

Pore Formation, Permeability, and Permselectivity in Porogen Derived Membranes

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SYNOPSIS

Porogen derived membranes, formed on decomposition of porogen molecules homogeneously dispersed in premembranes, were divided into two groups according to permeability and permeation mechanism. The more open membranes were formed when premembranes were cast on nonwoven polyester cloth support, or when decomposition products were extracted by solvent. The molecular cut-off found for these membranes was at about 1000 Daltons and permeability was mainly determined by permeants' diffusivity and concentration. Permeability through the denser membrane was mainly determined by the permeants' partial vapor pressure, leading to high permselectivities. These denser membranes allowed relatively high osmotic water permeation while practically blocking permeation of solutes, such as salt, in the opposite direction. These membranes were thus also suitable for concentration of aqueous solutions by water removal into concentrated electrolyte solutions. © John Wiley & Sons, Inc.

INTRODUCTION

Porogen derived membranes were formed by inducing decomposition of molecules ("porogens") homogeneously dispersed in premembranes. This new method of membrane formation was described and analysed in Ref. 1. Homogeneous dispersions of various porogens in polysulfone (PSF) and polyvinylchloride (PVC), decomposition of these porogens in premembranes, and metastable retention of decomposition products in the membranes formed are described in previous articles.²⁻⁴

The present article studies the effect of preparation parameters on permeability and permselectivity of transport through porogen derived membranes.

EXPERIMENTAL

Materials and methods are similar to those described previously.² In addition to casting on bottles, pre-

membranes were cast on nonwoven polyester cloth (Hollytex 3396, Filtration Science Corp.) and on woven polyester cloth (Polymon PES, 325-44, ASTM). The cloth was placed on a glass plate and a drop of the casting solution was spread on it, using a glass rod. The thickness of the films was in the range of 10–20 μm . Drying and methods of porogen decomposition were similar to those of films cast on bottles. Membranes obtained by casting on cloth are referred to in the following as supported membranes.

In permeation and permeability experiments, conventional analytical methods were used: acid-base titration, argentometry, conductivity measurements, colorimetry (erythrosine iodide indicator, absorption at 525 nm), and refractive index (polyethylene glycol solutions).

RESULTS

Pore Formation

Di-boc hydrazine (DBH, $\text{tbu-O-C : O-NH-NH-C : O-O-tbu}$, tbu-tertbutyl), di-boc diamino butane (DBDAB, $\text{tbu-O-C : O-NH-(CH}_2)_4\text{-NH-C : O-O-tbu}$), di-boc diamino hexane (DBDAH, $\text{tbu-O-C : O-NH-(CH}_2)_6\text{-NH-C : O-O-tbu}$), and mono-boc

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Table I Water Contents of PSF Porogen Derived Membranes Compared to Those of Membranes Obtained by Direct Casting of PSF Solution

Porogen	Porogen Content (mmol/g Composition)	Contact Time (h)	Water Content (%)
DBHd	0.25	55	1.2
	0.42	55	4.0
	0.68	55	6.7
	0.33	31	1.6
	0.33	101	1.7
	0.33	200	2.3
DBDAB	0.14	51	5.1
	0.41	51	7.6
DBDAH	0.3	25	3.9
	0.33	100	4.8
BAB	0.14	72	2.0
—	—	100	1.0

amino butane (BAB, $\text{tbu-O-C : O-NH-(CH}_2\text{)}_3\text{-CH}_3$) were used as porogens. PSF premembranes, containing these porogens, were treated in HCl solutions for porogen decomposition and then were immersed for prolonged periods in water. Water contents of these films (Table I) were considerably higher than those of films formed by casting of PSF with no porogen. Water content increased with initial po-

rogen content, indicating free volume and probable pore formation.

A direct indication of pore formation on porogen decomposition was the effect of this decomposition on rate of permeation. PVC and PSF premembranes were prepared containing as porogens: tertbutyl oleate (TBO), tertbutyl α -bromolaurate (TBABL, $\text{tbu-O-C : O-CHBr-(CH}_2\text{)}_9\text{CH}_3$), di-tertbutyl dodecanedioate (DTBDD, $\text{tbu-O-C : O-(CH}_2\text{)}_{10}\text{-C : O-O-tbu}$), glycerol triformine (GTF, $\text{CH}_2(\text{O-C : OH})\text{CH(O-C : OH)CH}_2(\text{O-C : OH})$), tertbutyl carbamate (TBC, tbu-O-C : O-NH_2), DBDAH, or di-tertbutyl oxalate (DTBO, $\text{tbu-O-C : O-C : O-O-tbu}$). Permeabilities were measured prior to porogen decomposition and after it. Results in Table II show that porogen decomposition increased permeability by 0.5–2 orders of magnitude.

