

Polysulfone Hollow Fiber Membranes Spun from Lewis Acid:Base Complexes. II. The Effect of Lewis Acid to Base Ratio on Membrane Structure

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Synopsis

Oxygen plasma ablation has been used to define the structure of polysulfone hollow fiber membranes spun from Lewis acid:base complex solvents in which the molar ratio of propionic acid to *N*-methylpyrrolidone was varied. It was found that the helium/nitrogen separation factor of the unetched samples increases with increasing PA/NMP molar ratios. This increase implies a decrease in surface porosity of the resultant hollow fiber as larger fractions of the total NMP in the solvent are complexed with propionic acid. The results also suggest that the differences between the outer separating layer and the supporting matrix increase with increases in the PA/NMP molar ratios. Therefore, a more rapid transition from the separating layer to the porous supporting matrix exists in hollow fiber membranes spun from the higher PA/NMP ratios.

INTRODUCTION

Integrally skinned phase inversion membranes were successfully fabricated from dopes of polysulfone in solvents containing Lewis acids, such as propionic acid, and Lewis bases, such as *N*-methylpyrrolidone.¹ Such pairs were shown to form Lewis acid:base complexes in stoichiometric ratios.¹ Formation of the complex allows the spinning dope to be loaded with larger amounts of nonsolvent than can be achieved with more conventional solvent/nonsolvent mixtures. Because the complex is rapidly disrupted by the presence of water during the coagulation step, the sol-to-gel transition is accelerated yielding a hollow fiber membrane which exhibits increased free volume, reflected by an elevated T_g , and concomitantly improved transport rates with a surprising maintenance of selectivity provided that the solvent is rapidly and completely removed from the hollow fiber membrane.^{1,2}

Oxygen plasma ablation was shown to be a useful technique to study the structure of hollow fiber membranes.³⁻⁵ Hollow fiber membranes are amenable to study by oxygen plasma ablation because the treatment is confined to the surface regions of a polymer and does not alter its bulk properties.⁶⁻¹⁰ Also, oxygen plasma ablation is a low temperature process which precludes thermal alteration of the specimen.¹¹ Finally, the oxygen plasma ablation rate is independent of free volume differences from sample to sample.¹²

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The use of oxygen plasma ablation to study the structural differences between hollow fiber membranes spun from 1 : 1 molar ratios of the propionic acid : *N*-methylpyrrolidone Lewis acid : base complex (PA : NMP) and those spun from formylpiperidine/formamide (FP/FA), a conventional solvent/non-solvent pair, has been reported.¹³ It is shown that hollow fiber membranes spun from 1 : 1 molar ratios of the propionic acid : *N*-methylpyrrolidone Lewis acid : base complex have active separating layers approximately half the thickness of the FP/FA spun hollow fiber membranes and that this active separating layer is not equivalent to the microscopically observable skin of a membrane formed by the phase inversion process but is instead a component of it. Furthermore, it is shown that not only does the 1 : 1 PA : NMP spun membrane have a thinner transition zone between the active separating layer and the porous substrate but that this zone has a larger gradient in the increase of pore sizes across it than do the FP/FA spun hollow fiber membranes. Also, it is shown that the internal matrices of the PA : NMP hollow fiber membrane offer less resistance to gas transport than do those of the FP/FA spun hollow fiber membranes.

In this paper, the structural differences, determined by oxygen plasma ablation, of polysulfone hollow fiber membranes spun from dopes in which the molar ratio of propionic acid/*N*-methylpyrrolidone were varied from 1.09 to 0.33 are presented.

