

# Structures and Gas Permeabilities of Poly(vinyl Chloride)/Oligo(dimethylsiloxane) Blend Membranes

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## Synopsis

A series of polymer blend membranes with several weight ratios of poly(vinyl chloride) (PVC) and oligo(dimethylsiloxane) (ODMS) were prepared and the permeation behaviors of O<sub>2</sub> and N<sub>2</sub> were studied. These components are only partially miscible to each other, leading to a phase separation. In order to improve the compatibility of these polymer blends, the use of a graft copolymer PVC-g-ODMS was explored. The gas permeation studies, the thermal analyses, and the microscopic observations were made on PVC-g-ODMS/ODMS blend membranes, and the results indicate that these blend membranes have rather high gas permeabilities together with good mechanical properties.

## INTRODUCTION

Gas separation processes by using membranes are attractive because of their low energy requirements, and many kinds of polymer membranes were prepared to obtain high gas permeabilities. The gas permeability of poly(dimethylsiloxane) (PDMS) (e.g., silicone rubber) has been reported to be very high,<sup>1</sup> but its permselectivity and mechanical strength are not enough for practical uses. Recently, Masuda et al. prepared a new silyl compound, of which the gas permeability is 10 times higher than that of ordinary silicone rubber.<sup>2</sup> But the permselectivity of O<sub>2</sub> to N<sub>2</sub> is low (1.7). To improve these situations, copolymerization techniques have been explored.<sup>3-8</sup> A typical example is a block copolymer of PDMS and polycarbonate,<sup>9-12</sup> which gives a thin film of about 15 nm thickness.<sup>13</sup> Until now some efforts have been aimed toward creation of a thin polymer membrane by blending a second polymer to PDMS.<sup>14</sup> The vinyl polymers have wide applications to prepare composite polymer materials,<sup>14-20</sup> because they can improve mechanical strengths of polymer blends. Some blend polymers are homogeneous, while others are inhomogeneous to form micro or macrodomain structures, depending on mutual compatibilities of components.<sup>21</sup>

In this investigation, poly(vinyl chloride) (PVC) was chosen as one component of blend polymers. PVC has been used frequently as one of the blenders,<sup>15-19</sup> but it is not used for mixing with PDMS because it is immiscible to PDMS. We could, however, obtain thin membranes in spite of a limited

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composition range when PDMS of low molecular weight (oligo(dimethylsiloxane) (ODMS) was blended with PVC. Moreover, poly(vinyl chloride)-g-oligo(dimethylsiloxane) (PVC-g-ODMS) was prepared and used instead of PVC in order to improve the compatibility of the blend polymers. The nitrogen and oxygen gas permeabilities of these blend membranes were measured and discussed in relation to the membrane structure.

## EXPERIMENTAL

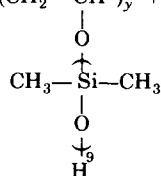
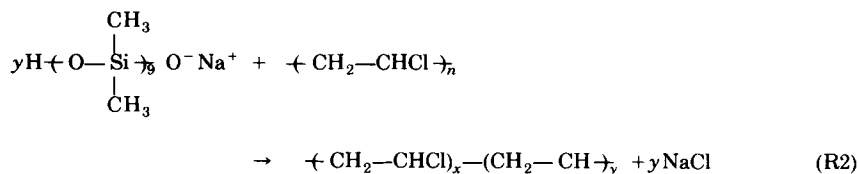
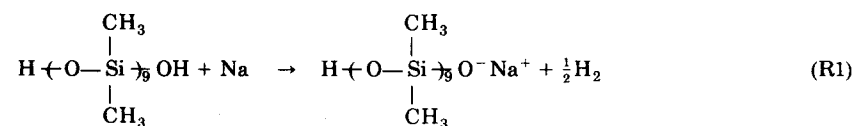
### Preparation of PVC/ODMS Blend Membranes

Poly(vinyl chloride) (degree of polymerization  $n = 1,100$ ) was obtained from Wako Chemicals and used without further purification. Oligo(dimethylsiloxane) ( $n = 9$ ) with silanol terminal groups was obtained from Petrarch Systems and used without further purification. The PVC/ODMS blend membranes were prepared by casting the mixed solutions of PVC and ODMS in tetrahydrofuran (THF) on glass plates. After preparation, the membranes were kept under vacuum at room temperature for two days to remove THF completely, and then were stripped off from the glass plates and kept in a desiccator. The weight ratios of PVC/ODMS in the blend membranes were 100/0, 90/10, 80/20, 75/25, 60/40, 50/50, 40/60, and 30/70, respectively. The membranes of 90/10, 80/20, 75/25, and 60/40 are translucent, and those of 50/50, and 40/60 are turbid and appear white. A THF solution of the ratio 30/70 gave also a turbid membrane but a thin oily film deposited on the surface of the glass plate was observed when the membrane was stripped off. All the membranes are asymmetric, and the glass side surface is smooth and glossy compared to the other side.

The vapor pressure of ODMS at 20°C is about 0.7 mmHg and ODMS in the membrane is apt to vaporize while the membranes are under vacuum. We dried the membranes for two days and checked the actual amount of ODMS in the membranes by proton nuclear magnetic resonance (NMR) measurements. From the integrated values of proton peaks assigned to  $-\text{CH}_2-$  (2.1, 2.3-ppm, doublet) of PVC and  $\text{CH}_3-$  (0 ppm; reference) of ODMS, the actual contents of ODMS were determined and are shown in Table I. These values were practically the same as the original values for the membranes

TABLE I  
ODMS Contents in the Blend Membranes

PVC/ODMS mixed	PVC/ODMS measured	PVC-g-ODMS/ODMS mixed	PVC-g-ODMS/ODMS measured
90/10	90/10	80/20	80/20
80/20	83/17	70/30	71/29
75/25	79/21	60/40	64/36
60/40	70/30	50/50	57/43
50/50	56/44	40/60	48/52
40/60	68/32	30/70	38/62



PVC-g-ODMS

Scheme 1

stored in a desiccator for two months, except for the case the membrane of 30/70. In the latter case, ODMS volatilizes continuously during keeping under vacuum or in a desiccator and, therefore, the actual content is not shown in Table I. All the samples were dissolved in deuterated THF and the spectra were obtained with a JEOL JNM-GX 270 FT NMR Spectrometer.

