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Effects of aging on the gas permeability and solubility in poly(1-trimethylsilyl-1-propyne) membranes synthesized with various catalysts

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Abstract

The effects of aging on the gas permeability and solubility in glassy poly(1-trimethylsilyl-1-propyne) (PMSP) membranes were investigated in terms of polymer characterization and storage environment. Under the aging conditions in the presence of vacuum pump oil vapor, in which a very small amount of vacuum pump oil vapor sorbed in the PMSP membrane served as an accelerator of physical aging rather than as a filler, the aging of the gas permeability of the PMSP membranes was dependent on their thickness, the polymerization catalyst and molecular weight. On the other hand, catalyst dependence on the gas permeability was not observed during annealing. Additionally, the aging of the gas sorption in the PMSP membranes was similar to that of the gas permeability. Storage in liquid nitrogen and exposure to carbon dioxide at 40 atm also affected the gas permeability and solubility in the PMSP membranes. These phenomena could be related to a difference in the glassy state of the as-cast membranes synthesized with various catalysts.

Keywords: Poly(1-trimethylsilyl-1-propyne); Gas permeability; Aging; Membrane contamination; Vacuum pump oil vapor

1. Introduction

The gas permeabilities of the poly(1-trimethylsilyl-1-propyne) (PMSP) membrane, which has a glass transition temperature of more than 250°C, are orders of magnitude higher than those of other polymeric membranes [1–29]. In addition, both the gas diffusivity and the gas solubility are higher than those of others, and these high properties are attributed to a very excessive free volume compared with other polymers. Based on this, the combination of high diffusivity and high solubility yield extraordinarily high permeability.

Interestingly, gas permeability coefficients in the PMSP membrane have been reported over a wide region compared with other polymers, e.g., the permeability coefficients for oxygen were between 1.3×10^{-6} and 3×10^{-7} (cm^3(STP) cm/(cm^2 s cmHg)) at 25 or 30°C [1–29]. A significant reduction in the gas permeability of this membrane was also observed during aging [2,3,8,9,11,16,19,20,27]. These results illustrate the importance that must be placed on the difference in morphology and hysteresis in as-cast membranes based on gas permeation measurements of PMSP compared with other glassy polymers.

The configuration of the PMSPs could be controlled by the properties of the polymerization catalysts when

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the preparation methods are the same. Even though the *cis–trans* content of the PMSP has not been quantitatively determined, the ^{13}C NMR [30,31] and ^{29}Si NMR [31] spectra of the PMSPs synthesized with $TaCl_5$ and $NbCl_5$ were different, and the solubilities of the PMSPs in organic solvents were also different [32–34]. The molecular weight, which was designed by controlling the monomer–catalyst feed ratio [32–34], affected the gas permeability of the PMSP [2].

Additionally, the non-equilibrium state of the as-cast PMSP membrane would be more unstable than that of other glassy polymers because of the hysteresis behavior of the gas permeability [2,3,5,8,9,11,16,19,20,27]. It is well known that annealing and conditioning affect the gas permeation, gas solution and glass transition properties [35–45]. The gas permeability of the PMSP was dramatically reduced by annealing [2,3,5,16]; however, changes in the glassy state have not been discussed in detail.

This membrane also showed a significant reduction in gas permeability near room temperature under vacuum [3,8,9,11,19,27]. The PMSP sorbs vacuum pump oil vapor [5,9,11,14,27] and some plasticizers from various packings used in the gas permeation measurements [5]. This unusual phenomenon is the most important reason for the reduction. The aging occurs physically; therefore, the sorbed contaminants would serve as a filler of free volume and as an accelerator of physical aging. In particular, we reported that a very small amount of vacuum pump oil vapor would serve as an accelerator of physical aging rather than as a filler of free volume. Moreover, the aging of the gas permeability of the PMSP membranes was dependent on the membrane thickness; that is, a heterogeneous aging from the surface to the center was observed under the aging conditions in the presence of vacuum pump oil vapor [27].

In this paper, we systematically studied the effects of aging on the gas permeability and solubility in the PMSP membranes synthesized with various catalysts based on the composite factors: physical aging, chemical aging (i.e. oxidation), and membrane contamination. In Section 3.2, the effects of aging on the gas permeation properties are reported during storage in a vacuum vessel and in air in the presence of contaminants, i.e. vacuum pump oil vapor and contaminants in air, respectively. Storage in air also affects chemical aging (i.e. oxidation). On the other hand, in the absence of contaminants (Section 3.3), effects of annealing, cooling, and CO_2-conditioning on the gas permeation properties are reported. Based on these results, we describe the aging system of the gas permeability and solubility in PMSP membranes synthesized with various catalysts.

2. Experimental

2.1. Materials

The PMSPs were synthesized using the same method described in some previous studies [26–29], which were performed according to Masuda et al.'s method [32–34].

The reagents used were purified just before each polymerization. The monomer was distilled with calcium hydride under dry nitrogen at atmospheric pressure. Tantalum(V) chloride ($TaCl_5$), niobium(V) chloride ($NbCl_5$), and triphenyl bismuthine (Ph_3Bi) as a cocatalyst were handled in a drybox equipped with diphosphorus pentaoxide under dry nitrogen and used without further purification. Toluene as a polymerization solvent was distilled with metallic sodium under dry nitrogen at atmospheric pressure after removing thiophenes, i.e. toluene was washed using sulfuric acid under cooling, washed with a 10% sodium carbonate solution, washed with water, and dried using calcium chloride.

