

# Preparation of Vinylpyridine Irradiation-Grafted Poly(4-Methyl-Pentene-1) Membrane for Oxygen Enrichment

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## Synopsis

By adjusting the casting conditions, the oxygen permeabilities of poly(4-methyl-pentene-1) (TPX) membranes prepared in this study are in the range of  $2.91\text{--}7.14 \times 10^{-9} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ s cm Hg}$  and permeability ratio of  $\text{O}_2/\text{N}_2$  between 2.7 and 4.4. To increase  $\text{O}_2\text{--N}_2$  selectivity, the vinylpyridine is  $\gamma$ -ray irradiation-grafted onto the substrate-TPX membrane. The factors that affect the structure and performance of the grafted membrane considered are: tightness of substrate, kind of solvent for grafting monomers, irradiation conditions, total irradiation dose, and operating temperature and pressure. The  $\text{O}_2/\text{N}_2$  selectivities of grafted TPX membranes are significantly improved comparing to that of nongrafted TPX membranes. For example, an  $\text{O}_2$  permeability of  $35.6 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ s cm Hg}$  and an  $\text{O}_2/\text{N}_2$  permeability ratio of 7.5 for the grafted membrane can be obtained.

## INTRODUCTION

Gas separation by membrane, such as oxygen enrichment from air, is being increasingly important due to its inherent energy efficiency. Silicone rubber membrane has been reported to be permeable to most of the gases than other polymer membranes. It has a permeability ratio  $P_{\text{O}_2}/P_{\text{N}_2}$  of about 2, and, therefore, it cannot be used to enrich the oxygen in the air to more than 30%. Poly(4-methyl-pentene-1) membranes with the next higher gas permeability but a higher permeability ratio  $P_{\text{O}_2}/P_{\text{N}_2}$  (2.9–4.15) were developed by Teijin Co. and Mitsui Co.<sup>1,2</sup> Matsushita Denko Co. has issued a patent<sup>3</sup> for polyvinylpyridine membrane with high  $\text{O}_2/\text{N}_2$  selectivity ratio of 12.2 and moderate oxygen permeability of  $2.7 \times 10^{-9} \text{ cm}^3(\text{STP}) \text{ cm/cm}^2 \text{ s cm Hg}$ . The requirements of a good oxygen enrichment membrane are good gas permeability, selectivity, and mechanical strength. Unfortunately, the above-mentioned membranes cannot meet all these requirements.

To develop composite and/or grafted membranes may provide the solution to improve the performances of these simple membranes. Graft copolymerization is a well-known method which can modify the chemical and physical properties of polymers.<sup>4</sup> The study of utilizing  $\gamma$ -ray irradiation which induces styrene and acrylonitrile to be grafted onto polyethylene membrane for gas separation was first presented by Myers et al.<sup>5</sup> Huang and Kanitz<sup>6</sup> investigated the permeation of gases through a series of poly(ethylene-styrene)-grafted copolymer membrane prepared by  $\gamma$ -ray irradiation. Kanitz and Huang<sup>7,8</sup> studied the permeation, diffusion, and separation of nitrogen and methane gases in a series of air- and vacuum-irradiated polyeth-

ylene and Teflon FEP films. Rogers et al.<sup>9</sup> studied the permeation and separation of helium and nitrogen gases through grafting methyl methacrylate onto polyisoprene membrane by  $\gamma$ -ray irradiation. Ward et al.<sup>10</sup> prepared the copolymer membranes of poly(dimethyl-siloxane) and polycarbonate and increased the  $O_2/N_2$  selectivities of siloxane membrane. Kawakami et al.<sup>11</sup> utilized the properties of vinylpyridine which possessed the affinity to oxygen and combined with the substrate, such as natural rubber and silicone rubber, to form a composite membrane by plasma deposition to improve the gas selectivities of the substrate membranes.

In this research, TPX membrane is used as a substrate which possesses excellent mechanical strength, high permeability, and fair selectivity. To increase  $O_2/N_2$  selectivity, the vinylpyridine is grafted onto the substrate, TPX membrane, to form a composite membrane. The factors that affect the structure and performance of the grafted membrane considered are: tightness of substrate, kind of solvent for grafting monomer, irradiation conditions, total irradiation dose, operating temperature, and pressure. The transport properties and mechanical strength of the  $\gamma$ -ray irradiation-grafted poly(4-methyl-pentene-1) membrane were studied.

## EXPERIMENTAL

### Materials

Poly(4-methyl-pentene-1) (TPX, MX-001) was supplied by Mitsui Co. Cyclohexene as supplied by Ferak Berlin Co. was used as a casting solvent. 4-vinylpyridine made by Merk Co. was used as the grafting monomer. Ethanol (Shimakyu's Pure Chemical Co.) and Benzene(Hayashi Pure Chemical Industries, Ltd.) were used as solvent for grafting monomer. All of the above chemicals are of reagent grade. Oxygen, nitrogen, argon, and helium of 99.9% purity were used.

### Membrane Preparation

The membrane was prepared from a casting solution of poly(4-methyl-pentene-1) in cyclohexene. The membrane was formed by casting the solution onto a glass plate to predetermined thickness by using a Gardner knife. The glass plate was evaporated for 5 min at ambient temperature and heated for specified times (10, 20, 40, 60, 120 min) at predetermined different temperatures (30, 50, 70, 90°C) in a well-circulated oven. Then the glass plate with the membrane was immersed in 4°C water for 2 h. The membrane was then peeled off and dried in vacuum for 24 h to remove solvent residue. The membrane thickness was 30  $\mu\text{m}$  in average.

