

# Polysulfone Hollow Fiber Membranes Spun from Aliphatic Acid (C<sub>2</sub>–C<sub>4</sub>) : *N*-Methylpyrrolidone Complexes—Structure Determination by Oxygen Plasma Ablation

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## Synopsis

Polysulfone hollow fiber membranes with increased free volumes as reflected by elevated glass transition temperatures can be obtained from a spectrum of Lewis acid : *N*-methylpyrrolidone (NMP) complexes provided that the complex is readily dissociated by water. The upper limit of the candidate Lewis acid for suitable complexes is an acceptor number between 49.1 (propionic acid) and 52.9 (acetic acid). Although the enhanced free volume yields an increase permeability with maintenance of selectivity, a knowledge of the structure and morphology of both the active separating layer and the substructure is needed to understand the performance of the membrane. Oxygen plasma ablation experiments have shown that the active separating layer of these membranes decreases in the order NMP/FA > acetic acid : NMP > propionic acid : NMP, butyric acid : NMP, and isobutyric acid : NMP with the differences among the last three being too small to resolve by the current experiment. Also, the surface and internal pore size and internal porosity appeared to increase in the order NMP/FA < acetic acid : NMP < propionic acid : NMP < isobutyric acid : NMP < butyric acid : NMP.

## INTRODUCTION

Integrally skinned phase inversion membranes were successfully spun from dopes of polysulfone in solvents containing Lewis acids and Lewis bases.<sup>1</sup> These form Lewis acid : base complexes in stoichiometric ratios.<sup>1</sup> Because of complex formation, the spinning dope contains higher concentrations of nonsolvent than can be achieved with more conventional solvent/nonsolvent mixtures. Because the complex is rapidly dissociated by water during the coagulation step, the sol-to-gel transition is accelerated, yielding a hollow fiber membrane that exhibits increased free volume, reflected by an elevated T<sub>g</sub>, and concomitantly improved transport rates with maintenance of selectivity provided that the solvent is rapidly and completely removed from the hollow fiber membrane.<sup>1,2</sup>

Oxygen plasma ablation was shown to be a useful technique with which to study the structure of hollow fiber membranes.<sup>3–5</sup> Hollow fiber membranes are amenable to study by oxygen plasma ablation because the treatment is confined

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TABLE I  
Nonsolvent Acceptor Number and T<sub>g</sub> Data for Hollow Fiber Membranes  
from 37% Total Solids Udel 3500 Dopes with NMP

Nonsolvent (wt %)	Complex <sup>a</sup>	Acceptor no.	T <sub>g</sub> (°C)	
			Initial	Reheat
Formamide (16)	–	39.8	185	191
Acetic acid (38)	+	52.9	189	191
Propionic acid (43)	+	49.1	195	190
Butyric acid (47)	+	48.3	195	191
Isobutyric acid (47)	+	47.0	197	191

<sup>a</sup> +, forms Lewis acid : base complex; –, does not form Lewis acid : base complex.

to the surface regions of a polymer and does not alter its bulk properties.<sup>6-10</sup> Also, oxygen plasma ablation is a low-temperature process that precludes thermal alteration of the specimen.<sup>11</sup> Finally, the oxygen plasma ablation rate is independent of free volume differences from sample to sample.<sup>12</sup>

In this series of papers, 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/nonsolvent pair, is reported.<sup>13</sup> It is shown that hollow fiber membranes spun from 1 : 1 molar ratios of the propionic acid : *N*-methylpyrrolidone complex have active separating layers approximately half the thickness of the FP/FA spun hollow fiber membranes and that this active separating layer is only a fraction of the microscopically observable skin. Furthermore, it is shown that not only does the 1 : 1 PA : NMP spun membrane have a thinner transition layer 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 in the FP/FA spun hollow fiber membranes. It is also shown that the internal matrices of the PA : NMP hollow fiber membrane offer less resistance to gas transport than those of the FP/FA spun hollow fiber membranes.

Oxygen plasma ablation has also been used to define the structure of polysulfone hollow fiber membranes prepared from dopes in which the propionic acid/*N*-methylpyrrolidone molar ratios were varied.<sup>14</sup> It was found that the helium/nitrogen separation factor of the unetched samples increases with increasing PA/NMP molar ratios. This implies a decrease in surface porosity of the resultant hollow fiber membranes as higher percentages of the total NMP are complexed with propionic acid. The results also indicate that the difference between the separating layer and the supporting matrix increases with increases in the PA/NMP molar ratio. Therefore, a more rapid transition from the separating layer to the supporting matrix exists in hollow fiber membranes spun from the higher PA/NMP ratios, which suggests that these hollow fiber membranes possess a more open cellular structure with larger pores.

In this paper, the structural differences, determined by oxygen plasma ablation, of polysulfone hollow fiber membranes spun from dopes of *N*-methylpyr-

TABLE II  
Performance<sup>a</sup> of Polysulfone Hollow Fiber Membranes Spun from Different Lewis Acid/*N*-Methylpyrrolidone Complexes  
as Function of Oxygen Plasma Ablation Time

Time (min)	NMP/FA (T <sub>g</sub> = 185°C)			Acetic acid : NMP (T <sub>g</sub> = 189°C)			Propionic acid : NMP (T <sub>g</sub> = 195°C)			Butyric acid : NMP (T <sub>g</sub> = 195°C)			Isobutyric acid : NMP (T <sub>g</sub> = 197°C)		
	P/l (He)	P/l (N <sub>2</sub> )	α	P/l (He)	P/l (N <sub>2</sub> )	α	P/l (He)	P/l (N <sub>2</sub> )	α	P/l (He)	P/l (N <sub>2</sub> )	α	P/l (He)	P/l (N <sub>2</sub> )	α
0	31.5	1.12	34.1	47.6	1.76	27.5	285	72	4.0	632	190	3.3	725	252	2.9
1	28.0	1.30	25.0	71.4	14.9	5.1	661	268	2.5	2160	928	2.3	2070	885	2.3
2	27.4	1.13	26.1	83.0	22.5	3.7	1160	511	2.3	3310	1450	2.3	2980	1340	2.2
2½	30.0	2.95	10.3	112	36.1	3.1	1360	638	2.1	3697	1639	2.3	3130	1430	2.2
3	30.6	2.04	15.2	105	33.5	3.1	1416	697	2.1	4370	1990	2.2	3440	1610	2.1
4	31.4	2.36	11.3	112	38.6	2.9	1700	856	2.0	4674	2140	2.3	4140	1980	2.1
8	35.9	5.08	7.2	125	48.9	2.6	1820	935	1.9	5440	2550	2.1	4610	2230	2.1
12	43.7	10.5	4.6	250	109	2.3	1890	1005	1.9	5370	2470	2.2	4220	2000	2.1
20	54.8	15.7	3.5	296	132	2.2	2130	1144	1.9	5822	2710	2.1	4450	2160	2.1
30	77.7	26.6	2.9	402	191	2.1	2210	1200	1.8	6130	2870	2.1	4460	2150	2.1

<sup>a</sup> All permeabilities are in units: × 10<sup>6</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup>-sec-cm Hg.