EXPERIMENTAL

Test cells were prepared from hollow fiber membranes spun from 37% total solids polysulfone (Amoco Udel 3500) dopes in propionic acid : *N*-methylpyrrolidone Lewis acid : base complexes in which the PA/NMP molar ratios varied from 1.09 to 0.33. Fifteen test cells of each type were made, as described in the first paper in this series.¹³ These 15 were subdivided into five sets of three cells each. Therefore, triplicate samples of each hollow fiber membrane were studied under each condition. Samples were subjected to oxygen plasma ablation for 1, 2, 3, or 5 min. Three samples remained as the unetched controls. The ablation experiments were carried out in the Plasma Technology System 80 barrel etcher. A radiofrequency of 13.6 MHz was maintained at 30 W during these experiments. The oxygen flow rate was 20 sccm, and the temperature within the etcher remained in the 27–28°C range throughout all of these experiments. The oxygen plasma ablated samples and unetched controls were measured for their helium and nitrogen flux rates and the results calculated as described in the preceding paper.¹³

The glass transition temperatures of all the samples were obtained by DSC analysis from room temperature to 250°C. All samples were tested in duplicate in a Dupont 1090 differential scanning calorimeter at a 20°C/min heating rate. After the first heat, the samples were cooled and subsequently reheated. Precision of the measurements is at least $\pm 1.0^\circ\text{C}$.

RESULTS AND DISCUSSION

The uncoated helium and nitrogen permeation rates as a function of oxygen plasma ablation time for propionic acid : *N*-methylpyrrolidone complexes

TABLE I
Uncoated Helium and Nitrogen Permeation Rates^a of Polysulfone Hollow Fiber Membranes Spun with Various Propionic Acid:n-methylpyrrolidone Molar Ratios as Function of Oxygen Plasma Etch Time (30 W RF, 20 cc/min O₂ flow rate)

Etch time (min)	$P/l(\text{He}) \times 10^6$	$P/l(\text{N}_2) \times 10^6$	α	$P/l(\text{He}) \times 10^6$	$P/l(\text{N}_2) \times 10^6$	α	$P/l(\text{He}) \times 10^6$	$P/l(\text{N}_2) \times 10^6$	α	$P/l(\text{He}) \times 10^6$	$P/l(\text{N}_2) \times 10^6$	α
0	446	191	2.4	189	41	4.7	614	227	2.7	560	194	2.9
1	601	273	2.2	689	334	2.1	1345	508	2.3	1490	617	2.4
2	592	269	2.2	569	236	2.4	1427	629	2.3	1314	543	2.4
3	580	267	2.2	938	395	2.4	1617	744	2.2	1723	743	2.2
5	633	250	2.6	1118	500	2.3	1614	740	2.2	1699	724	2.3
0	312	86	3.6	288	72	4.0	296	70	4.2	267	61	4.5
1	1610	769	2.2	661	268	2.5	648	236	2.7	713	244	2.9
2	2429	1041	2.4	1159	511	2.3	1227	499	2.5	1900	808	2.4
3	3246	1457	2.2	1416	697	2.1	2870	1372	2.1	3075	1441	2.1
4				1697	856	2.0						
5	3320	1536	2.2				3472	1663	2.1	4179	2125	2.0

^aThe units of permeability are (cm³ (STP)/cm² sec cm Hg).

