

Gas Permeation and Sorption in Brominated Poly (1-Trimethylsilyl-1-Propyne) Membrane

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SYNOPSIS

Brominated poly(1-trimethylsilyl-1-propyne) (Br-PMSP), which was prepared by immersing a poly(1-trimethylsilyl-1-propyne) membrane in bromine water, had a new endothermic peak between 70°C and 80°C in its DSC curves. After storage in air at room temperature, the endothermic peak shifted to the low temperature side with time, and occurred between 30°C and 40°C. A distinct change in slopes near the endothermic temperature determined by the DSC analysis was observed in the Arrhenius plots of the permeability coefficients for various gases in all Br-PMSP membranes. However, the slope's change did not clearly appear with storage under the same conditions. The Br-PMSP membrane had a pressure-dependence of the permeability coefficients not only *below* the endothermic temperature, but also *above* one. The sorption behavior for propane in the Br-PMSP membrane was similar to that for other glassy polymers, and there was little change in the sorption behavior with time. In the case of carbon dioxide, a different behavior was observed at first; that is, the same isotherm shape in glassy polymers appeared below 20 atm, but it showed an upward curve above that. After storage in air, the upward behavior disappeared, and the isotherm showed the general shape in glassy polymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A study has been in progress for several years in this laboratory concerning the stabilization of the poly(1-trimethylsilyl-1-propyne) (PMSP) membrane because this membrane has a high potential for separating a gas mixture and a liquid one by selective permeation.¹⁻⁴ Some articles have reported on the various modifications and fundamental studies of this polymer. Many significant properties of this polymer have also been reported by several research groups.¹⁻²²

We have previously reported a study about the bromination of PMSP membranes and their gas permeability.²³ The brominated poly(1-trimethylsilyl-1-propyne) (Br-PMSP) membranes were prepared using the membrane reaction method. The bromination of the PMSP membrane occurred not

only on the surface but also in the bulk. The bromine mainly reacted at the carbon-carbon double bonds in the backbone chain, producing carbon-carbon single bonds, which was determined from the IR and UV-visible analyses. The glass transition temperature of the PMSP is above 350°C, but a new endothermic peak appeared between 50°C and 80°C in the DSC curves of all Br-PMSP in spite of the bromine content. A distinct change in slopes near the endothermic temperature determined from the DSC analysis was observed in the Arrhenius plots of the permeability coefficients for various gases in all Br-PMSP membranes. This suggested that a new local domain, which had a new glass transition temperature, was produced by the bromination. The Br-PMSP membrane itself had a very stable permeability coefficient.

Recently, in the course of this study, an unusual behavior was found such that the new endothermic peak in the DSC curves of all Br-PMSP shifted to the low temperature side with time. The objective in this article was to study the effect of the hysteresis on the permeability and physical solubility for pen-

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etrants in the Br-PMSP membranes, which were prepared by the chemical sorption of bromine.

EXPERIMENTAL

Preparation of Br-PMSP Membrane

The preparation of Br-PMSP membranes was done according to the same method described in a previous article.²³ The same PMSP previously synthesized²³ was used. The weight (M_w) and number (M_n) average molecular weights of the PMSP were 540,000 and 220,000, respectively. The homogeneous PMSP membranes with between 50 and 500 μm thicknesses were prepared from a toluene solution by the casting method. All membranes were immersed in methanol to keep the membranes fresh.

Bromination was carried out by immersing the PMSP membrane in bromine water containing 1 ~ 2% bromine at 25°C. The combined bromine content of the membrane was determined using the flask combustion method. The maximal bromine content was about 20 wt %, and the membranes above 15 wt % bromine content were brittle.²³

Characterization Analyses

DSC was determined using a Perkin-Elmer DSC 7 at a heating rate of 20°C/min. Gel permeation chromatography was done using a Tohso HLC-8020. M_w and M_n were determined on the basis of a polystyrene calibration. Bromine content was obtained by the flask combustion method using a Hamada FHO-1-A.