PVC/DTBO premembranes were treated with 50% HNO_3 solution (24 h), for porogen decomposition. Permeation rate, from 2M HCl + 2M H_3PO_4 solution through the membranes formed, was low (about 1 $\text{mmol/m}^2\text{h}$). These membranes were treated with 4M NaOH. As a result, permeation rate increased by a factor of 15–40. Similar experiments were made with membranes formed on porogen decomposition by 70% HNO_3 at 40°C or 45°C. For these membranes, NaOH treatment had no effect on permeability.

Table II The Effect of Porogen Decomposition on Permeability of Various Solutes

Film Composition				Permeability ($\text{mmol/m}^2\text{h}$)			
Polymer	Porogen	Polymer : Porogen Weight Ratio	Porogen Decomposition Procedure	0.1 M HF ^a		2 M HCl + 2 M H_3PO_4 ^a	
				g	h	g	h
PVC ^b	TBO	100 : 12.1	3 h 70% HNO_3 , RT	0.5	6.5 ^e	5.1	377 ^e
PVC ^b	TBABL	100 : 13.1	3 h 70% HNO_3 , RT	0.1	3.1 ^e		
PVC ^b	DTBDD	100 : 13.4	3 h 70% HNO_3 , RT	0.1	5.4 ^e	5.7	237 ^e
PSF ^b	GTF	100 : 15	2 h 50% HNO_3 , 40°C	0.1	2.9 ^e , 3.4 ^f	5.7	103 ^e , 87 ^f
PSF ^b	TBC	100 : 4.4	2 h 50% HNO_3 , 40°C	0.01	0.95 ^f		
PSF ^c	GTF + DBDAH	100 : 15 : 15	28.5% HCl in cell, RT ^d	0.37	2.8 ^f		
PVC ^c	DTBO	100 : 15	32% HCl in cell, RT ^d			2.9	12 ^f
PVC ^c	DTBO	100 : 30	32% HCl in cell, RT ^d			0.6	18 ^f
PSF ^c	DTBO	100 : 15	32% HCl in cell, RT ^d			3.8	95 ^f

^a Permeation was measured in permeation cell with, on one side of the membrane, a solution composed as indicated and, on the other, deionized water.

^b Films cast on nonwoven cloth support.

^c Films cast on casting bottles.

^d The premembrane was introduced into the permeation cell and contacted with concentrated HCl solution. At the end of this treatment the film was carefully rinsed.

^e Permeation through premembrane with no porogen decomposition treatment.

^{h,e} Films prepared identically to those in g and treated, as indicated, for porogen decomposition.

^{h,f} The films in g were treated, as indicated, for porogen decomposition, and then the permeation experiment was repeated.

(RT) Room temperature, (h) hour.

Treating membranes containing carboxylic acid as decomposition products (DPs), with methanol increased HF permeation through them by a factor of 3–20. The same increase in permeation rate was observed following extraction of decomposition products, such as tertbutyl chloride, bromide, iodide, or hydroxide (denoted *tbuX*). The effect of *tbuX* extraction from PSF membranes was stronger than that of *tbuX* extraction from PVC films. The effect of *tbuOH* extraction was stronger than that of *tbuCl* extraction.

Membranes, obtained by performing porogen decomposition while still attached to casting bottles, showed higher permeability than those detached from the bottle prior to decomposition. Still higher permeation was obtained when porogen decomposition was performed in films already mounted in the permeability measuring cell. Permeation rates through supported membranes were even higher, about 2 orders of magnitude larger, than those obtained by casting on glass bottles (Table III).

Permeability Measurements

Permeation rate increased with initial porogen concentration in the premembrane (see Fig. 3 in Ref. 1).

Membranes were prepared by porogen decomposition in premembranes of various polymers, porogens, and initial porogen concentrations. These membranes were studied in permeation of acids, salts, alkanols, and other solutes from aqueous solutions into water. The results (Tables IV and V) showed some clear trends:

- Permeation rates divided the membranes into “dense” and “open” membranes. The second group included membranes cast on support and

membranes obtained by extraction of decomposition products.