### Preparation of Graft Copolymer PVC-g-ODMS/ODMS

A solution of 70 g of ODMS, 50 mL of dry THF, and 1.15 g of sodium was placed into a 200 mL three-necked round-bottom flask with a reflux condenser and kept under nitrogen flow at 70°C. Hydrogen gas was evolved as the reaction proceeded. ODMS was reacted with sodium metal of one half the equivalent amount in order to obtain monosubstituted siloxane as a main product (Scheme 1). PVC, 30 g, was dissolved with mechanical stirring in 200 mL of dry THF, into which the solution containing monosubstituted siloxane was added drop by drop (about 1 drop/s) with a dropping funnel. The mixed solution was kept under stirring for 24 h at 50°C. All the treatments were done under nitrogen atmosphere. The colorless solution changed to a transparent pale yellow one. The product of the reaction was purified by reprecipitation in methanol, and then dried under vacuum at room temperature. The structure of the final product was confirmed by the proton NMR measurement on a deuterated THF solution. There appeared three peaks corresponding to  $-\text{CHCl}-$  (4.2 ~ 4.6 ppm; broad),  $-\text{CH}_2-$  (1.9 ~ 2.4 ppm; broad) and  $-\text{Si}(\text{CH}_3)_2$ , which is used as a reference (0 ppm). From the integrated values of these peaks, the reaction ratio was calculated to be 1/250. A gel permeation chromatography (GPC) measurement was done in order to confirm that the final product was not a mixture of PVC and ODMS but a graft copolymer. The low conversion might be due to large bulkiness of polymer chains surrounding the reacting center.

### Preparation of PVC-g-ODMS/ODMS Blend Membranes

The preparation of PVC-g-ODMS/ODMS blend membrane and the determination of exact contents of ODMS were carried out by a similar method as described in the foregoing section of the preparation of PVC/ODMS blend membranes. The weight ratios of PVC-g-ODMS/ODMS were 100/0, 80/20, 70/30, 60/40, 50/50, 40/60, and 30/70, respectively. The membrane of 100/0 is transparent, those of 80/20, 70/30, and 60/40 are translucent, and those of 50/50, 40/60, and 30/70 are white and turbid.

Trials to prepare blend membranes from ODMS with higher molecular weight ( $n = 20$  or larger) were in vain. In all cases liquid ODMS was separated from the membrane when its mixed solution with PVC or PVC-g-ODMS was dried on a glass plate. We could obtain uniform membranes only when ODMS of  $n = 9$  was used. Mechanical strengths of all the membranes were checked by stretching 5 mm  $\times$  50 mm strips of samples by hand. All the samples were strong enough to stand elongation to double length in one direction.

### Measurements of Gas Permeabilities

Permeabilities ( $P$ ) of oxygen and nitrogen gases were measured with a gas permeability apparatus (Rikaseiki K-315) of which the principle is to measure a pressure increase caused by permeation of gas through the membrane under a constant difference of pressure across the membrane.<sup>22</sup> The pressure difference was kept always at 760 mmHg unless otherwise mentioned.

### Calorimetric Measurements

Calorimetric measurements were performed by using a differential scanning calorimeter (Perkin-Elmer Model DSC-2). Approximately 20 mg of each sample was used and a heating rate was 20°C/min. The glass transition temperature  $T_g$  was determined as the temperature at which the heat capacity changes by one half of the total change associated to the transition.

### Observations with Electron Microscopy

The cross-sectional views of the blend membranes were observed with a scanning electron microscope (Akashi, ALPHA-30). The specimens were coated with Au to prevent electrical charging.

## RESULTS AND DISCUSSION

### Morphology of Membranes

All the blend membranes are translucent or turbid, and this implies the formation of phase separation structure in the membranes. Observations with a photomicroscope exhibit uniform dispersion of microphases in the membranes (Fig. 1).

Figures 2 and 3 show the cross-sectional views of PVC/ODMS and PVC-g-ODMS/ODMS blend membranes. There we can see many holes initially filled with ODMS, which evaporated during the coating of Au on the specimens under high vacuum. Comparison of photo series suggests that the phase