Gas Permeation and Sorption Measurements

The gas permeabilities on both high- and low-upstream pressures were determined by the vacuum-pressure method.²⁴ The transport theory and calculation of the permeability coefficient were done according to the general method.²⁴⁻²⁶ The experimental method used in this study was an adaptation of the vacuum gas transmission technique using an MKS Baratron model 310BHS-100SP pressure transducer below 1 atm upstream pressure between 30°C and 90°C, and using an MKS Baratron model 370HA pressure transducer up to 40 atm at 35°C.

The gas sorption isotherms at elevated pressure were determined by the gravimetric method, and the experimental procedure was almost the same method described elsewhere.^{3,22} The sorptions of CO_2 and

C_3H_8 in a polymer at 35°C were measured using a Cahn model 2000 electrobalance and a quartz spring, respectively.

The pure gases, i.e., O_2 , CO_2 , and C_3H_8 were obtained from Showa Denko Co., Ltd., and Takachiho Co., Ltd., and used without further purification.

RESULTS AND DISCUSSION

Hysteresis of Transition Point in DSC Curves

There was no thermic change in the DSC curve of PMSP, but Br-PMSP stored in air at room temperature between the first day and 1 month had an endothermic transition point between 50°C and 80°C, which reversibly occurred in the heating cycle.²³ Figure 1 shows the DSC curves of the Br-PMSP (Br: 13.1 wt %) membrane stored in air at room temperature. It is clear that a new endothermic transition point appeared and shifted to the low temperature side with time. First, a small exothermic peak was observed next to the endothermic point. With sample storage in air, the exothermic peak disappeared and a new broad exothermic peak appeared near 250°C. Furthermore, the endothermic point shifted with time.

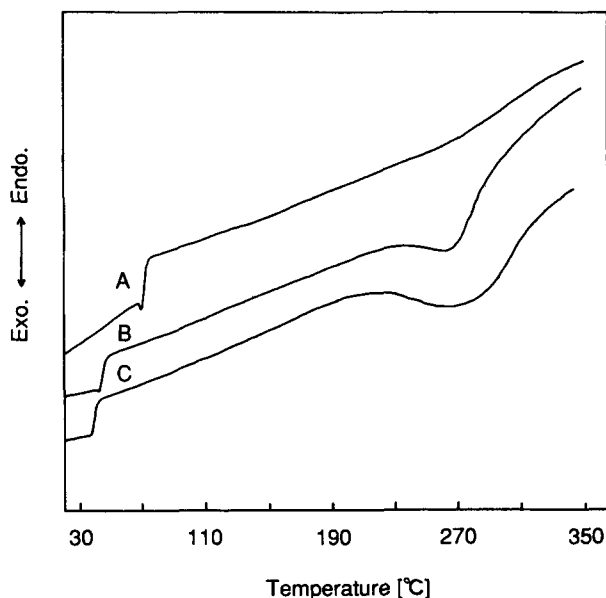
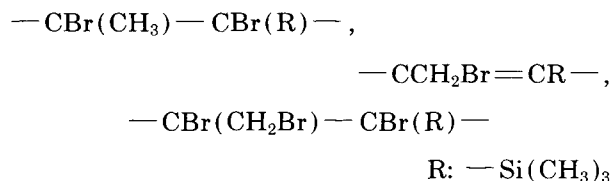


Figure 1 DSC curves of the brominated PMSP (Br: 13.1 wt %) membrane stored in air at room temperature for (A) 0 day, (B) 59 days, and (C) 80 days in the heating region between 20°C and 350°C.

After bromination, from the results described in a previous article,²³ the product was thought to have the following structures:



Furthermore, from the effects of water and oxygen in air, some C—Br bonds would change the C=O and OH groups. The endothermic transition was suggested to be attributable to a rotational change in the produced C—C bonds.

Figure 2 shows the time-dependence of endothermic temperature in the DSC curves of the Br-PMSP membranes stored in air at room temperature. In spite of the bromine content, the endothermic temperature linearly decreased, but after 80 days, it was constant between 30°C and 40°C.