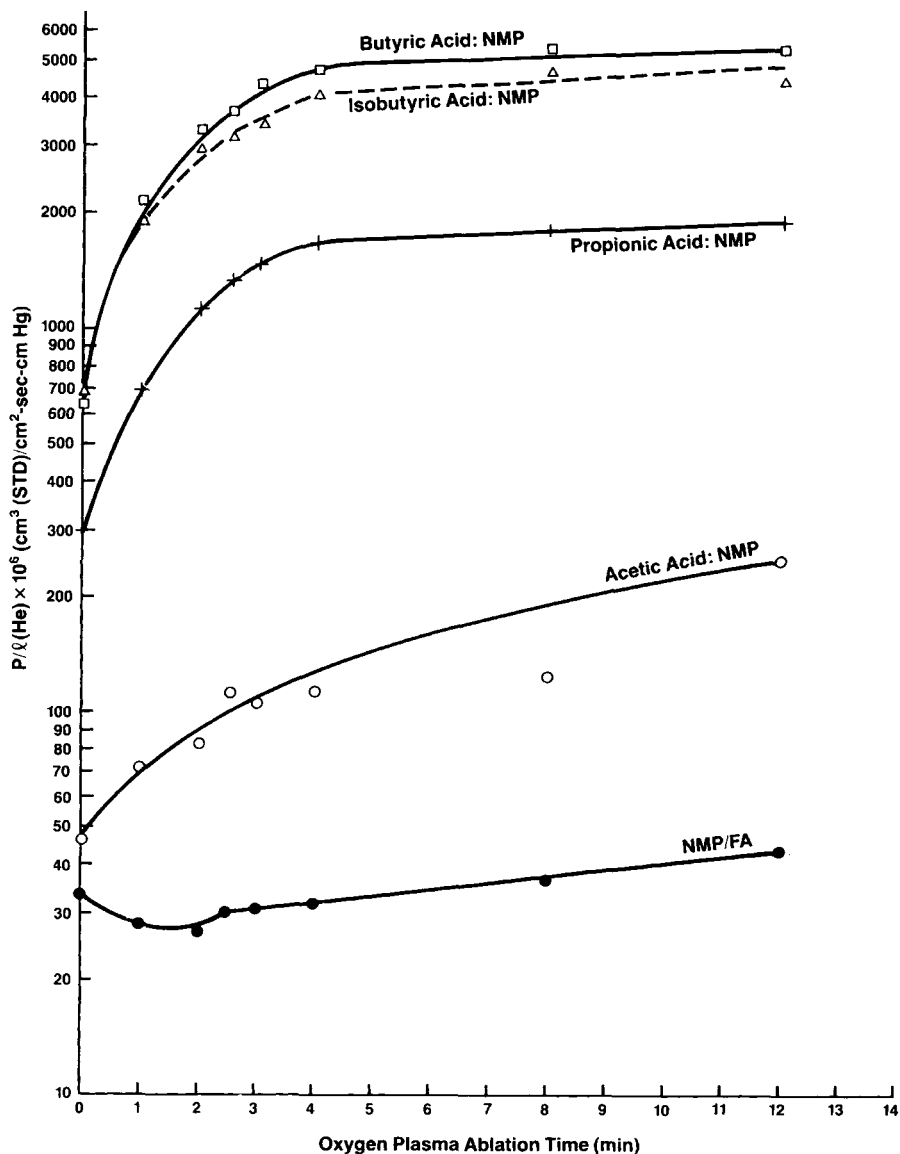


Fig. 1. Helium permeability of polysulfone hollow fiber membranes spun from various Lewis acid : NMP complexes as function of oxygen plasma ablation time.

olidone complexed with equimolar amounts of monobasic aliphatic acids (acetic acid, propionic acid, butyric acid, and isobutyric acid) are presented. Hollow fiber membranes spun from the noncomplexing *N*-methylpyrrolidone/formamide mixture were also examined.

### EXPERIMENTAL

Test cells were prepared from hollow fiber membranes spun from 37% total solids polysulfone (Amoco Udel 3500) dopes in solutions of *N*-methylpyrroli-

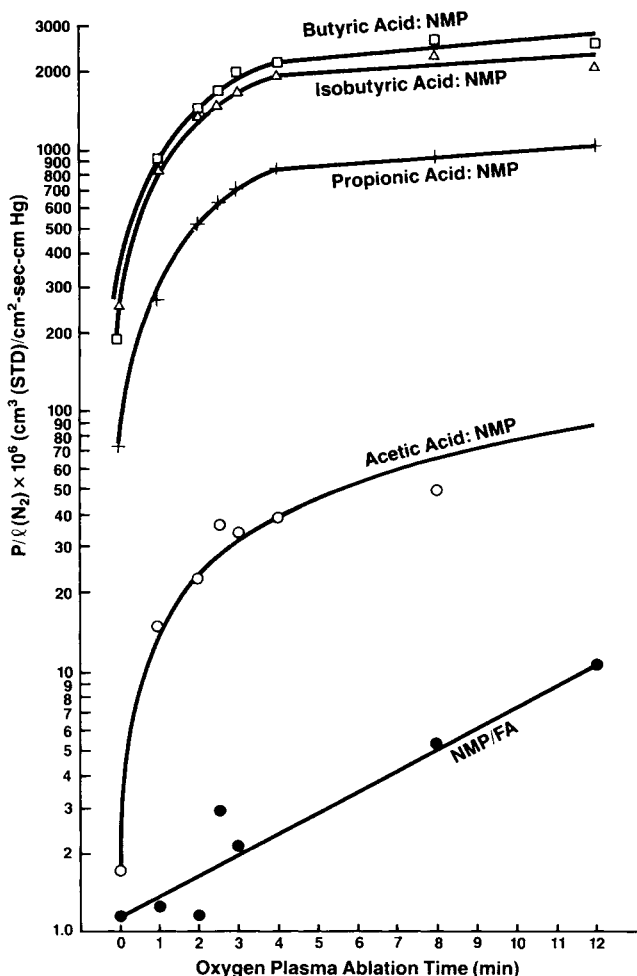


Fig. 2. Nitrogen permeability of polysulfone hollow fiber membranes spun from various Lewis acid : NMP complexes as function of oxygen plasma ablation time.

done complexed with equimolar quantities of acetic acid, propionic acid, butyric acid, or isobutyric acid. Test cells were also prepared from hollow fiber membranes spun from the noncomplexing *N*-methylpyrrolidone (84 wt %) formamide (16 wt %) solvent/nonsolvent mixture. Each test cell contained 10 hollow fibers approximately 15 cm in length. One end of the collection was encapsulated in a  $\frac{3}{8}$ " diameter epoxy seal. The seal fixes the cell in the gas test assembly and prohibits intermixture of the feed and product gases. The opposite ends of the hollow fiber membranes were sealed with a rapidly curing epoxy resin. Therefore, the only gas flow that can be measured emerging from the cell is that which is transported across the hollow fiber membranes. Eighteen test cells of each type were made. These 18 were divided into seven sets. Triplicate samples were exposed to an oxygen plasma for 1, 2, or 3 min. Duplicate samples were similarly

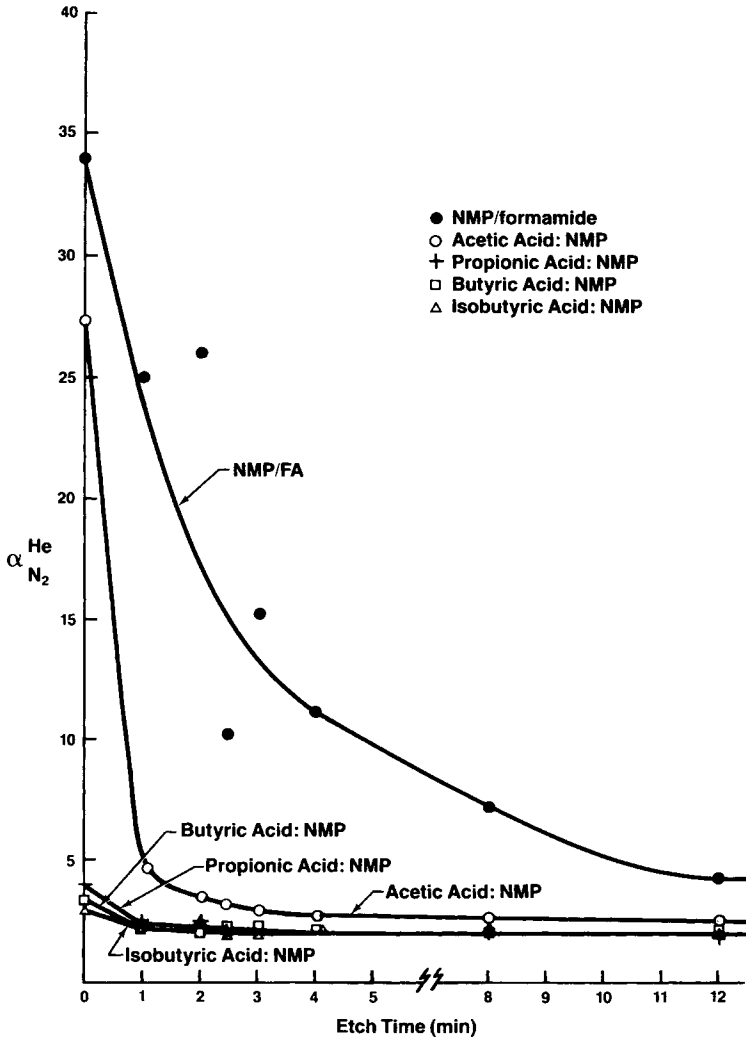


Fig. 3. Change in the helium/nitrogen separation factor as function of oxygen plasma ablation time of polysulfone hollow fiber membranes spun with *N*-methylpyrrolidone complexes with various aliphatic acids.

treated at 2.5, 4.0, and 8.0 min. Three samples were also maintained as unexposed controls.

