

Metastable Solutions and Interactions of Decomposition Products in Porogen Derived Membranes

A. M. EYAL, D. EDELSTEIN, B. HAZAN, and K. HAJDU

Casali Institute of Applied Chemistry, School of Applied Science and Technology,
The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

SYNOPSIS

Small incompatible molecules formed on porogen decomposition were found to be metastably dissolved in Porogen Derived Membranes, confirming previous analysis.¹ Degrees of metastable dissolution are determined by polymer and porogen characteristics, by porogen content, and by decomposition parameters (characteristics of reagent, its concentration, and decomposition temperature). These parameters determine the characteristics of decomposition products (DPs) formed, the rate of their formation, and the properties of the matrix through which they have to diffuse for phase separation. Extraction experiments indicated that, for many compositions, leaching out of DPs during contact with water is very slow. Porogen derived membranes are thus intermediate between polymeric membranes and supported liquid membranes, with the potential of combining high selectivity and reasonable stability. © John Wiley & Sons, Inc.

INTRODUCTION

A new method for producing permeable polymeric membranes was described and analyzed.¹ This method was based on chemical decomposition of molecules ("porogens") homogeneously dispersed in a polymeric matrix.

Briefly, the procedure for producing these Porogen Derived Membranes (PDM) consisted of:

1. Forming a uniform mass containing a polymer and at least one porogen,
2. Shaping the obtained polymeric mass to form a premembrane, and
3. Inducing a chemical decomposition of the porogen in the premembrane.

Previous articles^{2,3} described homogeneous molecular dispersion of various porogens in polysulfone (PSF) and in polyvinylchloride (PVC) and decomposition of these porogens (thermally or by reagents).

It was anticipated¹ that decomposition products, being less compatible with the polymeric matrix than the porogen, diffuse out during porogen decomposition, or right after it, thereby forming pores. Alternatively, decomposition products could be metastably trapped and thus could affect transport through the membrane. The present article studies phenomena related to decomposition products (DPs) during and after decomposition.

EXPERIMENTAL

Materials and methods were described in a previous article.²

RESULTS AND DISCUSSION

Metastable Solutions of Decomposition Products

*Metastable Solutions of *t*buX*

PVC premembranes, containing *t*-butyl esters of carboxylic acids or *N*-*boc* amines as porogens, were cast and dried in the procedure previously described²

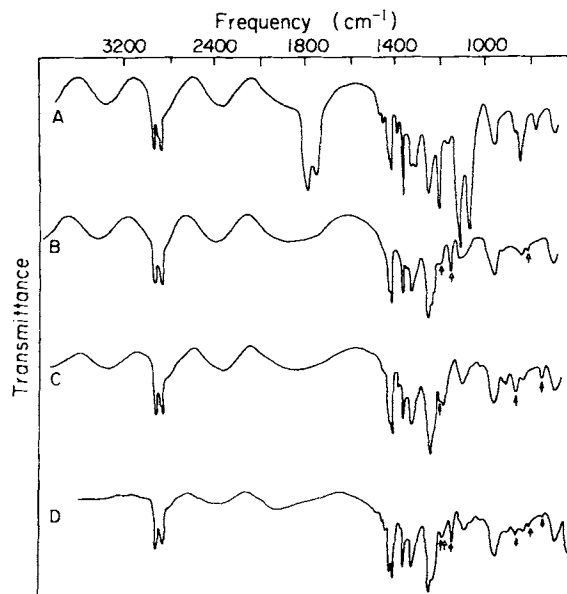
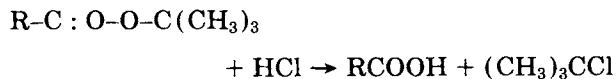


Figure 1 IR spectra of PVC : DTBDC premembranes before (A), and after contact with a decomposing reagent: HCl (B), HF (C), and HCl + HF (D).

and then were treated with solutions of acids for porogen decomposition. Using HCl, HBr, HI, or HF under the conditions already defined,³ decomposition approaches completion as determined by the disappearance of the carbonyl absorption from the IR spectra. Absorptions of the *t*-butyl (*t*bu) group (at about 1370 cm^{-1} and about 1150 cm^{-1}), however, were still observed (see Fig. 1), indicating the presence of *t*buX in the film: *t*buCl, *t*buBr, and *t*buI appeared in films treated with HCl, HBr, and HI, respectively. On using HF, however, *t*buOH is found rather than *t*buF (Fig. 1C). In a similar experiment, both HCl and HF were used for porogen decomposition. Premembranes, containing ditertbutyl oxalate (DTBO) as porogen, were first immersed in dilute HCl solutions and then were kept in the vapor phase above 48% HF solution. IR spectra of the resulting membranes show absorptions of both *t*buCl and *t*buOH.

Similar experiments were performed with PSF premembranes. IR spectra of membranes formed were complex, but the presence of *t*buX was indicated by absorption at 1370 cm^{-1} . *t*buCl in PSF membranes formed on di-*boc*-diamino hexane (DBDAH) decomposition by HCl was identified by GC-MS.

