

# Effect of the Casting Solvent on the Free-Volume Characteristics and Gas Permeability of Poly[1-(trimethylsilyl)-1-propyne] Membranes

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**ABSTRACT:** The effect of the casting solvent on the structure of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membranes was investigated experimentally. The PTMSP membranes were cast from solutions of cyclohexane, toluene, and tetrahydrofuran; the membranes were characterized by the positron annihilation lifetime spectroscopy (PALS) technique and by gas-permeation measurements of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>. The decay curves from the positron annihilation lifetime spectroscopy gave the best fit when two long-life components ( $\tau_3$  and  $\tau_4$ ,  $\tau_3 < \tau_4$ ) were employed. This suggests that two types of free volume existed in the PTMSP mem-

branes. The size and number density of  $\tau_4$ , which was characteristic for PTMSP, decreased in the following order of the casting solvents: cyclohexane > toluene > tetrahydrofuran. The order was consistent with the order of gas permeability. A good correlation was observed between the permeability and the structural parameter that denoted the free-volume size and the number density of  $\tau_4$ . © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 497–501, 2003

**Key words:** gas permeation; structure–property relations; membranes; diffusion

## INTRODUCTION

One of the most important factors for a membrane-separation process is the proper design of the membrane structure so that a higher performance is obtained for target mixtures.<sup>1</sup> Two types of membrane structures should be considered: the physical structure and the chemical structure. The chemical structure means the chemical composition of the membrane material. For example, the membrane material should be chosen so that the affinity of the membrane to the targeted component would be maximized to obtain higher selectivity. The membrane materials would be modified by the introduction of functional groups to increase the affinity or to add a specific interaction through the formation of complexes. The physical structure includes the pore size distribution of porous membranes, such as ultrafiltration and nanofiltration membranes. The pore size distribution should be optimized so that the higher performance for these filtration membranes would be obtained. For nonporous membranes, including those for gas separation and pervaporation, it has been recognized that physical structures such as the free-volume size and polymer density play a significant roll in membrane-separation performance.

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) is known as a super-glassy polymer.<sup>2–4</sup> Although its glass-transition temperature is higher than 530 K, the permeability of gases through PTMSP membranes has been reported to be extremely high even in comparison with rubbery membranes such as polydimethyl siloxane (PDMS). The high permeability of PTMSP membranes can be attributed to their very large free volumes. It has been reported, however, that the high permeability is significantly reduced by the long-term use of gas permeation. Such an aging process indicates that the free volume may not be an intrinsic property of PDMS but rather can be changed by several external conditions. On the contrary, the free-volume characteristics can be controlled to obtain proper membrane-separation performances through changes in the operational parameters in the membrane preparation process. The parameters may include the solvent for the casting solution or the solvent evaporation conditions, such as the evaporation temperature and duration. However, the effect of fabrication conditions on PTMSP membranes has not been fully investigated yet. For practical applications, it is essential to understand the consequences of membrane fabrication conditions, such as the effect of solvent selection on the physical structure of PTMSP membranes.

In this study, PTMSP membranes were prepared from casting solutions of different solvents, and the effects of the casting solvents on the physical structures of the membranes were elucidated through positron annihilation lifetime spectroscopy (PALS). The free-volume distribution of the membranes was

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characterized with the PALS technique.<sup>5</sup> The free-volume distribution obtained by the PALS technique was correlated with the gas-permeation performance through the membranes.

## EXPERIMENTAL

### Membrane preparation

1-Trimethylsilyl-1-propyne (TMSP) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Tantalum pentachloride ( $\text{TaCl}_5$ ; 99.9%) was purchased from Aldrich (Milwaukee, WI). Toluene, cyclohexane, and tetrahydrofuran (THF) were purchased from Wako Chemical Co. (Osaka, Japan). All the chemicals were used without further treatment or purification.