The oxygen plasma 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. After the helium and nitrogen permeabilities were measured, the triplicate samples were again placed in the Barrel Etcher to obtain samples with 12, 20, and 30 min total oxygen plasma exposure.

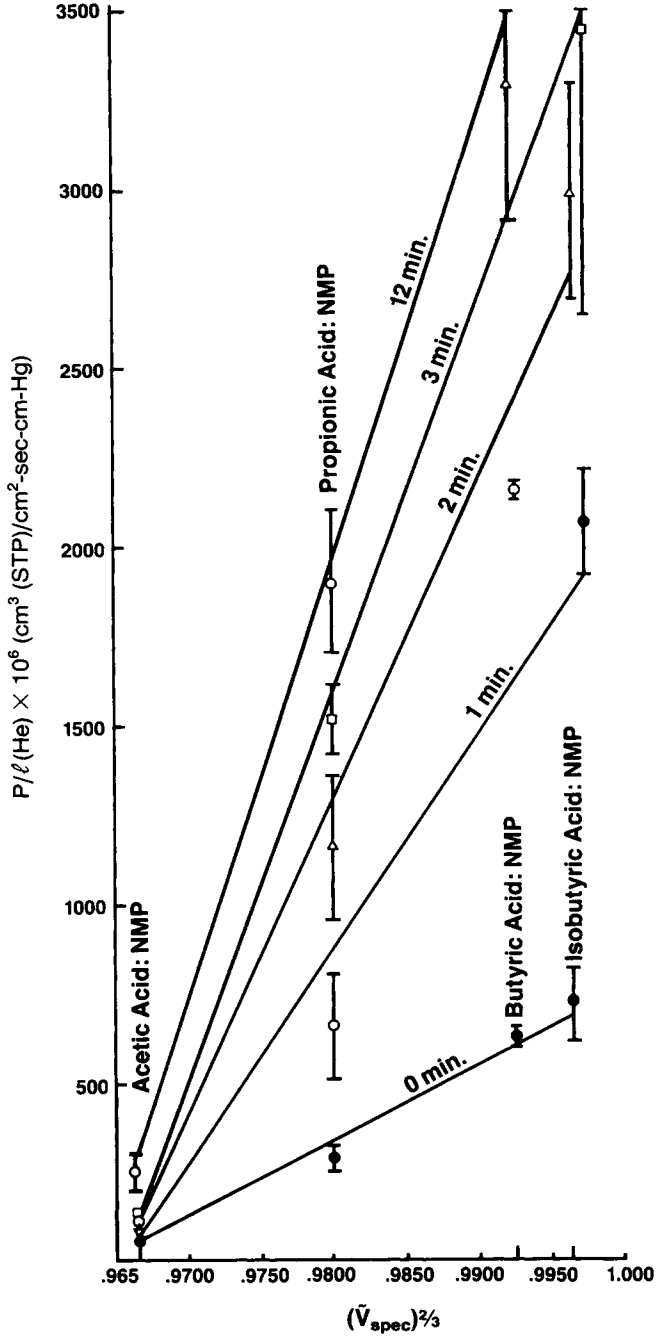


Fig. 4. Variation of helium permeability with  $(\bar{V}_s)^{2/3}$  of the Lewis acid : NMP complex as function of oxygen plasma ablation time.

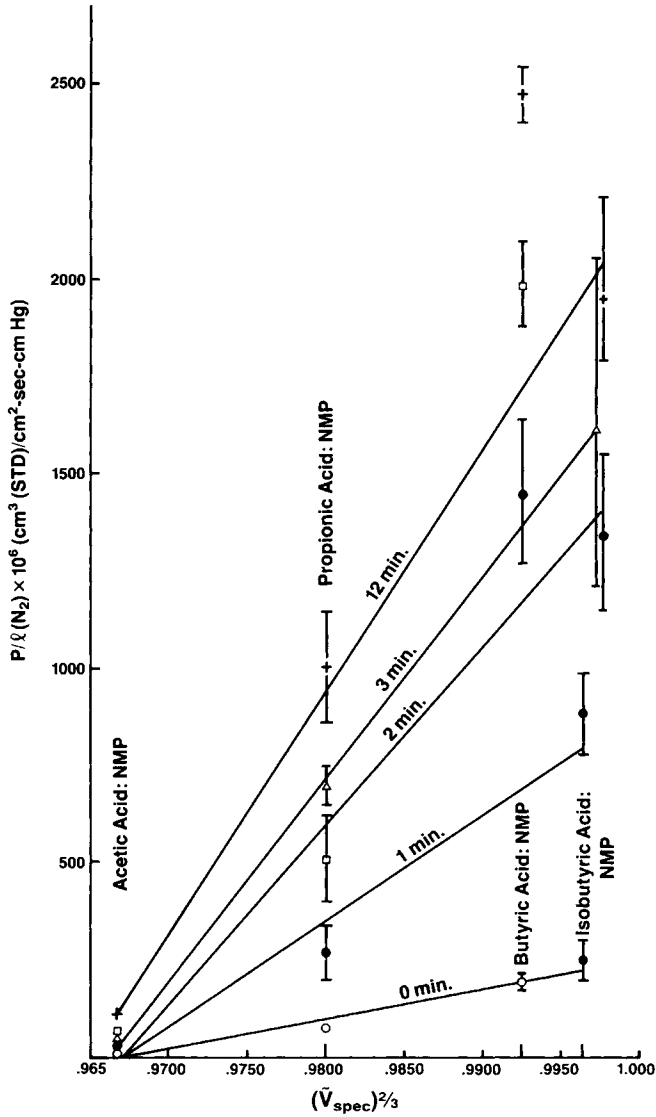


Fig. 5. Variation of nitrogen permeability with  $(\bar{V}_s)^{2/3}$  of the Lewis acid : NMP complex as function of oxygen plasma ablation time.

The oxygen plasma ablated samples and the unetched controls were measured for their uncoated helium and nitrogen flux rates at 100 psig at room temperature. The helium and nitrogen permeabilities were calculated by

$$P/l = \frac{Q}{A\Delta P} = \frac{Q}{n\pi DL\Delta P} \quad (1)$$



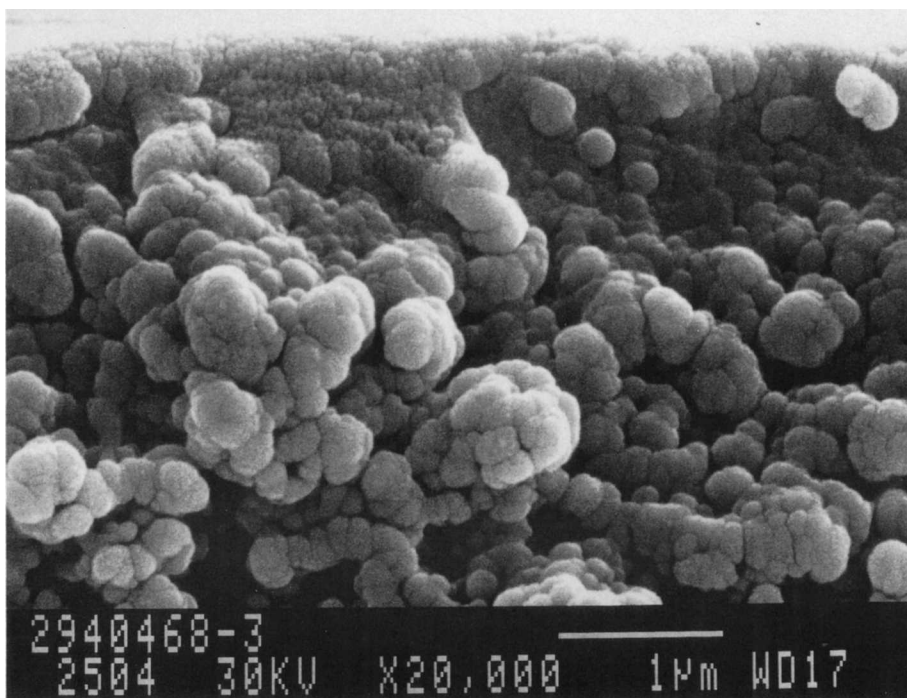


Fig. 6. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from NMP/formamide at 20K magnification.