The monomer and solvent used were more than 99.9% pure as determined by gas chromatography. The degree of dehydration of these reagents was determined using an MCI Model CA-05/VA-05 moisture meter according to the Karl Fischer method.

2.2. Polymerization

In the case of $TaCl_5$, the PMSPs previously synthesized [27,28] were used; polymerization was done in toluene at 80°C, [1-trimethylsilyl-1-propyne] = 1 M [27] and 0.3 M [28], $[TaCl_5] = 0.02$ M. The polymerization with other catalysts was carried out under dry nitrogen in toluene at 80°C ($TaCl_5$-Ph_3Bi) and 30°C ($NbCl_5$) for 24 h; [1-trimethylsilyl-1-propyne] = 1 M, [cat.] = 0.02 M and [cocat.] = 0.02 M. The products were isolated by precipitation from a large amount of methanol, filtered and dried under vacuum. Further-more, the obtained polymer was purified by the solution-precipitation method using the toluene–methanol system.

2.3. Membrane preparation

The PMSP membranes having various thicknesses were prepared by the casting method. The synthesized PMSP was dissolved in toluene, cast from a toluene solution onto a glass plate and dried under vacuum. All the membranes were immersed in methanol just before several measurements were taken to prevent hysteresis of the membranes.

2.4. Measurement of the gas permeability and sorption isotherm

The gas permeation and sorption measurements were performed according to the same method described in some previous studies [26–29]. The gas permeability was determined by the vacuum-pressure method using an MKS Baratron model 310BHS-100SP or 310BHS-10 pressure transducer at less than 1 atm upstream pressure. The gas sorption isotherms at an elevated pressure up to 1 atm were determined by the gravimetric method using a quartz spring. The vacuum pressure was controlled between 10^{-2} and 10^{-3} mm Hg. The vacuum pump oil used was Sanvac oil No. 160, which has a vapor pressure of 4.1×10^{-6} mm Hg at 10°C, which was purchased from the Asahi Vacuum Chemical Industry Co., Ltd. A silicone rubber packing that contained no bleeding agents was used for the gas permeation measurement. The pure gases were purchased from Showa Denko Co., Ltd. and Takachiho Co., Ltd., and were used without further purification.

3. Results and discussion

3.1. Polymer characterization

The FT-IR and ^{1}H NMR spectra of the products were consistent with those of PMSP described in some of the literature [22,26–28,30–32,46]. No thermal change appeared up to 250°C during the DSC measurements of all PMSPs. The weight-average molecular weights (M_w) of the products were determined by gel permeation chromatography based on polystyrene calibration or using the intrinsic viscosity–molecular weight relationship [32–34]. Intrinsic viscosities ($[\eta]$, dl/g) were measured in toluene at 30°C. The M_w values were 86×10^4 ($TaCl_5$(A)) [27], 54×10^4 ($TaCl_5$(B)) [28], 260×10^4 ($TaCl_5$-Ph_3Bi) and 35×10^4 ($NbCl_5$). The $[\eta]$ values (dl/g) were 6.0 ($TaCl_5$(A)) [27], 1.6 ($TaCl_5$(B)) [28], 9.3 ($TaCl_5$-Ph_3Bi) and 0.7 ($NbCl_5$).

We previously reported [46] that some PMSPs synthesized with $TaCl_5$ had a low viscosity and narrow polydispersity ratio compared with Masuda et al.'s case [32]; therefore, the relationship between their M_w and $[\eta]$ was out of range of the intrinsic viscosity–molecular weight relationship in [32]. In this study, only the $TaCl_5$(B) case [28] was not in accord with this relationship such as in [46]. These PMSPs were synthesized under the same conditions except for the feed component. A small amount of oxygen-containing compounds, e.g. H_2O, ethanol and acetic acid, served as a cocatalyst in the polymerization of 1-chloro-1-alkynes using molybdenum(V) chloride-tetrabutyl tin ($MoCl_5$-$n$$Bu_4Sn$); $[MoCl_5]/[nBu_4Sn]/[\text{oxygen-compound}] = 1/1/0.5$ [47]. Therefore, we considered the H_2O detected in the feed reagents. The molar ratio of $[H_2O]/[\text{cat.}]$ was less than 0.05 in most cases performed in this work, i.e. $TaCl_5$(A), $TaCl_5$-Ph_3Bi and $NbCl_5$. However, in the case of the previously synthesized PMSPs [28,46], i.e. $TaCl_5$(B) [28], the $[H_2O]/[\text{cat.}]$ was about 0.4. When H_2O ($[H_2O]/[\text{cat.}] = 2$) was purposely added in a polymerization system, the reaction also occurred, but little polymer was produced. As a consequence, the added H_2O should work as a terminator or an inhibitor of the polymerization. Based on these results, when the $[H_2O]/[\text{cat.}]$ was about 0.4, H_2O also should work as a cocatalyst during the polymerization of PMSP.