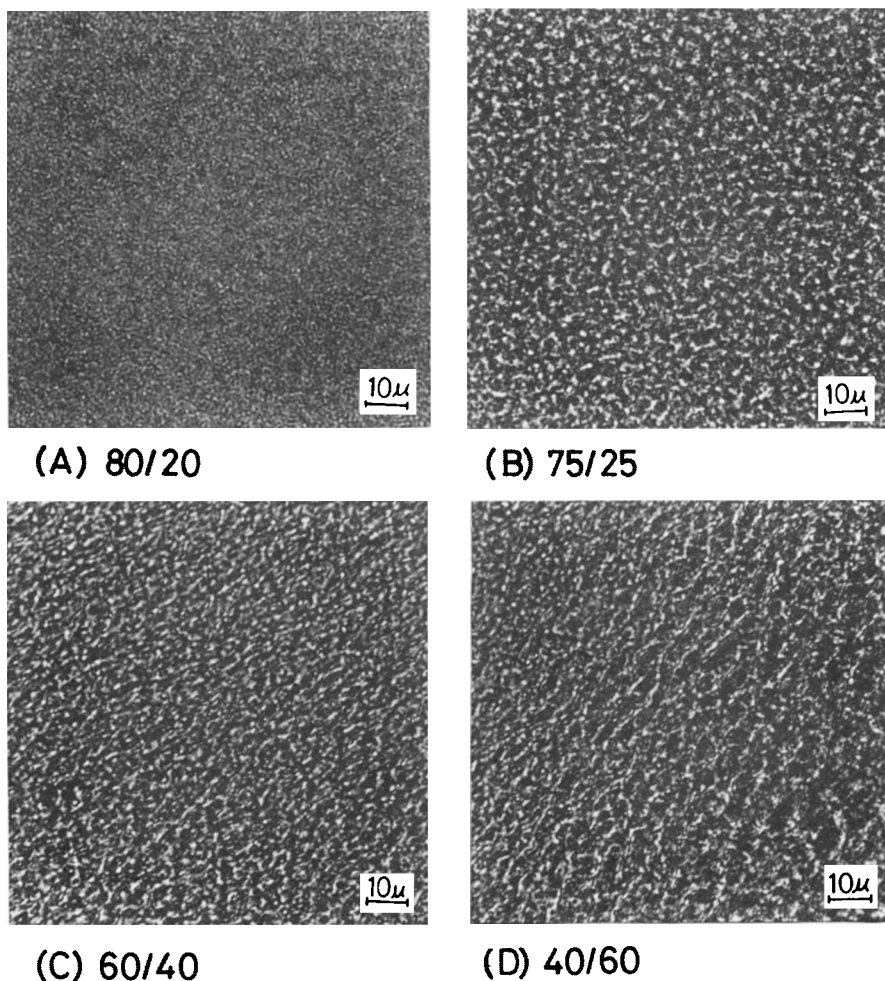
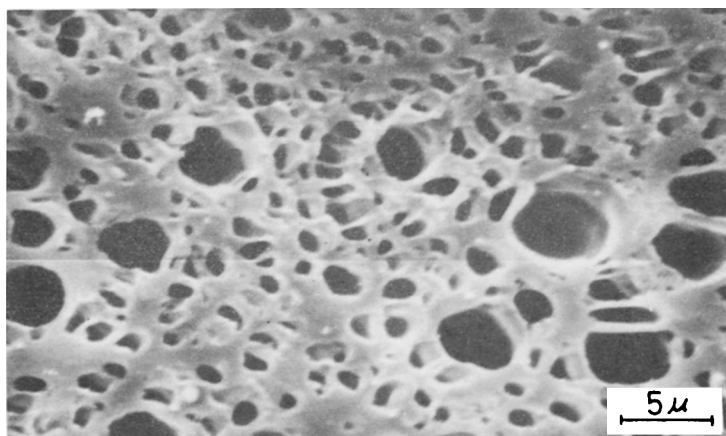
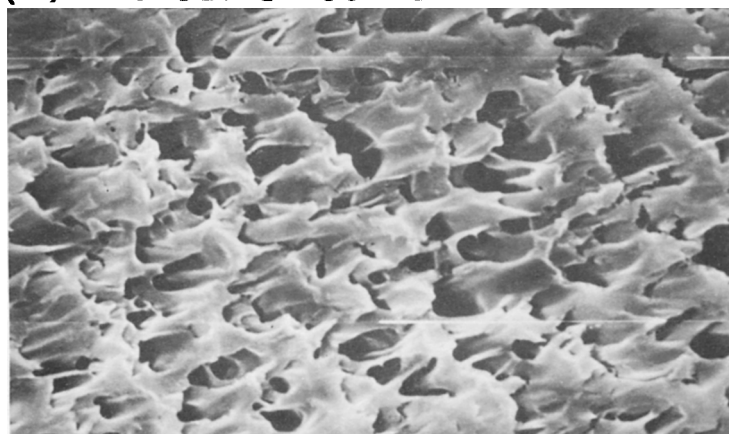


Fig. 1. Photomicroscopic views of the PVC/ODMS membranes.

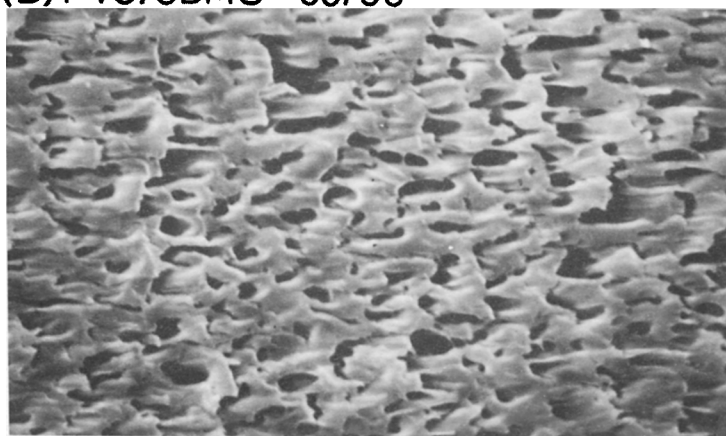
transition takes place more extensively as the content of ODMS increases. At lower contents of ODMS, PVC forms a continuous phase of matrix and microphases of ODMS are dispersed uniformly in the continuous phase. It seems that each phase of ODMS is isolated not to be interconnected; this suggests the phase separation takes place by the mechanism of nucleation and growth.<sup>23</sup> In both systems (PVC/ODMS and PVC-g-ODMS/ODMS systems), the ODMS microphase becomes interconnected when the content of ODMS increases beyond 50 wt% in the initial composition of blend systems. Then the blend polymer is formed of two continuous phases of PVC and ODMS; this implies that the phase separation takes place by spinodal decomposition.<sup>23</sup> A partially miscible binary system can decompose spontaneously into two phases. When the blend system is unstable, the composition of phase changes continuously during the phase separation; phase separation of this type is called a spinodal decomposition. On the other hand, when the blend system is metastable, the new phase begins to be formed from nuclei and their growth.<sup>24</sup>