### Gas Permeability Test of Membrane

The apparatus for measuring the permeability of the gas through the membrane is shown in Figure 1. The gas permeability was determined by the following equation:

$$P = q \cdot l / (p_1 - p_2) \cdot A \cdot t$$

where  $P$  = gas permeability [ $\text{cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cm Hg}$ ],  $q/t$  = volume flow rate of gas permeate [ $\text{cm}^3(\text{STP})/\text{s}$ ],  $l$  = the membrane thickness (cm),  $p_1, p_2$

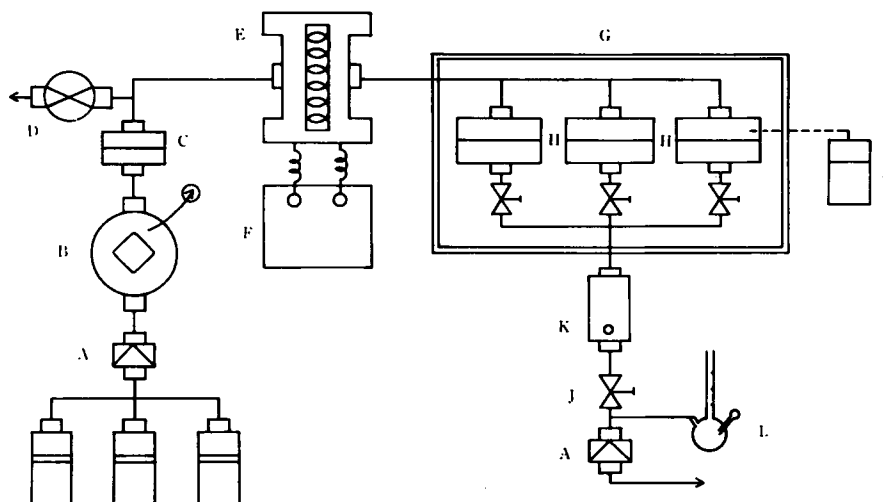


Fig. 1. Gas permeation apparatus: (A) check valve; (B) regulator/pressure gauge (0–11 kg/cm<sup>2</sup>); (C) gas filter; (D) vent; (E) heater; (F) temperature controller; (G) thermoisolator; (H) membrane cell S.S. filter holder 50 m/m OD; (I) digital thermometer TX-500; (J) shut-off valve; (K) flowmeter R-2-15-AA; (L) soapfilm meter.

= pressures on the high pressure side and low pressure side of the membrane, respectively (cm Hg), and  $A$  = effective membrane area (cm<sup>2</sup>).

### Graft Copolymerization

After testing the gas permeability, the TPX membrane was dried in vacuum and weighed. Then the TPX membrane was placed in a glass bottle. The grafting monomer solution was poured into it and completely soaked the membrane. The gas phase in the bottle is either air or pure nitrogen. Graft copolymerization was carried out by irradiation with  $\gamma$ -ray from <sup>60</sup>Co at room temperature, dose rate  $1.2 \times 10^4$  rad/h. After the irradiation, the grafted membrane was washed with ethanol several times to remove all the homopolymer and then dried in vacuum. The degree of grafting was calculated from the weight increase of the grafted membrane.

### Measurement of Tensile Strength

The tensile strength measurement of TPX and grafted TPX membranes were carried out on the Toyo Baldwin type Tensilon/UTM-III-100 instrument at various temperatures. The membranes were tested by ASTM method<sup>12</sup> for their tensile strengths and elongations in their dry states.

## RESULTS AND DISCUSSION

### Effect of Heat Treatment Temperature and Heat Treatment Time on Membrane Performance

Table I shows the effect of heat treatment temperature at 20 min heating time on TPX membrane performance in terms of gas permeability.

With increasing heat treatment temperature from 30 to 90°C, the gas permeability of oxygen decreases from 67.2 to  $29.1 \times 10^{-10}$  cm<sup>3</sup>(STP) cm/cm<sup>2</sup>

TABLE I  
Effect of Heating Temperature on TPX Membranes Performances<sup>a</sup>

Heating Temp (°C)	Gas permeabilities $P \times 10^{10}$			Separation factor ( $P_{O_2}/P_{N_2}$ )
	Ar	O <sub>2</sub>	N <sub>2</sub>	
30	55.2	67.2	24.9	2.7
50	40.7	47.3	14.3	3.3
70	28.7	33.7	9.58	3.5
90	24.5	29.1	6.68	4.4

<sup>a</sup> Heating time 20 min; operating temperature 25°C; operating pressure 6.8 kg/cm<sup>2</sup>; unit of permeability cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg.