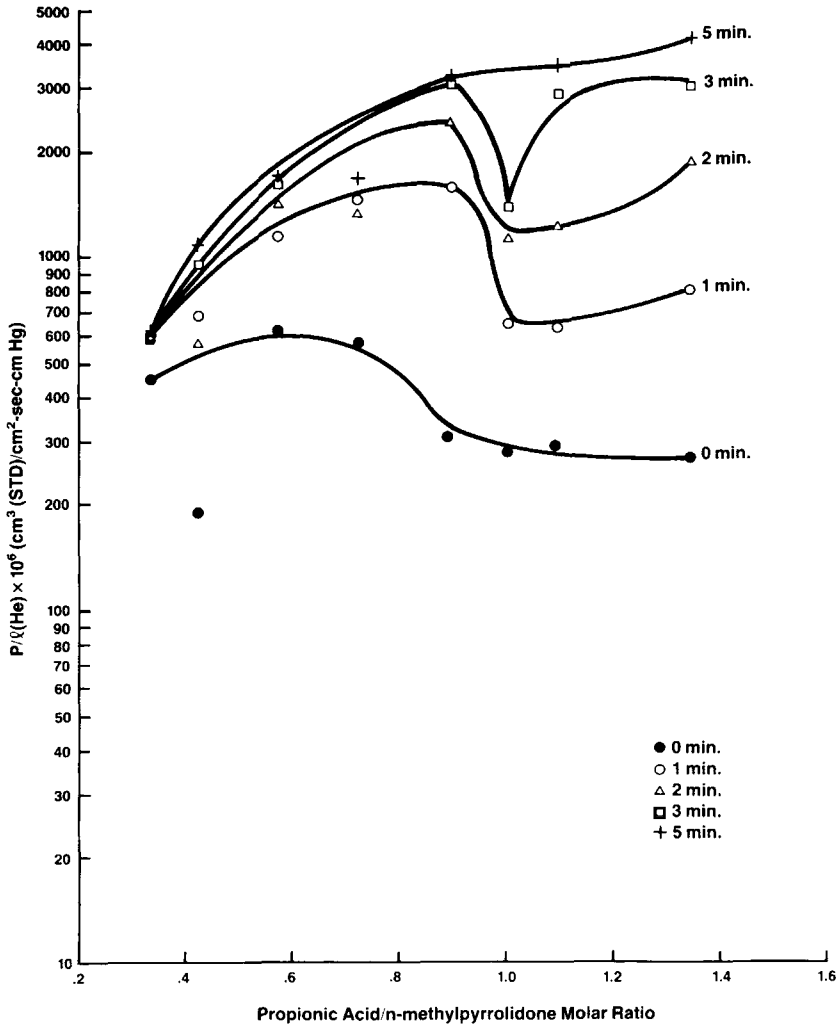


Fig. 1. $P_l/(He)$ vs. PA/NMP molar ratios as function of oxygen plasma ablation time.

(PA : NMP) with varying molar ratios is given in Table I. The results are shown graphically in Figures 1–3 for the changes in helium transport rate, nitrogen transport rate and helium/nitrogen separation factor, with the change in PA/NMP molar ratio. The results for samples etched at identical ablation times are connected by isoablation lines. The glass transition temperatures, which were obtained on the first heat, are shown in Table II for the hollow fiber membranes prepared from each dope composition.

Examination of Figures 1 and 2 reveals initial increases in both the helium and nitrogen permeabilities of the unetched hollow fiber membrane samples as the PA/NMP molar ratio is increased from 0.33 to 0.57. A decline in both is then observed with additional increases of the PA/NMP ratio. As oxygen plasma ablation proceeds, the maxima in the permeability curves vs. PA/NMP ratio appears to shift to a higher PA/NMP ratio of 0.89 at intermediate ablation times. Upon additional increases of the PA/NMP ratio, both the