(A) PVC/ODMS = 60/40

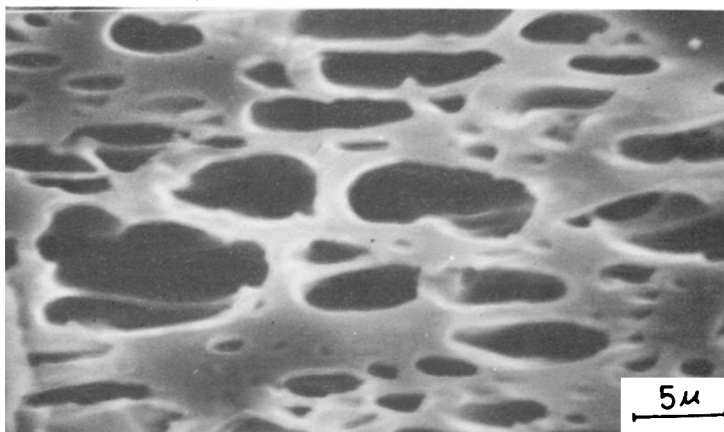


(B) PVC/ODMS = 50/50

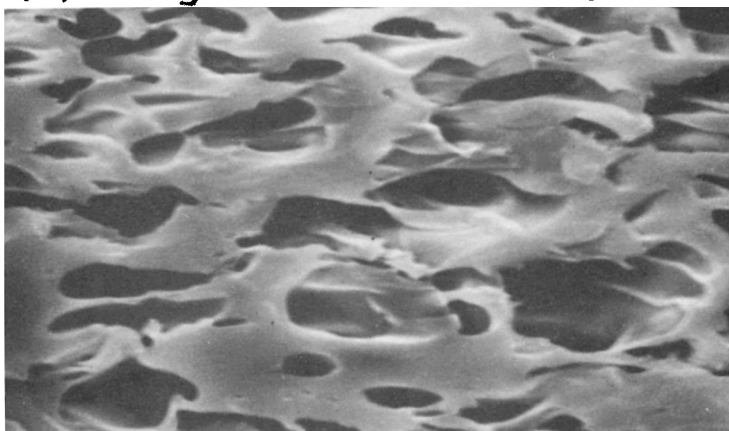


(C) PVC/ODMS = 40/60

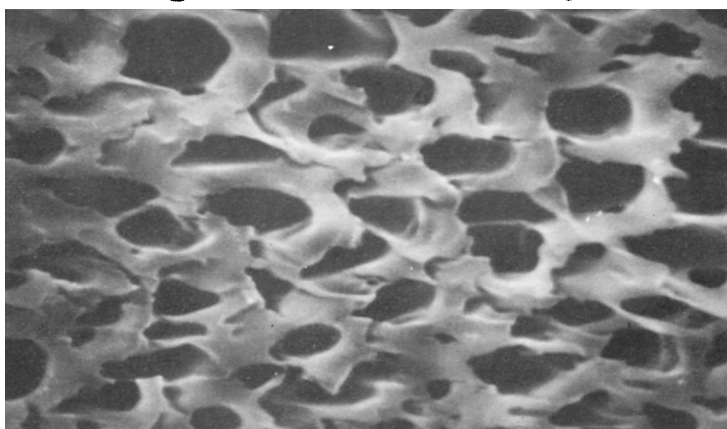
Fig. 2. Cross-sectional views of the PVC/ODMS membranes by SEM( $\times 3000$ ).



(D) PVC-g-ODMS/ODMS=60/40



(E) PVC-g-ODMS/ODMS=50/50



(F) PVC-g-ODMS/ODMS=40/60

Fig. 3. Cross-sectional views of the PVC-g-ODMS/ODMS membranes by SEM( $\times 3000$ ).

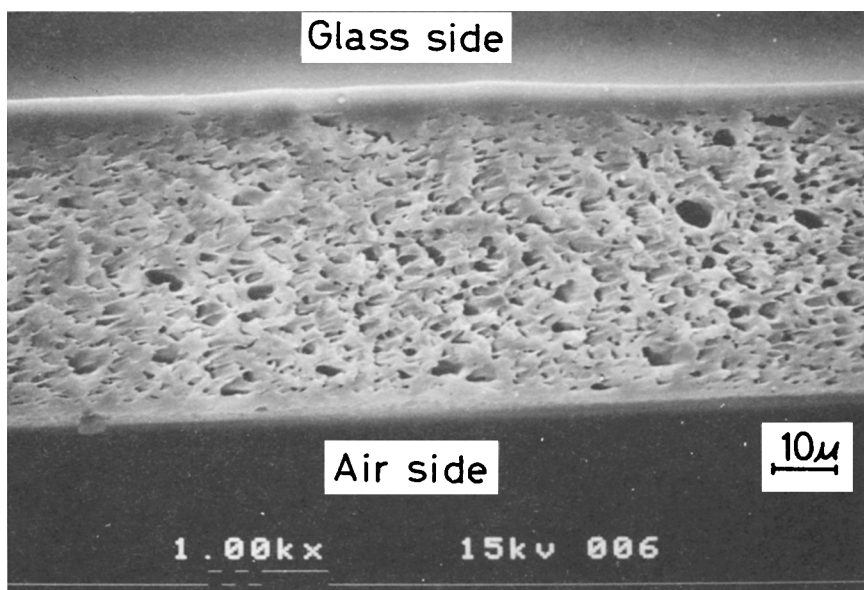


Fig. 4. Cross-sectional view of the membrane by SEM( $\times 1000$ ). PVC/ODMS = 50/50.

In the PVC/ODMS blend membranes, the measured content of ODMS is highest (44%) for the mixing ratio 50/50 and decreases to 32% when the mixing ratio increases to 60%, as shown in Table I. For higher mixing ratios, the actual ODMS content is hard to determine accurately. Moreover, the microphotographs and SEM photographs of the membrane of 60/40 are very different from those of the membrane of 40/60, although the actual content of ODMS is nearly the same for these two membranes. These results imply that the PVC-ODMS system becomes unstable at 40–50% of ODMS. The membrane structures change by the conditions of membrane formation in such an unstable region.

On the other hand, the actual ODMS content of PVC-g-ODMS/ODMS blend membrane increases monotonously with an increase in the mixing ODMS ratio. This shows clearly the miscibility of PVC to ODMS improves by graftization of PVC with ODMS.

It was found that the blend membranes are asymmetric and consists of three regions; a sponge-like region is sandwiched between two dense layers (Fig. 4). Both dense layers are not same, the layer of glass side is thicker than that of air side. The dense layers seem to be composed of PVC-rich or PVC-g-ODMS-rich phase, because the thickness of the dense layers decreases as ODMS content increases. As the  $O_2$  and  $N_2$  permeabilities of PVC have been reported to be about  $10^{-3}$  times lower than those of ODMS,<sup>25</sup> the permeation rates of gases through the whole membrane might be determined by the properties of the dense layer when its thickness is large (ODMS content is low).