where

- $P$  = the permeability of the separating layer  $\text{cm}^3(\text{STP})\text{-cm}/\text{cm}^2\text{-sec-cmHg}$ ,
- $l$  = the effective thickness of the separating layer,
- $Q$  = the gas flux,
- $n$  = number of fibers in the sampling,
- $D$  = outer diameter of the hollow fiber membrane,
- $L$  = active length of the fibers, and
- $\Delta P$  = the pressure difference between inner and outer surfaces of the hollow fiber membrane.

The separation factor, also referred to as the selectivity, of the gas pair is ratio of their permeation rates. For a gas pair, such as helium and nitrogen, the separation factor is given by

$$\alpha = \frac{P/l(\text{He})}{P/l(\text{N}_2)} \quad (2)$$

The glass transition temperature of all the samples was obtained by DSC analysis from room temperature to  $250^\circ\text{C}$ . All samples were tested in duplicate

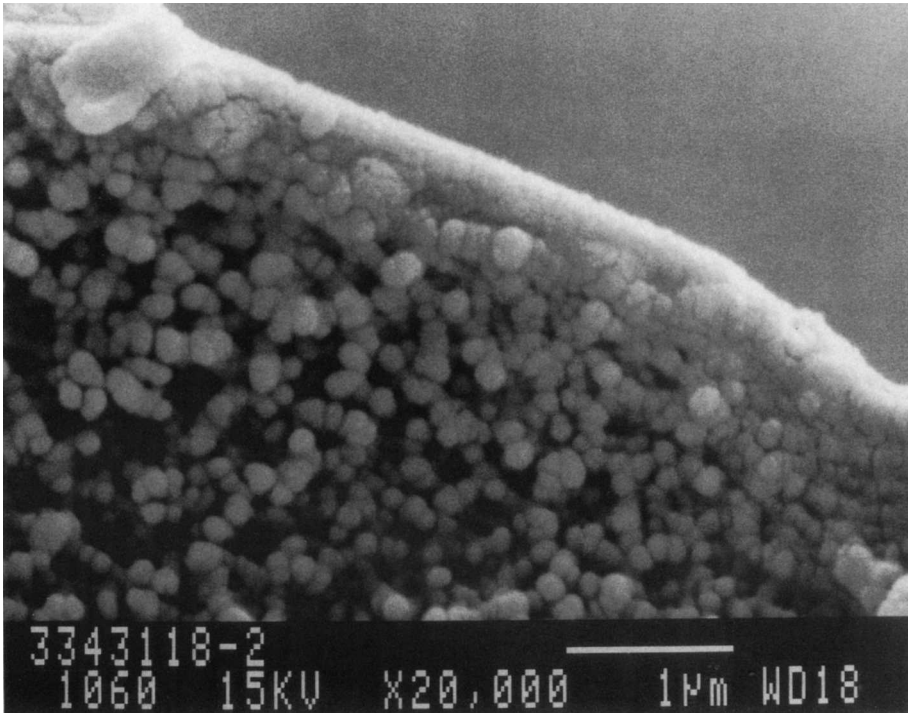


Fig. 7. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from propionic acid : NMP at 20K magnification.

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 DISCUSSIONS

The nonsolvents used in combination with *N*-methylpyrrolidone are listed in Table I. This table gives the weight percent of each nonsolvent used, the glass transition temperature of the resultant hollow fiber membrane in both the initial and reheat DSC scans, and the acceptor numbers obtained from the literature.<sup>1,15,16</sup> Formamide with an acceptor number of 39.8 does not form a complex with *N*-methylpyrrolidone, whereas acetic acid, propionic acid, butyric acid, and isobutyric acid do.<sup>1</sup> The strength of the Lewis acid : base complex decreases with declining acceptor numbers. Therefore, the relative stabilities of the complexes would be acetic acid > propionic acid > butyric acid > isobutyric acid. One would then expect more rapid coagulation of the nascent hollow fiber membrane upon contact with water in the order acetic acid < propionic acid < butyric acid < isobutyric acid due to the kinetics of the dissociation of the Lewis acid : base complex into its solvent/nonsolvent constituents. As shown in other papers in this series, a rapid transformation from sol-to-gel

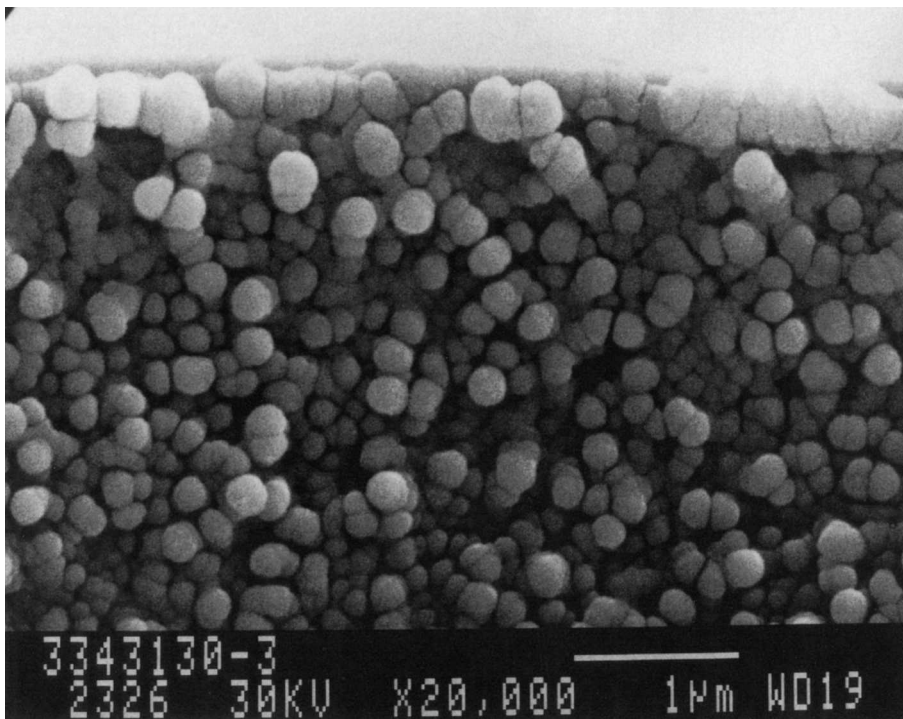


Fig. 8. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from isobutyric acid : NMP at 20K magnification.

increases the free volume of the resultant hollow fiber membrane, yielding a concomitant increase in its glass transition temperature.<sup>2,17,18</sup> The results of the initial calorimetric scans indicate that this indeed occurs with the glass transition temperatures and free volumes of the Lewis acid : base complexes decreasing in the order isobutyric acid : NMP (197°C) > butyric acid : NMP (195°C) = propionic acid : NMP (195°C) > acetic acid : NMP (189°C). These elevated glass transition temperatures are not equivalent to the elevated T<sub>g</sub> observed on a DSC curve due to superheating yielding a heat capacity overshoot resulting from enthalpic relaxation during annealing.<sup>2,17,18</sup>

Use of a Lewis acid : base complex ensures more rapid sol-to-gel transition, which enhances free volume, by permitting the incorporation of larger amounts of nonsolvent into the spinning dope than can be obtained with traditional solvent/nonsolvent formulations such as NMP/formamide. The NMP/FA mixture contains a 16 wt % formamide, and hollow fiber membranes spun from this mixture exhibit the lowest glass transition temperature (185°C) in this series. Because both the NMP/FA (T<sub>g</sub> = 185°C) spun hollow fiber membranes and the NMP : PA (T<sub>g</sub> = 195°C) spun hollow fiber membranes contain .1% residual *N*-methylpyrrolidone, the 10°C difference in the glass transition temperature must be attributed to free volume differences and not to the plasticization effect of residual *N*-methylpyrrolidone solvent. Based solely on the glass transition temperature results presented in Table I, one would predict



Fig. 9. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from NMP : acetic acid at 20K magnification.

gas transport rates of hollow fiber membranes to be related to the spinning solvent in the order isobutyric acid : NMP > butyric acid : NMP = propionic acid : NMP > acetic acid : NMP > NMP/formamide.