IR spectra thus show that *t*buCl is formed upon decomposition of tertbutyl esters and of *N*-*boc* amines by HCl:



*t*BuBr and *t*BuI are similarly formed upon using HBr and HI, respectively. Porogen decomposition by HF, however, resulted in *t*buOH due to water molecules penetrating with HF (the difference may result from the strong hydration of HF through H-bonding). In the decomposition of DTBDC, a water molecule may also result from the porogen molecule. These results point out that, while HF acts as a catalyst, HCl, HBr, and HI also act as reagents being consumed in the reaction.

Absorptions of *t*buX were small or absent in IR spectra of membranes obtained by using H_2SO_4 , methylsulfonic acid (MSA), or HClO_4 as external decomposition reagents. These residual absorptions may be attributed to incomplete decomposition or to *t*buOH formation.

PVC membranes, containing ditertbutyl dicarbonate (DTBDC) as porogen (w/w ratio of 100/16), were treated with HCl solution (37% w/w, 2 h, 40°) to complete porogen decomposition. Glass transition temperature (T_g) of these films was 51°, considerably lower than that of PVC, providing another indication of trapped decomposition products (DPs). After heating to 100°, the T_g changed to that of PVC (88°) due to evaporation of the DPs.

Evaporation of trapped DPs was studied thermogravimetrically. PVC or PSF premembranes, containing DTBO as porogen, were treated with HCl or HF for porogen decomposition. Thermogravimetric analysis of the membranes obtained (Table I) showed maximal rates of evaporation of DPs at about 100° and about 140° for PVC and PSF, respectively. Similar results were obtained for membranes obtained from DTBO and di-*N*-*boc* hydrazine (DBH) containing premembranes.

For comparison, a PSF film was immersed in *t*buCl. Its IR spectrum shows limited *t*buCl absorption, indicating some swelling. Thermogravimetric analysis (TGA) of this film showed complete evaporation of *t*buCl content at a temperature lower than 35°C.

*t*buX are thus small polar molecules, incompatible with the polymer, as was also shown by casting films from PVC + *t*buCl + THF and from PSF + *t*buCl + DCE (= dichloroethane) solutions. No *t*buCl absorptions were observed in IR spectra of these films. However, when formed on decomposition of molecularly dispersed porogens, *t*buCl molecules are retained, at least partially, in the polymer.

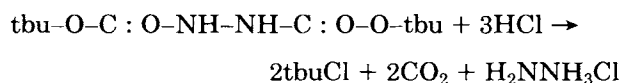
Table I Results of Thermogravimetric Analysis and Calculated Proportions of t-butyl Groups Trapped in the Films after Porogen Decomposition

Polymer	Polymer/Porogen (DTBO) Weight Ratio	Porogen Decomposition	Weight Loss		Temperature of Maximal Rate of Weight Loss	
			Relative to Film (%)	Trapped t-butyl ^a (%)	at 1°C/min	at 5°C/min
PVC	100/30	2 h in 37% HCl solution at 40°C	8.6	60	88	98
PVC	100/30	3 days in 37% HCl solution at 8°C	9.4	70	88	98
PVC	100/10	2 h in 37% HCl solution at 40°C	6.9	85		98
PVC	100/30	20 h in vapor phase above 48% HF at 25°C	6.9	60	85	
PSF	100/15	2 h in 37% HCl solution at 40°C	10.5	95		145
PSF	100/15	20 h in vapor phase above 48% HF at 25°C	4.1	45		145

^a Relative to calculated trapping of 100% tBuCl or tBuOH.

tBuCl and tBuOH are volatile (b.p. of 50.7° and 82.2°, respectively). Had they been in a thermodynamically stable molecular dispersion, they would have volatilized continuously when temperatures approached their boiling points, their virtually complete elimination taking place at 10 to 20 degrees C above b.p. These observations, the contents in the membranes exceeding, by an order of magnitude, solubilities as reported or determined by us and the derivation from a molecular dispersion of a soluble porogen in polymer, pointed to a molecular dispersion of this system. A state of metastable solution, named "anchoring" in Ref. 1, provided an explanation. Phase separation was prevented primarily by the cohesive forces between polymer chains, as indicated by several observations: (a) evaporation temperature was not determined by DP volatility and appeared unrelated to it, (b) evaporation temperatures from PSF were higher than those from PVC, (c) evaporation temperatures approximate glass transition temperatures.

Thermal analysis was used to calculate mean activation energies for evaporation of DPs from PSF membranes obtained on DBH (0.33 mmol/g in pre-membrane) decomposition by HCl.



7.3 KCal/mol and 31.6 KCal/mol were measured for tBuCl (temperature range 100°–140°) and for H₂NNH₃Cl (temperature range 165°–175°), respectively, confirming strong metastable binding.

Metastable Dissolution of Other DPs

In addition to C₄H₈ and tBuX, carboxylic acids were formed on decomposition of tBu-ester porogens in premembranes. IR spectra showed the presence of lauric, α-bromo lauric, oxalic, dodecanoic, 5-amino caproic, oleic, and malonic acid in PVC membranes and dodecanoic and terephthalic acid in PSF membranes after decomposition of the corresponding porogens. The acids were in various degrees of hydration, according to the decomposition method. Hydration of metastably dissolved acid can be affected by external conditions; prolonged contact with water vapor increased hydration, whereas heating removed water.