### Gas Permeabilities

The results of the gas permeability measurements are given in Tables II and III, and the permeabilities and separation factor are drawn against the actual



TABLE II  
Permeabilities for Oxygen and Nitrogen, and Separation Factors  
of PVC/ODMS Blend Membranes at 25° C

OVC/ODMS wt. ratio	Thickness ( $\chi$ m)	$P_{O_2}$ (cc(STP)cm/cm <sup>2</sup> s cmHg)	$P_{N_2}$ (cc(STP)cm/cm <sup>2</sup> s cmHg)	$P_{O_2}/P_{N_2}$
100/0	15	$1.37 \times 10^{-11}$	$3.01 \times 10^{-12}$	4.5
90/10	18	1.60	3.74	4.3
80/20	16	2.01	4.21	4.8
75/25	25	2.19	4.78	4.6
60/40	39	3.93	8.75	4.5
50/50	40	9.04	$2.04 \times 10^{-11}$	4.4
40/60 <sup>a</sup>	58	$2.32 \times 10^{-10}$	4.26	5.4
30/70 <sup>a</sup>	45	5.10	$2.01 \times 10^{-10}$	2.5

<sup>a</sup> Pressure difference across the membrane is 100 mmHg.

ODMS content in Figures 5 and 6 for the PVC/ODMS and PVC-g-ODMS/ODMS blend membranes, respectively. In general, gas permeabilities for  $N_2$  and  $O_2$  increase with an increase in ODMS content in the membrane. This trend is probably because the  $O_2$  and  $N_2$  permeabilities  $P_{O_2}$  and  $P_{N_2}$  of a silicone membrane are about  $10^3$  times larger than those of a PVC membrane.<sup>25</sup> The separation factor  $P_{O_2}/P_{N_2}$  of the PVC/ODMS blend membranes are nearly constant, irrespective of the change in their composition. These results could be explained by considering a similarity to the Monsanto PRISM separator system,<sup>26</sup> which is a hollow fiber system spun from polysulfone. The polysulfone membrane is porous and has a dense skin on an exterior surface. When a silicone rubber film is formed on the outside surface of the polysulfone membrane, it fills the pores left in the skin surface of the polysulfone hollow fiber, eliminating the leaks. Thereby, the gas permeability of the composite membrane is only slightly reduced compared with that of the original membrane and the separation factors are close to those inherent to polysulfone membrane.<sup>26</sup> By regarding PVC and ODMS in our system to polysulfone and silicone rubber film, respectively, in the PRISM separator system, the high permeability and high separation factors of the present membranes could be explained analogously to the case of the PRISM separator system.

TABLE III  
Permeabilities for Oxygen and Nitrogen, and Separation Factors  
of PVC-g-ODMS/ODMS Blend Membranes at 25° C

PVC-g-ODMS wt. ratio	Thickness ( $\mu$ m)	$P_{O_2}$ (cc(STP)cm/cm <sup>2</sup> s cmHg)	$P_{N_2}$ (cc(STP)cm/cm <sup>2</sup> s cmHg)	$P_{O_2}/P_{N_2}$
100/0	31	$2.18 \times 10^{-11}$	$3.58 \times 10^{-12}$	6.1
80/20	79	2.20	3.61	6.1
70/30	105	3.38	5.74	5.9
60/40	112	5.51	8.12	6.8
50/50	107	$1.06 \times 10^{-10}$	$1.60 \times 10^{-11}$	6.6
40/60 <sup>a</sup>	175	3.24	5.56	5.8
30/70 <sup>a</sup>	110	6.65	$1.34 \times 10^{-10}$	5.0

<sup>a</sup> Pressure difference across the membrane is 100 mmHg.

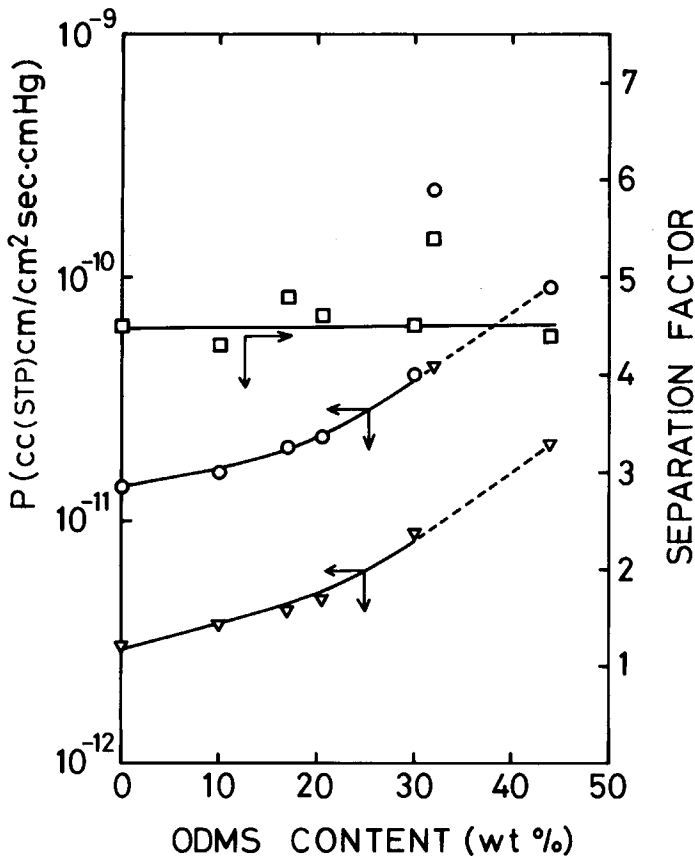


Fig. 5. Permeabilities for O<sub>2</sub> and N<sub>2</sub>, and separation factors of the PVC/ODMS membranes at 25°C. —○—, —▽—, —□—; permeabilities for O<sub>2</sub> and N<sub>2</sub>, and separation factor.

The PVC/ODMS blend membranes with actual ODMS content greater than 30 to ~40% do not show definite permeabilities of which values are dependent on the conditions of membrane formation. Although the actual ODMS contents in the mixing ratio of PVC/ODMS = 60/40 and 40/60 are nearly equal, the gas permeabilities are largely different; the difference might be explained by differences of their morphologies (Fig. 2). As discussed above, the ODMS microphases in the membrane of PVC/ODMS = 60/40 are dispersed and not interconnected in the continuous PVC phase. On the other hand, in the membrane of PVC/ODMS = 40/60, the ODMS phases are interconnected and the whole system resembles the PRISM membrane. The separation factors of these membranes are different, owing to the unstable conditions which could not be specified in the present experiments.