Slight coloration might be due to many things, most of which are related to minute quantities of often unknown substances that are intensely colored. Therefore, we were very careful as mentioned in the Experimental section. The initial PMSP membranes synthesized with $TaCl_5$(A) and $TaCl_5$-Ph_3Bi were colorless and transparent; however, that of $TaCl_5$(B) was slightly yellow and transparent. Masuda et al. [34] suggested that the color of substituted polyacetylenes might be dependent on the conjugated conformations of backbone chains.

Table 1

Effect of vacuum pump oil vapor on the permeability coefficient (P) for oxygen in PMSP membranes[a] synthesized with $TaCl_5$-Ph_3Bi

No.	Type	Pressure (mmHg)	Initial[b]	14 days[b]	P(14 days)/P(initial)[c]
1	membrane–oil rotary pump	10^{-2}–10^{-3}	11	1.0	9
2	membrane–cold trap[d]–oil rotary pump	10^{-2}–10^{-3}	13	3.6	28
3	membrane–cold trap[d]–oil rotary pump	10–15	13	6.8	52
4	membrane–PMSP column[d]–cold trap[d]–oil rotary pump	10^{-2}–10^{-3}	13	5.1	39
5	membrane–cold trap[d]–oil free pump	10–15	14	9.6	69

[a] Thickness: ca. 150 μm.

[b] $\times 10^{-7}$ cm^3 (STP) cm/(cm^2 s cmHg). Initial: between 24 and 36 h after a membrane was taken out of methanol.

[c] %.

[d] PMSP column, an adsorption column filled with PMSP powder; cold trap, liquid nitrogen.

3.2. *Effect of membrane contamination*

Table 1 shows the effect of vacuum pump oil vapor on the permeability coefficient for oxygen in the PMSP membranes synthesized with $TaCl_5$-Ph_3Bi. When an oil rotary vacuum pump was used, the effect of the oil vapor was not completely removed even though liquid nitrogen was used for the cold trap. In comparison with a non-cold trap system (type 1, a membrane in a vacuum vessel was directly vacuumed using an oil rotary pump), a decrease in the gas permeability was restrained using the cold trap placed between the membrane and the pump (type 2). However, the decrease in the gas permeability using the oil rotary pump (type 3) was larger than that using an oil-free pump (type 5). Using this property as one of the countermeasures for oil vapor contamination, an adsorption column filled with PMSP powder was placed between the membrane and the cold trap (type 4). A decrease in the gas permeability was more restrained compared with type 2. This means that the adsorption column would prevent the invasion of oil vapor. Vacuum pressure also affected the aging; that is, storage at lower pressure accelerated the aging (types 2 and 3).

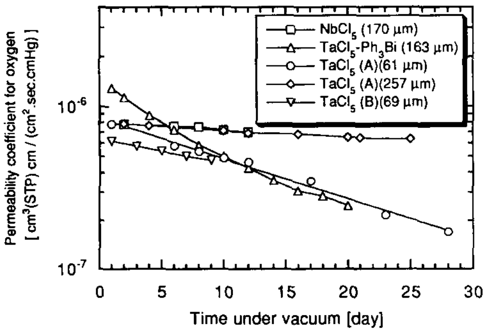

Fig. 1. Effect of aging time on the permeability coefficient for oxygen in the PMSP membranes synthesized with various catalysts at 30°C. Conditions: stored in a vacuum vessel at 30°C. $TaCl_5$(A): experimental data from [27].

Without a cold trap between the vacuum pump and the PMSP membrane, a distinct gravimetric increase due to oil vapor sorption was reported under 10^{-3}–10^{-4} mmHg at 35°C [14]. In this work using the cold trap, the gravimetric increase due to oil vapor was less than 0.1 wt% during storage under 10^{-2}–10^{-3} mmHg at 35°C for 7 days.

Based on these results, as we previously discussed [27], a very small amount of oil vapor would serve as an accelerator of physical aging rather than as a filler of free volume. The PMSP had a high adsorption as shown in Table 1 (type 4); therefore, the PMSP is probably useful not only as a membrane separation material but also as an adsorption material.

The chain configuration of substituted polyacetylenes, e.g. poly(*t*-butylacetylene), affects the gas permeation and sorption properties [2,48]. Unfortunately, the *cis*/*trans* ratio of disubstituted polyacetylenes, e.g. PMSP, has not been quantitatively determined although those of most of the mono-substituted polyacetylenes have been determined by NMR analysis. However, the PMSPs synthesized with different catalysts should not have the same structure because various properties, e.g. the ^{13}C NMR and ^{29}Si NMR spectra, and the solubilities of the PMSPs in organic solvents, were different [30–34].

Fig. 1 shows the aging effect on the gas permeability coefficients in the PMSP membranes synthesized with $TaCl_5$, $NbCl_5$ and $TaCl_5$-Ph_3Bi. All conditions were similar to the previous experiments [27]. Time 0 was when a membrane was taken out of the methanol solution. An oil rotary vacuum pump was used, and a cold trap with liquid nitrogen was placed between the pump and the membrane during storage under vacuum, the storage conditions of which were the same as shown in Table 1 (type 2). There was no pressure dependence of the gas permeability coefficients for oxygen, nitrogen and carbon dioxide at less than 1 atm in these membranes.