A change in the constant-pressure heat capacity (ΔC_p) of the Br-PMSP membranes also changed with time. These values of the Br-PMSP membranes and other polymeric membranes are summarized in Tables I and II, respectively. Methods for polymerization and membrane preparation of all polymers in Table II were carried out according to the same methods described in another article.²⁷ The ΔC_p values of other polymers were almost in agreement with those in reference 28, and all were below 0.6 ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$). However, the ΔC_p values of the

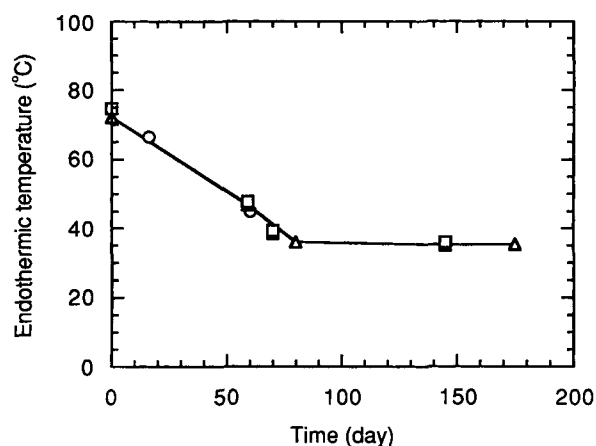


Figure 2 Time-dependence of endothermic temperature in the DSC curves of the brominated PMSP membranes stored in air at room temperature between the first day and 1 month. Bromine content (wt %): 3.3 (○), 10.8 (△), and 13.1 (□).

Table I Change in the Constant-Pressure Heat Capacity (ΔC_p) and the Endothermic Temperature (T_{Endo}) of the Br-PMSP Membranes

Bromine Content (wt %)	Time (day)	T_{Endo} (°C)	ΔC_p ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$)
3.3	0	74.7	1.38
	60	45.0	1.54
	70	38.5	1.39
10.8	0	72.1	1.32
	80 (1) ^a	36.9	1.68
	80 (2) ^a	40.2	1.74
	80 (3) ^a	35.5	1.84
	80 (4) ^a	35.1	1.84
13.1	0	74.7	—
	70	39.3	1.46

^a Heating rate: 1°C/min; region: 10–90°C; cycle: 4 times.

Br-PMSP membranes were above 1.0 ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$) and increased with time. In the case of repeating a heating-cooling cycle between 10°C and 90°C using the Br-PMSP membrane of 10.8 wt % bromine after 80 days, the value increased 0.16 ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$), i.e., from 1.68 to 1.84 ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$). After repeating three times, the value was constant. These results mean that the transition of the Br-PMSP membrane is different from the usual glass transition of polymers, which is a behavior of relieving frozen movements in a glassy state.

Table II Change in the Constant-Pressure Heat Capacity (ΔC_p) and the Endothermic Temperature (T_{Endo}) of Various Polymers

Polymer	T_{Endo} (T_g) (°C)	ΔC_p ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$)
Poly(dimethylsiloxane)	-123 ^a	0.50 ^a
Poly(3-methacryloxypropyl-tris(trimethylsiloxy)silane)	2	0.09
Poly(vinyl acetate)	28	0.53
Poly(vinyl chloride)	31 ^a	0.50 ^a
Poly(trimethylsilylmethyl methacrylate)	77 ^a	0.30 ^a
Polystyrene	82	0.30
Poly(methyl methacrylate)	101	0.21
Poly(phenylene oxide)	100 ^a	0.29 ^a
	105	0.32
	105 ^a	0.31 ^a
	199	0.11
	207 ^a	0.24 ^a

^a Ref. 28.

Figure 3 shows the FT-IR spectra of the Br-PMSP (Br: 2.4 wt %) membrane stored in air at room temperature. A change was not clearly observed. If a chemical reaction occurs during storage, a distinct change would be observed in the IR spectrum. Therefore, these results suggest that a physical change has priority over a chemical one.

From these results, the behavior, i.e., the endothermic point's shift, the appearance, and disappearance of the exothermic peaks, and the change in ΔC_p should be associated with a local change in the conformation and arrangement at the brominated sites and their neighborhood composed of the rigid backbone chains of the PMSP.

