MMA / TPX Homograft Membrane for Oxygen Enrichment

J. Y. LAI, J. J. SHIEH, *Department of Chemical Engineering, Chung Yuan University, Chung Li, Taiwan, Republic of China,* and
S. S. SHYU, *Department of Chemical Engineering, Central University, Chung Li, Taiwan, Republic of China*

Synopsis

Utilizing the factors of degradation and crosslinking of TPX polymer and high O_2/N_2 selectivity of MMA, the performances of MMA homografted TPX membrane are efficiently improved compared to those of pure TPX membrane. The degradation and crosslinking of TPX polymer solution with or without dissolved oxygen during irradiation were observed and proved in existence by the gas permeability, mechanical, and viscosity change study. High O_2/N_2 permeability ratio of 7.6 and fairly high oxygen permeability of 28×10^{-10} cm^3 cm/cm^2 s cm Hg of the membrane which was cast from the degassing polymer solution, with 20% degree of MMA grafting, can be obtained. Also the membrane for high oxygen permeability of 63×10^{-10} cm^3 cm/cm^2 s cm Hg with an O_2/N_2 permeability ratio of 4.5, which was cast from the polymer solution with dissolved oxygen, can be obtained under the condition of 60 h irradiation time and about 7% degree of grafting. O_2/N_2 selectivity of TPX membrane can be improved by homografting method with lower MMA grafting degree than that of heterografting method.

INTRODUCTION

The requirements of a good oxygen enrichment membrane are good gas permeability, O_2/N_2 selectivity, and mechanical strength. Unfortunately, some simple membranes, such as pure silicone rubber,[1] poly(4-methyl-pentene-1) (TPX) membrane, cannot meet all of these requirements. To prepare composite membranes may provide the solution to improve the performance of these simple membranes. Ward et al.[2] prepared the copolymer membranes of poly(dimethyl–siloxane) and polycarbonate and increased the O_2/N_2 selectivities of silcone membrane. Kawakami et al.[3] utilized the properties of vinylpyridine which possessed the affinity to oxygen and combined with some substrates, such as natural rubber and silicone rubber, to form a composite membrane by plasma deposition to improve the gas selectivities of the substrate membranes. Yamamoto et al.[4] and Inagaki et al.[5,6] also studied on oxygen enrichment membranes by plasma deposition technology. TPX/siloxane blend membrane for increasing permeability of TPX membrane was studied by Lai et al.[7]

Graft copolymerization is a well-known method which can modify the chemical and physical properties of polymers.[8-13] Vinylpyridine irradiation-heterografted poly(4-methyl-pentene-1) was studied by Lai and Wei[14] to improve the O_2/N_2 selectivity of TPX membrane.

Vinyl-monomer-homografted cellulose possessed higher branch number per cellulose chain and lower grafted polymer chain than those of heterografted

Journal of Applied Polymer Science, Vol. 37, 2907–2919 (1989)
 CCC 0021-8995/89/102907-13$04.00

cellulose was reported.[15,16] The modification effect of the membrane could be obtained by the homografting method by a lower grafting degree of monomer could be used than by the heterografting method.

The purpose of this study is intended to improve the O_2/N_2 selectivity of TPX membrane by homografting TPX with MMA, which possesses a high O_2/N_2 selectivity. The heterografting method for MMA/TPX membrane is also studied for comparison. The degradation and crosslinking of pure TPX caused from different irradiation conditions were studied by polymer viscosity, mechanical strength, and gas permeability changes. The factors that would affect the performances of membranes considered were TPX concentration of graft solution, kinds of medium solvent, MMA content, and irradiation conditions (such as irradiation time, with or without oxygen in solution during irradiation).

EXPERIMENTAL

Materials

Poly(4-methyl-pentene-1) (TPX, MX-001) was supplied by Mitsui Co. Cyclohexene supplied by Merk Co. was used as a medium solvent and casting solvent. Cyclohexane supplied by ALPS Chem. Co. was also used as a medium solvent. Methyl methacrylate (MMA) made by Merk Co. was used as a grafting monomer. Methanol and acetone (BDH chemicals) were used as a solvent for precipitation and extraction. All of the above chemicals are of reagent grade. Oxygen and nitrogen of 99.9% purity were used.

Homograft Copolymerization

Poly(4-methyl-pentene-1) was placed in a 250-mL flask, to which the medium solvent was added. After TPX was dissolved thoroughly, MMA monomer was added to the flask. The total amount of solution is 100 mL finally. Freezing, degassing, and melting cycles were repeated three times to remove oxygen, and then the flask was sealed. The case of solution with dissolved oxygen was also considered. The graft copolymerization was carried out by utilizing a high energy Co^{60} γ-ray irradiation method. The dose rate used was 0.1 Mrad/h. After irradiation, the reaction solution was poured into an excess of cold methnol, and the precipitate was filtered, dried, and weighed. The crude graft product was then kept in a Soxhlet apparatus for more than 48 h to extract PMMA homopolymer with acetone. The degree of grafting was calculated by the following equation:

$$\text{degree of grafting} = \frac{\text{wt grafted TPX} - \text{wt TPX}}{\text{wt TPX}}$$

Heterograft Copolymerization

The pure TPX membrane was dried in vacuum and weighed, and then was placed in a glass bottle. The grafting monomer solution was poured into the membrane and completely soaked the membrane. The solution was purged with nitrogen to remove oxygen. Graft copolymerization was carried out by irradiation with Co^{60} γ-ray at room temperature, dose rate 0.1 Mrad/h. After the irradiation, the grafted membrane was washed with acetone several times to remove all homopolymer and then dried in vacuum. The degree of grafting was calculated from the above-mentioned equation.