- The above groups differed also in the effect of permeant concentration on permeation rates. For open membranes, permeation was linearly dependent on concentration. For dense membranes the dependence was nearly logarithmic.
- In denser membranes, HF permeability was much higher than that of HCl, comparing similar, relatively low, up-stream solution concentrations. This phenomenon was not observed for open membranes.
- Study of relative permeabilities of several solutes through the more open membranes showed that permeability was mainly determined by concentration and by diffusivities of the permeants.
- An exception to the dependence on diffusivity was shown by larger molecules, such as polyethylene glycol, M.W. 6000, and erythrosine iodide indicator (E.I., 2',4',5',7'-tetraiodofluorescein disodium salt, M.W. 880). Their permeabilities were about an order of magnitude lower than expected, according to diffusivities (see Table VI). A similar, but considerably weaker effect (factors of 2–5), was observed for tetrabutyl ammonium bromide (M.W. 332) and citric acid (N.W. 192).

In experiments studying the permeation of solutes from concentrated solutions, water permeation in the opposite direction was observed. In most cases, membranes were of the denser type. Table VII summarizes permeation rates of solutes and of water in opposite directions for various membranes. (Water permeation rates were measured by volume change

Table III Comparison of Acids Permeation through Unsupported and Supported Membranes

Film Obtained from Premembrane Composed of:	Concentrated Side Composition	H ⁺ Permeation Rate (mmol/m ² h)	
		Unsupported ^a	Supported
PVC : TBO w/w ratio 100 : 12	2M HCl + 2M H ₃ PO ₄	5	396 ^b (7 : 1) ^d
PVC : TBABL w/w ratio 100 : 13	2M HCl + 2M H ₃ PO ₄	0.5	199 ^b (8 : 1) ^d
PSF : GTF : DBDAH w/w ratio 100 : 15 : 15	2M HCl + 2M H ₃ PO ₄	0.7	535 ^c (4 : 1) ^d
PSF : GTF : DBDAH w/w ratio 100 : 15 : 15	9.45M HCl	100	3800 ^d
PVC : DTBDD w/w ratio 100 : 13.4	2M HCl + 2M H ₃ PO ₄	5	237 ^d (7 : 1) ^d

^a The premembranes were cast on a cylindrical glass bottle. Porogen decomposition was induced on the dry film while still on the bottle.

^b Cast on nonwoven cloth.

^c Cast on woven cloth.

^d HCl : H₃PO₄ molar ratio in the permeate.

Table IV Permeation Rate ($\text{mmol}/\text{m}^2\text{h}$) through Membranes Prepared from Premembranes of Various Compositions

Upstream Permeant Solution	Permeants Diffusion Coefficient ($\times 10^9$)	PSF : GTF :		PSF : DBDH 100 : 10 (B)	PSF : GTF :		PSF : GTF :		PVC :		PVC :	
		DBDAH 100 : 15 : 15 Supp. (A1)	(A2)		DBDAH 100 : 15 : 15 (C)	DBDAH 100 : 15 : 15 (D)	NC : GTF 100 : 50 (E)	PVC : TBO 100 : 12.1 (F)	TBABL 100 : 13 Supp. (G)	TBABL 100 : 26 Supp. (H)	DTBDD 100 : 13.4 (I)	DTBDD 100 : 30 (J)
2MHCl + 2M H ₃ PO ₄	4.04/0.76	531	1147		0.7	5.6	377	171	225	237	140	
0.1M HF		36			2.7		6.9	3.0	9.6	3.5	3.1	
0.24M HF												
2.4M HF												
4.0M HF			165									
4.0M HCl	5.17		1		1.5	10.0						
4.0M HBr						9.0						
4.0M H ₃ PO ₄						0.8						
7.7M HCl (25% w/w)			11									
8.9M HCl (28.5% w/w)					81							
9.1M HCl (28.9% w/w)		6550										
9.4M HCl (30% w/w)		3775	65		100							
10.0M HCl (31.6% w/w)												
4M H ₃ PO ₄ + 0.24M HF	(0.48 ^{1.1M})	41										
2M citric acid	> 0.48	28										
2M Na citrate												
0.1M NH ₄ Cl	1.8		19						1.5			
4.0M NH ₄ Cl	2.2								0.3			
2.0M NH ₄ H ₂ PO ₄												
0.1M NH ₄ OH					26							
0.1M (CH ₃) ₄ NBr	1.1											
2.0M (CH ₃) ₄ NBr		224										
2.2M (C ₄ H ₉) ₄ NBr	0.39	13										
2.0M (CH ₃)OH	1.1	205										
2.0M CH ₃ CH ₂ OH	0.9	125										
0.0023M EI	0.3											
0.023M EI	0.3		0.05		0.001		0.003	0.001	0.01	0.003	0.002	
0.005M PEG 6000	0.14	0.003										

(Supp.) Supported. For acids, total H⁺ permeation rates were measured. (NC) Nitro cellulose, (EI) Erithrosine iodide indicator, (PEG) Polyethylene glycol.