Temperature-Dependence of Permeability

The gas permeation behavior with time was investigated, as shown in Figure 4, which shows the temperature-dependence of the permeability coefficient for oxygen in the Br-PMSP (Br: 10.8 wt %) membranes. During the first heating from 30°C to 90°C, a distinct change in slope was observed, and in the first cooling from 90°C to 30°C, the permeability coefficient linearly changed on the same line as the first heating between 60°C and 90°C; then the value at 30°C decreased after doing the heating-cooling cycle. In the second heating, continually, a transition point was not clearly observed. In the second cooling from 100°C to 30°C, the value changed on the same line as in the second heating. In the case of the membrane stored in air at room temperature for 2

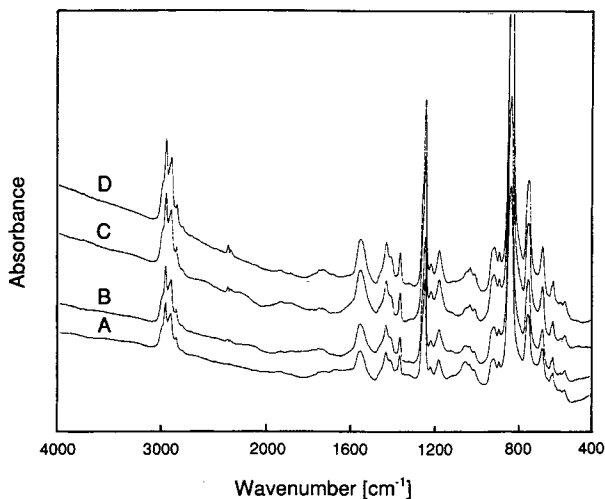


Figure 3 FT-IR spectra of the brominated PMSP (Br: 2.4 wt %) membrane stored in air at room temperature. (A) 0 day, (B) 21 days, (C) 96 days, (D) 217 days.

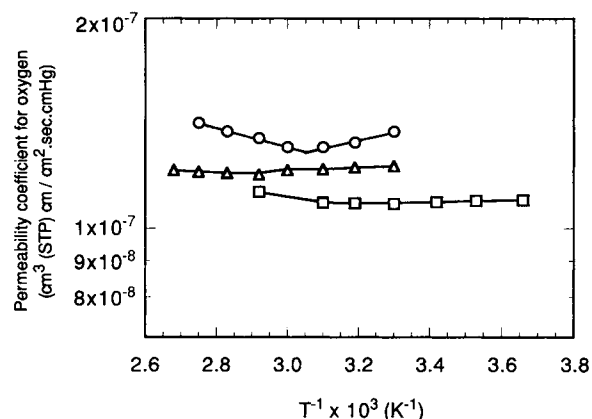


Figure 4 Temperature-dependence of permeability coefficient for oxygen in the brominated PMSP (Br: 10.8 wt %) membranes: the fresh membrane in the first heating (\circ), the fresh membrane in the second heating (Δ), and the membrane stored in air at room temperature for 2 months in the first heating (\square).

months, a distinct change in slope was not observed in the heating from 0°C to 70°C. The permeability coefficient at 30°C was smaller than that of the fresh membrane. Other gases (i.e., N_2 , CO_2 , H_2 , and CH_4) also showed the same results.

It was assumed from the results of the permeation and DSC analyses that the behavior was due to a relaxation of a new local domain, which was produced by the bromination. First, the brominated sites were fixed to the nonreacted PMSP chains, then the ΔC_p value was larger than those for other polymers, but the free volume would be large, meaning that there was a space that the chains could easily move in. Therefore, a distinct change in the permeability would occur, and the ΔC_p value would be smaller than those for the stored membranes. With time, the brominated sites and their neighborhood were relaxed by physical aging; therefore, the endothermic temperature would shift to the low temperature side. However, since free volume decreased, a higher energy for the rotation of the chains would be needed in comparison with the first; then the ΔC_p value increased, and an effect of the change in the permeability would be weakened.

Pressure-Dependence of Permeability

From the previously mentioned results, the transition was thought to result in a local change, not in an entire change in all chains. If the entire change occurs, such as the glass transition of polymers, a

rubbery behavior would be observed in its permeability above the transition temperature.