Irradiation Effect on Pure TPX Polymer Solution

In order to study the irradiation effect on TPX itself. Pure TPX solutions with different irradiation doses were prepared. The pure TPX polymer solution was prepared with the same procedure as that of the homograft copolymerization solution except without MMA.

The inherent viscosity of irradiated TPX solution was measured by a Ubbelohde viscometer with cyclohexene as a solvent at 30°C.

Membrane Preparation

Homograft membrane was prepared from a casting solution of grafted copolymer in cyclohexene or cyclohexene/acetone mixture solvent. Pure TPX membrane prepared by casting TPX in cyclohexene solution with different irradiation dose was cast under the same conditions as our previous report.[14] Heterograft membrane was prepared as in our previous report except that the monomer was MMA instead of vinyl pyridine. All the membranes were prepared under the conditions of heat treatment temperature of 30°C and heat treatment time of 40 min.

Gas Permeability and Mechanical Strength Tests of Membranes

Gas permeability of membranes and measurement of tensile strength were the same as reported previously.[14]

RESULT AND DISCUSSION

Performance of Pure TPX Membranes

As shown in Figure 1, the oxygen permeabilities increase up to a maximum and then decrease while the O_2/N_2 selectivities decrease to a minimum and then increase as irradiation time increases for the membrane cast from the TPX solution with dissolved oxygen during irradiation. For the oxygen permeabilities and O_2/N_2 selectivities of membranes cast from the TPX solution without oxygen, we follow the opposite trend as irradiation time increases. The reason to cause these observed gas permeability changes might be the effects of degradation and crosslinking. In order to prove these effects, the viscosity and mechanical strength changes were studied

Effect of Irradiation Time on Viscosity of TPX Polymer Solution

Figure 2 shows the effect of irradiation time on the viscosity of the TPX polymer solution. Viscosity of the TPX polymer solution with dissolved oxygen decreases to a minimum, while that of the solution without oxygen

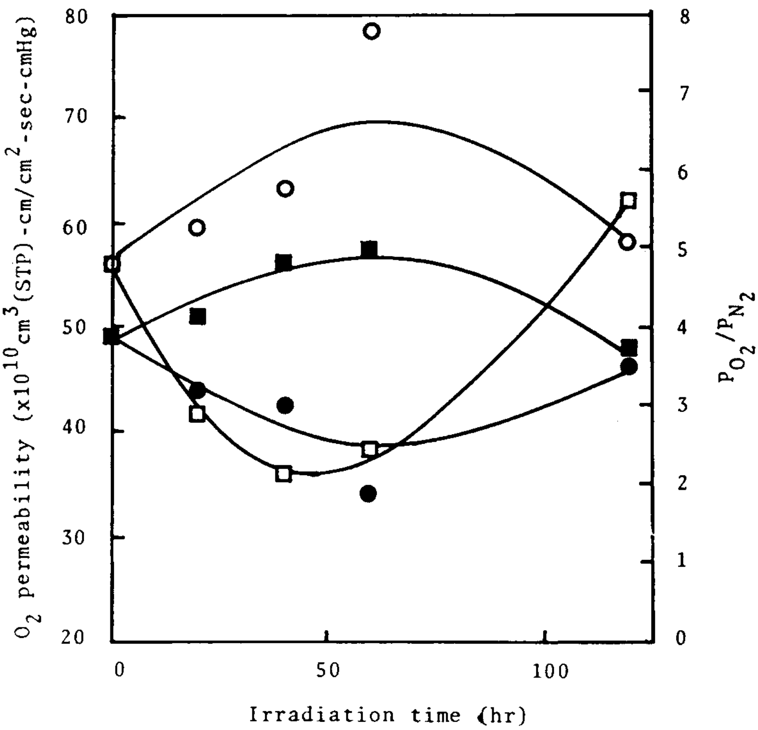

Fig. 1. Performance of pure TPX membranes: 5 wt % TPX in cyclohexene; dose rate 0.1 Mrad/h. Solution condition: (□) without O_2; (○) with dissolved O_2(□, ○) O_2 permeability coefficient; (■, ●)PO_2/PN_2.

