Synthesis and Gas Permeability of Copoly (trimethylsilylpropyne-phenylpropyne) Membranes

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Copoly(trimethylsilylpropyne-phenylpropyne) membranes were prepared with TaCl$_5$ and Ph$_3$Bi in order to modify the deterioration of gas permeability of poly(trimethylsilylpropyne)(PMSP) membrane which is the highest pas permeability of all synthetic membranes. Before, preparing the copolymer, a homopolymer of phenylpropyne(PP) was prepared and the gas permeabilities were examined. Although they were about two orders of magnitude lower than those of PMSP membrane, the gas permeabilities of the copolymer membranes with 10 mol % PP was not influenced and was not deteriorated after thermal hysteresis. These results were discussed by moderate decrease of C$_H$' which is hole saturation constant of Langmuir domain of the membranes.

Introduction

Recently, much attention has been directed toward evaluating poly(1-trimethylsilylpropyne, PMSP, as a membrane because PMSP exhibits the highest gas permeability of all synthetic polymer membranes and is expected its potential utility in industrial applications such as separation of oxygen and nitrogen from the air. Moreover, PMSP also has unusual transport behavior [1-6].
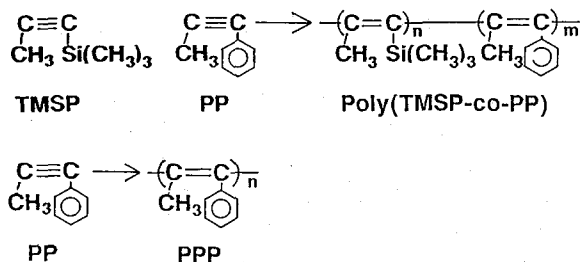
In general, membranes for industrial oxygen separation are required to have both high oxygen permeability, high separation factor and durability. Although PMSP has a high permeability coefficient to gases, the separation factor for O$_2$/N$_2$ as an example is the lowest and also the permeability coefficients decrease markedly with time and/or thermal hysteresis [4, 6]. Such unusual gas permeability may be due to the extraordinary large excess free volume, compared with other glassy polymers, which is a large capacity for sorbing vapors even at quite low vapor pressures, and also due to the collapse of micro voids in unrelaxed domains which may contain excess free volume in the form of pre-existing micro voids.

However, it is uncertain what the distribution of microvoids are and what particular micro void configurations influence the aging of PMSP membranes. The authors considered that the extraodinary large excess free volume results in large values of the dual mode

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parameter, namely C'_H which is denoted the hole saturation constant of Langmuir absorption, in the glassy polymer. As C'_H is reduced by some extent, the separation factors are typically improved and the durability of the membrane is also improved.

The objective of the present investigation is to improve separation factor and the durability without sacrificing the high permeability coefficients to gases by copolymerizing trimethylsilylpropyne, TMSP, with 1-phenylpropyne, PP. whose chemical structure resemble to TMSP.

$$C{\equiv}C \qquad C{\equiv}C \longrightarrow {-}(C{=}C)_n{-}{-}(C{=}C)_m$$
$$CH_3 \ Si(CH_3)_3 \quad CH_3 \bigcirc \qquad CH_3 \ Si(CH_3)_3 \ CH_3 \bigcirc$$

TMSP   **PP**   **Poly(TMSP-co-PP)**

$$C{\equiv}C \longrightarrow {-}(C{=}C)_n$$
$$CH_3 \bigcirc \qquad CH_3 \bigcirc$$

PP   **PPP**

Experimental

Polymerization and Polymer Characterization

Polymerization of 1-phenylpropyne (PP). The following is the standard polymerization conditions to obtain a polymer sample for the preparation of a membrane: According to Masuda's method [7], in a nitrogen atmosphere, $TaCl_5$ and n-Bu_4Sn (each of 0.02 M) were dissolved in 1.0 ℓ toluene and then PP (1.0 M) was added in this solution. Then, the polymerization was carried out at 80°C for about 24 hrs. The polymer thus obtained, were isolated by precipitation in a large amount of methanol, filtered and dried. Polymer, poly(1-phenylpropyne), PPP, yield was 80%.