Table V Permeation Rate (mmol/m²h) through Membranes Prepared from Premembranes of Various Composition

Upstream Permeation Solution	Permeants Diffusion Coefficient (× 10 ⁵)	PVC : BAHA	PVC : BAHA	PVC : BAHA	PVC : BAHA	PVC : BAHA 100 : 30 Supp.		PVC : DTBO 100 : 15 Supp.			
		100 : 10 Supp. (K)	100 : 15 Supp. (L)	100 : 20 Supp. (M)	100 : 25 Supp. (N)	(O)	(P)	(Q)	(R)	(S)	(T)
2M HCl + 2M H ₃ PO ₄		16	96	141	116	38	31	40	187	47	198
0.1M HCl						1.1					
2.0M H ₃ PO ₄	0.76			20				7.6			
2.0M H ₃ PO ₄		10					14	36	155	35	
2.0M Maleic Acid								2.3			21
2.0M Citric Acid	0.48 ^{1.1M}		2.8	12	6			2.4	124	2.3	9.8
2.0M Acetic Acid								5.5	38	10	46
2.0M LiBr	(1.3 ^{0.1M})	7	24	56	32		12	13.5	56	17	59
2.0M (CH ₃) ₄ HBr				48	26						
2.0M (C ₄ H ₉) ₄ NBr	0.39	1.2	21	14			2.1	2.8	4.1	2.4	6.5

(Supp.) Supported. For acids total H⁺ permeation rates were measured. (BAHA) Mono-boc-amino hexanoic acid (tbu-O-C:O-NH-(CH₂)₅COOH).

or by decrease in solution concentration). Water permeation rates were 1–4 orders of magnitude larger than solute permeation rates. Figure 1 shows that for PSF membranes, water permeation increased linearly with solute permeation, while for NC, such a correlation did not exist.

characterization of membranes. Many results were therefore gathered for a variety of membranes. For denser membranes (total H⁺ permeation from 2M HCl + 2M H₃PO₄ solutions of less than 10 mmol/m²h), permselectivities of at least 6 were measured, permselectivity being defined as

$$\frac{HCl_d/H_3PO_{4d}}{HC_u/H_3PO_{4u}}$$

Permselectivity

HCl/H₃PO₄ Selectivity

Measurements of permeation from 2M HCl + 2M H₃PO₄ solutions were introduced as a routine in

where d and u denote downstream and upstream concentrations, respectively. More open membranes,

Table VI The Effect of Molecular Size: A Coefficient Obtained by Dividing Permeation Rate by the Concentration in the Upstream Solution and by 10⁵ × Diffusion Coefficient, Given for Most of Membranes in Tables IV and V

Membrane ^a	A ₁	A ₂	D	F	G	H	I	J	L	M	N	P	Q	R	S	T
M HCl + 2M H ₃ PO ₄	72	155	0.09	51	23	31	32	19	13	19	16	4.2	5.5	25	6.4	27
0.1 N HF			12	30	13	42	15	13								
2N LiBr									9	21	13	4.6	5.2	21	6.5	23
0.023M EI		7.5														
0.0023M EI				4.4	1.5	14.5	4.4	2.9								
2M Citric Acid	81								2.8	12	6		2.4	12	2.3	9.8
0.1M (CH ₃) ₄ NBr				60	28	40	49	25								
2M (C ₄ H ₉) ₄ NBr	13								27	18		2.7	3.6	5.2	3.1	8.3
PEG 6000	4.3															

^a The symbols used in Table VI denote the same membranes as in Tables IV and V.