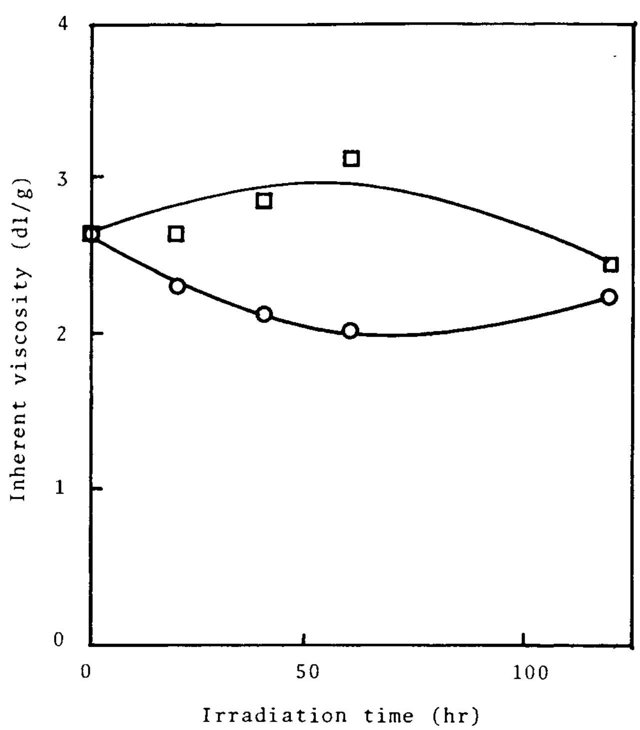

Fig. 2. Effect of irradiation time on inherent viscosity of TPX polymer solution: 5 wt % TPX in cyclohexene: dose rate 0.1 Mrad/h. solution condition: (□) without O_2; (○) with dissolved O_2.

increases to a maximum and then decreases, as irradiation time increases. This viscosity change study of the TPX polymer solution after irradiation would provide the support of the explanation of degradation for solution with the presence of dissolved oxygen and slight crosslinking for solution without oxygen.[17-19]

Mechanical Strength of Membrane

Figure 3 shows that tensile strength increases and elongation decreases with increasing degree of MMA homografting. Figure 4 shows the effect of irradiation time on tensile strength and elongation of pure TPX membranes that were cast from the solutions with or without dissolved oxygen during irradiation. As irradiation time increases, the tensile strength increases up to a maximum and then decreases for the membrane which was free from oxygen during irradiation. This could be explained by the fact that slight crosslinking was formed around 40–60 h irradiation time, and degradation was caused for higher irradiation time. For the membrane cast from solution with dissolved oxygen, the tensile strength decreases to a minimum and then increases as the irradiation time increases. It indicates that the degradation of TPX polymer possibly caused with the presence of oxygen for irradiation time up to 40 h.

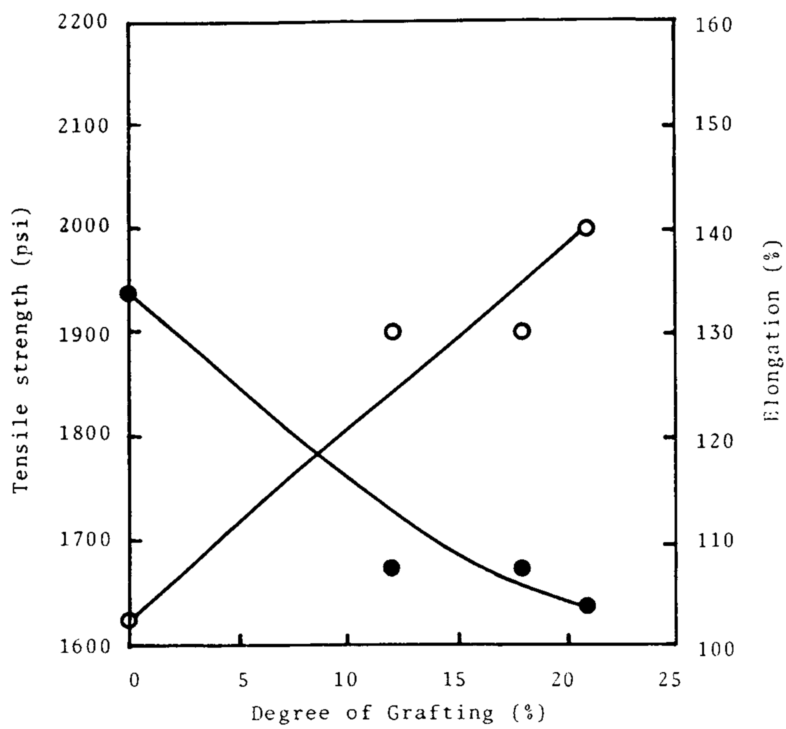

Fig. 3. Mechanical strength of homografted membranes: irradiation time 40 h; dose rate 0.1 Mrad/h; medium solvent, cyclohexene; Solution condition, with dissolved O_2; (○) tensile strength; (●) elongation.