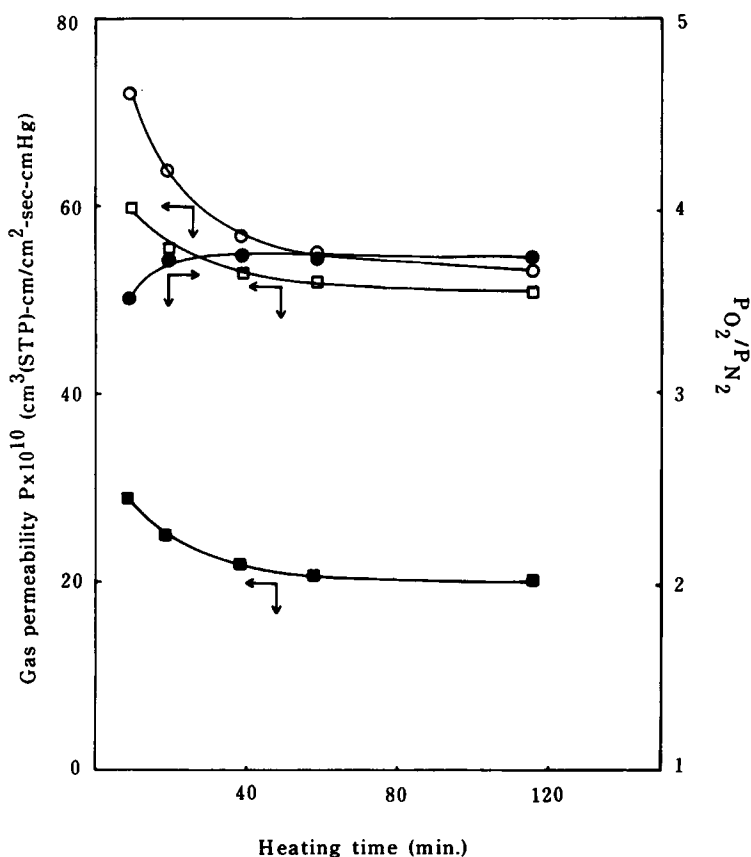


Fig. 2. Effect of heating time on gas permeability and separation factor (for 30°C heat-treated membranes): operating temp 25°C; operating pressure 6.8 kg/cm<sup>2</sup>; (○) O<sub>2</sub>; (□) Ar; (■) N<sub>2</sub>; (●)  $P_{O_2}/P_{N_2}$ .

s cm Hg, that of nitrogen decreases from 24.9 to 6.68 cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg. As a result, the permeability ratio of O<sub>2</sub> to N<sub>2</sub> is 2.7 and 4.4 at 30 and 90°C heat treatment temperatures, respectively.

Figure 2 shows the effect of heat treatment time at 30°C on gas permeability. As can be seen, the gas permeabilities of O<sub>2</sub> and N<sub>2</sub> decrease with rising heat treatment time up to 60 min. Similar results were also found in the

membrane that were heat-treated at 50, 70, and 90°C. This could be because of the effect of heat treatment on decreasing crystalline region, pore size, and void volume.<sup>13-15</sup>

From the above results, it shows that the gas permeability and selectivity between O<sub>2</sub> and N<sub>2</sub> of TPX membrane can be effectively controlled by adjusting the heat-treatment temperature and heat-treatment time.

### Estimation of Mean Pore Size of Membrane

There are many methods for estimation of mean pore size of the membrane.<sup>16</sup> Each of these methods has more or less errors. Pore size determined by the SEM method is certainly more reliable for porous membranes. However, for homogeneous membrane with pore size less than 100 Å such as ones used in our work, it is difficult to determine the pore size by SEM. According to Liepmann's theory<sup>17</sup> for homogeneous membrane, when  $2r/\lambda = 0.1$ , where  $r$  is radius of pore and  $\lambda$  is mean free path, only 1% of permeate gas is not due to the free molecular flow. This theory is quite acceptable<sup>18</sup> and is used as our basis to estimate mean pore size of TPX membranes.

The equation used to calculate the mean free path of the gas is

$$\lambda = 3.2\mu/P_t \cdot (RT/2\pi g_c M)^{1/2}$$

where  $\lambda$  = mean free path (cm),  $\mu$  = gas viscosity (cP),  $R$  = ideal gas constant (8.314 J/mol K),  $M$  = molecular weight of gas (g/mol),  $T$  = absolute temperature (K),  $g_c$  = gravitational conversion factor (kg m/N s<sup>2</sup>), and  $P_t$  = The operating pressure at the point of deviation of 1% from the straight line of permeate gas volume flow rate vs. operating pressure curve (kg/cm<sup>2</sup>). Once  $\lambda$  is calculated by eq. (1) and substituted into the relationship  $2r/\lambda = 0.1$ , then  $2r$  can be determined.

The pore sizes estimated by Liepmann's method with He gas are 39.0, 40.4, 42.2, and 44.9 Å for 30, 50, 70, and 90°C, heat-treated TPX membrane, respectively.

### Effect of Monomer Concentration, Irradiation Environmental Condition and Total Irradiation Dose on the Degree of Grafting

Figure 3 shows that the degree of grafting increases with increasing monomer concentration and irradiation time. In the first 20 h, the degree of grafting increases rapidly with irradiation time; then the rate of grafting is slowed down. This could be explained by the fact that as more and more polyvinylpyridine is grafted onto the TPX membrane, it slowed down the diffusion rate of vinylpyridine monomer into TPX membrane. For constant monomer concentration and irradiation time, the degree of grafting is higher when irradiating in an atmosphere of nitrogen than in air. During  $\gamma$ -ray irradiation grafting in the presence of oxygen, diperoxide, or hydroperoxide compounds may be produced and become a resistance to the grafting.<sup>19</sup>

### Effect of Monomer Solvent on Degree of Grafting

The solubility parameters of ethanol/H<sub>2</sub>O (1:1), ethanol, benzene, and TPX are 18.1, 12.7, 9.2, and 7.4, respectively. At  $2.4 \times 10^5$  rad, total dose for