Table VII Water Permeation through Membranes into Permeant Solution

Polymer	Porogen	Porogen Content mg/100 mg Polymer	Permeant	Permeation Rates mol/m ² h	
				Permeant	Water
PSF	DBDAH	10	9.45M HCl	0.044 (H ⁺)	7.3
			6.3M HCl + 3.2M LiCl	0.034 (H ⁺)	5.5
			3.1M HCl + 6.3M LiCl	0.017 (H ⁺)	6.8
			9M LiCl	0.001 (H ⁺)	6.4
NC	GTF	50	4M H ₃ PO ₄	0.0005	4-9
			2M HCl + 2M H ₃ PO ₄	0.005 (H ⁺)	6-9
			4M NH ₄ Cl	0.002	7-12
NC	GTF	100	2M (CH ₃) ₄ NBr	0.001	6-9
			2M HCl + 2M H ₃ PO ₄	0.002-0.02 (H ⁺)	4-8
			36% Na ₃ Cit	0.001	5-7
PSF	DBDAH	10	30% HCl	0.012-0.081	1-12
PSF	DBDAH	8	25% HCl	0.0062	1.3
		10	25% HCl	0.0065	1.8
		15	25% HCl	0.013	3.1
		20	25% HCl	0.017	3.7
		30	50% CH ₃ OH	0.08	0.3
PSF	GTF	30	4M H ₃ PO ₄	0.005	2
			30% HCl	0.016	2
			4M NH ₄ Cl	0.002	0.2-0.5
			30% HCl	0.09-0.17	5-11
PSF	GTF + DBDAH	15 + 15	2M HCl + 2M H ₃ PO ₄	0.22-0.88	6-15
PSF	GTF + DBDAH ^a	15 + 15	2M HCl + 2M H ₃ PO ₄	0.22-0.88	6-15

^a Supported on woven cloth.

with total H⁺ permeation rates of several hundreds mmol/m²h, show permselectivities of ≥ 5 (see Fig. 2). For membranes with still higher permeability, permselectivity decreases with increasing permeation rate.

HCl/LiCl Selectivity

PSF membranes were prepared from PSF/DBDAH premembranes (cast on glass bottles) by inducing porogen decomposition with HCl. These membranes were studied for permeations from concentrated HCl, LiCl, and HCl + LiCl solutions. The results (Table VIII) show preferred HCl permeation with permselectivity of ≥ 40 .

Methanol/Ethanol Selectivity

A preliminary study compared methanol and ethanol permeation through more open membranes and through dense membranes. Open membranes were prepared from PSF-DBDAH-GTF w/w ratio 100 : 15 : 15 premembranes, cast on polyester cloth, showing an average total H⁺ permeation rate of 560 mmol/m²h from 2M HCl + 2M H₃PO₄ solution.

Dense membranes were prepared from PSF-GTF w/w ratio of 100 : 30 premembranes, cast on casting bottles, showing total H⁺ permeation rate from 2M HCl + 2M H₃PO₄ of few mmol/m²h.

The methanol permeation rate through the more open membranes was about 2 times higher than that of ethanol (average of 140 mmol/m²h and 65 mmol/m²h, respectively). Permeation rates through denser membranes were < 10 mmol/m²h for ethanol (from solution with H₂O : ethanol molar ratio of 1 : 1) and 100 mmol/m²h and 80 mmol/m²h for methanol (from solutions with H₂O : methanol molar ratios of 0.76 and 1.78, respectively).

DISCUSSION

Porogen decomposition in premembranes resulted in formation of small volatile fragments (CO₂, C₄H₈, C₄H₉Cl, or C₄H₉OH), part of which left the polymeric matrix. Total free volume of a few percent resulted initially as discrete pores of few Å diameter forming internal surfaces of several hundred square meters per cm³. These enormous surfaces were obviously unstable and rearrangement of the polymeric