The permeability coefficient for simple gases in most rubbery polymers has no pressure-dependence, but for hydrocarbons, e.g., C_3H_8 in various silicone polymers, it increases with increasing upstream pressure.²⁹ In the case of glassy polymers, there is a pressure-dependence of permeability coefficients for CO_2 and hydrocarbons. With increasing upstream pressure, the permeability decreases, or decreases once and then increases as a result of plasticization. Some theories about these behaviors have been proposed.³⁰⁻³²

Figures 5 and 6 show the effect of upstream pressure on the permeability coefficient for C_3H_8 in the fresh PMSP membrane and the Br-PMSP (Br: 13.1 wt %) membrane above and below Br-PMSP transition temperatures. With increasing upstream pressure, all permeability coefficients decreased regardless of the measured temperature. Above the transition temperature, the permeability in the Br-PMSP membrane showed similar behavior in glassy polymers. This means that the entire change did not occur from a glassy state to a rubbery state in the Br-PMSP membrane above the transition temperature. For the purpose of analyzing what sites were brominated, sorption measurements were carried out.

Time-Dependence of Sorption Behavior

Sorption isotherms for C_3H_8 in the PMSP and Br-PMSP membranes are shown in Figure 7. The measurement was done below Br-PMSP transition temperature with elevating pressures. These curves

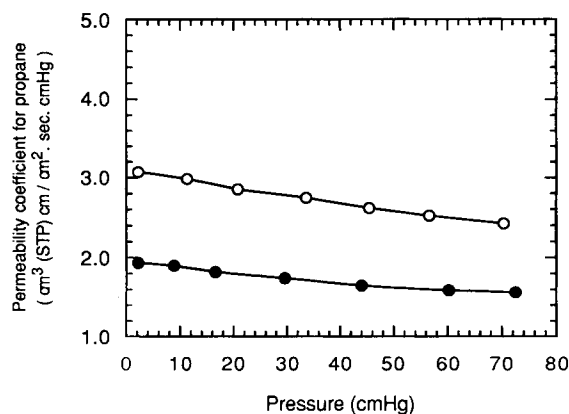


Figure 5 Effect of upstream pressure on permeability coefficient for propane in the fresh PMSP membrane at 35°C (○) and 70°C (●).

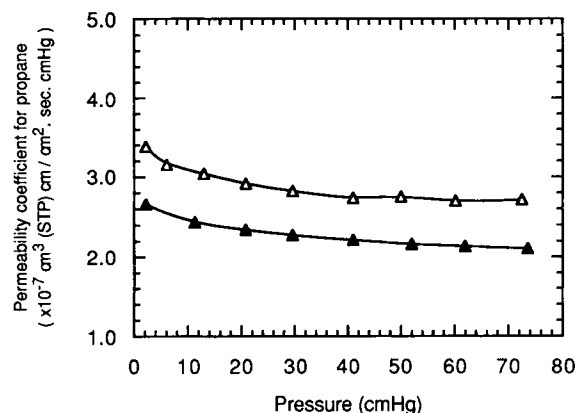


Figure 6 Effect of upstream pressure on permeability coefficient for propane in the brominated PMSP (Br: 13.1 wt %) membrane at 35°C (△) and 70°C (▲).

exhibit the typical isotherm's shape observed in glassy polymers, and have been known to be analyzed using the dual-sorption model.³³⁻³⁵

$$C = K_D p + C'_H b p / (1 + b p)$$

where C is the equilibrium concentration of the sorbed gas, K_D is the solubility constant in the Henry's law limit, C'_H is the hole saturation constant of Langmuir absorption, b is the Langmuir affinity constant, and p is the equilibrium gas pressure. In particular, C'_H is useful for an estimation of the space in the microvoids composed of polymer chains with frozen movements in the glassy state.

The parameters K_D , C'_H , and b as a function of bromine content are shown in Figures 8-10, respec-

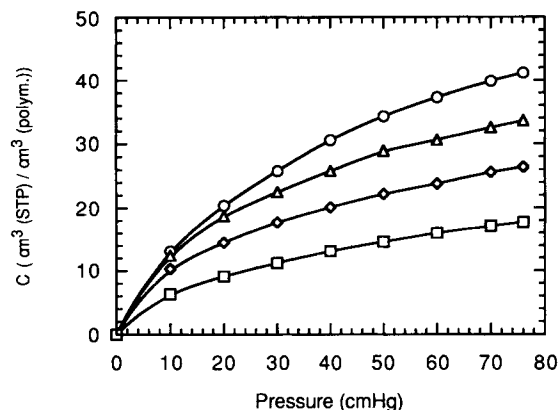


Figure 7 Sorption isotherms for propane in the PMSP (○) membrane and brominated PMSP membranes containing 7.4 (△), 11.9 (◇), and 14.2 (□) wt % bromine at 35°C.