Copolymerization of 1-trimethylsilylpropyne, TMSP, and PP. The almost identical method as the polymerization of PP was adopted [8]. The typical polymerization method for poly(TMSP-co-PP) (9:1) was as follows: In a nitrogen atmosphere, $TaCl_5$ (0.02 M) and and Ph_3Bi (0.02 M) were dissolved in toluene and then TMSP (0.80 M) and PP (0.20 M) were added. Polymerization was carried out at 70°C for about 24 hrs. The polymer isolated by precipitated was filtered and dried. Purification of the copolymer was carried out by dissolving the polymer into toluene, followed by reprecipitation. Copolymer yield was 85%. The molecular weight of these polymer and copolymers was determined by gel permeation chromatography using Tohsoh HLC-802UR and found to be about 900,000. The chemical structure of PPP and poly(TMSP-co-PP) was determined by FT-IR Perkin Elmer 1800 and ^1H NMR and ^{13}C NMR using JEOL FT-NMR-GSX270 (270MH$_Z$).

Measurement of sorption isotherm and gas permeability

Sorption of propane in a polymer at 35°C was measured by a gravimetric technique using quartz spring. The detailed discussions of the method of measurement and calculation of sorbed amount have been published elsewhere [5].

The experimental method of gas permeability used in this study was an adaptation of the high vacuum gas transmission technique with an MKS Baratron Model 310BHS-100S pressure transducer [4]. The general theory of gas transport in polymers and detailed discussions of the methods of measurement and calculation of the permeability, diffusion and solubility coefficients have also been published in elsewhere [9].

Results and Discussion

Confirmation of structure of poly(1-trimethylsilylpropyne-co-1-phenylpropyne, poly(TMSP-co-PP)

The chemical structure of PPP and poly(TMSP-co-PP) are suggested by a broad absorption spectra of ^{1}H NMR for polymers to be mixture of cis-transoidal or trans-cisoidal and trans-transoidal structures. The steric hindrance of a large trimethylsilyl group inhibits the cis-cisoidal configuration of the polymer [10].

Chemical structures of PPP and poly(TMSP-co-PP)

Fig. 1 shows the comparison between ^{1}H NMR spectra of PMSP and that of poly(TMSP-co-PP) and also that of PPP as a reference sample. About 0.1 ppm in the spectra shows hydrogen in trimethylsilylpropyne, and near 2 ppm peak shows the hydrogen in methyl group. Also, about 7 ppm spectrum shows the hydrogen in phenyl group which is present in the copolymer.
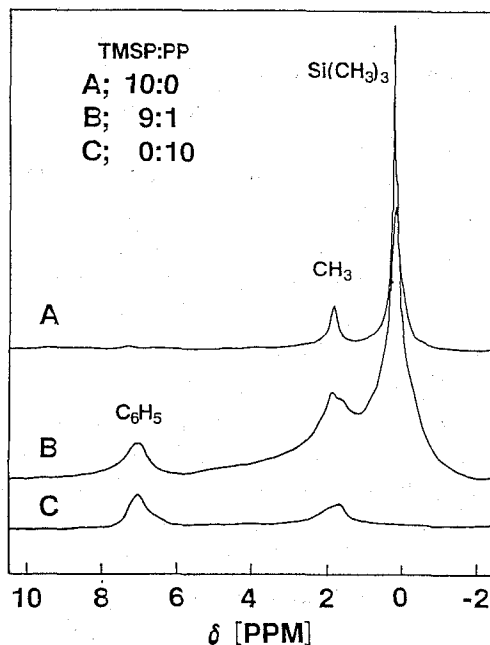

Fig. 1. ^{1}H NMR spectra of PMSP, poly(TMSP-co-PP) (9:1) and PPP.

Stability of permeability coefficients of PPP

In the case of very thin PMSP membranes, remarkable reduction of gas permeability was observed after repeating the thermal treatment at 75°C for 24 hrs, between measurement intervals. The same experimental conditions as PMSP membranes was adopted for the evaluation of thermal stability.

Comparing the thin PMSP membrane, the permeability coefficients for various gases in PPP did not decrease as shown in Figs. 2, 3. In order to make the transport properties
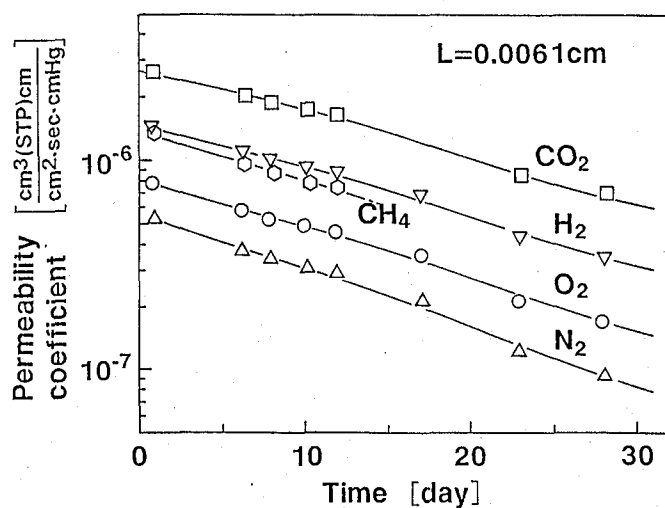