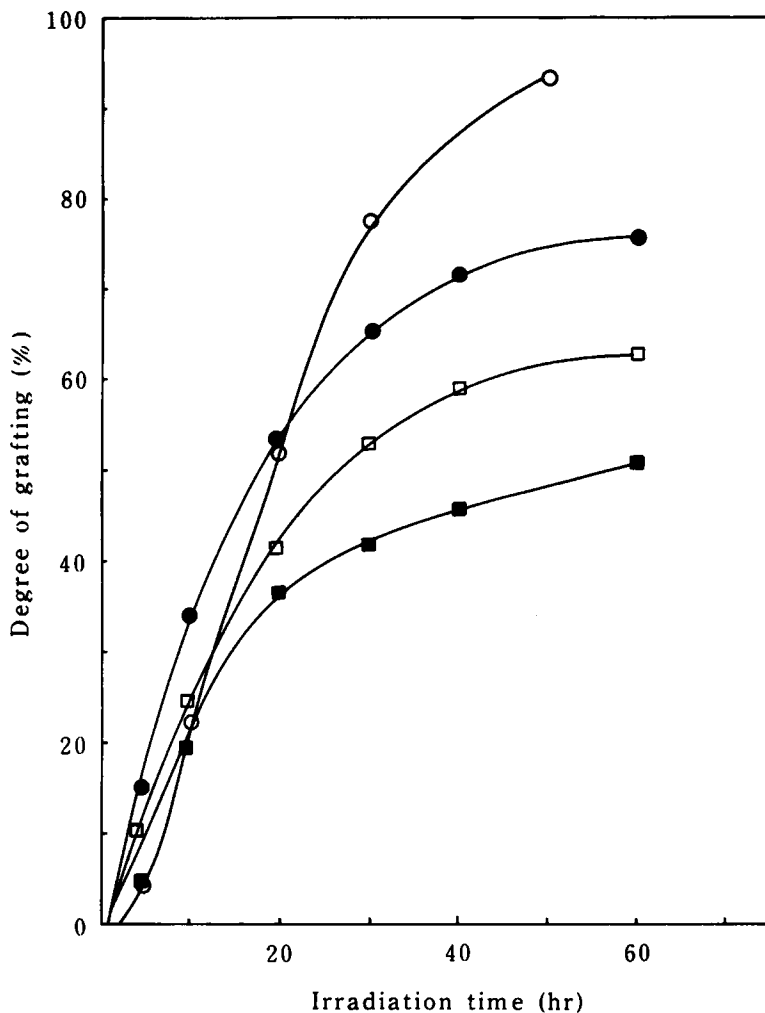


Fig. 3. Degree of grafting of TPX-g-4-vinylpyridine membranes vs. irradiation time: dose rate  $1.2 \times 10^4$  rad/h; solvent: ethanol/H<sub>2</sub>O = 1 : 1; (○) 20 vol % in N<sub>2</sub>; (●) 40 vol % in air; (□) 20 vol % in air; (■) 10 vol % in air.

20% monomer concentration, the degrees of grafting are 50.8, 15.9, and 12.3% when ethanol/H<sub>2</sub>O (1 : 1), ethanol, and benzene are used as solvent, respectively. It shows that higher degree of grafting can be obtained when the monomer solvent has higher solubility parameter difference from that of the TPX substrate.

#### Effect of Grafting Degree on Membrane Performance

In order to make comparison, the gas permeabilities before and after irradiation of the same membrane were tested. Table II shows that the gas permeabilities of O<sub>2</sub> and N<sub>2</sub> decrease with increasing degree of grafting of vinylpyridine. However, O<sub>2</sub>/N<sub>2</sub> selectivities of grafted TPX membranes are significantly improved comparing to that of nongrafted TPX membranes. For

TABLE II  
Performances of TPX-*g*-4-Vinylpyridine Membranes<sup>a</sup>

Nongrafted membranes gas permeabilities $P \times 10^{10}$			Irradiation time (h)	Degree of grafting (%)	4-vinylpyridine- <i>g</i> -TPX membranes gas permeabilities $P \times 10^{10}$		
O <sub>2</sub>	N <sub>2</sub>	$P_{O_2}/P_{N_2}$			O <sub>2</sub>	N <sub>2</sub>	$P_{O_2}/P_{N_2}$
71.4	25.8	2.8	20	50.7	46.7	7.98	5.9
66.3	25.1	2.7	30	73.4	35.6	4.91	7.5
62.2	24.5	2.6	50	88.7	26.4	2.43	11.1

<sup>a</sup>30°C, 20 min heat-treated membranes; monomer concentration 20 vol % in C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O = 1 : 1; dose rate  $1.2 \times 10^4$  rad/h; operating temperature 25°C; operating pressure 6.8 kg/cm<sup>2</sup>; unit of gas permeability cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg.

TABLE III  
Performances of TPX-*g*-4-Vinylpyridine Membranes<sup>a</sup>

Irradiation time (h)	Degree of grafting (%)	Gas permeabilities $P \times 10^{10}$		
		O <sub>2</sub>	N <sub>2</sub>	$P_{O_2}/P_{N_2}$
5	4.7	38.3	10.5	3.7
10	19.4	36.2	5.57	5.5
20	50.1	38.1	6.32	6.1
30	79.2	20.2	1.97	10.6

<sup>a</sup>50°C, 20 min heat-treated membranes; monomer concentration 20 vol % in C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O = 1 : 1; dose rate  $1.2 \times 10^4$  rad/h; operating temp 25°C; operating pressure 6.8 kg/cm<sup>2</sup>; unit of gas permeability cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg.