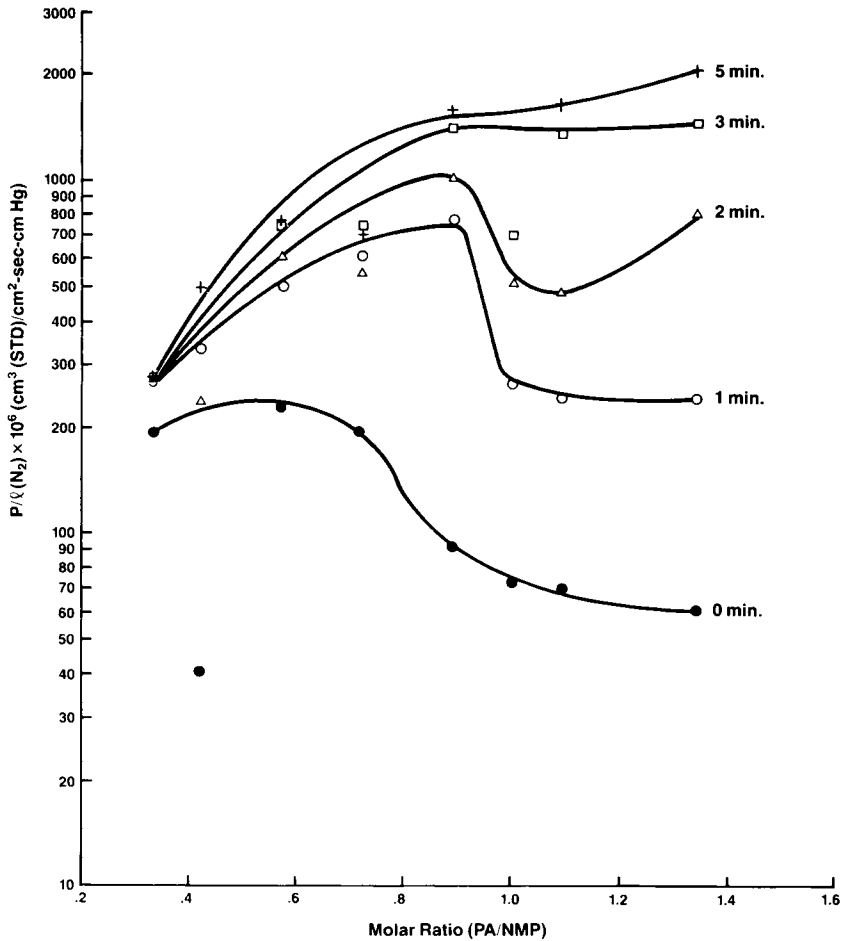


Fig. 2. $P/l(N_2)$ vs. PA/NMP molar ratios as function of oxygen plasma ablation time.

helium and nitrogen permeabilities experience declines with minima appearing at a PA/NMP molar ratio of 1.0. The minima disappear at longer etch times (5 min). Because the outer separating layer is removed with 2 min of ablation,¹³ the isoablation lines at 2 min or more reflect the gas transport rates through matrices unimpeded by the separating layer. Therefore, the isoablation lines are related to the decrease in resistance of the supporting matrix to gas flow. Therefore, the gas flux is controlled by the porosity and tortuosity of the matrix which is related to dimensions of the pores and the degree of their open cellular structure. Consequently, as the PA/NMP molar ratio of the spinning solvent is increased, the internal resistance of the porous supporting matrix diminishes. This is consistent with the appearance of a more open cellular structure with larger pores. As the pores increase in size, so do both the number and sizes of the holes in the walls of the cells.

It can be seen that the greatest change from the separating layer to the porous supporting matrix as measured by changes in the helium and nitrogen permeation rates with oxygen plasma surface ablation occur in polysulfone