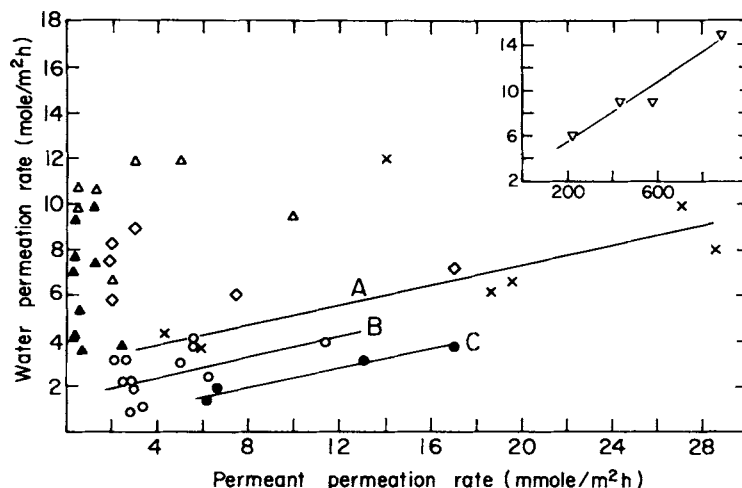


Figure 1. Water permeation into the concentrated permeant solution as a function of permeant permeation in the other direction. (X) (curve A) and (O) (curve B) permeation of HCl from 30% aqueous solution through membranes formed by HF and HCl induced (respectively) porogen decomposition in PSF-DBDAH (weight ratio 100 : 10) premembranes. (●) (curve C) permeation of HCl from 25% aqueous solution through membranes formed by HCl induced porogen decomposition in PSF-DBDAH (weight ratios 100 : 8-20) premembranes. (Δ▲ and ◇) represent permeations of HCl + H₃PO₄ from 2M + 2M solutions, H₃PO₄ from 4M solutions and NH₄Cl, respectively, from 4M solutions through membranes formed by NH₄OH induced porogen decomposition in GTF-NC premembranes (weight ratio 50 : 100). ▽ HCl + H₃PO₄ permeation from 2M + 2M solutions through membranes formed by HCl induced decomposition of porogens in PSF-GTF-DBDAH (weight ratio 100 : 15 : 15) supported premembranes.

matrix took place. Avoiding pore fusion to dense matrix was therefore required. Porosity was thus expected to be determined by many parameters, such as polymer and porogen characteristics, their weight ratio in the premembrane, casting parameters, porogen decomposition parameters, etc.

Temperature of porogen decomposition and rate

of plasticizer (porogen) elimination seemed to be important factors. As was previously discussed,³ inducing decomposition by an external or by an internal reagent required conditions that would allow the reagent's migration. These conditions certainly allowed some polymer rearrangement, which may have resulted in contraction. Decomposition by a-

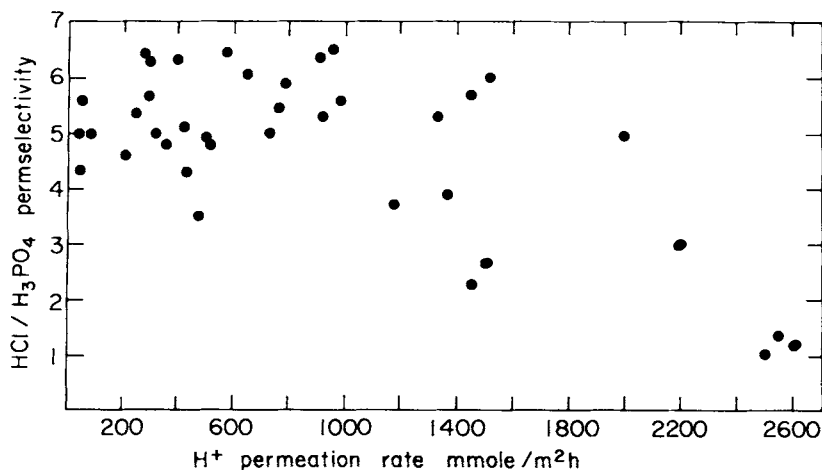


Figure 2. HCl : H₃PO₄ permselectivity as a function of total H⁺ permeability for "open" membranes (supported or methanol treated).

Table VIII HCl and LiCl Permeation Rates through Films Obtained from PSF : DBDAH (w/w Ratio of 100 : 10) Premembranes by Porogen Decomposition in HCl Vapors

Concentrated Side Composition equ/L			Permeation Rate mmol m ⁻² h ⁻¹	
H ⁺	Li ⁺	Cl ⁻	H ⁺	Cl ⁻
9.45	—	9.45	45	45
6.30	3.17	9.47	34	34
3.15	6.33	9.48	14.7	15.8
—	9.50	9.50	—	0.7

diation was expected to allow pore formation in rigid media. Suitable porogens, however, were not found yet (decomposition of salts of N-boc amino acids require temperatures of about PSF T_g^2).

Alternatively, membrane formation may be divided into two stages, performed at different conditions: (a) porogen decomposition and (b) pore formation by extraction of metastably dissolved decomposition products. Permeation measurements showed that such extraction of DPs at low temperature (and in absence of plasticizer) resulted in considerable enhancement of permeability. (In the case of DTBO in PVC decomposition by 70% HNO₃ at 40°C, treatment with NaOH solution showed no effect, since in those decomposition conditions, acid is not retained in the matrix.)