TABLE IV  
Performances of TPX-*g*-4-Vinylpyridine Membranes<sup>a</sup>

Irradiation time (h)	Degree of grafting (%)	Gas permeability $P \times 10^{10}$		
		O <sub>2</sub>	N <sub>2</sub>	$P_{O_2}/P_{N_2}$
5	3.8	30.9	6.50	4.1
10	21.4	27.4	4.26	6.5
20	48.4	24.8	3.55	7.1
30	79.7	17.9	1.71	10.7

<sup>a</sup>70°C, 20 min heat-treated membranes; monomer concentration 20 vol % in C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O = 1 : 1; dose rate  $1.2 \times 10^4$  rad/h; operating temperature 25°C; operating pressure 6.8 kg/cm<sup>2</sup>; unit of gas permeability cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg.

30°C and 20 min heat-treated grafted TPX membrane, the oxygen permeabilities are 46.7, 35.6, and  $26.4 \times 10^{-10}$  cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg and  $P_{O_2}/P_{N_2}$  ratios are 5.9, 7.5, and 11.1 for 50.7, 73.4, and 88.7% degrees of grafting, respectively. This shows similar results to those of the styrene-grafted PE membrane obtained by Myers et al.<sup>5</sup>

Similar results are observed for tighter (higher-temperature heat-treated) TPX membranes. As can be seen in Tables III–V, the gas permeabilities decrease with increasing heat treatment temperatures. For an example, at

TABLE V  
Performances of TPX-g-4-Vinylpyridine Membranes<sup>a</sup>

Irradiation time (h)	Degree of grafting (%)	Gas permeabilities $P \times 10^{10}$		
		O <sub>2</sub>	N <sub>2</sub>	$P_{O_2}/P_{N_2}$
5	5.1	23.2	5.59	4.2
10	19.0	20.3	3.30	6.3
20	53.4	14.1	1.68	8.6

<sup>a</sup>90°C, 20 min heat-treated membranes; monomer concentration 20 vol % in C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O; dose rate  $1.2 \times 10^4$  rad/h; operating temperature 25°C; operating pressure 6.8 kg/cm<sup>2</sup>; unit of permeability cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg.

20 h irradiation time, the oxygen permeabilities are 46.7, 38.1, 24.8, and 14.1 cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg, and  $P_{O_2}/P_{N_2}$  ratios are 5.9, 6.1, 7.1, and 8.6 for 30, 50, 70, and 90°C heat-treated grafted TPX membranes, respectively. We can prepare membranes with desired gas permeability and O<sub>2</sub>/N<sub>2</sub> selectivities (between 2.6 and 11.1) by adjusting the heat treatment temperature, degree of grafting, and irradiation time.

#### Effect of Operating Temperature on Membrane Gas Permeability

Figure 4 shows that the permeability of 30°C heat-treated membrane is increased with increasing operating temperature in the considered range of 30–60°C and is found to follow the Arrhenius law,  $P = P_0 \exp(-E_p/RT)$ . This is also true for higher-temperature heat-treated membranes. The activa-

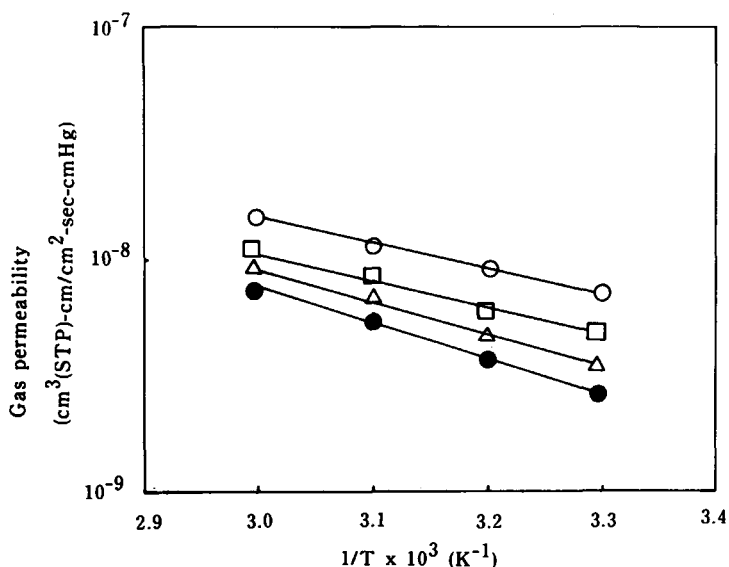


Fig. 4. Effect of operating temperature on gas permeability (for 20 min heat-treated membranes): operating pressure 6.8 kg/cm<sup>2</sup>; (○) 30°C heat-treated; (□) 50°C heat-treated; (△) 70°C heat-treated; (●) 90°C heat-treated.