The helium and nitrogen permeation rates, as well as their respective separation factors, as a function of oxygen plasma etch time, are given in Table II. Examination of Table II reveals that  $T_g$  is an acceptable indicator of the relative performance of the hollow fiber membranes. It also suggests that free volume of the hollow fiber membrane, as defined by the  $T_g$ , is indicative of the free volume of the active separating layer. However, a knowledge of the structure and morphology of the hollow fiber membrane is necessary to understand the performance of the membrane. The results are also shown graphically in Figures 1-3.

Examination of Figures 1 and 2 reveals marked differences among the helium and nitrogen permeabilities of the hollow fiber membranes spun from differing Lewis acid : NMP complexes, as well as between those of the complex spun hollow fiber membranes and the membranes spun from the noncomplexing NMP/FA mixture. The helium permeability of the acetic acid : NMP complexes unetched is 1.5 times that of the NMP/FA spun hollow fiber membranes. The propionic acid : NMP spun membranes 9 times greater, the butyric acid : NMP spun membranes 20 times greater, and the isobutyric acid : NMP spun membranes 23 times greater than NMP/FA spun hollow fiber membranes. After

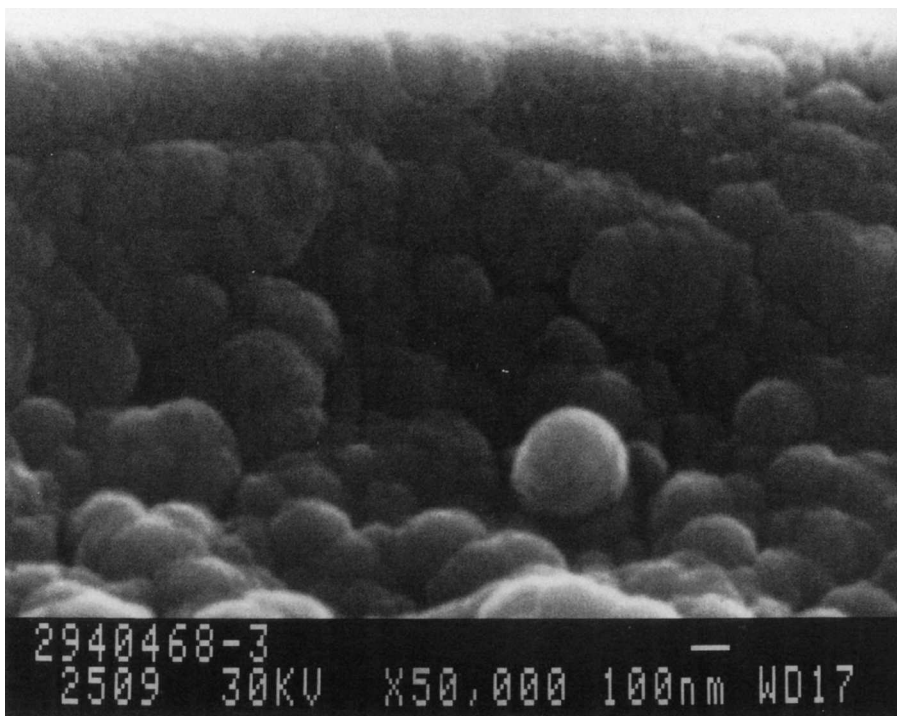


Fig. 10. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from NMP/formamide at 50K magnification.

30 min of oxygen plasma ablation, structural differences among the matrices become very pronounced. The helium permeability of the acetic acid spun hollow fiber membranes is 5 times that NMP/FA spun hollow fiber membranes, and the helium permeabilities of the propionic acid/NMP spun membranes are 28 times greater, the butyric acid : NMP spun membranes 79 times greater, and the isobutyric acid : NMP spun membranes 57 times greater than the hollow fiber membranes spun from the noncomplexing NMP/FA solutions. The flows should reach limiting values controlled by passage of the gas along and out the fiber bores.

Figure 3 shows the change in the helium/nitrogen separation factor as a function of oxygen plasma ablation time for hollow fiber membranes spun from *N*-methylpyrrolidone complexed with either acetic acid, propionic acid, butyric acid, or isobutyric acid in a 1 : 1 molar ratio. The figure also shows the results from polysulfone hollow fiber membranes spun from NMP and the noncomplexing formamide mixture. The differences between the polysulfone hollow fiber membranes spun from the Lewis acid : base complexes and the noncomplexing NMP/formamide mixture are dramatic. The hollow fiber membrane spun from the NMP/FA mixture has a dense, thick active separating layer with a high separation factor ( $\alpha = 34$ ) for the etched, uncoated samples. This high uncoated separation factor also indicates an exceedingly low fraction of pores or defects protruding through the relatively thick separating layer. Suc-

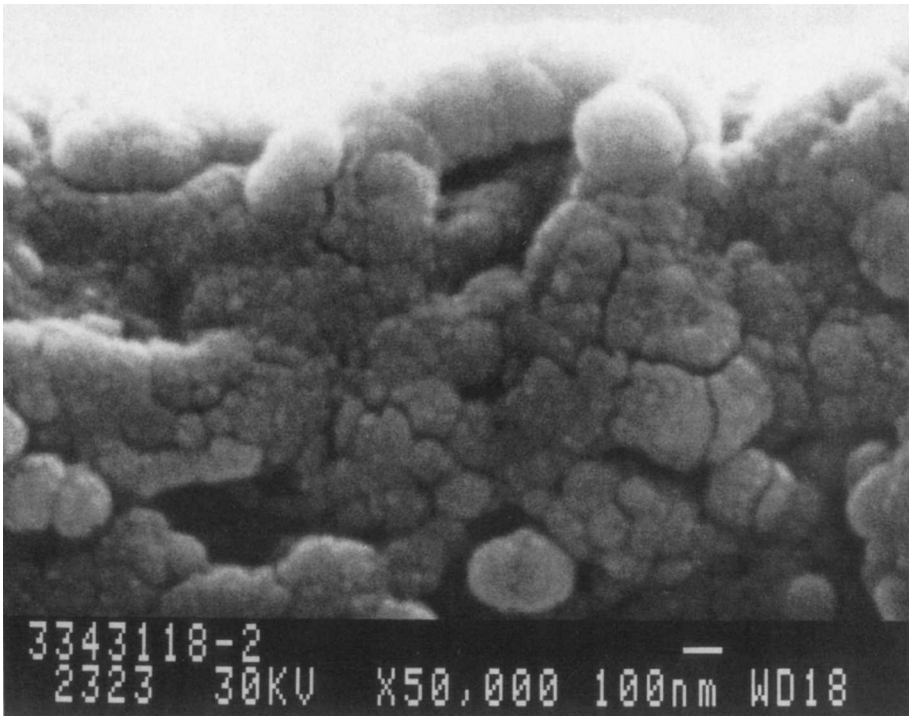


Fig. 11. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from propionic acid : NMP at 50K magnification.

cessive removal of the outer layers of this hollow fiber membrane yields a gradual decline in separation factor abetted by exposure of micropores beneath the surface of both small size and predominately closed cellular structure. Even after 30 min of oxygen plasma ablation, the separation factor of 2.9 remains above that of 2.65 predicted by Knudsen flow for helium and nitrogen. Consequently, after the removal of at least 350 nm of the surface, the internal pores remain smaller than the mean-free-path length of the diffusing gases, i.e., less than 13 nm at 100 psig at 20°C. The mean-free-path length is given by

$$\lambda = \frac{3\mu}{2p} (\pi RT/2M)^{1/2} \quad (3)$$

where

$\lambda$  = mean-free-path length,

$M$  = the molecular weight of the diffusing species,

$p$  = the pressure,

$\mu$  = the viscosity of the diffusing species,

$R$  = the universal gas constant, and

$T$  = the absolute temperature.