The polymerization of TMSP was carried out with a procedure that was essentially the same as that of Masuda et al.<sup>2</sup> with minor modifications. TMSP (25 mL) was dissolved in 40 mL of toluene in a round-bottom flask under a nitrogen atmosphere at room temperature. The solution was then heated to 353 K. The catalyst solution was prepared in a separate flask (1105.7 mg of  $\text{TaCl}_5$  in 500 mL of toluene). The polymerization was started by the addition of the TMSP solution to the catalyst solution with a syringe at 353 K. After a given time of polymerization, the solution was diluted with toluene (ca. 2 L), and the polymer was precipitated by dropwise addition of the solution into methanol. The precipitated polymer was allowed to stand overnight, was filtered off, was washed with methanol, and was dried to a constant weight.

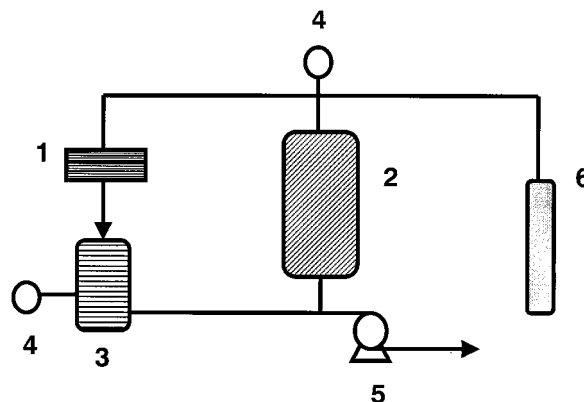
The membrane casting was carried out on a Teflon mold from a casting solution of the polymer. The solvents used for casting in this study were toluene, THF, and cyclohexane. The concentration of the polymer was fixed at 0.54 wt % for all the solvents. The solvents were allowed to evaporate at room temperature under a nitrogen flow in a glove box.

### Membrane characterization

For the membrane-structure characterization, the PALS technique was used. The permeation performance was measured with a single gas-permeation experiment.

### PALS technique

PALS measurements were carried out with an automated EG&G Ortec (Oak Ridge, TN) fast-fast coincidence system with a  $^{22}\text{Na}$  resolution of 0.25 ns. Before the measurements, the equipment and samples were thermally stabilized at  $295 \pm 0.5$  K. The  $^{22}\text{NaCl}$  source was a 2-mm-diameter spot source of 25  $\mu\text{Ci}$  sandwiched between two 2.54-mm titanium foil sheets. Data were collected in air at 295 K on membrane



**Figure 1** Schematic drawing of the gas-permeation experimental apparatus: (1) membrane cell, (2) gas reservoir of the upstream side, (3) gas reservoir of the downstream side, (4) pressure gauge, and (5) rotary vacuum pump.

samples stacked up to a 10-mm thickness, and they were analyzed with the PFPOSIT-88 program. The shortest lifetime component was fixed at 0.125 ns, which was characteristic of *o*-positronium self-annihilation. The equipment was calibrated with 99.99% pure annealed and chemically polished aluminum samples and was confirmed to give two lifetimes (0.166 ns, 98.6%, and 0.474 ns, 1.4%) by the best fit. A source correction was not used in the analysis. The peak counts (30,000) were collected for each sample, and the error bars were determined by population standard deviations of the results. Each spectrum took approximately 2 h to collect. The lifetime parameters reported in this study are the averages of at least 10 measurements.