Hydrochloric salts of diamines were found in PSF membranes after decomposition of (CH₃)₃COOCNH-(CH₂)_nNHCOOC(CH₃)₃ porogens. Thermogravimetric studies and chemical analysis showed that in the case of n = 0, monohydrochloride was formed, while for the others, dihydrochlorides were the retained species. NH₄Cl was trapped in PSF membranes on decomposition of tertbutyl carbamate.

Thermal decomposition of metal salts of N-boc amino acids in premembranes resulted in metastable dissolution of metal complex of the corresponding acid or products of its decarboxylation.²

With HNO₃ solutions as external reagents for DTBO decomposition in PVC films, absorptions at 1610, 1160, and 880 cm⁻¹, or 1670 and 1310 cm⁻¹, were observed in IR spectra (Fig. 2). The relevant decomposition product was not identified.

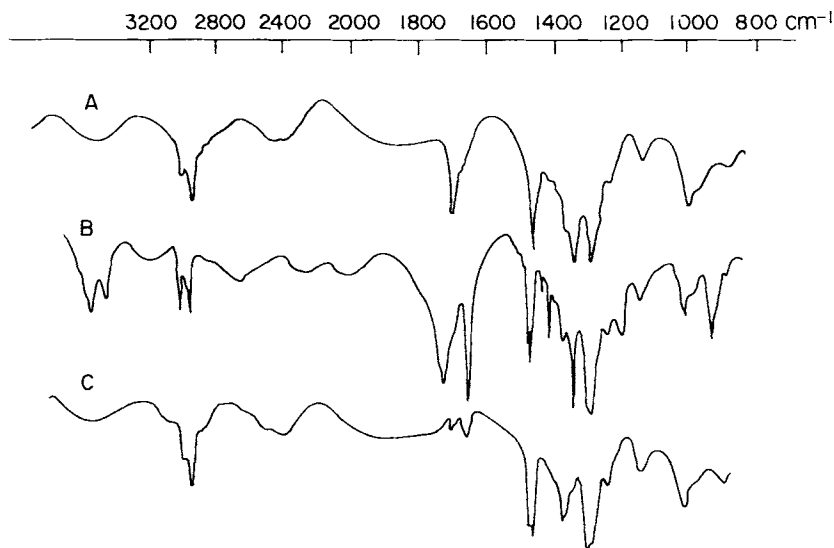


Figure 2 IR spectra of PVC-DTBO premembranes treated at room temperature with 70% HNO_3 for 2 h. (A); with 50% HNO_3 for 20 h, (B); and held in water for 1 h after HNO_3 treatment (C).

Degree of Metastable Dissolution

Metastable dissolution can be evaluated in terms of the extent of retention of DPs by the membrane and the stability of these metastable dispersions under various conditions. These are lumped under metastable dissolution.

Effects of parameters, such as polymer and porogen characteristics, porogen concentration, reagent used, and decomposition temperature, were studied.

Effect of Polymer Characteristics

TGA provided data for calculating metastable dissolution as % of total *tbu* content in the porogen. Results (Table I) showed:

1. in both PVC and PSF, more *tbuCl* (formed on decomposition by HCl) was found than *tbuOH* (formed on decomposition by HF),
2. *tbuCl* content in PSF was higher than in PVC, and
3. *tbuOH* content in PVC was higher than in PSF.

Marked differences between PVC and PSF were observed, also with respect to retention of oxalic acid, in these experiments. Thus, oxalic acid was clearly identified in the IR spectra of PVC membranes, but was absent in those of PSF membranes. Similar results were observed on treating ditertbutyl

dodecanedioate (DTBDD) containing premembranes with 70% HNO_3 at -12° (Table II).

Effect of Porogen Characteristics

PSF/DBH and PSF/DBDAB premembranes were treated in vapors of HCl solutions for porogen decomposition. After drying, they were thermogravimetrically analyzed to determine *tbuCl* retention. The results (Table III) showed that, compared on the same initial porogen concentration basis, membranes resulting from DBH containing premembranes retained *tbuCl* more strongly than membranes resulting from DBDAB.

IR spectra of PVC films, formed upon treating premembranes containing various *tbu*-ester porogens with 70% HNO_3 at 30° (in the case of BAHA 6°C), showed that lauric, α -bromolauric, oleic, and dodecanoic acid were retained while oxalic and 5-amino caproic acid were completely eliminated (see Table II). Lowering decomposition temperature to -12° did not change the results. Similar behavior was observed for premembranes containing a mixture of DTBDD and DTBO; dodecanoic acid was retained while oxalic acid was not.

Effect of Porogen Content

Table III shows that metastable dissolution decreased with increasing initial porogen concentration. Similar results were observed for PVC/DTBDC premembranes treated for 2 h in 37% HCl solution at 40°C (Table I).