In order to obtain some information on the mechanism of gas permeation, the diffusion coefficient  $D$  was determined by the time lag method. The solubility coefficient  $S$  was calculated from the following relation,  $P = DS$ .<sup>27</sup> The values of  $D$  and  $S$  are shown in Figures 7 and 8 for the PVC/ODMS and the PVC-g-ODMS/ODMS blend membranes, respectively. In both cases the solubility coefficient  $S$  is nearly constant, but the diffusion coefficient  $D$

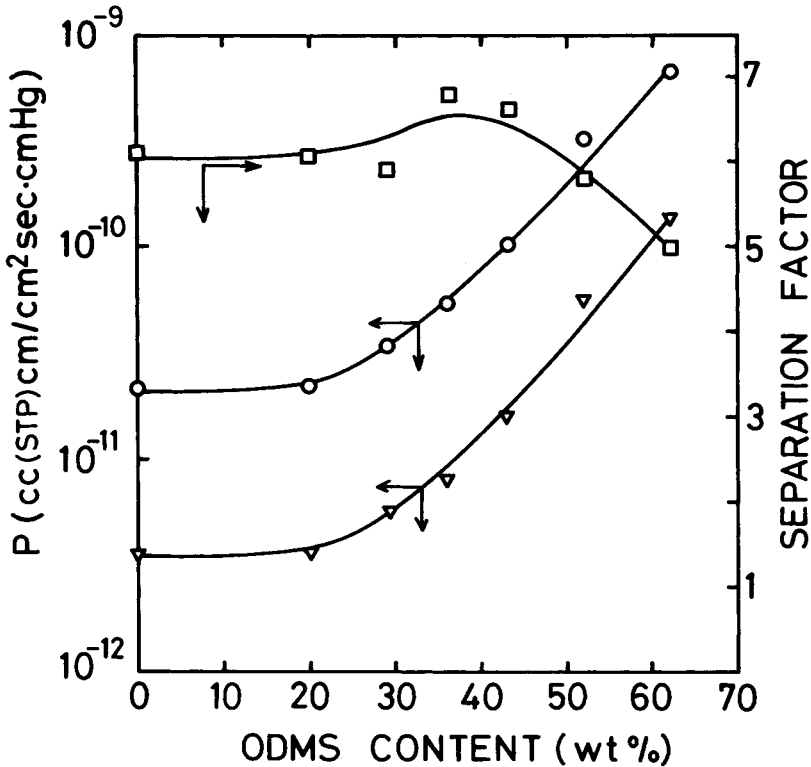


Fig. 6. Permeabilities for O<sub>2</sub> and N<sub>2</sub>, and separation factors of PVC-g-ODMS/ODMS membranes at 25°C. -○-, -▽-, -□-; permeabilities for O<sub>2</sub> and N<sub>2</sub>, and separation factor.

increases gradually as the ODMS content increases, except in the case of PVC/ODMS = 68/32 (Fig. 7). These values were not determined in a case of PVC/ODMS = 30/70, because continuous evaporation of ODMS made it difficult to measure the time lag.

#### Glass Transition Temperature

The glass transition temperature  $T_g$  of each membrane is shown in Figure 9. For the two series of blend membranes  $T_g$  once decreases and almost regains original  $T_g$  temperature with an increase in ODMS content. According to Fox,  $T_g$  of a blend polymer is given by

$$T_g^{-1} = w_1 T_{g_1}^{-1} + w_2 T_{g_2}^{-1} \quad (1)$$

when the miscibility of two components is good.<sup>28</sup>  $T_{g_i}$  and  $w_i$  are  $T_g$  and weight fraction of  $i$ -th component, respectively. As  $T_g$  of PVC and PDMS are 354K and 146K,<sup>29</sup> respectively, we should observe a sharp decrease with an increase in ODMS content, which is completely different from the observed data. Thus, it was confirmed that the compatibilities of two components in the PVC/ODMS and PVC-g-ODMS/ODMS systems are not very good. The membrane is made of PVC-rich and ODMS-rich phases, and  $T_g$  is mainly determined by the PVC-rich phase.

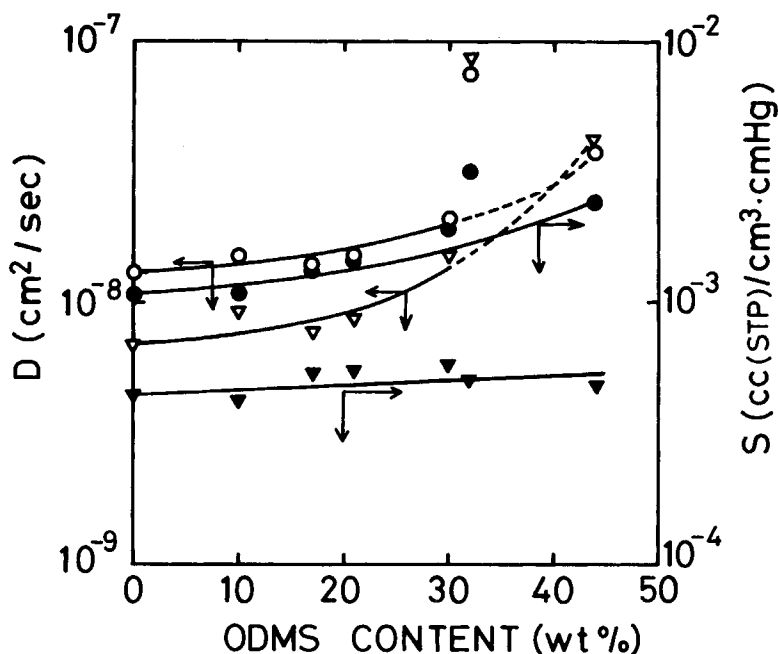


Fig. 7. Diffusion and solubility coefficients of the PVC/ODMS membranes for  $O_2$  and  $N_2$  at  $25^\circ C$ .  $\circ$ -,  $\nabla$ -; diffusion coefficients for  $O_2$  and  $N_2$ .  $\bullet$ -,  $\blacktriangledown$ -; solubility coefficients for  $O_2$  and  $N_2$ .