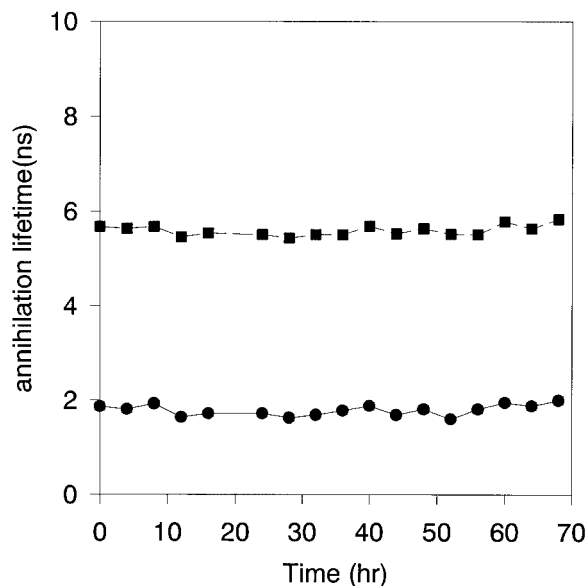
### Permeability measurements

The permeability measurements were carried out with a device designed according to ASTM Standard 1434 D (Rika-Seiki Co.). Figure 1 shows a schematic diagram for the experimental apparatus. The membrane was mounted in a stainless steel cell 48 mm in diameter. The downstream side of the membrane was evacuated before the measurements, whereas the pressure of the upstream side was fixed at 1 bar during the experiments. Only steady-state flux measurements were employed in this study because the lag time for the permeation was too short on account of the extremely large permeability of PTMSP membranes.

## RESULTS AND DISCUSSIONS

### PALS

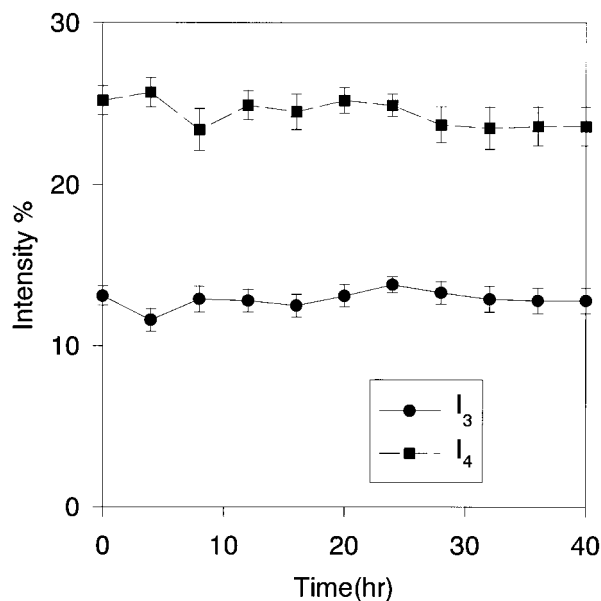
Two types of longer lifetime components were obtained from the fitting of the decay curves for the PTMSP membranes. We label the components,  $\tau_3$  for the shorter one and  $\tau_4$  for the longer one, according to



**Figure 2** Annihilation lifetimes for PTMSP membranes cast from toluene solutions.

Yampol'skii et al.<sup>6</sup> Figure 2 shows a time profile of the annihilation lifetimes up to 70 h for the PTMSP membranes cast from toluene. The observed lifetimes were almost unchanged during the measurements. Figure 3 shows the time course of the annihilation intensity for each annihilation lifetime for the membranes cast from toluene solutions. The lifetime fluctuated slightly with time, and the average intensity  $I_3$  for the shorter lifetime  $\tau_3$  was smaller than that for the longer lifetime,  $I_4$  for  $\tau_4$ .

The results for the PALS measurements of PTMSP membranes cast from solutions with different solvents



**Figure 3** Intensity of annihilation spectra for PTMSP membranes cast from toluene solutions.

**TABLE I**  
Lifetimes and Lifetime Intensities of PALS for PTMSP Membranes Cast from Different Solvents

Solvent	$\tau_3$ (ns)	$I_3$ (%)	$\tau_4$ (ns)	$I_4$ (%)
Cyclohexane	$2.04 \pm 0.08$	$11.0 \pm 0.2$	$6.23 \pm 0.08$	$28.8 \pm 0.3$
Toluene	$1.82 \pm 0.24$	$12.1 \pm 0.3$	$5.93 \pm 0.08$	$24.7 \pm 0.4$
THF	$2.05 \pm 0.20$	$15.1 \pm 1.0$	$5.18 \pm 0.08$	$14.7 \pm 0.8$