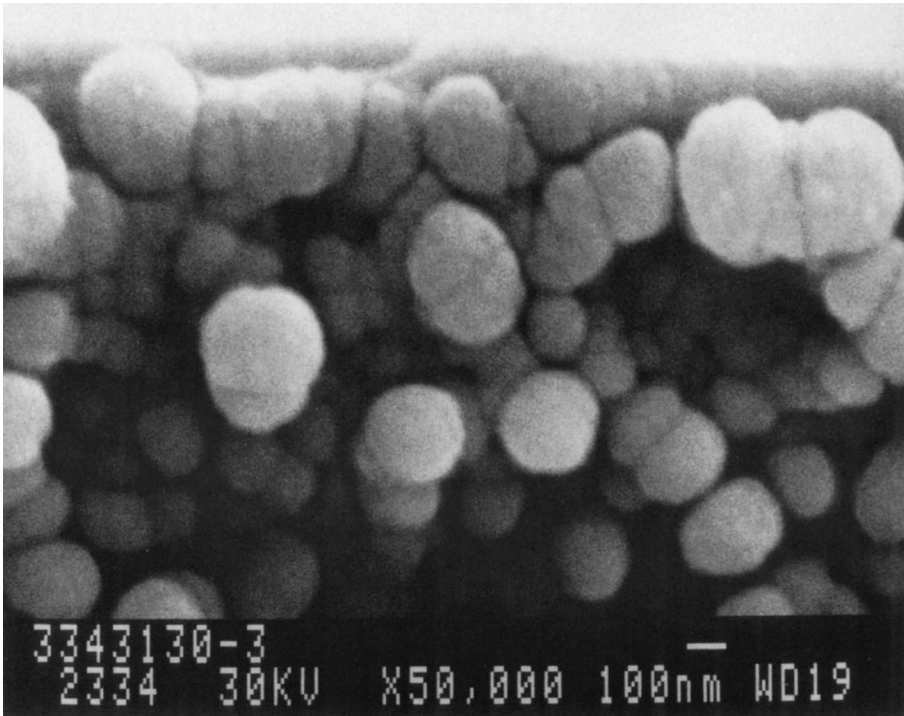


Fig. 12. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from isobutyric acid : NMP at 50K magnification.

The hollow fiber membrane spun from the acetic acid : NMP complex also exhibits a high separation factor ( $\alpha = 27.5$ ) for the unetched, uncoated samples. Its loss in separation factor with ablation time is more rapid than that seen in the NMP/FA spun hollow fiber membrane. If the active separating layer is defined by the thickness of the layer that must be removed to obtain Knudsen flow, then the active separating layer is removed within 8 min of oxygen plasma ablation, suggesting that the active separating layer is about 80–110 nm thick. An ablation rate of  $11.2 \pm 1.1$  nm/min was used for these estimates. It was determined by weight loss with oxygen plasma exposure time.<sup>13</sup> This ablation rate was used to estimate the active separating layer thickness because the experiments were conducted in the flow controlled region in which etch rate is independent of discharge power.<sup>19,20</sup>

The hollow fiber membranes spun from NMP complexed with either propionic acid, butyric acid, or isobutyric acid all show much lower separating factors in the 2.9 to 4.0 range for the uncoated, unetched fibers. This suggests a much higher degree of porosity in the active separating layer. Prior to coating with polydimethylsiloxane, Knudsen and Poiseuille flows are significant contributors to the total gas transport across the hollow fiber membranes. With each of these hollow fiber membranes, the separation factor falls below 2.65 within the first minute of oxygen plasma ablation, suggesting that the active separating layer is about 10–12 nm in thickness.

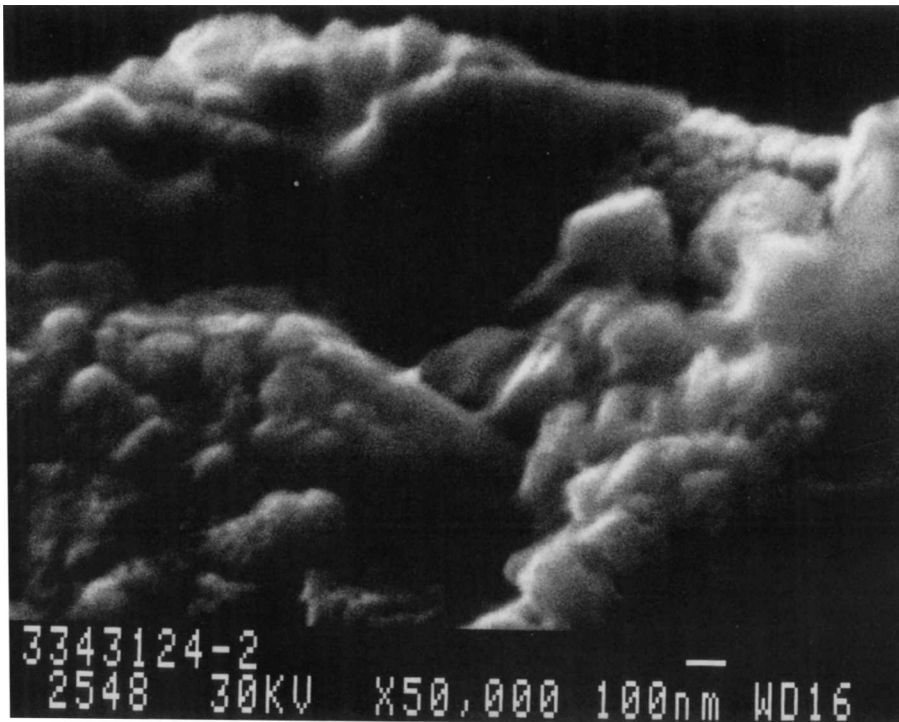


Fig. 13. SEM photomicrograph of outer edge of a cross section of a hollow fiber membrane spun from acetic acid : NMP at 50K magnification.

It appears that pores gradually increase in size and internal resistance to flow decreases due to increased porosity and reduced tortuosity with sequential removal of the outer layers of the hollow fiber membranes. It appears that the dimensional rates of change of the pore size, porosity, and tortuosity depend on the nature of the complexing Lewis acid. Not only do the acceptor numbers, which are related to the kinetics of coagulation, change in the Lewis acid series but so do their sizes. In Figures 4 and 5, the helium and nitrogen permeabilities were plotted vs. the two-thirds power of the specific volumes of the complexes, determined with a pycnometer at 30°C. An interesting trend is revealed by the data, which may not be coincidental. The flux rate appears to vary linearly with  $(V_s)^{2/3}$  within experimental error. This implies that the pores sizes are proportional to the specific volumes of the complexes and their cross sectional area proportional to  $(V_s)^{2/3}$ . It is the cross sectional area of the pores that controls the flux of gas through the pores. Furthermore, this relationship persists in the acetic acid : NMP, propionic acid : NMP, butyric acid : NMP, and isobutyric acid : NMP complex spun hollow fiber membranes etched at times beyond those needed to remove the separating layer. Aggregation of the complexes into solvent clusters may influence the mechanism through which these pores of increasing size are formed. It appears from this study that the internal matrices of hollow fiber membranes spun from propionic acid : NMP, butyric acid : NMP, and isobutyric acid : NMP complex solvents are open cellular in