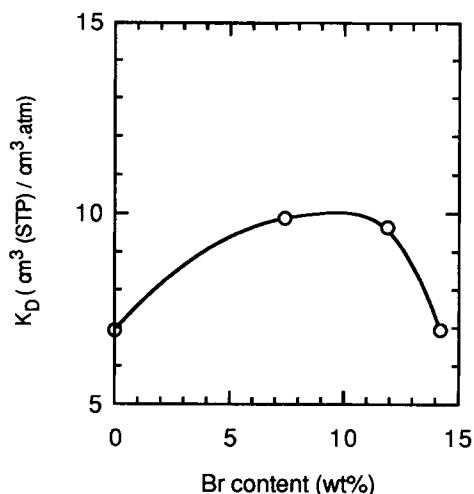


Figure 8 Relationship between bromine content and K_D for propane in the brominated PMSP membranes at 35°C.

tively. With increasing bromine content, the K_D and b values increased once and then decreased, and the C'_H value constantly decreased. Both a glassy domain and a rubbery one in the PMSP would be brominated, but these results mainly gave information about bromination of the glassy domain. These results mean that the glassy domain in the PMSP had reacted, and some brominated sites in the glassy state changed to the rubbery state.

The endothermic temperature in the DSC curves of the Br-PMSP membranes decreased with storage in air at room temperature. Therefore, the sorption

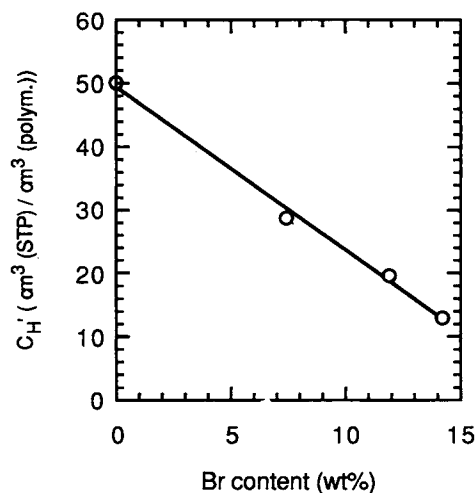


Figure 9 Relationship between bromine content and C'_H for propane in the brominated PMSP membranes at 35°C.

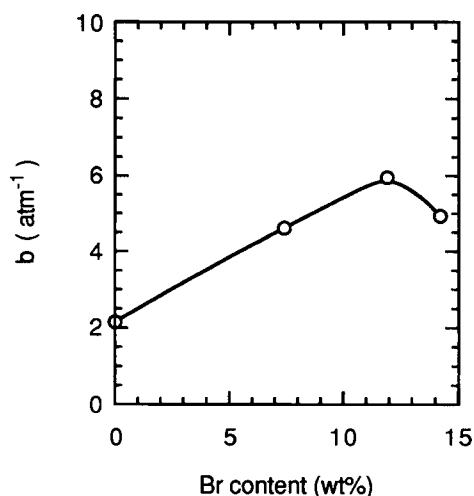


Figure 10 Relationship between bromine content and b for propane in the brominated PMSP membranes at 35°C.

measurement for C_3H_8 in the Br-PMSP (Br: 11.9 wt %) membranes was carried out under the same conditions, and the sorption isotherms are shown in Figure 11. A shape change in the isotherms was expected from a glassy type to a rubbery one because the endothermic temperature approached the measurement temperature with time. However, the shapes were the same in Figure 7. A slight decrease in the C value was observed with time. Therefore, these curves were analyzed using the dual-sorption model, and the parameters K_D , C'_H , and b are plotted as a function of storage time in Figure 12. This means that the C value's decrease with time depended on a slight decrease in both the K_D and C'_H