are summarized in Table I. For the shorter lifetime components,  $\tau_3$ , the membranes cast from solutions of cyclohexane had almost the same value as those membranes cast from THF. The membranes from toluene had a slightly smaller value, but it was within the experimental error. Therefore, the value of  $\tau_3$  would be practically unaffected by the casting solvent. The intensity corresponding to the shorter lifetime,  $I_3$ , increased in the following order of the solvents: cyclohexane < toluene < THF. However, the value of the longer lifetime component,  $\tau_4$ , depended more strongly on the casting solvent. The membranes cast from THF solutions had the shortest  $\tau_4$ , and the membranes from cyclohexane solutions had the longest  $\tau_4$ . The corresponding intensity,  $I_4$ , decreased in the same order as the lifetime (cyclohexane > toluene > THF).

This bimodal lifetime indicates that two types of free volume with different sizes existed in the PTMSP membranes; both components could be interpreted to correspond to the pickoff process of *o*-positronium in the free volume of the polymer. The longer lifetime suggests a larger free volume, and the larger intensity indicates a larger number density of the free volume. The bimodal long-living components for PALS were also reported by Yampol'skii et al.<sup>6</sup> for PTMSP membranes ( $\tau_3 = 2468$  ps and  $\tau_4 = 6668$  ps for fresh membranes). They found that the longer component was characteristic for PTMSP membranes. They also found that the intensity and lifetime of the longer component decreased during the aging process, whereas the intensity of the shorter component increased with aging,<sup>7</sup> and they suggested that the relatively larger free volume in PTMSP would be reduced in both size and number density by aging. In this case, the lifetime and the intensity of the longer component,  $\tau_4$ , decreased with the following order of the casting solvents: cyclohexane > toluene > THF. This result suggests that the size and number density of the larger free volume decreased in this order. However, the intensity of the shorter component,  $\tau_3$ , decreased in the reverse order, cyclohexane < toluene < THF, whereas the lifetime was almost unaffected by the choice of the solvent. This result suggests that the number density of the smaller free volume also decreased in the aforementioned order, but the size was unaffected by the casting solvent. Therefore, the free-volume size distribution of PTMSP membranes could be changed by changes in the casting solvent. The

effect would be similar to that from the aging of PTMSP membranes. In other words, PTMSP membranes cast from THF would be more aged than those cast from cyclohexane solutions.

### Gas permeability

The results for the gas-permeation experiments are summarized in Table II. The permeability of all the components (oxygen, nitrogen, and carbon dioxide) studied through the membranes decreased in the following order of the casting solvents; cyclohexane > toluene > THF. The oxygen permeability through the membranes cast from cyclohexane solutions was almost 5 times larger than that for membranes from THF solutions. The separation factor of oxygen over nitrogen was not affected very much by the casting solvent.

The order of the permeability among the membranes cast from the different solvents agreed with the orders of the longer component,  $\tau_4$ , obtained by the PALS measurements. In addition, the order of the corresponding intensity,  $I_4$ , was consistent with the order of the permeability. However, the intensity of the shorter lifetime,  $\tau_3$ ,  $I_3$ , was opposite to the order of the permeability. Because the longer component of the lifetime could be considered the characteristic component for the PTMSP membranes, and because of the larger size and number density, the free volume corresponding to  $\tau_4$  would be the dominant path for the permeation through the PTMSP membranes. To elucidate this structure-performance correlation, we conducted the following analysis on the basis of a quantitative treatment.