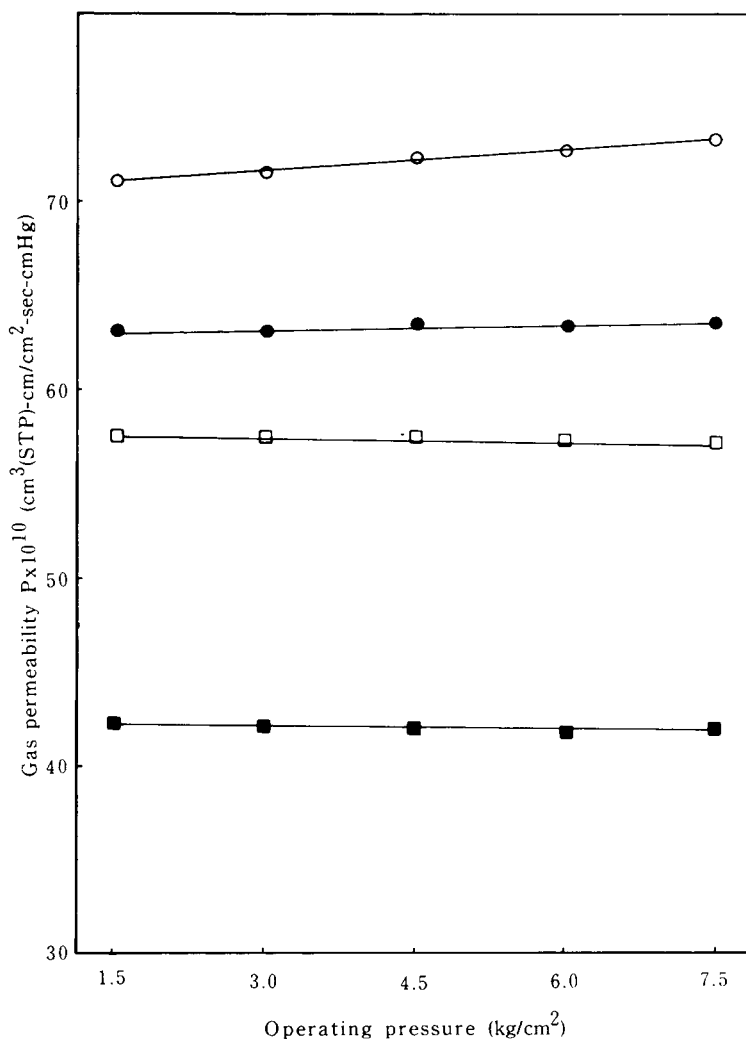


Fig. 5. Effect of operating pressure on gas permeability (30°C, 20 min heat-treated membranes): operating temperature 25°C; (○) He; (●) O<sub>2</sub>; (□) Ar; (■) N<sub>2</sub>.

tion energy ( $E_p$ ) for gas permeation through TPX membrane obtained by the Arrhenius law is higher for higher-temperature heat-treated membrane.  $E_p$  values of oxygen for 30, 50, 70, and 90°C heat-treated TPX membranes are 4.4, 4.8, 5.4, and 6.2 kcal/mol, respectively.

#### Effect of Operating Pressure on Membrane Gas Permeability

Figure 5 shows that the permeability is not affected by pressure up to 7.0  $\text{kg}/\text{cm}^2$  for N<sub>2</sub>, O<sub>2</sub>, and Ar, but the permeability of He gas slightly increased with increasing pressure. Compared to N<sub>2</sub>, O<sub>2</sub>, and Ar, the permeability of He is relatively high because its molecular size is smaller. Hence the pore blocking

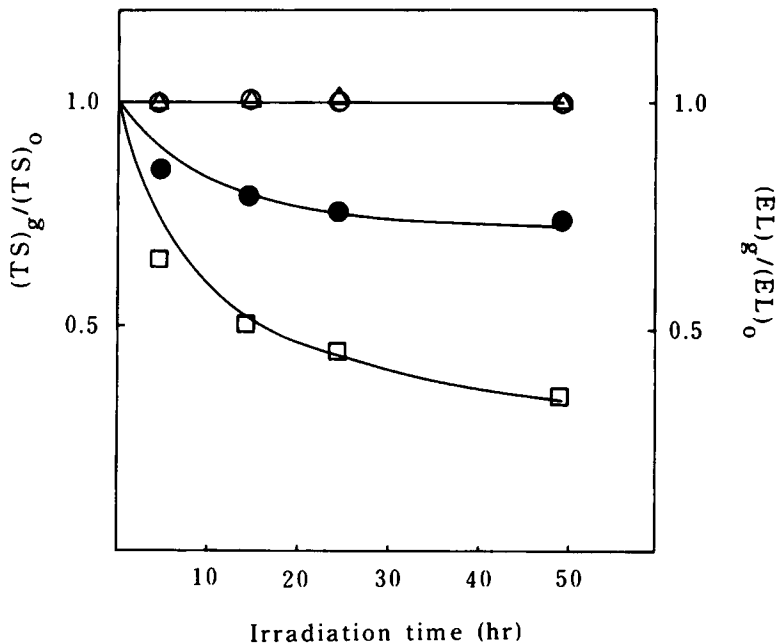


Fig. 6. Plot of tensile strength and elongation decay vs. irradiation time: dose rate  $1.2 \times 10^4$  rad/h at room temp; drawing rate 50 mm/min; drawing temp, room temp; (○) tensile strength decay in  $N_2$ ; (●) tensile strength decay in air; (△) elongation decay in  $N_2$ ; (□) elongation decay in air.

effect for He does not play such a significant role as the other mentioned gases.

### Mechanical Strength of Membrane

In order to study the effect of irradiation on membrane strength, the tensile strength and elongation of nongrafted membrane for different degree of irradiation were tested at first. The average strength is 210 kg/cm<sup>2</sup> and elongation is 76% for prepared TPX membrane. Figure 6 shows that both tensile strength and elongation decrease with increasing  $\gamma$ -ray dose when irradiated in air. On the other hand, the mechanical strength has no appreciable change up to a total dose of  $6 \times 10^5$  rad. when irradiated in nitrogen instead of in air. Similar result was reported for  $\gamma$ -ray irradiation of polystyrene in air and nitrogen by Bowmer.<sup>20</sup> During  $\gamma$ -ray irradiation, the presence of oxygen might cause the production of hydroxyl or carbonyl group and hence decrease the molecular weight of the grafted polymer and the mechanical strength of the grafted membrane. The mechanical strength shows a decrease with increasing degree of grafting even when irradiated in  $N_2$ . As shown in Figure 7, for example, the tensile strength and elongation of membrane with 73.4% degree of grafting are 210 kg/cm<sup>2</sup> and 40%, respectively. This decay in the mechanical strength should be mainly caused by the grafting of polyvinylpyridine from the above results on the  $\gamma$ -ray irradiated nongrafted TPX membrane. After  $\gamma$ -ray irradiating, the membrane may possibly be crosslinked, interpenetrating polymer network (IPN) formed, or