Table II Metastable Dissolution, According to IR Spectra, of Acids Formed on Decomposition of Various Poroogens by Various Reagents

A	The Acid Formed is Retained (at Least Partially)						The Acid Formed is Not Retained					
	B	C	D	E	F		A	B	C	D	E	F
TBL	10	PVC										
ABTBL	13.3	PVC	70% HNO ₃	30°C	2 h							
TBO	12.1	PVC	HCl vap	RT	4 d ^a							
DTBDD	6.7-30	PVC ^b	70% HNO ₃	30°C	2 h							
DTBDD	6.7-30	PVC ^b	70% HNO ₃	-12°C	15 d							
DTBDD	6.7-30	PVC ^b	HCl vap	RT	4 d ^a							
DTBDD	6.7-30	PVC ^b	32% HCl	40°C	1 d + RT 5 d							
DTBDD	6.7-30	PVC ^b	ASA ^e	45°C	3 d							
DTBDD	6.7	PSF	50% HNO ₃	RT	2 d		DTBDD	6.7	PS	70% HNO ₃	-12°C	5 d
DTBO	15, 30	PVC	1% MSA ^e	65°C	20 m							
DTBO	15, 30	PVC	HCl vap				DTBO	6.7-30	PVC	70% HNO ₃	30°C	2 h
DTBO	15, 30	PVC	HF vap							70% HNO ₃	-12°C	16 d
DTBO	15, 30	PVC	32% HCl	RT	4 d							
			≤ 50%									
DTBO	15, 30	PVC	HNO ₃	RT	1 d		DTBO	6.7	PS	50% HNO ₃	RT	20 h
DTBO	15, 30	PVC	70% HNO ₃	RT	30 m					70% HNO ₃	-12°C	6 d
DTBDD + DTBO	6.7		70% HNO ₃	30°C	2 h ^c							
	1.3-13.3	PVC	70% HNO ₃	-12°C	9 d + 30°C 2 h							
DTBDD + DTBO	13.1		70% HNO ₃	30°C	2 h ^{c,d}							
	0-6.9	PVC	70% HNO ₃	-12°C	15 d ^c							
BAHA	10, 20	PVC	30% HCl	RT	1 d		BAHA	20	PVC	70% HNO ₃	6°C	20 m
DTBH	20	PVC	32% HCl	40°C	1 d							
DTBTF	5-30	PSF	HCl vap	RT	5 d							

(A) Poroegen, (B) mg Poroegen per 100 mg polymer, (C) Polymer, (D) Reagent used for inducing decomposition treatment, (E) Temperature, (F) Treatment period.

All films treated with HNO₃ were kept/held in water for several days after treatment.

(m) Minute, (h) Hour, (d) Day, (RT) Room temperature, (vap) Premembrane bearing casting bottles were held in vapor phase above the solutions.

^a Membranes made and treated similarly while on non-woven cloth, also contained the acid as shown by dissolution and recasting.

^b Retention decreases with increasing poroegen initial content (above 13 mg/100 mg polymer, opaque membranes are obtained from clear premembranes).

^c Only dodecanoic acid is retained.

^d Films are opaque. Opacity increases with increasing DTBO initial content.

^e ASA and MSA are internal reagents (see c).

Table III *t*buCl Metastable Dissolution in PVC Films During Porogen Decomposition

Porogen	Porogen Concentration in Premembranes mmol/g Composition	<i>t</i> buCl Retention (%)
DBH	0.25	100
DBH	0.41	95
DBH	0.68	66
DBDAB	0.138	100
DBDAB	0.23	93
DBDAB	0.41	80

Transparent PVC premembranes containing DTBDD, DTBO, or their mixtures as porogens, were treated with 70% HNO₃ at 30°C. Membranes formed from premembranes, initially containing 13.1, 16, 20, or 30 DTBDD per 100 PVC (w/w), were at least partially opaque, indicating phase separation. Opacity increased with initial porogen content. Films, obtained from PVC/DTBDD/DTBO premembranes with PVC/DTBDD w/w ratio of 100/6.7 and PVC/DTBO ratios of up to 100/13.3, were clear. Films, resulting from PVC/DTBDD/DTBO premembranes with PVC/DTBDD w/w ratio of 100/13.1, were opaque, the opacity increasing with DTBO content. Similar dependence on initial porogen content was observed also for films obtained from PVC/DTBO premembranes (although oxalic acid formed in these conditions completely diffused out of the film).

Effect of Decomposition Parameters

Oxalic acid was found in membranes obtained by treating DTBO containing premembranes with HF or HCl (either in solution or in vapor phase). Treating with 70% HNO₃ solution for 2 h at 30°C resulted in films with no indication of acid retention. Similar results were found for 5-amino caproic acid in membranes obtained from BAHA (mono boc-5-amino hexanoic acid) containing premembranes.

PVC membranes obtained from premembranes with high porogen (DTBDD, DTBO, or mixtures) content were opaque when decomposition was induced by 70% HNO₃ at 30°C (2 h), but clear if induced by 70% HNO₃ at -12° (15 days).

Oxalic acid, *t*buX, and nitric acid related DPs were found in PVC membranes obtained by treating PVC/DTBO premembranes at ambient with 50% (or less) HNO₃ solution or with 70% HNO₃ solution for 30 min. These DPs are not retained in mem-

branes formed using 70% HNO₃ for 2 h at ambient or at higher temperature.