As is evident from Fig. 1, catalyst dependence of the gas permeability was observed. The configuration of the PMSPs could be controlled by the polymerization catalysts. Therefore, this indicates that the aging of the gas permeability would be dependent on the chain configuration of the PMSP. The cis/trans ratio has not been quantitatively determined; however, Costa et al. [30] reported that the PMSP synthesized with $NbCl_5$ had a higher content of long cis or trans sequences compared with $TaCl_5$. Izumikawa et al. [31] described that the PMSP synthesized with $NbCl_5$ was a *cis*-rich structure compared with $TaCl_5$, and polymerization conditions, e.g. solvent, temperature and cocatalyst, hardly affected the geometric structure. Under the aging conditions used, the gas permeability in the PMSP membrane synthesized with $NbCl_5$ was more stable compared with $TaCl_5$ and $TaCl_5$-Ph_3Bi; that is, a quasi-stable state of an as-cast membrane with $NbCl_5$ would be more stable compared with the others. Using the same catalyst, i.e. $TaCl_5$(A) and $TaCl_5$(B), the aging behavior differed slightly. We have already described the thickness dependence of the gas permeability of the PMSP membranes [27] and the copolymer composed of 1-trimethylsilyl-1-propyne and pentamethyldisilyl-1-propyne [49]. The gas permeability of the thinner membrane was more sensitive than that of the thicker membrane. Additionally, these initial permeabilities differed slightly.

The effect of membrane thickness on the initial permeability coefficient for oxygen in the PMSP membranes is shown in Fig. 2. The initial value was between 24 and 36 h after a membrane was taken out of methanol. An interesting tendency was observed. The initial permeability in the PMSP membranes synthesized with $TaCl_5$(B) and $NbCl_5$ was about 7×10^{-7} (cm^3(STP) cm/(cm^2 s cmHg)), and that with $TaCl_5$-Ph_3Bi was about 1.3×10^{-6} (cm^3(STP) cm/(cm^2 s cmHg)). In the case of $TaCl_5$(A), the initial permeability of the membranes having a thickness of more than 400 μm was in the same order of $TaCl_5$-Ph_3Bi, but that of the thin membranes was about 7×10^{-7} (cm^3(STP) cm/(cm^2 s cmHg)). As we will show later in Fig. 4 and Fig. 6, the sorption concentration for propane in the thick membrane (more than 400 μm) synthesized with $NbCl_5$ was smaller than that with $TaCl_5$(A) and was similar to that of the thin membrane (less than 100 μm) synthesized with $TaCl_5$(B). Based on these results, the initial gas permeability could be related to the initial free volume of the PMSP membranes. Therefore, these results are probably based on the initial packing of the polymer chains of the as-cast membranes, and the initial packing would be dependent on chain configuration of the PMSP. The result for $TaCl_5$(A) is assumed as follows; the permeability of the thin membrane was reduced before measuring the initial permeability, i.e. during storage under vacuum or the initial free volume of the thin membrane was essentially smaller than that of the thick membrane.

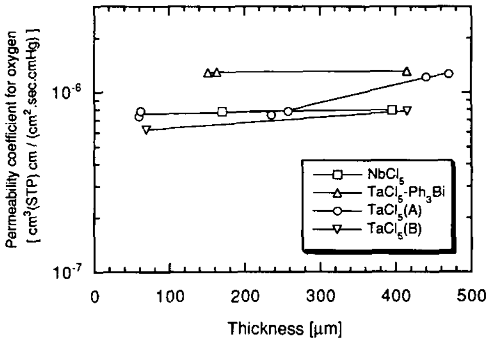

Fig. 2. Effect of membrane thickness on the initial permeability coefficient for oxygen in the PMSP membranes synthesized with various catalysts at 30°C. Initial: between 24 and 36 h after a membrane was taken out of methanol.

This difference in the aging may be due to a difference in the glassy state, which is probably dependent on the configuration of the as-cast PMSP membranes synthesized with various catalysts because the conditions were the same except for the configuration. Oil vapor naturally diffuses from the surface to the center. Based on the effects of membrane thickness on the initial permeability (Fig. 2) and aging (Fig. 1), the glassy state on the surface should be a dominant factor during aging.

During storage under vacuum over a period of 30 days, the gas sorption concentration of the thin membrane synthesized with $TaCl_5$(A) was also dramatically reduced in addition to the decrease in the gas

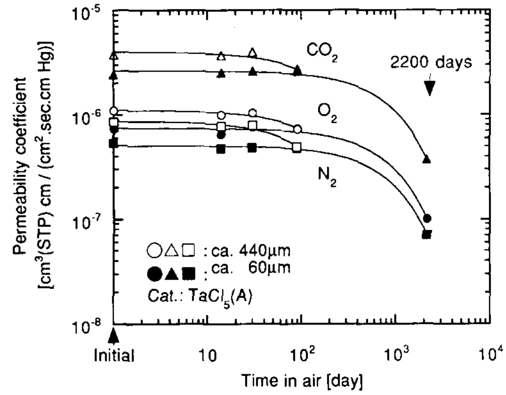

Fig. 3. Effect of aging time on the permeability coefficients for oxygen, nitrogen and carbon dioxide in the PMSP membranes with two different thicknesses at 30°C. Conditions: stored in air at room temperature. Experimental data till 30 days: from [27]. Catalyst: $TaCl_5(A)$.