Fig. 3. Effect of thermal hysteresis on gas permeability of PPP membrane at 30°C. Heat treatment was carried out at 75°C under vacuum between measurements.
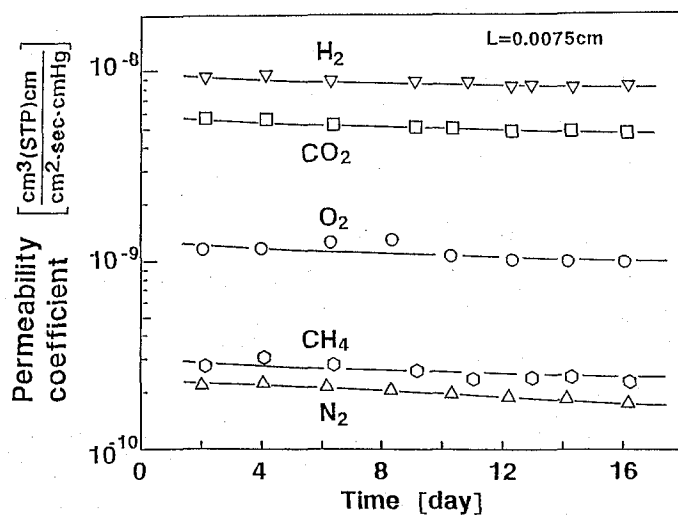

Fig. 2. Deterioration of gas permeability of PMSP membrane kept in vacuum vessel at 30°C.

Table 1. Permeability(P), Diffusivity(D), Solubility(S) at 30°C, apparent activation energies for permeation(E_P), Diffusion(E_D), heat of solution (ΔH) and separation factor of PPP

Gas	$P^{*1} \times 10^{10}$	$D^{*2} \times 10^8$	$S^{*3} \times 10^2$	E_P^{*4}	E_D^{*4}	ΔH^{*4}
H_2	117.7	1540	0.077	1.97	—	—
O_2	16.5	18.0	0.916	1.74	5.16	−3.42
N_2	3.51	4.03	0.873	2.73	6.40	−3.67
CO_2	88.6	9.92	8.93	−0.30	4.83	−5.13
CH_4	5.24	1.76	2.98	3.54	6.66	−3.12
C_2H_6	3.87	0.13	30.2	4.05	8.47	−4.42
$P(O_2)/P(N_2)$	4.70					
$P(H_2)/P(N_2)$	33.5					
$P(CO_2)/P(CH_4)$	16.9					

*1: cm^3 (STP)·cm/cm^2·sec·cmHg   *2: cm^2/sec
*3: cm^3 (STP)/cm^3 (polymer)·cmHg.   *4: Kcal/mol

clear, the coefficients of permeability, diffusivity and solubility are shown in Table 1. The oxygen permeability of poly(1-phenylpropyne) is 16.5 Barrer and the ideal separation factor for oxygen/nitrogen is 4.7. The permeability coefficient of oxygen is about two orders of magnitude lower than that of PMSP. The lower permeability coefficients are presumably mainly due to the low diffusivity by stacking effect of phenyl groups as a side chain group.

The sorption isotherms for propane in PMSP and PPP at 35°C are shown in Fig. 4. These curves are concave to the pressure axis and could be representative of dual-mode sorption [11]. The parameters are calculated by using the following equation and summarized in Table 2.
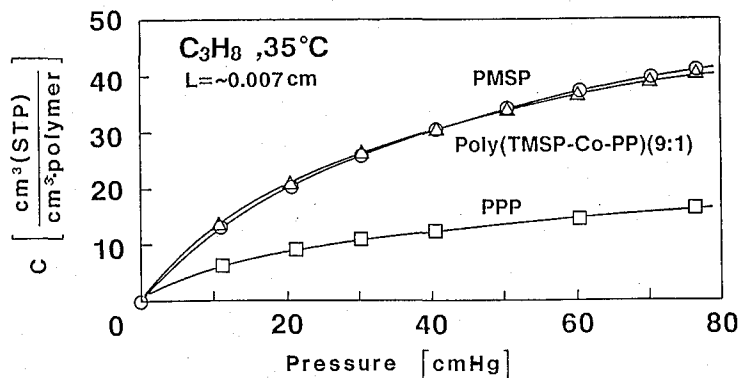
$$C = K_D P + \frac{C_H{}'bp}{1+bp}$$

Fig. 4. Sorption isotherm for C_3H_8 in PMSP, poly(TMSP-co-PP) (9:1) and PPP membranes.