Dodecanoic acid was retained in membranes obtained by treating PSF/DTBDD premembranes with 50% HNO₃ at ambient for 48 h, but not in those treated with 70% HNO₃ at -12° for 5 days.

Discussion of Degree of Metastable Dissolution

Metastable dissolution obviously depended on porogen and polymer, on their ratio, and on decomposition conditions. These parameters determined the characteristics of DPs formed, the rate of their formation, and the characteristics of the matrix through which they have to diffuse for phase separation.

Acid induced decomposition of *t*bu esters or of *N*-boc amines may have resulted in C₄H₈, which evaporated completely, or *t*buX, which may have been retained. In the first case, the acid acted as a catalyst, while in the second, HX or water was consumed. The amount of *t*buX retained in the polymer was also affected by the amount of *t*buX formed and therefore was determined also by the accessibility of the reagents, which in turn was affected by the polymer. The relatively low proportion of *t*buOH in PSF films after porogen decomposition by HF, may thus be ascribed to limited formation rather than to weak anchoring (the amount of water being the limiting factor).

Once formed, the incompatible volatile *t*buX tended to phase separate and to diffuse out of the film. This diffusion was affected by the rigidity and by the density of the polymeric matrix. Polymer characteristics, and plasticizing effect of porogen not yet decomposed, were therefore of importance. Metastable dissolution was thus higher in PSF than in the less rigid PVC. It increased with decreasing initial porogen concentration and, for di-*N*-boc diamines, with decreasing M.W. (for the effect of molecular size on plasticizing effect, see *T_g* data in Ref. 2). Furthermore, porogen concentration and size determined the initial distances between decomposition products.² Low initial concentration of porogen and porogen of small M.W. contributed to retention also by increasing diffusion distances required for phase separation.

For less volatile DPs (carboxylic acids, amines) the degree and rate of C₄H₈ and *t*buX formation and evaporation also affected matrix properties. Thus, unlike when HCl or HF were used, porogen decomposition by HNO₃ did not leave *t*buX in the film and therefore formed, at least initially, a larger free

volume, providing for easier migration of acid or amine nitrate out of the membrane.

The role of volatile DPs formation, and the concentration of the remaining porogen acting as plasticizer still present in the polymeric medium, were also affected by the decomposition rate, as determined by the decomposition reagent, its concentration, and decomposition temperature.³ In rapid decompositions (completed in about 1 h), a combination of larger volumes of gas formed and relatively rapid plasticizer elimination left, at least initially, an open system, which provided for phase separation. In slower decomposition, during most of the process there was still enough plasticizer to allow polymer flow to close openings and trap a considerable part of the DPs. In very slow decomposition, most of the slowly formed DPs could diffuse out while the polymer rearranged into a dense medium.

Extraction of Decomposition Products

Water, methanol, and their mixtures were used to extract retained decomposition products. Extraction rates were expected to provide data characterizing metastable dissolution.

Extraction of *tbuX*

Membranes formed on porogen decomposition in premembranes, using HCl or HF as reagents, were tested in permeation experiments. IR spectra of these membranes showed a decrease of *tbuX* absorptions as compared with those prior to the experiments. Hence, permeation of solute or osmotic permeation of water caused extraction of DPs. Ex-

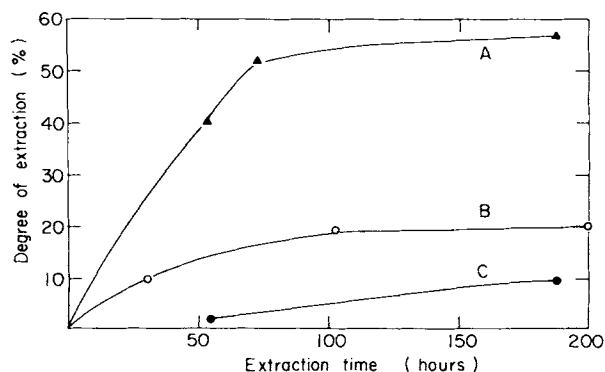


Figure 3 Extraction into water at 32°C of *tbuCl* retained in film after treating PSF-DBHD premembranes by HCl for porogen decomposition. The initial porogen concentrations were 0.68 mmol/g composition (A) 0.33 mmol/g composition (B) and 0.25 mmol/g composition (C).

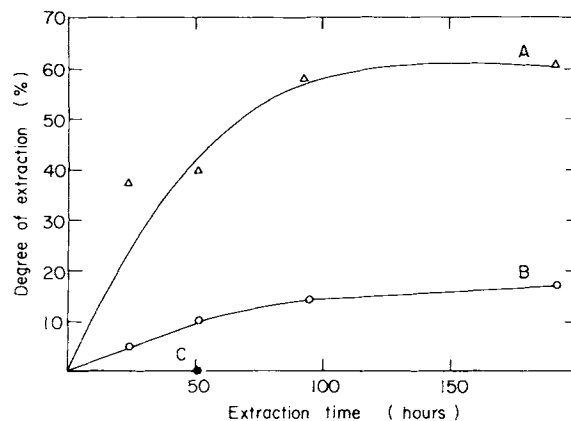


Figure 4 Extraction into water at 32°C of *tbuCl* retained in film after treating PSF-DBDAB premembranes by HCl for porogen decomposition. The initial porogen concentrations were: 0.41 mmol/g composition (A), 0.21 mmol/g composition (B) and 0.13 mmol/g composition (C).

traction from PVC membranes is faster than extraction from PSF membranes.