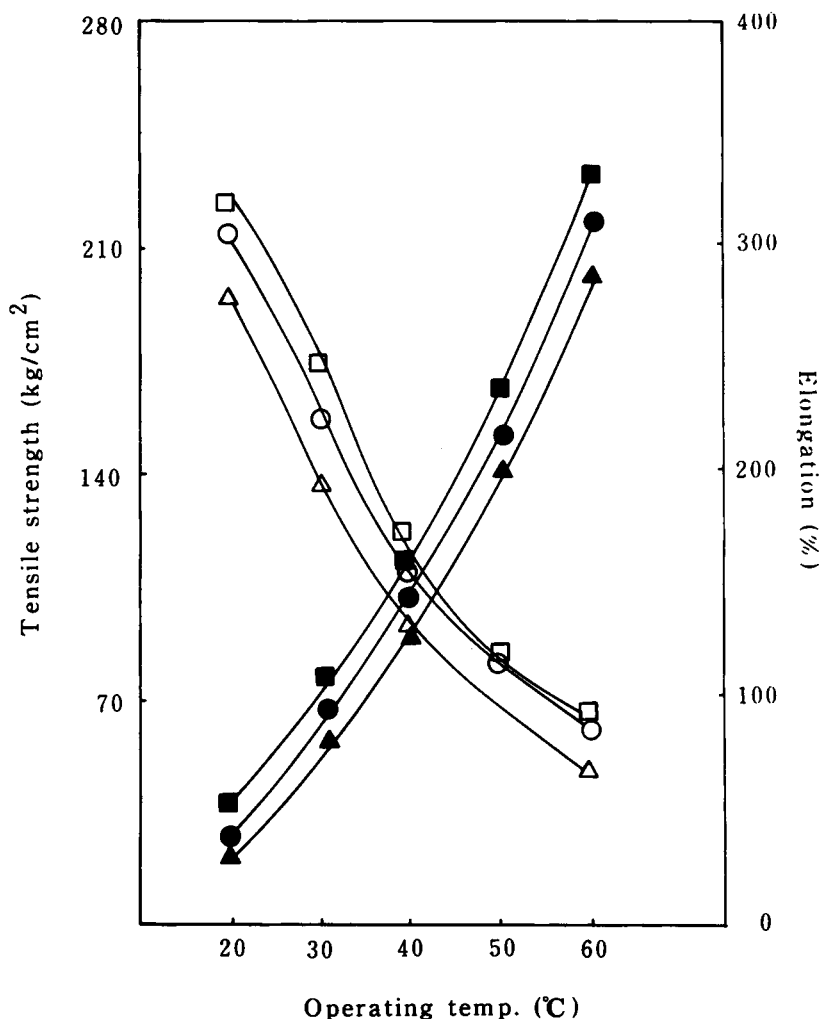


Fig. 7. Effect of operating temperature on tensile strength and elongation of various degree of 4-vinylpyridine grafting; drawing rate 50 mm/min; (□) tensile strength of 52% degree of grafting; (○) tensile strength of 73.4% degree of grafting; (Δ) tensile strength of 88% degree of grafting; (■) elongation of 52% degree of grafting; (●) elongation of 73.4% degree of grafting; (▲) elongation of 88% degree of grafting.

polyvinylpyridine merely grafted. However, the mechanical strength should be increased if the membrane was crosslinked. It would not be changed if an interpenetrating polymer network was formed. From the mechanical decay of the irradiated membrane, it is believed that polyvinylpyridine was grafted onto the TPX membrane and not crosslinked or IPN formed.

#### Comparison to the Results of Previous Workers

Table VI shows the comparison of the data obtained so far by other authors with those of this study. Teijin Co. issued many patents on TPX membranes in which the  $P_{O_2}/P_{N_2}$  ratios were in the range of 2.9–3.49. The ratio of 3.49

TABLE VI  
Comparison of Previous Data with This Study<sup>a</sup>

Membranes	$P_{O_2} \times 10^{10}$	$P_{O_2}/P_{N_2}$	References
TPX (ultrathin)	$1.8 \times 10^{-4b}$	2.9	Teijin Co. <sup>1</sup>
TPX (23 $\mu$ m)		3.49	Teijin Co. <sup>21</sup>
TPX	27	4.15	Mitsui Co. <sup>2</sup>
Poly(4-vinylpyridine)	28	12.2	Matsushita Denko Co. <sup>3</sup>
4-vinylpyridine-coated nature rubber by plasma deposition	13.6	5.8	Kawakami et al. <sup>11</sup>
4-vinylpyridine-coated silicone rubber by plasma deposition	115	4.9	Kawakami et al. <sup>11</sup>
TPX, 90°C, 20 min heat-treated	29.1	4.4	This study
TPX, 30°C, 20 min	71.4	2.8	This study
TPX- <i>g</i> -4-vinylpyridine (73.4% grafting)	35.6	7.5	This study
TPX- <i>g</i> -4-vinylpyridine (88.7% grafting)	26.4	11.1	This study

<sup>a</sup>Unit of permeability  $\text{cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cm Hg}$ .