In the PVC/ODMS membranes, miscibility is very poor and the blend system with the mixing ratio higher than 40% becomes unstable and undergoes phase separation. The resulting membrane structures are not reproducible under the present conditions of membrane formation and, therefore, different  $T_g$  values were observed even for nearly the same value of actual ODMS content. On the other hand, in the PVC-g-ODMS/ODMS membranes the miscibility of two components improves to give a definite trend of  $T_g$  against the actual ODMS content. However, it seems difficult to explain clearly this trend of  $T_g$ . A possibility is to consider an inhomogeneity of graft polymers PVC-g-ODMS. Since the graft polymers were used without a fractionation after preparation, it is natural to consider that the polymers consist of graft polymers with various degrees of graftization. The mixed solutions of PVC-g-ODMS and ODMS are stable at smaller contents of ODMS but the graft polymers with a lower degree of graftization separate to form a PVC-rich phase, when the mixed ratio of ODMS is higher than about 50%. The resultant membrane has a higher  $T_g$  value.

The  $T_g$  value of PVC-g-ODMS is higher by  $3^\circ C$  than that of PVC, which might be a result of formation of double bonds in the main chain of PVC caused by basic elimination of HCl. Shindo et al.<sup>30</sup> measured  $T_g$  of dehydrochlorinated and original PVC and found it changed in the range of  $80$ – $82^\circ C$ . They said no significant differences were formed outside of the precision of their measurements, estimated to be  $\pm 2^\circ C$ . Repeated measurements, however, imply a small increase of  $T_g$  by graftization. To confirm the formation of double bonds, an ultraviolet (UV) spectrum of PVC-g-ODMS in THF solution was measured using a Hitachi spectrometer Model 360. Absorption assigned to

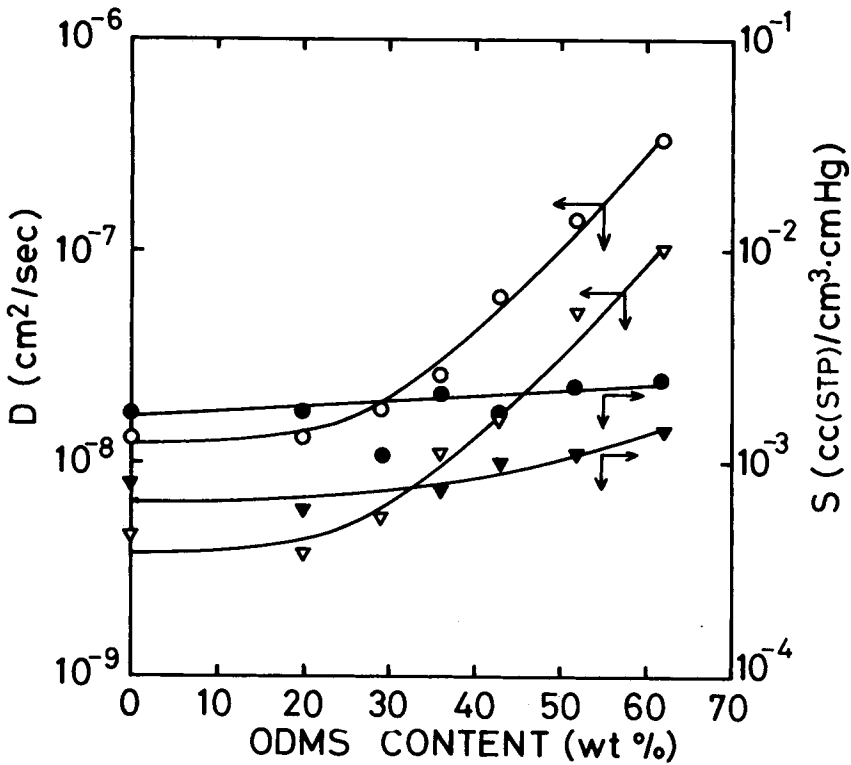


Fig. 8. Diffusion and solubility coefficients of the PVC-g-ODMS/ODMS membranes for O<sub>2</sub> and N<sub>2</sub> at 25°C. -○-, -▽-; diffusion coefficients for O<sub>2</sub> and N<sub>2</sub>. -●-, -▼-; solubility coefficients for O<sub>2</sub> and N<sub>2</sub>.

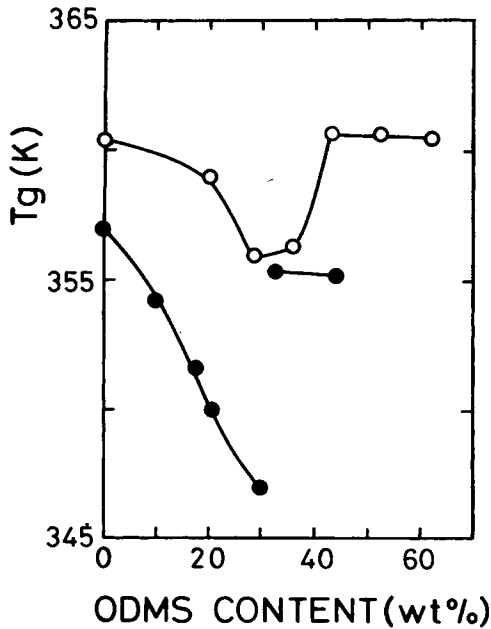


Fig. 9. Glass transition temperatures  $T_g$  of the PVC/ODMS and PVC-g-ODMS/ODMS membranes versus the actual ODMS content. -○-, -●-;  $T_g$  of the PVC-g-ODMS/ODMS and PVC/ODMS membranes, respectively.