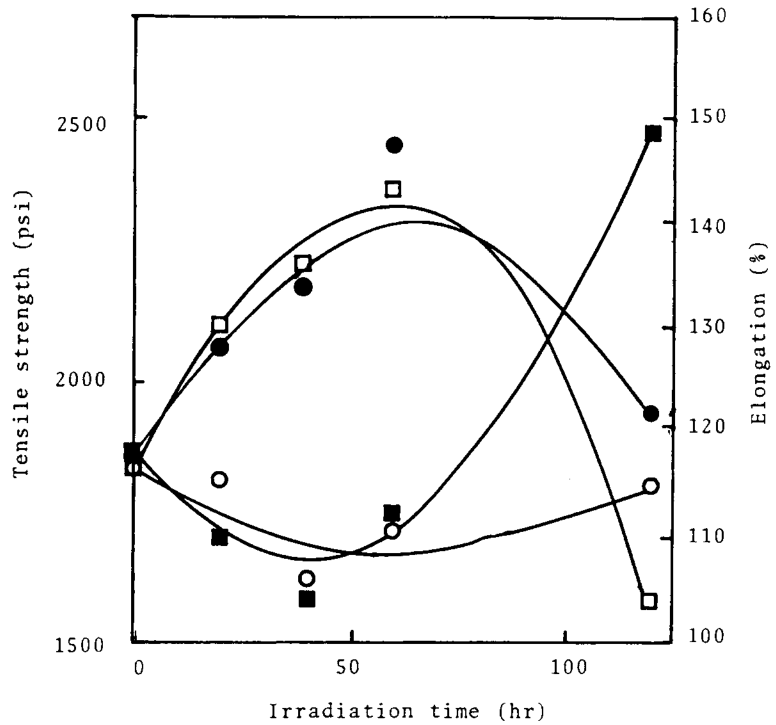

Fig. 4. Effect of irradiation time on mechanical strength of pure TPX membranes: 5 wt % TPX in cyclohexene; dose rate 0.1 mrad/h; solution condition: (□) without O_2, (○) with dissolved O_2; (□, ○) tensile strength, (■, ○) elongation.

Effect of TPX Concentration on the Degree of Grafting

It is observed in Figure 5 that there is an optimum TPX concentration (22 g/100 mL solution) at which the degree of grafting is maximum. It could be explained that the maximum extension of the backbone polymer occurs at 2 g TPX/100 mL soluton and at this concentration of TPX, the pentration of polymer chains is maximum, with increase in the concentration of TPX, grafting is found to decrease. This indicates that, beyond optimum concentration, gel effect becomes pronounced. The formation of gel increases the viscosity of the reaction solution and the movement of the growing grafted polymer chains is restricted with the result that the attack on the active site of TPX backbone is decreased.[20] Hereafter 2 g TPX/100 mL solution was used for the result of this report.

Effect of Irradiation Time and MMA Content on the Degree of Grafting

Figure 6 shows the effect of irradiation time and MMA content on the degree of grafting of MMA onto TPX for the grafting solution with dissolved oxygen during irradiation. It is observed that, with an increase in irradiation time, degree of grafting increases, reaches a maximum at 40 h, and then falls off. This is different from Tsuzuki et al.,[15,16] who report that the degree of styrene grafting onto cellulose increased linearly with increasing irradiation

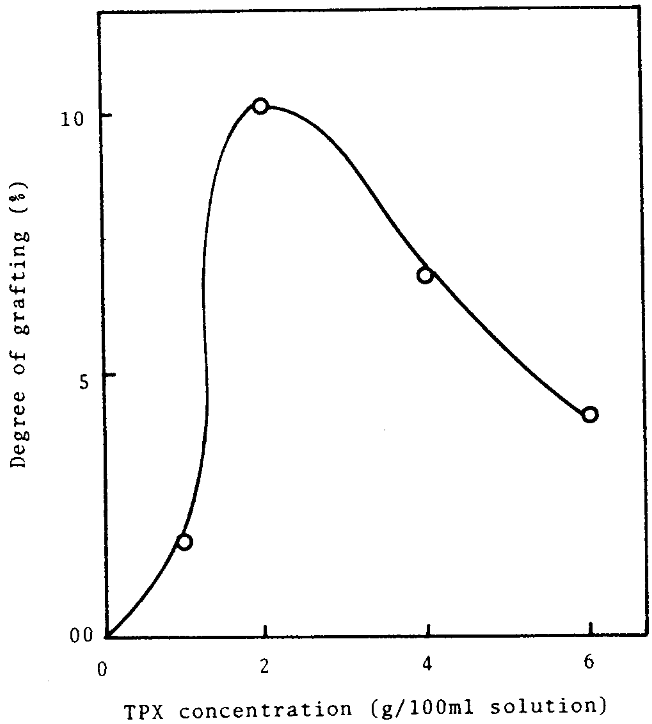

Fig. 5. Effect of TPX concentration on the degree of MMA grafted onto TPX: irradiation time 20 h, dose rate 0.1 Mrad/h; medium solvent; cyclohexane; MMA concentration 10 vol %; solution condition, with dissolved O_2.

time. This could be explained by the fact that polystyrene was crosslinked while PMMA was degraded after irradiation.[21] In the beginning of irradiation, the degree of grafting increased due to the active sites increasing, and then the degradation of PMMA occurred after sufficient energy was irradiated (0.1 Mrad/h × 60 h in this study): hence degree of grafting decreased. It is also observed that the degree of grafting increases as MMA content increases. The solution with higher than 30% MMA content was changed from clear to opaque. It is indicated that the phase separation occurred due to the addition of nonsolvent (MMA).[22,23] It was suggested from this experimental that MMA concentration should not exceed 30% for good membrane formation.