<sup>b</sup>Unit of permeation rate  $\text{cm}^3(\text{STP})/\text{cm}^2 \text{ s cm Hg}$ .

was for 23  $\mu$ m thickness membrane.<sup>21</sup> The ultrathin membranes have  $P_{O_2}/P_{N_2}$  ratios below 3.14.<sup>22</sup> Mitsui Co. issued a patent for TPX membrane with a permeability of  $2.7 \times 10^{-9} \text{ cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cm Hg}$  and  $P_{O_2}/P_{N_2} = 4.15$ .<sup>2</sup> Compared to these data, our TPX membranes possess higher  $O_2/N_2$  selectivities and permeabilities. Compared to the high  $P_{O_2}/P_{N_2}$  ratio, 12.2 of poly(4-vinylpyridine) membrane of Matsushita Denko Co.,<sup>3</sup> the selectivities of our grafted membranes are slightly lower but the strength are better. The excellent gas permeability with fairly high  $P_{O_2}/P_{N_2}$  ratio of vinylpyridine plasma-deposited silicone rubber membrane was reported by Kawakami et al.<sup>11</sup> Compared to Kawakami's data, our grafted TPX membranes possess lower gas permeabilities but higher selectivities and mechanical strength. This may be simply due to the fact that higher content of polyvinylpyridine could be obtained in this study compared with the plasma deposition.

## CONCLUSION

By adjusting the heat treatment conditions, the oxygen permeabilities of TPX membranes are in the range of  $67.2\text{--}29.1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cm Hg}$ , and the permeability ratio of  $O_2/N_2$  is between 2.7 and 4.4. The mean pore size of prepared TPX membranes are estimated to be in the range of 39.0–44.9 Å diameter by Liepmann's method. The membranes are proved to be pinhole-free by microscopy.

With increasing degree of grafting, the permeability of the grafted membrane decreases and selectivity increases. The degree of grafting is higher for  $\gamma$ -ray irradiating in nitrogen and using  $C_2H_5OH/H_2O$  as monomer solvent. The selectivities of oxygen against nitrogen through vinylpyridine-grafted TPX membranes are significantly improved compared to that through non-

grafted TPX membranes. For example, an O<sub>2</sub> permeability of  $35.6 \times 10^{-10}$  cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg and an O<sub>2</sub>/N<sub>2</sub> permeability ratio of 7.5 for the grafted membrane can be obtained. The conditions of preparation are 30°C and 20 min heat-treated TPX as substrate, vinylpyridine 20 vol % in C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O as grafting solution. The prepared grafted membranes with 73.4% degree of grafting still possess 210 kg/cm<sup>2</sup> tensile strength and 40% elongation at 0.36 Mard total dose in N<sub>2</sub>.

The authors wish to thank the National Science Council of The Republic of China for financial support. The authors also wish to express our appreciation to Professor Tohru Kaiwai of Tanaka-Chiyo Women's College, Japan, for valuable discussions.

### References

1. Jpn. Pat. 79 146277 (1979).
2. "Methylpentene Polymers 'TPX,'" Bulletin 2000, Petrochemical Industries, Ltd., Oct. 1976.
3. Jpn. Pat. 76 72976 (1976).
4. R. W. MacDonald and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **26**, 2239 (1981).
5. A. W. Myers, C. E. Rogers, V. Stannett, and M. Szwarc, *J. Appl. Polym. Sci.*, **4**, 159 (1960).
6. H. K. Lonsdale and H. E. Podall, *Reverse Osmosis Membrane Research*, Plenum, New York and London, 1972, p. 236.
7. J. F. Kanitz and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 2739 (1970).
8. J. F. Kanitz and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **15**, 67 (1971).
9. C. E. Rogers, *Permeability of Plastic Films and Coatings*, H. B. Hopfenberg, Ed., Plenum, New York and London, 1974, p. 157.
10. W. J. Ward III, W. R. Browall and R. M. Salemme, *J. Membr. Sci.*, **1**, 99 (1976).
11. M. Kawakami, Y. Yamashita, M. Iwamoto, and S. Kagawa, *J. Membr. Sci.*, **19**, 249 (1984).
12. L. E. Nisen, Ed., *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974, Vol. 1, p. 292.
13. R. E. Kesting, *Synthetic Polymeric Membrane*, McGraw-Hill, 1971, p. 24.
14. J. Napp, W. H. M. Yang, and N. A. Peppas, *J. Appl. Polym. Sci.*, **28**, 2793 (1983).
15. S. W. Lasoski, Jr. and W. H. Cobbs, Jr., *J. Polym. Sci.*, **36**, 21 (1959).
16. I. Cabasso, K. Q. Robert, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.*, **21**, 1883 (1977).
17. H. Liepmann, *J. Fluid Mech.*, **10**, 65 (1961).
18. S. Sourirajan, *Reverse Osmosis and Synthetic Membrane*, Publication Ottawa, Canada, Kia ORL, 1977, p. 529.
19. A. Chapiro, Ed., *Radiation Chemistry of Polymeric System*, Wiley-Interscience, New York, 1962, p. 601.
20. T. N. Bowmer, L. K. Cowen, J. H. O'Donnell, and D. J. Winzor, *J. Appl. Polym. Sci.*, **24**, 425 (1979).
21. Jpn. Pat. 80 41809 (1980).
22. Jpn. Pat. 81 166232 (1981).

Received January 14, 1986

Accepted April 1, 1986