permeability [27]. On the contrary, the thicker membranes were not influenced by gas permeability and solubility. These results are discussed in relation to a decrease in C_H', which is one of the dual-sorption parameters using Eq. (1) and is related to the unrelaxed volume in a glassy polymer [50–52].

$$C = k_D p + C_H' bp/(1+bp) \qquad (1)$$

where C is the equilibrium concentration of the sorbed gas, k_D is the solubility constant in Henry's law limit, C_H' is the hole saturation constant of Langmuir adsorption, b is the Langmuir affinity constant and p is the equilibrium gas pressure. PMSP has the largest C_H' value for all the synthetic polymers; therefore, this membrane has the highest permeability along with the highest diffusivity [4,12,14,18,25]. A decrease in C_H' means a reduction in the unrelaxed volume; therefore, relaxation of the unrelaxed volume of the PMSP membrane would heterogeneously occur from the surface to the center [27].

In the course of this study, the sorption properties of the PMSP membranes stored for over 4 years were investigated compared with storage in air. As shown in Fig. 3, during storage in air at atmospheric pressure, the gas permeability of the thin membrane synthesized with $TaCl_5(A)$ was stable, although a distinct reduction in the gas permeability was observed during storage under vacuum. The initial gas permeabilities of the thick membrane were higher than that of the thin membrane; however, these values approached those of the thin membrane, and after 90 days, these values were the same. The PMSP membranes were easily autooxidized during storage in air [46]; however, oxidation did not affect the gas permeability compared with storage under vacuum. There appears to be a decrease in gas permeability as the membrane aging time in air is increased from 90 days to 2200 days. The permeability coefficient for oxygen in the thin membrane was about 1×10^{-7} ($cm^3(STP)\ cm/(cm^2\ s\ cmHg)$) after storage in air for 2200 days. Langsam et al. [11] described that the use of commercial antioxidants at up to 2 wt% improved the long term stability of the PMSP. Chen et al. [22] reported that the gas permeabilities were stable after 6 months storage in ambient air; the initial permeability coefficient for oxygen was 7.87×10^{-7} ($cm^3(STP)\ cm/(cm^2\ s\ cmHg)$) and the value after storage was 7.25×10^{-7} ($cm^3(STP)\ cm/(cm^2\ s\ cmHg)$). Yampol'skii et al. [20] showed that the gas permeability coefficient for oxygen in the PMSP stored in air for 4 years was about 1×10^{-8} ($cm^3(STP)\ cm/(cm^2\ s\ cmHg)$); the initial being about 3×10^{-7} ($cm^3(STP)\ cm/(cm^2\ s\ cmHg)$). This difference in aging of the gas permeability during storage in air was probably dependent on a combination of physical aging, chemical aging, and contamination. However, the contamination was probably a dominant factor on aging of the gas permeability during storage in air between 90 and 2200 days.

Fig. 4 shows the sorption isotherms for propane in the aged PMSP membranes. The PMSP membranes were stored in glass tubes at 10^{-2}–10^{-3} mmHg for 12 h using a liquid nitrogen cold trap between the

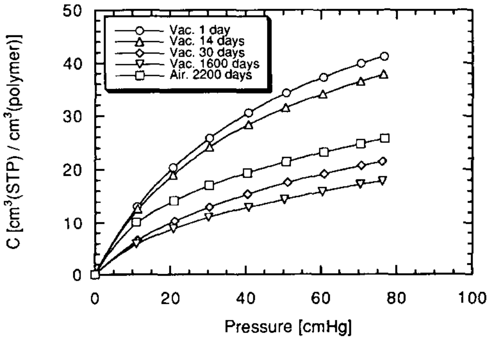

Fig. 4. Sorption isotherms for propane in aged PMSP membranes at 35°C. Conditions: stored in a vacuum vessel for 1, 14, 30 and 1600 days and in air at room temperature for 2200 days. Experimental data (stored under vacuum for 1, 14 and 30 days): from [27]. Thickness: about 70 μm (in vacuum) and 106 μm (in air). Catalyst: $TaCl_5(A)$.

Table 2
Dual-mode sorption parameters for propane in aged PMSP membranes[a] at 35°C

No.	Condition		K_D^b	$C_H{}'^c$	b^d	Ref.
1	20 h	under vacuum	0.0912	50.1	0.0283	[27]
2	14 days	under vacuum	0.113	40.0	0.0355	[27]
3	30 days	under vacuum	0.0758	22.3	0.0307	[27]
4	1600 days	under vacuum	0.0938	13.3	0.0537	This work
5	30 days	in air	0.182	36.4	0.0432	[27]
6	2200 days	in air	0.121	19.2	0.0762	This work

[a] Experimental data: Fig. 4, thickness; samples 1–5: ca. 70 μm, sample 6: 106 μm.
[b] $cm^3(STP)/(cm^3(polymer)\ cmHg)$.
[c] $cm^3(STP)/cm^3(polymer)$.
[d] $1/cmHg$.

membrane and the pump. These tubes were then heat sealed at both ends using a flame, wrapped in aluminum foil, and stored at room temperature. When the membranes were stored in air, the membranes were sandwiched between filter papers. The type of storage did affect the sorption properties. With continuing storage time, the sorption concentration decreased, and the $C_H{}'$ value also decreased as shown in Table 2. From 30 days to 1600 days, the decrease in the sorption concentration was small compared with that from 1 and 30 days. This means that the glassy state should approach the stable state. In the case of storage in air, the sorption properties were also influenced over the first 30 days, although the gas permeability was constant. After storage for 2200 days, the sorption concentration decreased along with a decrease in the gas permeability. The initial PMSP membranes were colorless and transparent. The membranes stored in a vacuum vessel for 1600 days maintained this appearance; however, those stored in air for 2200 days became light yellow and transparent. Yampol'skii et al. [20] also reported that a PMSP membrane stored in air for 4 years was tinted yellow. Witchey-Lakshmanan et al. [14] mentioned that the PMSP became yellowed due to sorbing vacuum pump oil vapor. Therefore, these observations suggest the sorption of contaminants during storage in air.