Effect of Medium Solvent on the Degree of Grafting

Figure 7 shows the effect of medium solvent on the degree of MMA grafted onto TPX. The differences between cyclohexane and cyclohexene are that the former has a single bond and higher *G*-value, free radical value per 100 eV absorbed, and the latter has a double bond and lower *G*-value.[17] This explains the fact that the result of the degree of grafting for using cyclohexane as medium solvent is higher than for using cyclohexene. However it was found that the homografted polymers using cyclohexane as medium solvent made it rather difficult to form membrane, so that cyclohexene was used as medium solvent for most of this study.

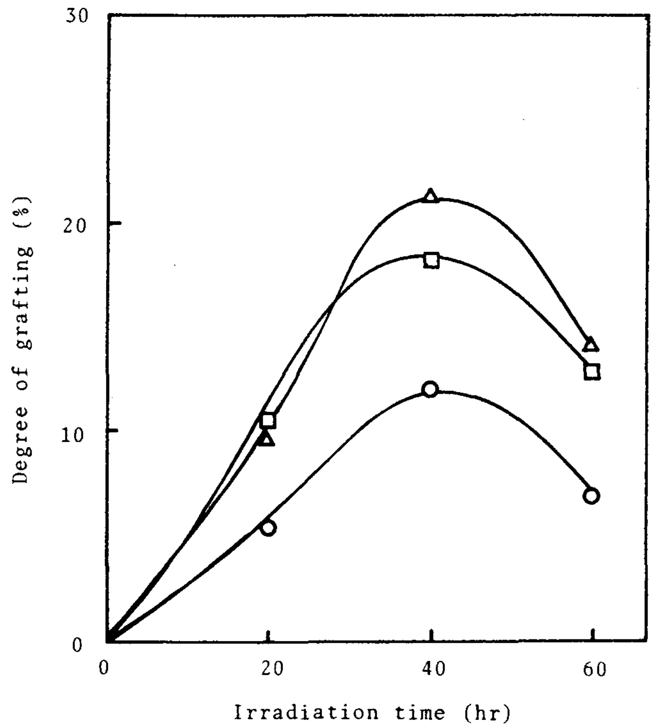

Fig. 6. Effect of irradiation time and MMA content on the degree of MMA grafted onto TPX: dose rate 0.1 Mrad/h; medium solvent, cyclohexene; solution condition, with dissolved O_2; MMA concentration: (○) 10 vol %; (□) 20 vol %; (△) 30 vol %.

Effect of Oxygen on Degree of Grafting

As shown in Figure 8, under the same irradiation dose the MMA grafting degree of TPX with dissolved oxygen is higher than that of TPX without oxygen by freezing, degassing, and melting processings. The higher degree of grafting is caused by the peroxide and peroxy radicals which were produced in the presence of oxygen during irradiation.[17–19]

Performances of Membranes Cast from Grafting Solutions with / without Oxygen during Irradiation

As shown in Figure 9, the oxygen/nitrogen permeability ratio increases rapidly, and oxygen permeability decreases as the degree of grafting increases for the membrane cast from degassing solution during irradiation. But for the membrane cast from the polymer solution with dissolved oxygen during irradiation when the degree of grafting increases, the oxygen/nitrogen permeability ratio increases only slightly.

The performances shown in Figure 9 were adjusted to the MMA volume percents to provide different degrees of grafting for constant irradiation time of 40 h.

The O_2/N_2 permeability ratio of MMA homografted TPX membrane is significantly improved, compared to that of nongrafting TPX membrane. For

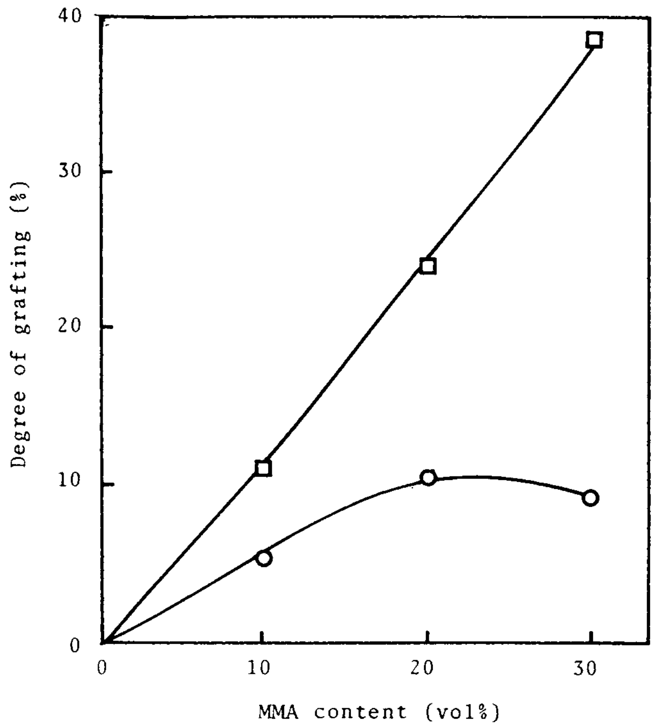

Fig. 7. Effect of medium solvent on the degree of MMA grafted onto TPX: irradiation time 20 h; dose rate 0.1 Mrad/h; solution condition, with dissolved O_2; medium solvent: (○) cyclohexene; (□) cyclohexane.

example, an oxygen/nitrogen permeability ratio of 7.6 and 28×10^{-10} cm^3 cm/cm^2 s cm Hg oxygen permeability of the membrane which was cast from the degassing polymer solution, with 20% degree of grafting, can be obtained. The oxygen permeability and oxygen/nitrogen permeability of nongrafted TPX membrane are 56×10^{-10} cm^3 cm/cm^2 s cm Hg and 3.9, respectively.