PSF membranes containing *tbuCl* or *tbuOH* were introduced into permeation measuring cells containing 30% HCl solution on one side and deionized water on the other (permeation cell is described in Ref. 1). After 6 days in a mechanical shaker at ambient, about 30% of retained *tbuOH* was extracted while *tbuCl* extraction was only a few percent. About 40% of retained *tbuCl* was extracted after 16 days.

Figures 3 and 4 summarize results of *tbuCl* extraction by water at 32°C from PSF membranes

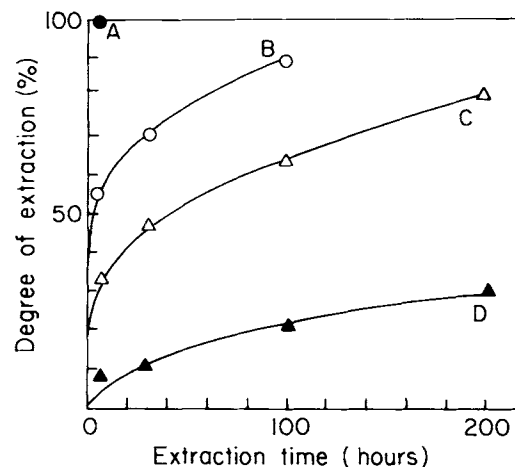


Figure 5 Extraction into methanol, methanol-water mixtures and water of *tbuCl* retained in the film after HCl treatment of PSF-DBHD premembranes. The methanol: water molar ratios were: (A) 1:0, (B) 0.5:0.5, (C) 0.3:0.7, and (D) 0:1.

formed by treating PSF/di-N-boc diamine containing premembranes with HCl vapors. The figures show that extraction is not complete and that extraction increases with initial porogen concentration and with porogen molecular weight.

Figure 5 summarizes results of *tbuCl* extraction by water, methanol, and their mixtures from PSF membranes formed by treating PSF/DBH premembranes with HCl vapors. The effect of increasing methanol proportions is clear.

Extraction of Carboxylic Acids

Metastably dissolved oxalic acid was extracted more easily than metastably dissolved dodecanoic acid. While the first was completely extracted during several days immersion in water at ambient (or several hours at elevated temperatures), the second showed only modest extraction, even by solutions of NH_4OH or NaOH .

IR spectrum of PVC membranes, obtained by treating PVC/ABTBL (α -bromo *t*-butyl laurate) premembrane with HNO_3 [Fig. 6(A)], showed absorption at about 1750 cm^{-1} due to retained α -bromo lauric acid. Immersion of this film in a solution of NH_4OH resulted in transformation of the carboxylic acid to carboxylate as shown by shift of IR absorption to about 1580 cm^{-1} [Fig. 6(B)]. The base permeated into the membrane and interacted with the retained acid. Similar results were obtained with retained dodecanoic acid and with terephthalic acid. Immersing in HF solution converted the carboxylate back to carboxylic acid [Fig. 6(C)], confirming the

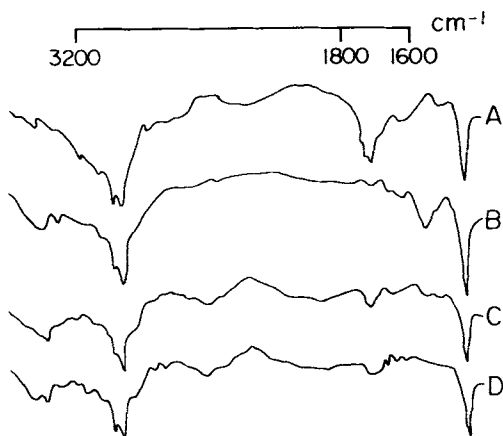


Figure 6 IR spectra of PVC film obtained by treating ABTBL containing film with HNO_3 (A); followed by treatment with concentrated NH_4OH (B), and then with 2M HF solution (C), and with water (D).

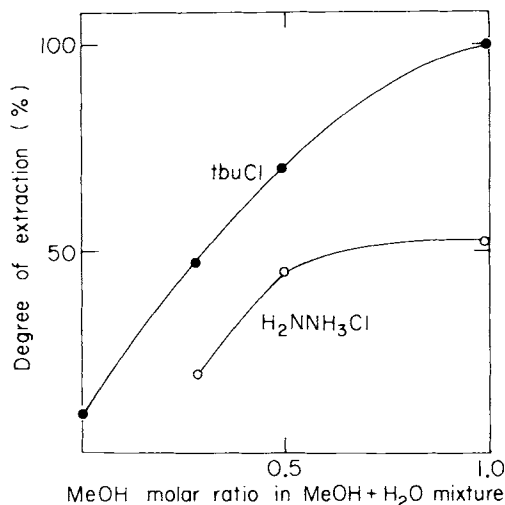


Figure 7 Extraction by methanol-water mixtures (32°C , 31 h contact) of *tbuCl* and $\text{H}_2\text{NNH}_3\text{Cl}$ formed by HCl induced porogen decomposition in PSF-DBH premembranes. Initial porogen concentration was 0.33 mmol/g composition.

identification of the carboxylate. Figure 6(D) is the IR spectrum of this membrane after being kept in water; it indicates that retention persisted through these transformations.