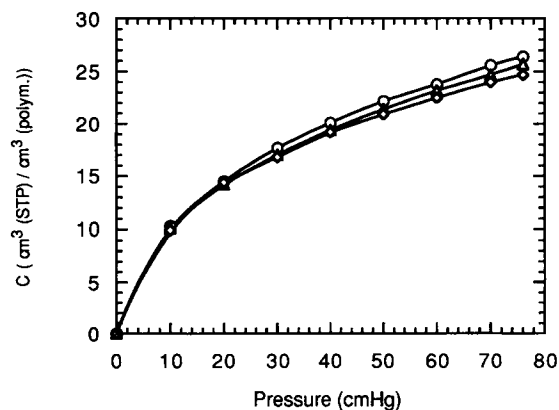


Figure 11 Sorption isotherms for propane in the brominated PMSP (Br: 11.9 wt %) membranes stored in air at room temperature for 0 day (O), 149 days (Δ), and 174 days (\diamond).

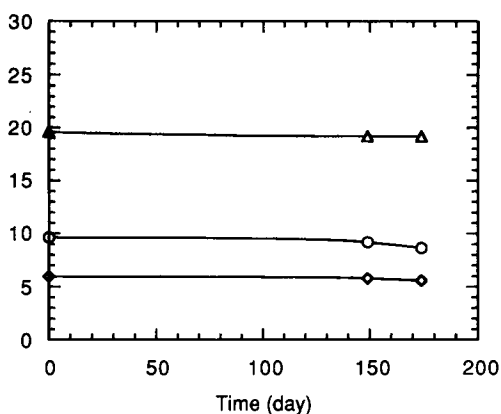


Figure 12 Time-dependence of K_D (\circ), C'_H (Δ), and b (\diamond) for propane in the brominated PMSP (Br: 11.9 wt %) membranes stored in air at room temperature.

values. The range of the decrease is small; however, these results suggest, along with the result of the hysteresis in the permeability, that the brominated sites and their neighborhood were relaxed by physical aging. Therefore, both a slight decrease in the microvoids, i.e., the decrease in the C'_H value and a slight increase in flexibility in the rubbery domain, i.e., the decrease in the K_D value, occurred with time.

These results can also support the explanation of the results of the DSC and permeation analyses.

High-Pressure Permeability and Solubility

The permeability and solubility for CO_2 in the PMSP and Br-PMSP membranes were carried out with increased pressure, up to 40 atm. Figure 13 shows the effect of the upstream pressure on the

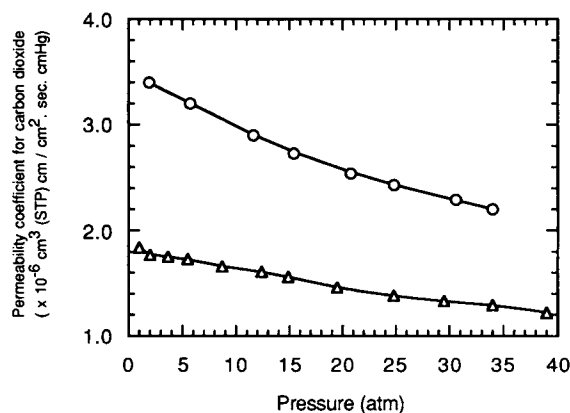


Figure 13 Effect of upstream pressure on permeability coefficient for carbon dioxide in the fresh PMSP (\circ) and brominated PMSP (Br: 2.6 wt %, Δ) membranes at 35°C.

permeability coefficient for CO_2 in the PMSP and Br-PMSP (Br: 2.6 wt %) membranes, while the sorption isotherms for these membranes are shown in Figure 14. There was a similar pressure-dependence of the permeability coefficients in both membranes, as shown in the case for C_3H_8 . The sorption isotherm in the PMSP membrane showed a similar curve for C_3H_8 , but those in the Br-PMSP membranes had different curves, i.e., the shape had an upward curve above 20 atm. The same shape of the isotherms has been found in various polymer-vapor (water) and polymer-gas systems, and especially, in the latter case, an attempt was made to analyze it using the modified dual-sorption equations with the new parameter related to the interaction between a polymer and a gas.³⁶⁻⁴¹ For a polymer- CO_2 system, the T_g of the used polymers was about 60°C, e.g., poly(vinyl benzoate) = 65.5°C³⁷; poly(ethyl methacrylate) = 61°C.⁴⁰ Although the shape was linear near the T_g , the same type isotherms were observed near room temperature. This was due to the large plasticizing effect of sorbed CO_2 . The Br-PMSP- CO_2 system might be influenced by the same effect at the local brominated domains.