Effect of Grafting Degree on Performances of Membranes Cast from Polymer Solution with Dissolved Oxygen

The data of membranes with zero degree of grafting as shown in Figure 10 represent that of membranes prepared from pure TPX polymer solution in the presence of dissolved oxygen with 20, 40, and 60 h irradiation times. Oxygen permeability of the mentioned pure TPX membrane increases as irradiation time increases because of the polymer degradation caused by irradiation. Figure 10 shows that gas permeabilities decrease and PO_2/PN_2 ratios increase with increasing MMA grafting degree for membranes with different irradiation times. The degree of grafting was controlled by different MMA contents for each fixed irradiation time. With increasing degree of grafting, gas permeability of 20 h irradiation treated membrane decreases much more seriously than that of the membrane dose for a longer irradiation treatment. Because the TPX polymer degradation would affect the increase of gas permeability while the grafted MMA plays a major role on decreasing effect. The gas

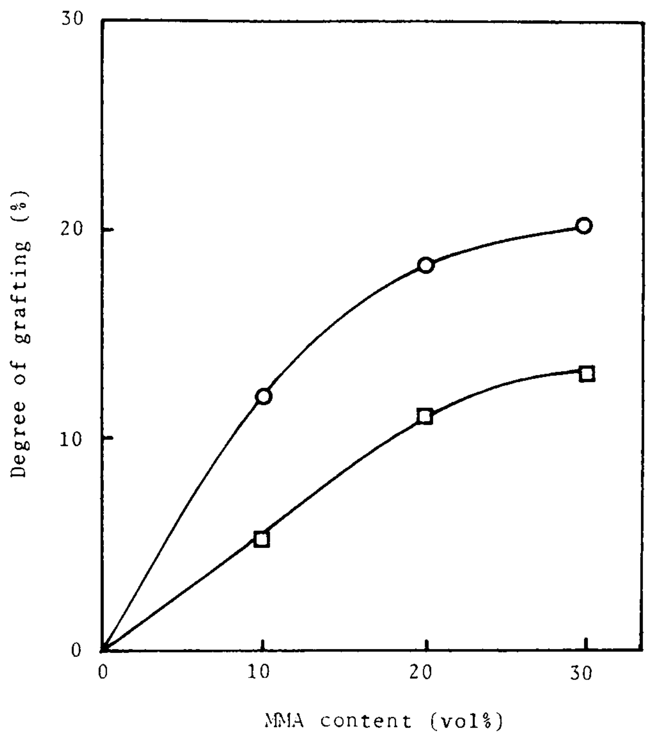

Fig. 8. Effect of oxygen in grafting solution on the degree of MMA grafted onto TPX: irradiation time 20 h; dose rate 0.1 Mrad/h; medium solvent, cyclohexene; solution condition: (□) without O_2; (○) with dissolved O_2.

permeabilities decrease with increasing grafting degree not so seriously for 40 and 60 h irradiation treated membranes.

From this result, it suggests that the MMA homografted TPX membrane with high gas permeability and high PO_2/PN_2 ratio should be obtained under the condition of 60 h irradiation time and around 7% degree of grafting.

Comparison of Membranes by Homografting and Heterografting Methods

As shown in Figure 11, the oxygen permeability decreases seriously and the oxygen/nitrogen permeability ratio increases slightly as grafting degree increases for membranes prepared by heterografting method. Compared to performances of heterografted membranes, the high oxygen permeabilities and oxygen/nitrogen permeability ratios of membranes could be obtained by the homografting method; a much lower grafting degree of MMA could be used than that of the heterografting method. For example, the oxygen permeability of 42×10^{-10} cm^3 cm/cm^2 s cm Hg and O_2/N_2 permeability ratio of 5 could be prepared by homografting method with 10% MMA grafting degree while 32×10^{-10} cm^3 cm/cm^2 s cm Hg oxygen permeability with O_2/N_2 permeability ratio of 5 should be prepared by the heterografting method with 60% MMA grafting degree.