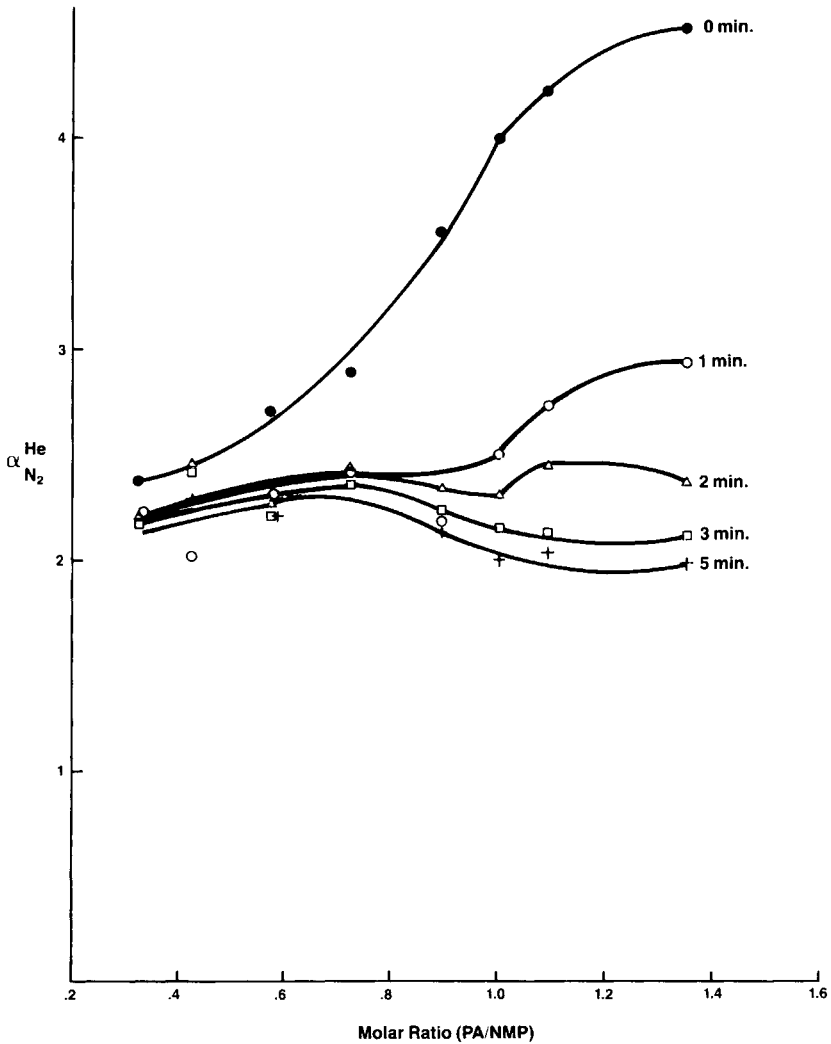


Fig. 3. Separation factor (He/N_2) vs. propionic acid/NMP molar ratios as function of oxygen plasma ablation time.

hollow fiber membrane spun at 0.89 PA/NMP molar ratios. This indicates a more rapid transition from the outer separating layer to the open cellular substrate. These hollow fiber membranes have an uncoated, unetched helium/nitrogen separation factor of 3.57, which indicates a separating layer with lower porosity than obtained with those spun with lower PA/NMP ratios. Similar results also may be expected at PA/NMP greater than 1. It may be that a slight excess of either *N*-methylpyrrolidone or propionic acid may be beneficial to scavenge traces of water which could disrupt the Lewis acid:base complex in the dope.

Examination of Figure 3 reveals an increase in separation factor of the unetched samples with decreasing NMP content, i.e., increasing propionic acid/*N*-methylpyrrolidone molar ratios. This implies a decrease in surface

TABLE II
First Heat Glass Transition Temperature as Function of
Lewis Acid/Lewis Base Molar Ratios

PA/NMP molar ratio	T_g (°C)
0.33	187
0.42	187
0.57	197
0.72	197
0.89	197
1.00	195
1.09	197
1.34	197

porosity of the resultant hollow fiber membrane as increasing percentages of the total NMP in the spinning dope are complexed with propionic acid. The hollow fiber membrane spun from the 0.33 PA/NMP molar ratio solvent has a separation factor of 2.35, which is less than that of 2.65 predicted for Knudsen flow by the equation

$$\frac{Q(\text{He})}{Q(\text{N}_2)} = \left(\frac{M_{\text{N}_2}}{M_{\text{He}}} \right)^{1/2} = \left(\frac{28}{4} \right)^{1/2} = 2.65 \quad (3)$$

where Q = the flux rate of the gas and M = the molecular weight of the gas. This implies that pores with diameters greater than the mean-free-path length of the diffusing species penetrate through the outer surface layer of the hollow fiber membrane. As the molar ratio of propionic acid to *N*-methylpyrrolidone approaches 1.00, the separation factors increase suggesting a more perfect outer separating layer with pores whose diameters are smaller than the mean-free-path lengths of the diffusing gases.