Table 2. Dual-mode sorption parameters for C_3H_8 in PMSP, PPP and their copolymers at 30°C

TMSP : PP	K_D [*1]	C'_H [*2]	b [*3]
10 : 0	0.0912	50.14	0.0283
9 : 1	0.1099	43.59	0.0365
0 : 10	0.0769	12.47	0.0722

[*1] cm^3 (STP)/cm^3 polymer·cmHg
[*2] cm^3 (STP)/cm^3 polymer
[*3] 1/cmHg

C'_H value for propane in PPP membrane is very small compared with that of PMSP, where-as the b value is about 3 times larger than that of PMSP, in spite of the same level of the solubility coefficient, K_D, as PMSP, and also the higher separation factor for oxygen/nitrogen, 4.70. These values are comparable to those of poly(4-methylpentene-1) which has been used in membrane type oxygen enrichment apparatus for medical use. The high solubility coefficient in ambient temperature decreased with increasing temperature, however, the activation energy for diffusion is high. Therefore, the balancing effect of those opposing temperature dependencies results in an activation energy for permeation which is also positive except for the permeation of CO_2. These are quite unique phenomena exhibited by the PMSP membrane. The model of Meares suggest that the activation energy is expressed as follows [12]:

$$E_D = \lambda (CED) \frac{1}{4} d^2$$

where CED is cohesive energy density between the segments, λ is a jump distance for a penetrant to jump in diffusion process, and d is the diameter of a cylindrical diffusion zone. The high D value means that interaction between polymer segments is high. These results suggest that even if the backbone chain is rigid, the interaction between phenyl group in the different neighbor main chains occurs and at the same time, the absorption of oily vapor materials from the surrounding vapor space also reduced like other glassy polymers, thereby improving the durability of PPP.

The permeability and durability of poly(TMSP-co-PP) membrane

Copolymers of TMSP, which forms a very high gas permeable membrane and 1-phenyl-propyne, which forms a lower gas permeable membrane but excellent durability, would be expected to give membranes with higher gas permeability and durability.

The sorption isotherm for propane in poly(TMSP-co-PP) (9:1) membrane was also shown in Fig. 4. C'_H, b and K_D are shown in Table 2. The C'_H of copolymer reduced about 13 % from the initial value of PMSP. The gas permeability coefficients of various gases are listed in Table 3. The data in Table 3 show that the permeability is reduced by

Table 3. Comparison of permeability coefficient of PMSP, poly(TMSP-co-PP) and PPP membranes to gases at 30°C

MSP : PP	$P \times 10^{10}$ [cm^3 (STP)·cm/cm^2·sec·cmHg]				
(mol %)	H$_2$	O$_2$	N$_2$	CO$_2$	CH$_4$
10 : 0	13900	7850	5510	28100	12980
9 : 1	9490	5230	3140	17400	6760
6 : 4	605	438	153	874	802
0 : 10	118	17	4	89	5

approximately 30-40 %. At the moment, it is impossible to calculate the size of the micro voids, which formed in PMSP and poly (TMSP-co-PP) (9:1), however, it can be estimated that small size of micro voids is very hard to form, because the activation energy for diffusion of oxygen and carbon dioxide is almost the same as those of PMSP membrane. The gas permeability coefficients of poly(TMSP-co-PP) (6:4) are remarkably reduced, and E_D is increased two times. The additional phenylpropyne inhibits the formation of large micro voids, and therefore, the permeability coefficients reduced drastically and the separation factor increased from 1.2 to 3.5. The permeability coefficient of oxygen (153 Barrer) is about one fourth the value of poly(dimethylsiloxane) but the separation factor is much higher.