### Correlation between the gas permeability and the annihilation lifetime

Nakanishi and Jean<sup>8</sup> derived a relationship between the cavity size (assuming a spherical shape potential and the positronium lifetime without free volume being 0.5 ns), in polymeric materials and the lifetime of positronium,  $\tau$ , as follows:

$$\tau \text{ (ns)} = \frac{1}{2} \left\{ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \frac{2\pi R}{R_0} \right\}^{-1} \quad (1)$$

TABLE II  
Steady-State Gas Permeability for the PTMSP  
Membranes Cast from Different Solvents

Solvent	Oxygen <sup>a</sup>	Nitrogen <sup>a</sup>	Carbon dioxide <sup>a</sup>	Selectivity of O <sub>2</sub> /N <sub>2</sub>
Cyclohexane	2.34	1.56	7.02	1.49
Toluene	1.46	1.03	3.81	1.42
THF	0.446	0.299	2.08	1.49

<sup>a</sup> cm<sup>3</sup> STP cm/cm<sup>2</sup>s cmHg.

TABLE III  
Size of the Free Volume Calculated Based  
on PALS Results

Solvent	$R_3$ (nm)	$R_4$ (nm)
Cyclohexane	0.286 ± 0.008	0.528 ± 0.002
Toluene	0.269 ± 0.023	0.516 ± 0.008
THF	0.290 ± 0.018	0.484 ± 0.016

where  $R$  is the radius of the spherical cavity and  $R_0$  is the modified radius:

$$R \text{ (nm)} = R_0 - 0.166 \quad (2)$$

The cavity radii calculated with eqs. (1) and (2) are tabulated in Table III for the membranes cast from different casting solvents. The cavity radii corresponding to the shorter lifetime,  $\tau_3$ , were 0.269–0.290 nm. The cavity radii for the longer lifetime,  $\tau_4$ , were 0.484–0.528 nm. The Lennard–Jones potential parameters,  $\sigma$ , which denoted the molecular radius, were 0.346 and 0.3698 nm<sup>9</sup> for oxygen and nitrogen, respectively. Therefore, it could be assumed that the permeation of gaseous molecules would take place mainly through the larger cavities in the PTMSP membranes.

In general, the permeation of gaseous molecules through the cavity can be interpreted with sorption-diffusion theory.<sup>1,3</sup> The permeability of gaseous molecules,  $P$ , would be given by the product of the diffusivity,  $D$ , and the solubility,  $S$ :

$$P = D \times S \quad (3)$$

The diffusivity of the molecule in the membrane would be given by eq. (4) according to the diffusion theory in free volume:

$$D = D_0 \exp\left(-\frac{B}{V_f}\right) \quad (4)$$

where  $B$  and  $D_0$  are constants depending on the membrane material and permeating species and  $V_f$  is the specific volume of the free volume per apparent volume of the membrane. The specific volume would be related to the cavity size by introduction of the factor  $\alpha$  and

$$V_f = \alpha IR^3 \quad (5)$$

where  $\alpha$  depends on the shape of the cavity. In eq. (5), the intensity is introduced to consider the number density of the free volume. However,  $S$  would be proportional to the specific volume of the free volume:

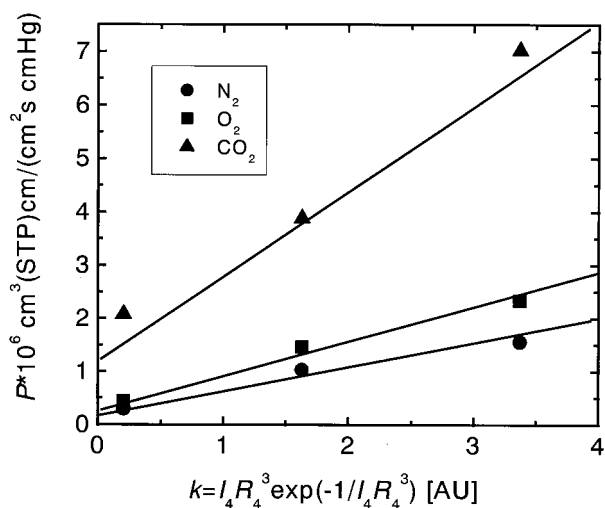
$$S = \beta' V_f = I \times \beta R^3 \quad (6)$$

where  $\beta$  is the shape parameter for sorption. The intensity of PALS is employed in eq. (6) because the sorption amount should depend on the total volume of the free volume as well as its size. From eqs. (4)–(6), the permeability is proportional to the product of  $R^3$  and the exponential of  $R^3$ .