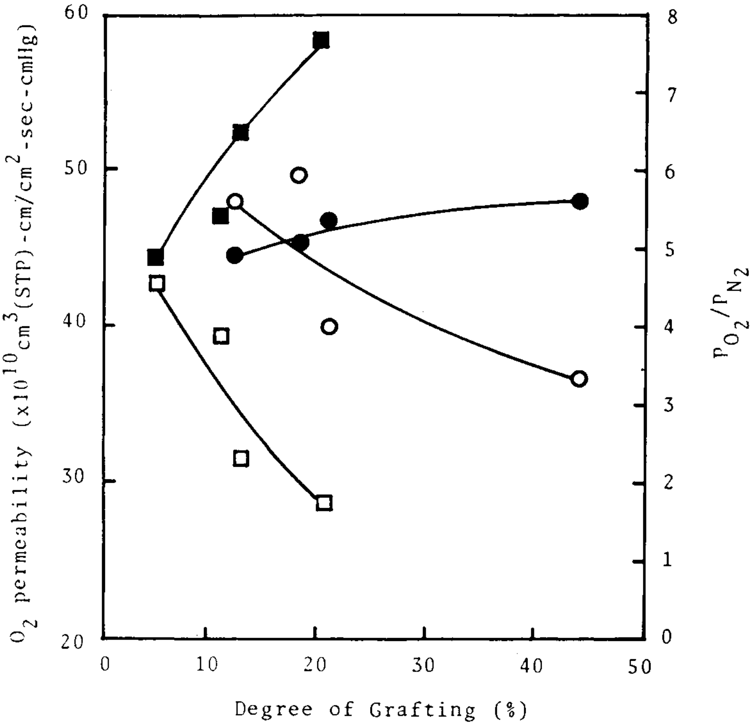

Fig. 9. Performance of membranes casting from grafting solution with/without O_2 during irradiation: irradiation time 40 h; dose rate 0.1 Mrad/h; medium solvent, cyclohexene; solution condition: (□) without O_2; (○) with dissolved O_2; (□, ○) O_2 permeability coefficient; (■, ●) PO_2/PN_2

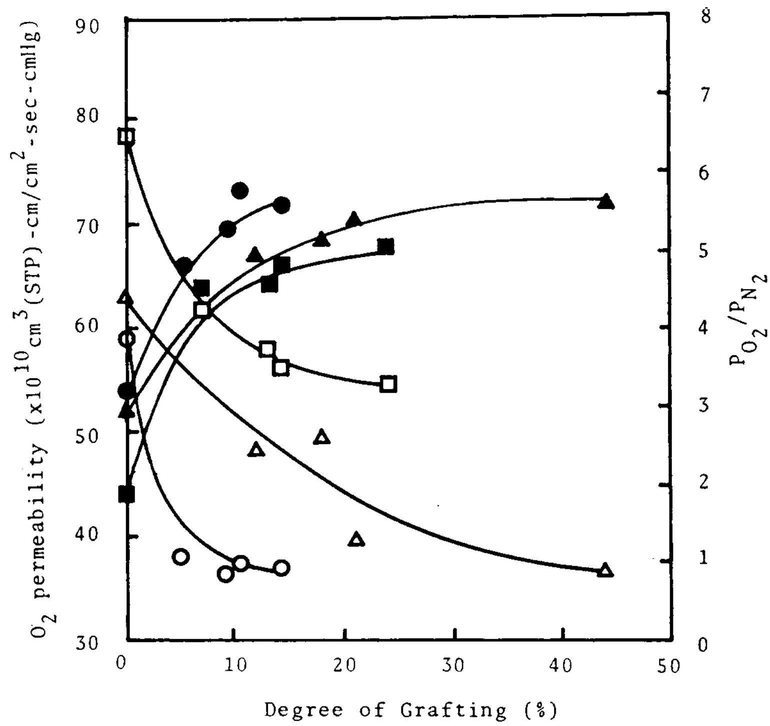

Fig. 10. Effect of grafting degree on performance of membranes casting from grafting solution with dissolved O_2 during irradiation: dose rate 0.1 Mrad/h; irradiation time: (○) 20 h; (△) 40 h; (□) 60 h; (○, △, □) O_2 permeability coefficient; (●, ▲, ■) PO_2/PN_2

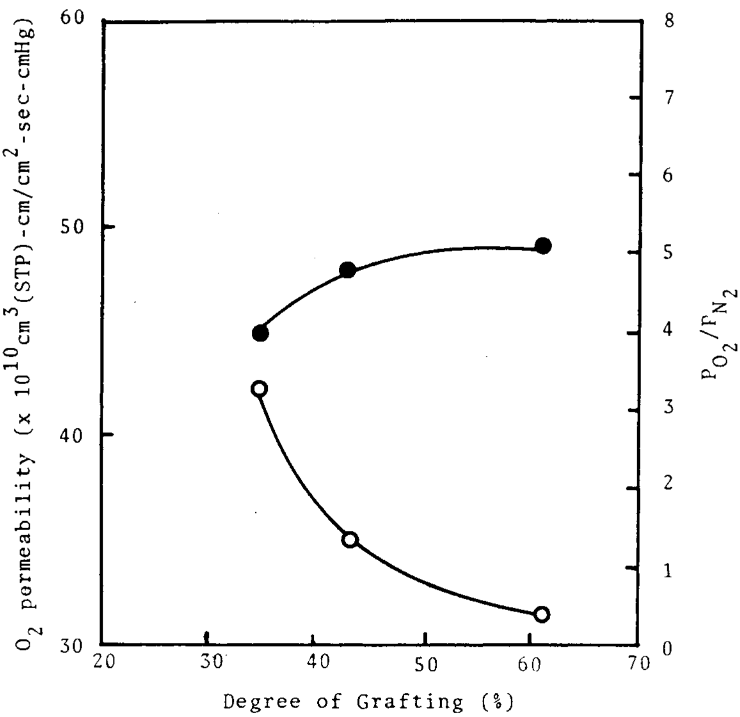

Fig. 11. Effect of heterografting degree on performance of membranes: irradiation time 20 h; dose rate 0.1 Mrad/h; medium solvent, dioxane; (○) O_2 permeability coefficient; (●) PO_2/PN_2.