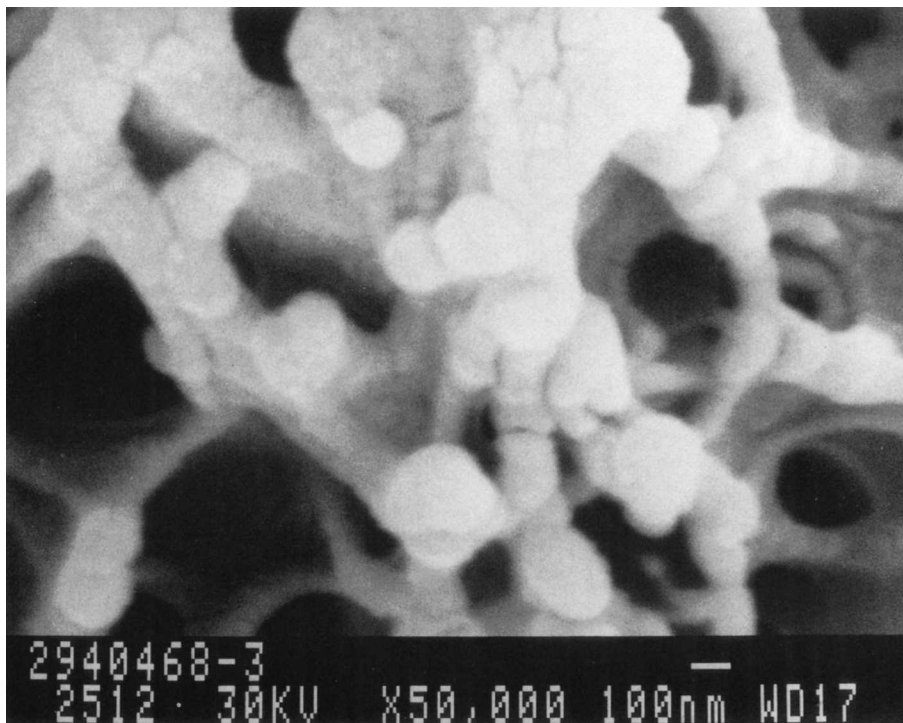


Fig. 14. SEM photomicrograph of the porous substructure of a hollow fiber membrane spun from NMP/formamide at 50K magnification.

structure with pores sizes that are related to the size of the Lewis acid : base complex.

Hollow fiber membranes spun from *N*-methylpyrrolidone/formamide, acetic acid : *N*-methylpyrrolidone, propionic acid : *N*-methylpyrrolidone, and isobutyric acid : *N*-methylpyrrolidone were examined by scanning electron microscopy. Photomicrographs were obtained from cross sections of these hollow fiber membranes at both their outer edges and within their porous substructures. Figures 6–9 show the outer edges of these hollow fiber membranes at a 20K magnification, while Figures 10–13 show the same regions at 50K magnification. The photomicrographs of the hollow fiber membranes spun from the NMP/FA mixture, Figures 6 and 10, reveal what appears to be a thick dense skin, which may be up to 400 nm thick. It appears that the skin is composed of nodule aggregations, also referred to as micelles, so tightly packed at the surface that their boundaries are very difficult to define, if at all, with the resolution of the scanning electron microscope. Beneath this layer the individual micelles become more readily identifiable but remain in a tightly packed assembly. As the outer layers of this membrane are sequentially ablated by the oxygen plasma, the separation factor declines as defects in the skin are reached. Gas flow through these defects becomes a significant contributor to the total amount of gas transported across the hollow fiber membrane. However, the defects are few and the skin sufficiently thick that the total amount of gas transported remains low.

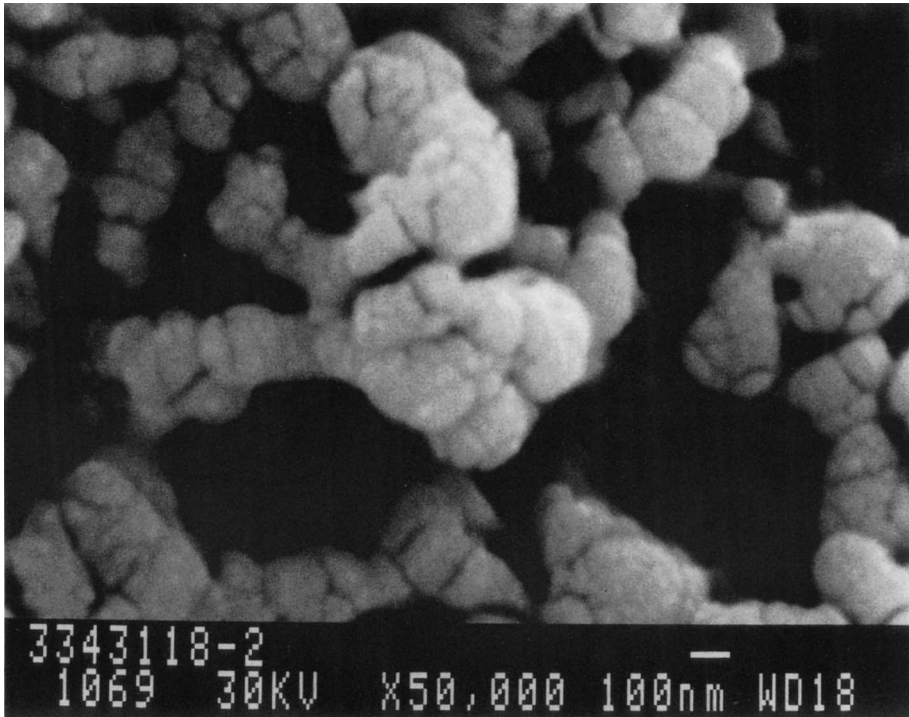


Fig. 15. SEM photomicrograph of the porous substructure of a hollow fiber membrane spun from propionic acid : NMP at 50K magnification.

The photomicrographs of the cross sections of the hollow fiber membranes spun from propionic acid : NMP (Figs. 7 and 11) and from isobutyric acid : NMP (Figs. 8 and 12) revealed structures predicted by oxygen plasma ablation. The skins of both are thinner than the skin of the NMP/formamide spun hollow fiber membrane. Also, the photomicrographs indicate that the skin of the isobutyric acid : NMP spun hollow fiber membrane is thinner than the skin of the propionic acid : NMP spun hollow fiber membrane although oxygen plasma etching studies could not distinguish any difference between the active separating layer components of these skins. In the case of the propionic acid : NMP spun hollow fiber membrane, it is difficult to define the boundary between the skin and the supporting matrix while this boundary is quite apparent in the hollow fiber membrane spun from isobutyric acid : NMP. Comparisons of Figures 6–8 and Figures 10–12 reveal another interesting feature of their structures beneath the skins. The spherical micelles are less tightly packed as one progresses from hollow fiber membranes spun from NMP/formamide to those spun from propionic acid : NMP to those spun from isobutyric acid : NMP. This indicates an increasingly higher porosity, indicative of lower substructure resistance to gas flow, as one proceeds through the series but also a porous substructure that is located closer to the hollow fiber membrane surface.

The structure of the hollow fiber membrane spun from acetic acid : NMP (Figs. 9 and 13) appears, at first, to be anomalous. Unlike the more distinctive

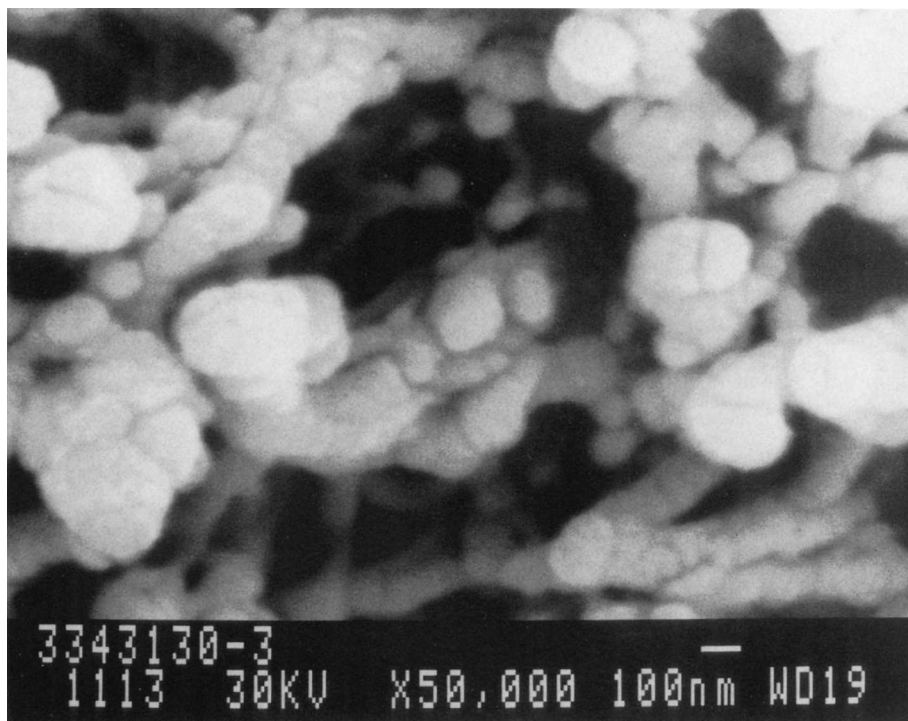


Fig. 16. SEM photomicrograph of the porous substructure of a hollow fiber membrane spun from isobutyric acid : NMP at 50K magnification.