Based on these results, in the case of storage for a long time period, the aging behavior under vacuum is dependent on physical aging, which would be influenced by a very small amount of vacuum pump oil vapor as an accelerator. On the contrary, the aging behavior in air at atmospheric pressure was probably determined by a combination of physical aging, oxidation effects, i.e., chemical aging, and especially the sorption of contaminants in air.

3.3. Aging without membrane contamination

As previously mentioned, the aging conditions under vacuum would cause a heterogeneous relaxation of the PMSP membrane. It is well known that annealing below the glass transition temperature is effective for reducing the unrelaxed volume of glassy polymers. Annealing causes a decrease in the unrelaxed volume, and the decrease then causes a reduction in permeability and solubility [35,36,40,41,43]. Thermal energy would affect not only the surface but also the bulk of the PMSPs; therefore, a homogeneous relaxation should be expected. In addition, it is also known that exposure of glassy polymers to gases (vapors) and liquids causes a change in the state and properties of the glassy polymers [35–45]. CO_2-conditioning causes an increase in free volume, then gas permeability and solubility increase [35–39]. Exposure to gases (vapors) and liquids also causes changes in the glass transition properties in the differential scanning calorimetry curves [44,45]. The gas permeability of the PMSP was reduced by annealing [2,3,5,16]; however, changes in the glassy state and the solubility behavior have not been discussed in detail.

The PMSP was easily auto-oxidized in the presence of oxygen and was also decomposed by heating [46,53]. Additionally, in order to eliminate the effect of vacuum pump oil vapor, annealing of the PMSP membranes was carried out in nitrogen. The membrane was stored under vacuum for 12 h after being taken out of methanol, annealed for 1 h, and placed into the gas permeation and sorption apparatuses, then measured for permeability between 12 and 18 h after annealing. These membrane thicknesses were about 400 μm.

The relationship between annealing temperature and the permeability coefficients for oxygen and nitrogen is shown in Fig. 5. The gas permeabilities decreased with increasing annealing temperature in the cases of both catalysts, although the thick membranes were stable under vacuum over a period of 30 days at 30°C. Fig. 6 shows the sorption isotherms for propane in the annealed PMSP membranes. With increasing annealing temperature, the sorption of propane decreased. A distinct change in the gas permeability and solubility

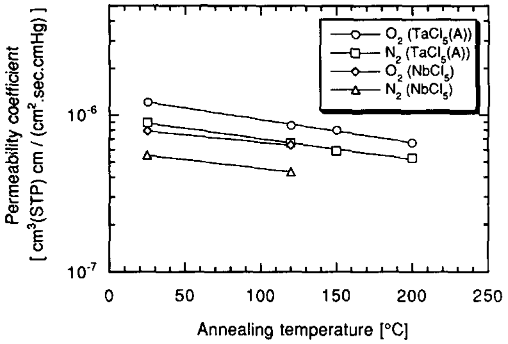

Fig. 5. Effect of annealing temperature on the permeability coefficients for oxygen and nitrogen in the PMSP membranes synthesized with $TaCl_5$(A) and $NbCl_5$ at 30°C. Conditions: annealed in nitrogen at 1 atm for 1 h. Thickness: about 400 μm.

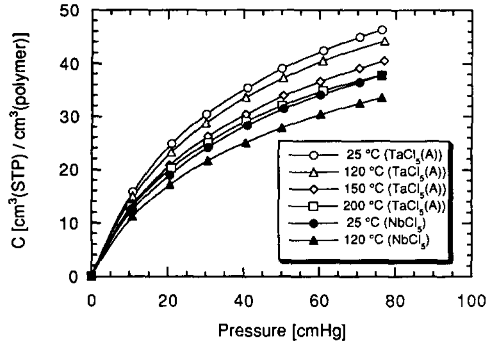

Fig. 6. Sorption isotherms for propane in annealed PMSP membranes synthesized with $TaCl_5$(A) and $NbCl_5$ at 35°C. Condition: annealed in nitrogen at 1 atm for 1 h at 120, 150 and 200°C. Thickness: about 400 μm.

of most glassy polymers required a long annealing time [35,36,40,41,43]. On the contrary, in this case, only a 1-h annealing affected the permeability and solubility. This indicates that a nonequilibrium state would be more unstable compared with most glassy polymers. These isotherms were concave to the pressure axis, the shapes of which are clearly observed in glassy polymers. As previously mentioned, these isotherms were analyzed using the dual-mode sorption model. The dual-mode sorption parameters were calculated using Eq. (1) and were plotted as a function of annealing temperature (Fig. 7a–c). Of these parameters, C_H' showed the largest change. The PMSP synthesized with $TaCl_5$(A) initially had a large C_H' when compared with $NbCl_5$. However, they both had the same aging behavior. With increasing annealing temperature, the C_H' decreased in the PMSP membranes synthesized with $TaCl_5$(A) and $NbCl_5$. A decrease in the C_H' means that the bulk of the thick membrane would be relaxed by annealing.