Another way of reducing matrix contraction is by performing porogen decomposition while the film is under tension. Permeation studies showed that stretching on a casting bottle or in a permeation measurement cell during porogen decomposition increased membrane permeabilities. The effect of adhesion to the support was even stronger, resulting in increasing permeability by about 2 orders of magnitude.

Permeability through the more open membranes was determined by permeant diffusivity and concentration, as expected for the pore transport mechanism. For denser membranes, obtained from pre-membranes cast on glass bottles, the permeation rate was a function of solute partial vapor pressure. It agreed with a model involving dissolution of permeant molecules into the membrane and molecular diffusion in it. This model explained the increase of HCl permeation rate by a factor of about 200 on increasing HCl concentration from 2M to 9.5M.

Permeation mechanism determined permselectivity,

as shown by relative permeation of methanol and ethanol: whereas the permeability ratio for more open membranes resembled the ratio of diffusion coefficients, about 2, it reached 9 for denser membranes. A similar phenomenon was observed in comparing HF and HCl permeation from dilute solutions, the first showing higher permeation in denser membranes.

The HCl partial vapor pressure for a 2M solution is low and HCl/H₃PO₄ permselectivity in both kinds of membranes resembled the diffusivity ratio (coefficients of 4.04×10^{-5} and 0.76×10^{-5} for 2M HCl and 2M H₃PO₄, respectively). Permselectivities of less than 5 indicated larger pores or pinholes.

Permeation from concentrated HCl and LiCl solutions provided another example of activity driven permselectivity. At these concentrations, HCl partial vapor pressure, and thus permeability through dense membranes, were high. As a result, HCl/LiCl permselectivity was ≥ 40 , which was about one order of magnitude higher than the diffusivity ratio. HCl activity in HCl + LiCl mixture, and therefore its permeability, further increased due to common ion effect.

Water permeation through PSF membranes increased with increasing solute permeation in the opposite direction, indicating water permeation through pores formed on porogen decomposition. Water permeation through dense membranes was affected by acid concentration (which determined osmotic pressure) and by the method of porogen decomposition, which determined membrane characteristics, e.g., porogen decomposition by HF resulted in C₄H₉OH,² which was more easily extracted⁴ than C₄H₉Cl formed on decomposition by HCl. Water/solute permeation correlations in denser membranes showed similar slopes. The slope for the more open membranes was different (lower water permeability), indicating a different permeation mechanism.

Permeation of relatively small molecules (M.W. of up to about 100) through the more open membranes was proportional to the diffusion coefficient. Erythrosine iodide permeation showed clear deviation from this correlation, with permeation rates about an order of magnitude lower than rates correlating with diffusion coefficient (Table VI). Permeation of erythrosine iodide was practically blocked by the membranes, indicating cut-off at about 1000 Daltons. Lowered permeabilities were also observed for tetrabutyl ammonium bromide and for citric acid, though the M.W. was much below 1000. This was probably due to the bulky structure

of these molecules, resulting in strong interactions with pore surfaces.

CONCLUSIONS

Permeability through porogen derived membranes was affected by composition of casting solution, by casting and drying methods, and by parameters of porogen decomposition. The most important ones were the surface on which the premembrane was cast and stretching or inhibition of contraction during porogen decomposition. Additional treatments, such as extraction of retained decomposition products, provided for considerable effects on permeation. Membranes formed belonged to two groups, according to permeability and to permeation mechanism. Permeabilities could reach up to about 1500 mmol H⁺/m²h in permeation from 2M HCl + 2M H₃PO₄ solution without losing permselectivity. Permselectivity through the more open membranes was determined by permeant diffusivities. For the denser membranes, it was determined by partial vapor pressure of permeant rather than by concentration. The more open membranes showed cut-offs of about 1000 Daltons. The denser membranes allowed relatively high osmotic water permeation, while

practically blocking permeation of solutes, such as salt, in the opposite direction.

Porogen derived membranes, of the more open kind, allowed separations according to diffusivity and to molecular weight. They also had the potential of separation according to chemical characteristics, due to decomposition products anchored in proximity to transport channels. Membranes of the denser kind were suitable for separation of volatile constituents of solution and for concentration of solutions by water permeation into concentrated salt solutions.

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