CONCLUSION

The degradation of TPX polymer of casting solution with dissolved oxygen was proved by the decrease of tensile strength, viscosity, and increase of elongation. The slight crosslinking of TPX polymer of the degassing casting solution was believed to be caused by the fact of appreciable increase of tensile strength, viscosity, and decrease of elongation. By utilizing the factors of degradation, slight crosslinking, and high O_2/N_2 selectivity of MMA, the performances of TPX membrane can be efficiently improved. With increasing degree of grafting, the permeability of MMA homograft copolymerized membrane decreases and its selectivity increases.

The O_2/N_2 permeability ratio of MMA homografted TPX membrane is improved, compared to that of nongrafting TPX membrane. For example, an O_2/N_2 permeability ratio of 7.6 and 28×10^{-10} cm^3 cm/cm^2 s cm Hg oxygen permeability of the membrane, cast from the degassing polymer solution during irradiation for 20% degree of grafting, can be obtained. MMA-homografted TPX membrane with high gas permeability and fairly high O_2/N_2 permeability ratio can be prepared under the conditions of 60 h irradiation time to cause suitable TPX polymer degradation of grafting solution with dissolved oxygen. For example, with an oxygen permeability of 63×10^{-10} cm^3 cm/cm^2 s cm Hg and an O_2/N_2 permeability ratio of 4.5 for 60 h irradiation, about 10% degree homografted membrane can be obtained.

Compared to performances of heterografting membranes, the high oxygen permeability and oxygen/nitrogen permeability ratio of membranes could be obtained by the homografting method; a much lower grafting degree of MMA could be used than that of the heterografting method.

The authors wish to thank the National Science Council of the Republic of China for financial support.

References

1. Jpn. Pat. 79 146277 (1979).
2. W. J. Ward III, W. R. Browall, and R. M. Salemme, *J. Membr. Sci.*, **1**, 99 (1976).
3. M. Kawakami, Y. Yamashita, M. Iwamoto, and S. Kagawa, *J. Membr. Sci.*, **19**, 249 (1984).
4. M. Yamamoto, J. Sakata, and M. Hirai, *J. Appl. Polym. Sci.*, **29**, 2981 (1984).
5. N. Inagaki and D. Tsutsumi, *Polym. Bull.*, **16**, 131, (1986).
6. N. Inagaki and J. Ohkubo, *J. Membr. Sci.*, **27**, 63 (1986).
7. J. Y. Lai, G. J. Wu, and S. S. Shyu, *J. Appl. Polym. Sci.*, **34**, 559 (1987).
8. R. W. MacDonald and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **26**, 2239 (1981).
9. A. W. Myers, C. E. Rogers, V. Stannett, and M. Szware, *J. Appl. Polym. Sci.*, **4**, 159 (1960).
10. H. K. Lonsdale and H. E. Podall, *Reverse Osmosis Membrane Research*, Plenum, New York, and London, 1972, p. 236.
11. J. F. Kanitz and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 2739 (1970).
12. J. F. Kanitz and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **15**, 67 (1971).
13. C. E. Rogers, *Permeability of Plastic Films and Coatings*, H. B. Hopfenberg, Ed., Plenum, New York and London, 1974, p. 157.
14. J. Y. Lai and S. L. Wei, *J. Appl. Polym. Sci.*, **32**, 5763 (1986).
15. M. Tsuzuki, I. Hagiwara, N. Shiraishi, and T. Yokota, *J. Appl. Polym. Sci.*, **25**, 2721 (1980).
16. M. Tsuzuki, I. Hagiwara, N. Shiraishi, and T. Yokota, *J. Appl. Polym. Sci.*, **25**, 2909 (1980).
17. A. J. Swallow, *Radiation Chemistry*, Longman, London, 1973.
18. G. Odian, *Principles of Polymerization*, 2nd ed., Wiley, New York, 1981.
19. T. Seguchi, S. Hashimoto, K. Arakawa, N. Hayakawa, W. Kawakami, and I. Kuriyama, *Radiat. Phys. Chem.*, **17**, 195 (1981).
20. B. N. Misra, I. K. Mehta, M. Kanthwal, and S. Panjloo, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 2177 (1987).
21. E. J. Lawton, A. M. Bueche, and J. S. Balwit, *Nature*, **172**, 76 (1953).
22. N. Nishioka and K. Kosai, *Polym. J.*, **13**, 1125 (1981).
23. N. Nishioka and K. Kosai, *Polym. J.*, **15**, 159 (1983).
24. N. Nishioka and K. Kosai, *Polym. J.*, **15**, 591 (1983).

Received February 18, 1988
Accepted May 6, 1988