The effect of hysteresis on the sorption behavior in the Br-PMSP (Br: 2.6 wt %) membrane is shown in Figure 15. After storage in air for 2 months, the upward curve above 20 atm observed in the fresh membrane disappeared, and the curve was similar to that of the PMSP membrane. An isotherm in a silicone rubber- CO_2 system is well-known to show an upward curve in the sorption isotherm.⁴² When a silicone structure is added in a glassy polymer, the sorption isotherm is expected to show the same shape as the Br-PMSP- CO_2 system. However,

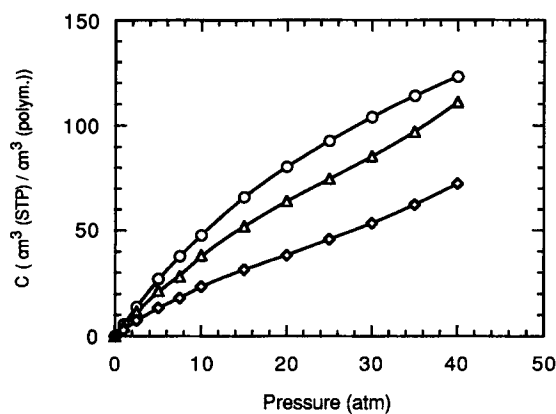


Figure 14 Sorption isotherms for carbon dioxide in the PMSP (\circ) membrane and brominated PMSP membranes containing 2.6 (Δ) and 14.2 (\diamond) wt % bromine at 35°C.

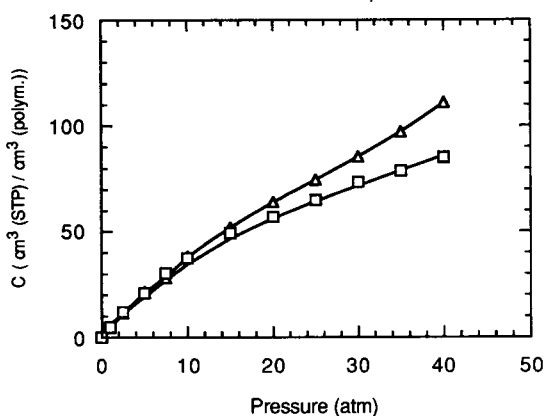


Figure 15 Sorption isotherms for carbon dioxide in the fresh brominated PMSP (Br: 2.6 wt %) membrane (Δ) and the membrane stored in air at room temperature for 2 months (\square) at 35°C.

sorption in polyimide containing siloxane units in the chain showed typical glassy behavior.⁴³ The polyimide was composed of 2,2-bis(3,4-decarboxyphenyl)hexafluoropropane (6-FDA); 4,4'-diaminodiphenylether (DADE); and α,ω -bis(3-aminopropyl)polydimethylsiloxane (DMS). The morphology of this membrane would have a microphase separation, i.e., microsioxane domains in the matrix, because there were two T_g in the DSC curve, i.e., at about -120°C and above 250°C . Although only 2.6 wt % bromine affected the change in the isotherm of the PMSP membrane, the silicone-polyimide containing the maximum siloxane content of 24% had a typical glassy isotherm. The reason for this may be due to the effect that the rigid polyimide matrix is tightly packed with siloxane domains. After storage, the Br-PMSP membrane affected the physical aging already mentioned; then the rich units of the rigid PMSP would prevent movement of the brominated domains.

CONCLUSIONS

The state in the Br-PMSP membrane, which was prepared by the chemical sorption of bromine, is suggested as follows. The Br-PMSP membrane had a hysteresis, which results in physical aging from a quasi-stable state to a stable one in the local brominated domains. The domain would be composed of the brominated sites, which have the produced carbon-carbon single bonds, and their neighborhood. The movement in the domains heightened, and approached a more stable state with changing morphology. Some distinct changes in the perme-

ability and sorption behavior in the fresh Br-PMSP membranes are due to this effect. With time, the state approached the stable one; then the distinct changes in the permeability and sorption behavior were not observed, although an endothermic transition clearly appeared in the DSC curve of the Br-PMSP membrane.

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