$$P \propto I \times R^3 \exp(-1/IR^3) \quad (7)$$

In Figure 4, the experimentally obtained permeability is plotted versus the parameter  $k_4 = I_4 R_4^3 \exp(-1/I_4 R_4^3)$ . A linear relationship between the permeability and  $k_4$  was obtained for each component. However, the correlation line did not go through the origin, especially for  $\text{CO}_2$ . This was because permeation took place in the smaller free-volume sites denoted by  $\tau_3$ , and the plasticization effect was strong for  $\text{CO}_2$  so that the free-volume size increased when  $\text{CO}_2$  penetrated the polymer matrix.

The aforementioned results demonstrate that the solvent strongly affected the free volume of PTMSP membranes and, consequently, the permeation performance as well. These effects should be related to the properties of the solvents and the polymer. PTMSP is considered a highly hydrophobic polymer. Table IV summarizes the dielectric constants and dipole moments for the solvents used in this study.<sup>9</sup> Apparently, more polar solvents resulted in smaller permeability and smaller cavity sizes and densities. Because PTMSP is hydrophobic, less polar solvents would be better for



**Figure 4** Correlation between the free-volume parameter  $k$  and the permeability  $P$  through PTMSP membranes.

**TABLE IV**  
Properties of the Casting Solvents<sup>8</sup>

Solvent	Dielectric constant (-)	Dipole moment (D)
Cyclohexane	2.02	0
Toluene	2.57	0.45
THF	7.58	1.75

PTMSP. In a good solvent, the polymer chain is more relaxed, and in a poor solvent, the polymer chain has a coil structure that results in the larger cavity size. This trend agrees with the general polymer morphology in solution.

## CONCLUSIONS

The following conclusions can be drawn from this study:

1. The physical structure of PTMSP membranes, that is, the free-volume distribution, varies with the casting solvent. The use of a better solvent for PTMSP, such as cyclohexane, resulted in a larger size and number density of the free volume, whereas the use of a poor solvent such as THF resulted in a smaller size and number density.
2. The size and number density of the free volume obtained by the PALS technique was well correlated with the gas-permeability data through the membranes.

## References

1. Mulder, M. *Basic Principles of Membrane Technology*, 2nd ed.; Kluwer: Dordrecht, 1996; Chapter 4.
2. Masuda, T.; Isobe, E.; Higashimura T. *J Am Chem Soc* 1983, 105, 7473.
3. Masuda, T.; Isobe, E.; Higashimura, T. *Macromolecules* 1985, 18, 841.
4. Paul, D. R.; Yampol'skii, Y. P. *Polymeric Gas Separation Membranes*; CRC: Boca Raton, FL, 1994.
5. Wijmans, J. G.; Smolders, C. A. In *Synthetic Membranes: Science, Engineering and Application*; Bungay, P. M.; Lonsdale, H. K.; de Pinho, M. N., Eds.; NATO ASI Series C: Mathematical and Physical Sciences; NATO: Washington, DC, 1986; p 181.
6. Yampol'skii, Y. P.; Shantorovich, V. P.; Chernyakovskii, F. P.; Kornilov, A. I.; Plate, N. A. *J Appl Polym Sci* 1993, 47, 85.
7. Yampol'skii, Y. P.; Shishatskii, S. M.; Shantorovich, V. P.; Antipov, E. M.; Kuzmin, N. N.; Rykov, S. V.; Khodjaeva, V. L.; Plate, N. A. *J Appl Polym Sci* 1993, 48, 1935.
8. Nakanishi, H.; Jean, Y. C. *J Polym Sci Part B: Polym Phys* 1989, 27, 1419.
9. Dean, J. A. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: New York, 1992.