Under the conditions in the presence of vacuum pump oil vapor in a vacuum vessel at 30°C, the gas permeability of the PMSP membranes synthesized with $TaCl_5$ and $NbCl_5$ of about 400 μm thickness was not influenced over the period of 30 days. The gas permeability of the thin membranes synthesized with $TaCl_5$

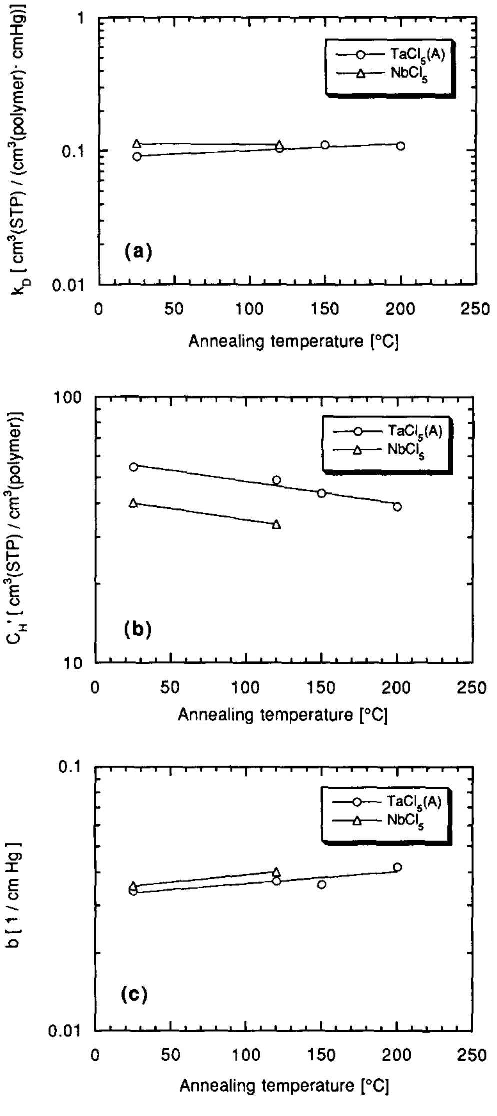

Fig. 7. Relationship between annealing temperature and the dual-mode sorption parameters of PMSP membranes synthesized with $TaCl_5$(A) and $NbCl_5$. Experimental data: Fig. 6. Dual-mode sorption parameters: (a) K_D, (b) C_H' and (c) b.

was dramatically reduced; however, a distinct reduction in the gas permeability in the membranes synthesized with $NbCl_5$ was not observed during that period. On the contrary, the annealing effects on the gas permeability in the thick PMSP membranes were the same in spite of the polymerization catalysts.

The movement of atoms would be inhibited at lower temperature. Using thin membranes synthesized with $TaCl_5$(A), the effects of cooling on the aging of the gas permeability were investigated. A membrane was taken out of methanol, dried using filter paper, and without pre-vacuum, stored in liquid nitrogen (ca. − 196°C), in a freezer (ca. − 10°C) and at 25°C for 24 h. The membrane was placed into the gas permeation and sorption apparatuses, and the permeability was measured at 30°C between 12 and 18 h after cooling.

Fig. 8 shows the effect of storage temperature on the gas permeability coefficients in the thin PMSP membranes. Storage under the cooling conditions delayed the reduction in the gas permeabilities. In terms of a change in the sorption capacity of the PMSPs, the sorption for propane was measured and is shown in Fig. 9. The sorption isotherm of the PMSP membrane stored in liquid nitrogen for 24 h had a similar concave shape as observed in Fig. 4. The sorption concentration of propane of this membrane was larger than that of the PMSP membrane stored at 25°C for 24 h. This means that a decrease in the unrelaxed volume would be inhibited by cooling.

As shown in Fig. 2, the thickness dependence of the gas permeability in the PMSP membrane synthesized with $TaCl_5$(A) indicated that the permeability of the thin membrane was reduced before the initial permeability was measured, i.e. during storage under vacuum, or the initial free volume of the thin membrane was essentially smaller than that of the thick membrane. Based on these results, the former case should be reasonable. However, the initial permeability after storage in liquid nitrogen was smaller than that of the thick membrane; therefore, the combination of both cases should give the thickness dependence.