The durability of poly(TMSP-co-PP)

As has been mentioned, the thin PMSP membranes, with thickness less than 60 μm, are well known to deteriorate with time by keeping them in the air and/or vacuum. Therefore, the same thickness of the co-polymer membrane were examined. The results are shown in Fig. 5. This figure shows that the gas permeability coefficients were stabilized by
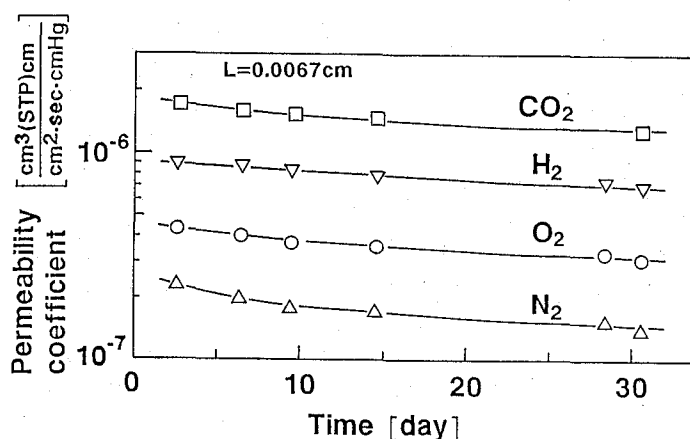

Fig. 5. Durability of gas permeability of poly(TMSP-co-PP) (9:1) membrane kept in vacuum vessel at 30°C.
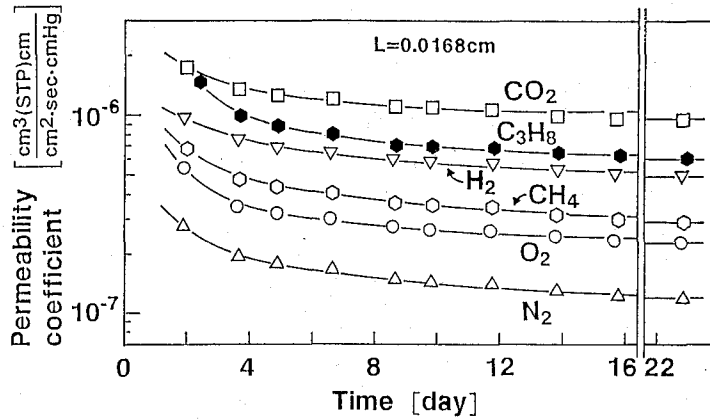
Fig. 6. Effect of thermal hysteresis on gas permeability of poly(TMSP-co-PP) (9:1) membrane at 30°C. Heat treatment was carried out at 75°C under vacuum between measurements.
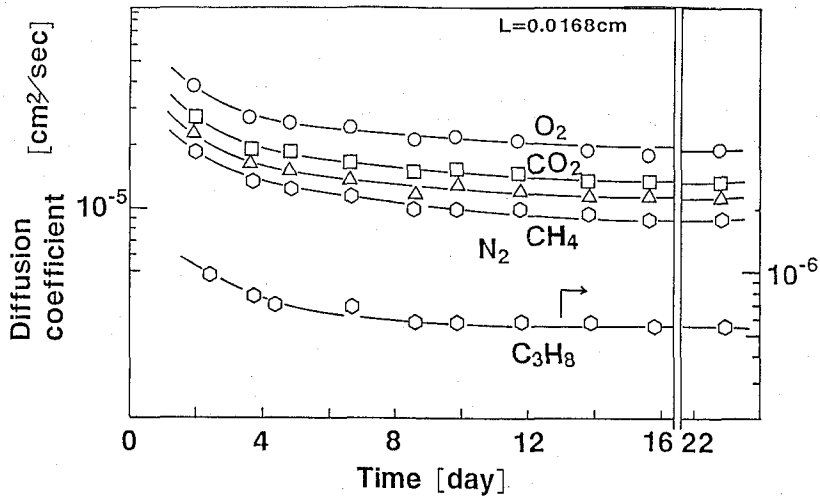

Fig. 7. Effect of thermal hysteresis on gas diffusivity of poly(TMSP-co-PP) (9:1) membrane at 30°C. Heat treatment was carried out at 75°C under vacuum between measurements.

addition of 10 mole % of phenylpropyne in the polymer. The markedly better results were obtained after the repeated thermal treatment at 75°C for 24 hrs as shown in Fig. 6. Both the permeability and the diffusivity were found to decrease within a first few days as shown in Figs. 6, 7. This time some deterioration might occur like collapsing of middle size of the micro voids.

Conclusions

The markedly deterioration of gas permeabilities of poly(1-tri-methylsilylpropyne) was improved without sacrificing the gas permeability by control of the C'_H with the addition of 1-phenylpropyne as a comonomer. The excess free volume including large micro voids in PMS P membrane reduced by stacking effect of phenyl groups between inter-segments in the copolymer membrane. About 10 mol % of 1-phenylpropyne is enough for stabilization of the gas permeability.

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