Terephthalic acid was retained in PSF membranes after porogen decomposition in PSF/DTBTF (di-*t*-butyl terephthalate) premembranes. As in the case of α -bromolauric acid, immersion in solutions of bases converted the acid into the salt form. However, in the case of terephthalic acid, this conversion enhanced extraction with water. Terephthalate-containing films were treated with HCl vapors for conversion of the salt back to the acid form. Extraction experiments showed that the acid formed was extracted more easily than the acid prior to conversion to terephthalate—the interaction with the base made an irreversible change in the system.

Similar experiments were made with membranes obtained from PSF/DTBO and PVC/DTBDD premembranes. In the first, conversion to salt affected extraction as in PSF/DTBTF, while the second behaved similarly to PVC/ABTBL.

Membranes were obtained by inducing decomposition in PVC/DTBDD premembranes (using acetic methyl-sulfonicanhydride (ASA) as internal precatalyst³ or HNO_3). These membranes were immersed for 1 day in: (a) water, (b) 5% (w/w) methanol in water, (c) 25% w/w methanol in water, and (d) methanol. Partial and complete extractions of the dodecanoic acid were observed in solutions (c) and (d) respectively.

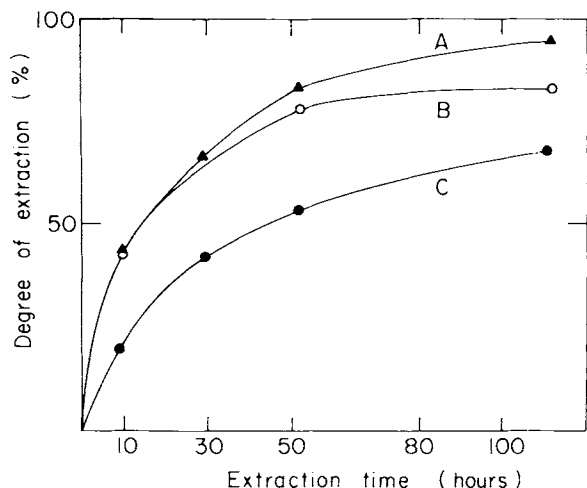


Figure 8 Extraction by methanol of $\text{H}_2\text{NNH}_3\text{Cl}$ formed by HCl induced porogen decomposition in PSF-DBHd premembranes. The initial porogen concentrations were: (A) 0.68 mmol/g composition, (B) 0.41 mmol/g, and (C) 0.25 mmol/g composition.

Extraction of Amine Hydrochlorides

PSF premembranes containing the porogen TBC (t-butyl carbamate), DBH, BAB (N-boc aminobutane), DBDAB, DBDAH, BABA (boc aminobutanoic acid), or BAHA were treated in HCl vapors for

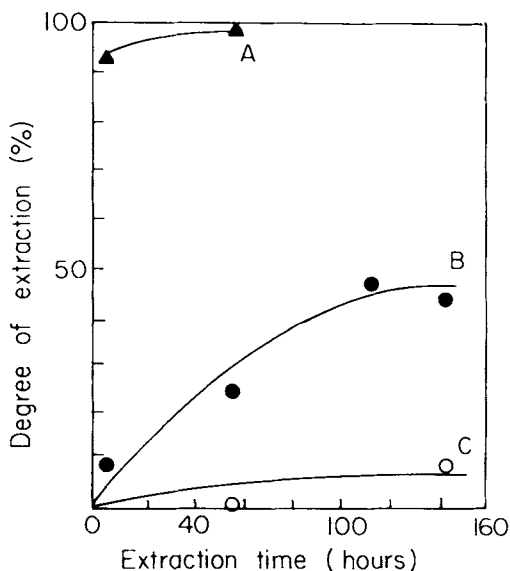


Figure 9 Extraction by methanol of $\text{ClH}_3\text{N}-(\text{CH}_2)_4\text{NH}_3\text{Cl}$ formed by HCl induced porogen decomposition in PSF-DBDAB premembranes. The initial porogen concentrations were: (A) 0.41 mmol/g composition, (B) 0.22 mmol/g composition, and (C) 0.13 mmol/g composition.

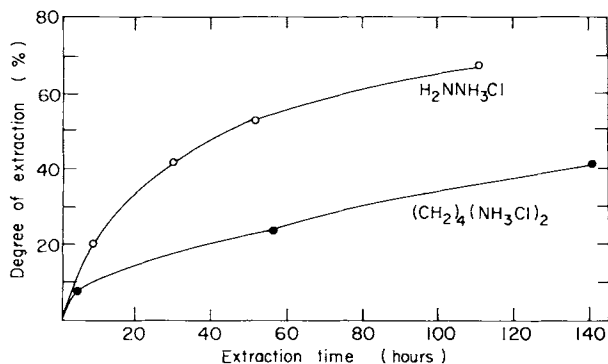


Figure 10 Extraction by methanol of $\text{H}_2\text{NNH}_3\text{Cl}$ and $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{NH}_3\text{Cl}$ formed by porogen decomposition in PSF premembranes. Initial porogen concentrations were 0.25 and 0.22 mmol/g composition, respectively.

porogen decomposition. PSF membranes, containing the corresponding amine hydrochlorides, resulted. Extraction of these retained DPs was studied at 32° .