In addition, CO_2-conditioning would affect the glassy state of the PMSP membrane. The PMSP membranes synthesized with $TaCl_5$(A) having about a 70 μm thickness were exposed to carbon dioxide at 40 atm for 24 h at 30°C. As shown in Fig. 10, the gas permeabilities in the conditioned membrane were higher than those of the membranes stored in carbon dioxide at less

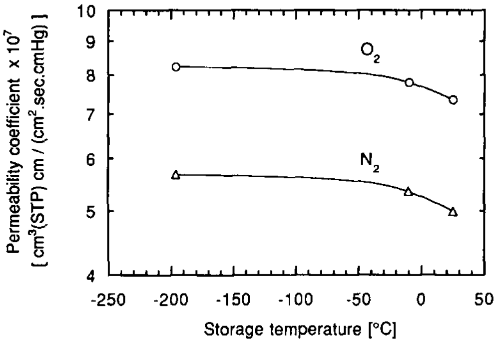

Fig. 8. Effect of storage temperature on the permeability coefficients for oxygen and nitrogen in PMSP membranes at 30°C. Conditions: stored for 24 h at 25°C, ca. − 10°C (in a freezer) and − 196°C (in liquid nitrogen). Thickness: about 70 μm. Catalyst: $TaCl_5$(A).

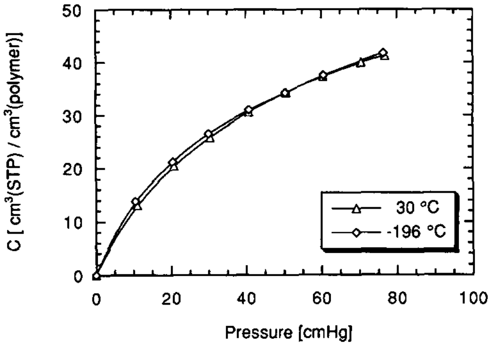

Fig. 9. Sorption isotherms for propane in stored PMSP membranes at 35°C. Conditions: stored in liquid nitrogen for 24 h (◇) and in carbon dioxide for 24 h at 30°C (△). Thickness: about 70 μm. Catalyst: $TaCl_5$(A).

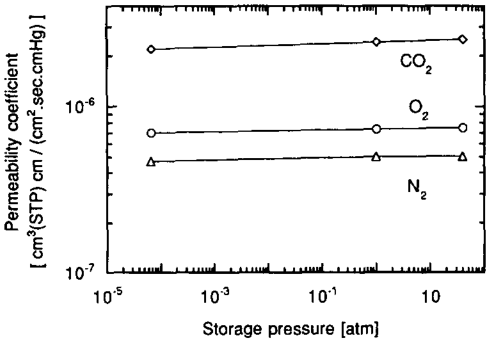

Fig. 10. Effect of CO_2-exposed pressure on the permeability coefficients for oxygen, nitrogen and carbon dioxide in PMSP membranes at 30°C. Conditions: exposed to carbon dioxide for 24 h at 30°C. Thickness: about 70 μm. Catalyst: $TaCl_5$(A).

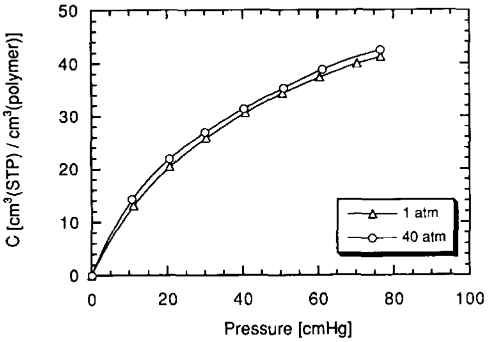

Fig. 11. Sorption isotherms for propane in CO_2-exposed PMSP membranes at 35°C. Conditions: exposed to carbon dioxide at 40 atm (○) and 1 atm (△) for 24 h at 30°C. Thickness: about 70 μm. Catalyst: $TaCl_5$(A).

than 1 atm. Polymers are swollen by the conditioning and the free volume increases. Fig. 11 shows the sorption isotherms for propane in the thin PMSP membranes. These membranes were conditioned under the same conditions shown in Fig. 10. After CO_2-conditioning, the sorption concentration of the membrane increased. However, the changes in the gas permeability and solubility were small compared with those of other glassy polymers [35–39]. Both the gas permeability and solubility were also smaller than those of the thick membrane. Therefore, this indicates that the thin PMSP membrane should be reduced before the initial measurements, although the membrane would be swollen by conditioning.

4. Conclusions

We systematically studied the effects of aging on the gas permeability and solubility in the PMSP membranes synthesized with various catalysts. The aging system of the gas permeability and solubility in the PMSP membrane was based on relaxation of the unrelaxed volume in the absence of a large amount of contaminants. Annealing effects on the gas permeability and solubility in the PMSP membranes synthesized with various catalysts were the same.

However, a difference in the aging of the PMSPs synthesized with $TaCl_5$ and $NbCl_5$ was observed during storage under vacuum in the presence of a very small amount of vacuum pump oil vapor at 30°C. The difference may be due to a difference in the glassy state, which is probably dependent on the configuration of the as-cast PMSP membranes synthesized with various catalysts because the conditions were the same except for the configuration. The thickness dependence of the aging was observed. This was probably due to a diffusion effect of oil vapor; that is, oil vapor naturally diffuses from the surface to the center. Based on the effects of membrane thickness on the initial permeability and aging, the glassy state on the surface should be a dominant factor during aging in the presence of a very small amount of vacuum pump oil vapor.

The annealing energy for relaxation of the unrelaxed volume would hide the difference in the glassy state of the as-cast membranes because the aging behavior of the gas permeability and solubility were the same in the thick membranes synthesized with $TaCl_5$ and $NbCl_5$.

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