The results also indicate that the differences between the outer separating layer and the supporting matrix increase as the PA/NMP molar ratio increases. For example, in the PA/NMP molar ratios in the 0.89–1.34 range dramatic decreases in separation factor occur after 1 min of oxygen plasma ablation, i.e., after removal of at least 11–12 nm from the effective separating layer. With these high PA/NMP molar ratios dopes, the solvent becomes a poorer solvent for the polysulfone promoting coagulation of the polymer from the dope.¹ Therefore, moisture in the air induces dissociation of the PA : NMP complex in the outer surface of the nascent hollow fiber membrane in the air gap between the spinnerette and the coagulation bath. A tighter, more uniform, i.e., lower porosity, outer separating layer results.

Hollow fiber membranes spun from dopes of lower PA/NMP molar ratio solvents are less susceptible to coagulation at their outer surfaces during the nascent fiber's short residence time in this air gap. Therefore, gelation and desolvation are retarded, and additional time is available during which sol inhomogeneities arise which are subsequently frozen into the structure following gelation.¹

CONCLUSIONS

Oxygen plasma ablation has been used to define the structure of polysulfone hollow fiber membranes prepared from 37% total solids dopes in Lewis acid : base solvents in which the propionic acid/*N*-methylpyrrolidone molar ratios were varied. It was found that the helium/nitrogen separation factor of the unetched samples increases with increasing PA/NMP molar ratios. This increase implies a decrease in surface porosity of the resultant hollow fiber membrane as higher percentages of the total NMP in the spinning dope are complexed with propionic acid. The results also suggest that the differences between the outer separating layer and the supporting matrix increase with increases in the PA/NMP molar ratios. Therefore, a more rapid transition from the separating layer to the porous supporting matrix exists in hollow fiber membranes spun from the higher PA/NMP ratios. These hollow fiber membranes possess a more open cellular structure with larger pores.

The results also suggest that a slight excess of either *N*-methylpyrrolidone or propionic acid may be beneficial to scavenge traces of water which could disrupt the Lewis acid : base complex in the dope.

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References

1. R. E. Kesting, A. K. Fritzsche, M. K. Murphy, A. C. Handermann, C. A. Cruse, and R. F. Malon, U.S. and Foreign patents applied for.
2. A. K. Fritzsche, R. E. Kesting, and M. K. Murphy, *J. Membr. Sci.*, to appear.
3. A. K. Fritzsche, *Proc. Am. Chem. Soc. Polym. Mater. Sci. Eng.*, **56**, 41 (1987).
4. A. K. Fritzsche, in *Applications of Polymers*, R. B. Seymour, Ed., Plenum, New York, 1987, pp. 17-27.
5. A. K. Fritzsche, paper presented at Sixth Annual IUCCP Symposium on Functional Polymers, Texas A & M University, College Station, TX, March 1988.
6. R. H. Hansen, in *Interface Conversion*, P. Weiss and G. D. Cheevers, Eds., Elsevier, New York, 1968.
7. H. Yasuda, C. E. Lamaze, and K. Sakaoku, *J. Appl. Polym. Sci.*, **17**, 137 (1973).
8. G. A. Byrne and K. C. Brown, *J. Soc. Dyers Colour.*, **88**, 113 (1972).
9. M. Hudis, *J. Appl. Polym. Sci.*, **16**, 2397 (1972).
10. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.*, **11**, 1461 (1967).
11. R. H. Hansen, J. V. Pascale, T. Benedictus, and P. M. Rentzepis, *J. Polym. Sci. A*, **3**, 2205 (1965).
12. E. L. Lawton, *J. Polym. Sci. A-1*, **10**, 1857 (1972).
13. A. K. Fritzsche, C. A. Cruse, and R. E. Kesting, *J. Appl. Polym. Sci.*, (preceding paper).

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