skins seen in the other samples, the skin of the acetic acid : NMP spun hollow fiber membrane appears at 20K magnification to be monotonous. At this magnification no structure within the skin can be discerned, but instead it appears to have a thickness similar to or greater than that of the hollow fiber membrane spun from NMP/formamide. However, inspection of Figure 13 at 50K magnification does reveal spherical micelles, although these do not appear quite as distinct as those observed in the other photomicrographs. However, the arrangement of these micelles implies that the skin thickness, as well as the active separating layer of the acetic acid : NMP spun hollow fiber membrane, is intermediate between those spun from NMP/formamide and propionic acid : NMP.

Photomicrographs were also made of the porous substructures in the interior of the cross sections of the hollow fiber membranes. These photomicrographs at 50K magnification are shown in Figures 14–17. Because it was difficult to obtain photomicrographs at the same distances from the outer surfaces of the hollow fiber membranes, no estimate of their relative pore sizes could be made. However, it does appear that the cellular structure of the substructures of hollow fiber membranes spun from the Lewis acid : base complexes (Figs. 15–17) are more open than the cellular structure of the hollow fiber spun from the NMP/formamide mixture (Fig. 14). This implies that the substructure of this membrane has a higher tortuosity and a greater resistance to flow than do the substructures of the hollow fiber membranes spun from the Lewis acid : base com-

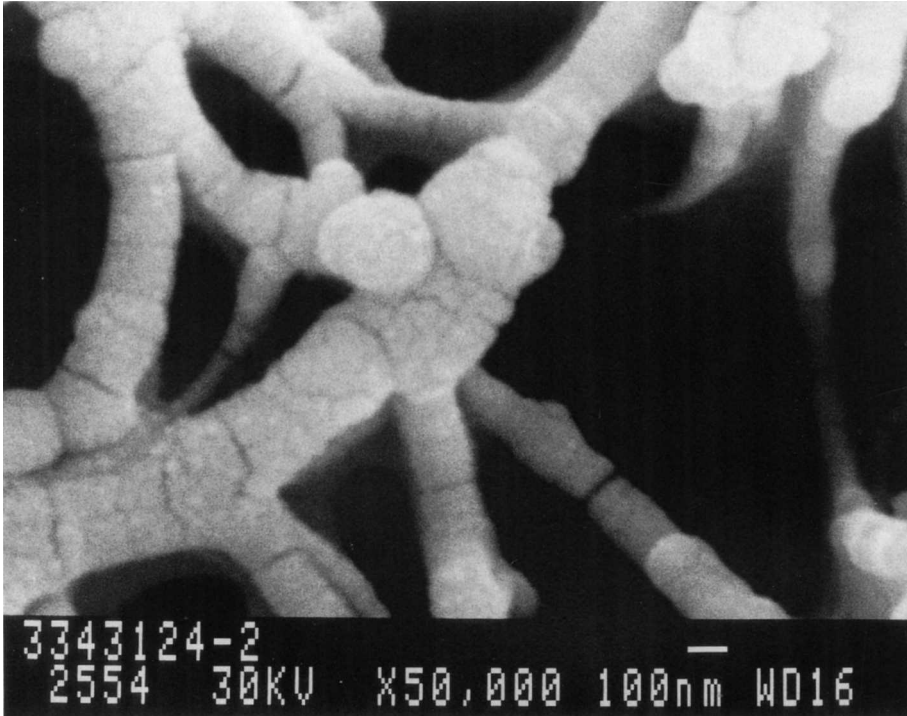


Fig. 17. SEM photomicrograph of the porous substructure of a hollow fiber membrane spun from acetic acid : NMP at 50K magnification.

plexes. It should also be noted that the pore size of the substructure of the acetic acid : NMP spun hollow fiber membrane (Fig. 17) appears to be greater than the others. Although all of the hollow fiber membranes were spun from the same total solids dope under similar conditions, the wall thickness of the acetic acid : NMP spun hollow fiber membrane was 35% greater than that of the others. Therefore, this apparent increase in pore size within the acetic acid : NMP hollow membrane is probably only an artifact of coagulating the same amount of material in a larger volume.

### CONCLUSIONS

It has been shown that polysulfone hollow fiber membranes with increased free volume as reflected by elevated glass transition temperatures can be obtained from a variety of Lewis acid : NMP complexes provided that the complex is readily dissociated by water. The upper limit of the candidate Lewis acid for suitable complexes is an acceptor number between 49.1 (propionic acid) and 52.9 (acetic acid). Based on glass transition temperature measurements obtained by calorimetry, the relative permeabilities of a series of hollow fiber membranes spun from different Lewis acid : NMP complexes may be surmised. However, a knowledge of the structure and morphology of both the active sep-

arating layer and its internal supporting matrix is necessary to understand the performance of the membrane.

Oxygen plasma ablation experiments have shown that the active separating layer of these membranes decreases in the order NMP/FA > acetic acid : NMP > propionic acid : NMP, butyric acid : NMP, and isobutyric acid : NMP with the differences among the last three being too small to resolve by the current experiment. Also, the surface and internal pore size and internal porosity appeared to increase in the order NMP/FA < acetic acid : NMP < propionic acid : NMP < isobutyric acid : NMP < butyric acid : NMP.

It also appeared that the pore size and porosity of the internal supporting matrix of the hollow fiber membranes increased with sequential removal of the outer layers of the hollow fiber membrane. The increase in flux of gas through a hollow fiber membrane with increasing oxygen plasma ablation seems to be proportional to the two-thirds power of the specific volume of the complex from which it was spun.

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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 Patent applications.
2. A. K. Fritzsche, R. E. Kesting, and M. K. Murphy, *J. Membrane Sci.*, **46**, 135 (1989).
3. A. K. Fritzsche, *Proc. ACS Div. 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, *Structure of Asymmetric Hollow Fiber Membranes by Oxygen Plasma Ablation*, presented at the Sixth Annual IUCCP Symposium on Functional Polymers, Texas A&M University, College Station, Texas, 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. A1 Polym. Chem.*, **10**, 1857 (1972).
13. A. K. Fritzsche, C. A. Cruse, R. E. Kesting, and M. K. Murphy, *J. Appl. Polym. Sci.*, **40**, 19 (1990).
14. A. K. Fritzsche, C. A. Cruse, R. E. Kesting, and M. K. Murphy, *J. Appl. Polym. Sci.*, to appear.
15. U. Mayer, V. Gutman, and W. Geger, *Monats. Chemie*, **106**, 1235 (1975).
16. U. Mayer, *Pure Appl. Chem.*, **51**, 1697 (1979).
17. A. K. Fritzsche, M. K. Murphy, C. A. Cruse, R. F. Malon, and R. E. Kesting, *Asymmetric Hollow Fiber Membranes with Graded-Density Skins*, paper presented in Symposium on Separations by Membranes at Annual Meeting of AIChE, Washington, DC, November 27-December 2, 1988.
18. A. K. Fritzsche, M. K. Murphy, C. A. Cruse, R. F. Malon, and R. E. Kesting, *Gas Separ. Purif.*, **3**(3), 106 (1989).
19. T. Yasuda, M. Gazicki, and H. Yasuda, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **38**, 201 (1984).
20. H. Yasuda, *Plasma Polymerization*, Academic Press, New York (1985).

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