Methanol/water mixtures were used for extraction of tbuCl and of $\text{H}_2\text{NNH}_3\text{Cl}$ from films obtained on porogen decomposition in PSF/DBH premembranes. Results are summarized in Figure 7, showing that tbuCl is extracted more easily than the hydrazine salt.

Methanol was used for extraction of amine hydrochloride from membranes resulting from PSF/DBH and PSF/DBDAB premembranes. Results, summarized in Figures 8 and 9, show increased extraction with increasing initial porogen content.

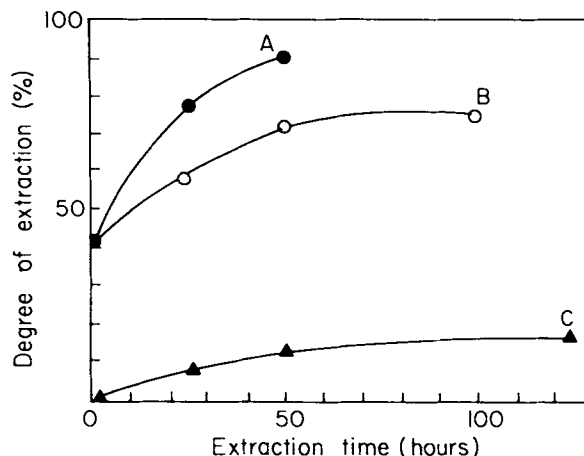
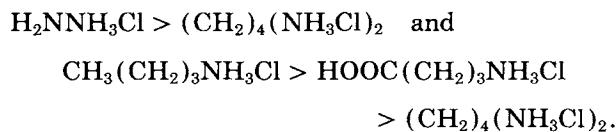


Figure 11 Extraction by methanol of (A) $\text{CH}_3(\text{CH}_2)_3\text{NH}_3\text{Cl}$ (B) $\text{HOOC}(\text{CH}_2)_3\text{NH}_3\text{Cl}$, and (C) $\text{ClH}_3\text{N}(\text{CH}_2)_4\text{NH}_3\text{Cl}$ formed by porogen decomposition in PSF premembranes. Initial porogen concentrations were 0.15, 0.14, and 0.14 mmol/g composition, respectively.

The effect of amine hydrochloride characteristics on extraction rate was studied. Results in Figures 10 and 11 show the following sequences of extractability.



In another experiment, comparing extraction by methanol at 30°, the following sequence of decreasing extractability was observed.



Discussion of Extraction Experiments

Retained DPs and the medium in which they are retained form systems that interact with permeating solvent molecules. As a result, the metastable structure may be affected so as to lower the activation energy for phase separation. Extraction results confirm conclusions obtained, as described in the section "Discussion of Degree of Metastable Dissolution," according to the degree of retention: (a) *tbuX* is retained less strongly than amine hydrochlorides, (b) retention decreases with increasing initial porogen concentration.

Extraction experiments also provided data as to the effects of molecular size and functionalities of DPs:

1. Activation energy for separation of dodecanoic acid was higher than that of oxalic acid and for $(\text{CH}_2)_4(\text{NH}_3\text{Cl})_2$ it is higher than for $\text{H}_2\text{NNH}_3\text{Cl}$. These molecules differ in size, in number of charges, and in (CH_2) -chain. The difference in degree of retention was therefore not surprising, though it was difficult to assign a single overriding reason for the difference.
2. Activation energy for separation of $(\text{CH}_2)_4(\text{NH}_3\text{Cl})_2$ was higher than that of $\text{CH}_3(\text{CH}_2)_3\text{NH}_3\text{Cl}$. As the former has two polar groups located at the opposite ends of

the chain, migration might have been very slow, the polar groups "pulling" in different directions. In addition, bifunctional DPs may conceivably form a network of interactions throughout the polymeric composition, thereby stabilizing anchoring.

3. The high activation energy for separation of 5-amino butanoic acid, compared to that of diamino hexane, may be due to lower free volume formation (only one N-boc group is decomposed per porogen molecule).

CONCLUSIONS

Small, incompatible decomposition products were found homogeneously dispersed in PSF and PVC membranes formed on porogen decomposition. The degree of this retention was determined by polymer and porogen characteristics, by porogen content, and by porogen decomposition parameters. Extraction experiments indicated that, for many membranes, leaching out of decomposition products during contact with water was very slow. Thus, stable membranes containing hydrochloric acid salts of diamines, carboxylic acids, and metal complexes were attainable. These metastably dissolved decomposition products interacted with molecules permeating into the membrane. Porogen derived membranes thus had the potential of combining the advantages of polymeric and of supported liquid membranes: reasonable stability and high selectivity.

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