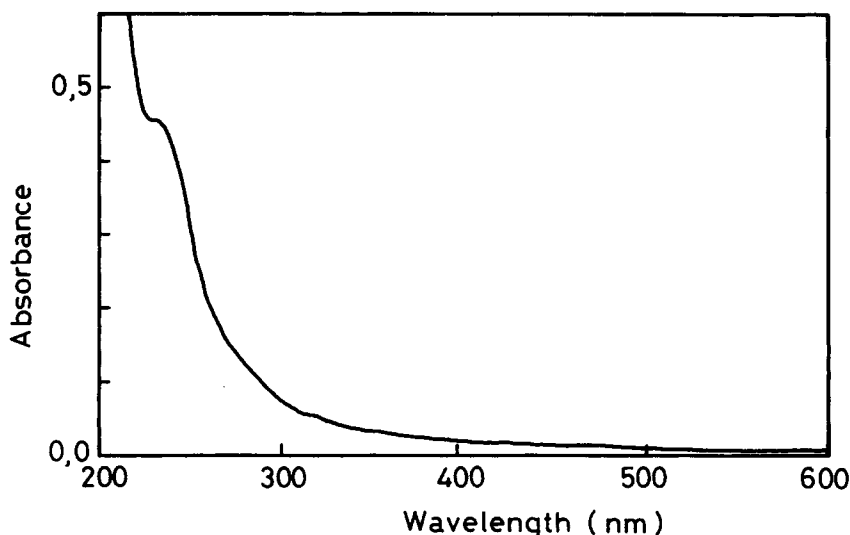


Fig. 10. UV spectrum of PVC-g-ODMS in a THF solution. Reference is a THF solution of PVC. Broad peak is assigned to conjugated double bonds.

a polyene structure was observed (Fig. 10). From the peak height at about 220 nm, which is assigned to dienes,<sup>31</sup> the amount of dienes is about  $10^{-4}$  in molar ratio against  $\text{CH}_2\text{CHCl}$  unit. Since the peak position of an isolated double bond is about 190 nm, a quantitative estimation of the amount of double bonds was impossible, but we might be able to say that the total amount of double bonds including polyenes is about  $10^{-3}$  at highest versus  $\text{CH}_2\text{CHCl}$  unit.

## CONCLUSIONS

Blending of PVC or PVC-g-ODMS with ODMS makes stable and mechanically strong membrane in a fairly wide range of ODMS content. By the use of PVC-g-ODMS the miscibility of PVC to ODMS was improved to a rather large extent. The blend system gives membranes of phase separation structure constructed of the PVC-rich or PVC-g-ODMS-rich region and the ODMS-rich region. Gas permeation rates and separation factors of these membranes are practically determined by the PVC-rich or PVC-g-ODMS-rich region, and the membrane of a relatively high gas permeability and a high separation factor for  $\text{O}_2$  against  $\text{N}_2$  was obtained.

## References

1. K. Kammermeyer, *Ind. Eng. Chem.*, **49**, 168 (1957).
2. T. Masuda, E. Isobe, T. Higashimura, and K. Takada, *J. Am. Chem. Soc.*, **105**, 7473 (1983).
3. M. Morton, A. A. Rembaum, and E. E. Bostick, *J. Appl. Polym. Sci.*, **8**, 2707 (1964).
4. Y. Minoura, M. Mitoh, A. Tabuse, and Y. Yamada, *J. Polym. Sci., A-1*, **7**, 2753 (1969).
5. W. G. Davis and D. P. Jones, *Ind. Eng. Chem., Prod. Res. Dev.*, **10**, 168 (1971).
6. A. Noshay, M. Matzner, and T. C. Williams, *Ind. Eng. Chem., Prod. Res. Dev.*, **12**, 268 (1973).
7. G. Cameron and M. S. Chisholm, *Polymer*, **26**, 437 (1985).

8. Y. Kawakami, T. Aoki, H. Hisada, Y. Yamamura, and Y. Yamashita, *Polym. Commun.*, **26**, 133 (1985).
9. Y. Tezuka, A. Fukushima, and K. Imai, *Makromol. Chem.*, **186**, 685 (1985).
10. H. A. Vaughn, *J. Polym. Sci. Part B, Polym. Lett.*, **7**, 569 (1969).
11. R. P. Kambour, *J. Polym. Sci. Part B, Polym. Lett.*, **7**, 573 (1969).
12. D. G. LeGrand, *J. Polym. Sci. Part B, Polym. Lett.*, **7**, 579 (1969).
13. W. J. Ward III, W. R. Browall, and R. M. Salemme, *J. Memb. Sci.*, **1**, 99 (1976).
14. S. Wu, *J. Macromol. Sci., Revs. Macromol. Chem.*, **C10**, 1 (1974).
15. Y. J. Shur and B. Ranby, *J. Appl. Polym. Sci.*, **19**, 1337 (1975).
16. Y. J. Shur and B. Ranby, *J. Appl. Polym. Sci.*, **19**, 2143 (1975).
17. Y. J. Shur and B. Ranby, *J. Appl. Polym. Sci.*, **20**, 3105 (1976).
18. Y. J. Shur and B. Ranby, *J. Appl. Polym. Sci.*, **20**, 3121 (1976).
19. B. Albert, R. Jerome, P. Teyssie, G. Smyth, N. G. Boyle, and V. J. McBrierty, *Macromolecules*, **18**, 388 (1985).
20. J. E. Sax and J. M. Ottino, *Polymer*, **26**, 1073 (1985).
21. M. Matsuo, C. Nozaki, and Y. Jyo, *J. Electron Microsc.*, **17**, 7 (1968).
22. C. E. Rogers, in *Polymer Permeability*, J. Comyn, Ed., Elsevier, London, 1985, Chap. 2.
23. T. Nishi, T. T. Wang, and T. K. Kwei, *Macromolecules*, **8**, 227 (1975).
24. J. W. Cahn, *J. Chem. Phys.*, **42**, 93 (1965).
25. B. P. Tikhomirov, H. B. Hopfenberg, V. Stannett, and J. L. Williams, *Makromol. Chem.*, **118**, 177 (1968).
26. H. K. Lonsdale, *J. Memb. Sci.*, **10**, 81 (1982).
27. H. Yasuda and K. J. Rosengren, *J. Appl. Polym. Sci.*, **14**, 2839 (1970).
28. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
29. J. Brandrup and E. H. Immergut, ed., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.
30. Y. Shindo, B. E. Read, and R. S. Stein, *Makromol. Chem.*, **118**, 272 (1968).
31. Y. Shindo and T. Hirai, *Makromol. Chem.*, **155**, 1 (1972).

Received March 13, 1986

Accepted June 10, 1986