Chemically Induced Porogen Decomposition in Premembranes for Porogen Derived Membranes

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SYNOPSIS

Studies of chemically induced porogen decomposition in Porogen Derived Membranes show that substantially complete decomposition of porogen molecules, molecularly dispersed in the polymeric matrix, is attainable. Several hours are required for decomposition by reagents penetrating into the premembrane at ambient. Decomposition rate is determined by characteristics of polymer, porogen, and reagent used, by polymer/porogen weight ratio, by reagent concentration, and by temperature. The concept of decomposition by an internal catalyst was also validated. In addition to direct relevance to the new method of membrane formation, the study provides better understanding of phenomena of general interest, such as transport of small molecules through changing polymeric matrices. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

A new method for producing permeable polymeric membranes was described and analyzed in a previous article.[1] This method is based on inducing chemical decomposition in molecules ("porogens") that are homogeneously dispersed in a polymeric matrix. Decomposition products, being smaller and less compatible, either leave the polymeric matrix, forming pores, or are trapped, and may affect transport through chemical interaction.

Various t-butyl and di-t-butyl esters, N-boc and di-N-boc amines, metal salts of N-boc amino acids, and glycerol–formic acid esters provide potential porogens as they decompose to give small volatile fragments. These molecules can be homogeneously and practically molecularly dispersed in polyvinyl-chloride (PVC) and polysulfone (PSF) to form premembrane.[2] The upper limit of porogen concentration depends on characteristics of the polymer and the porogen, as well as on solvent used for casting, and on drying procedure and temperature.

Porogen decomposition by heating or irradiation has the inherent virtue of eliminating the need for external reagent penetration into the premembrane. The choice of suitable porogens is limited, however. A heat decomposable porogen should be stable at the drying temperature, but should decompose while the polymer is still stable and, preferably, while under the T_g of the premembrane. Irradiation decomposable porogens should provide for decomposition at wave lengths which are not absorbed by the polymer or by impurities that may catalyse polymer decomposition.

The choice is much larger in porogen decomposition by chemical reagents, which may be consumed in the reaction or may act as catalysts. Strong acids induce decomposition in molecules having $COOC(CH_3)_3$ and/or $NHCOOC(CH_3)_3$ group, according to well known reactions.[3-5] For decomposition of a porogen molecularly dispersed in a premembrane, contact with the decomposition-inducing reagent is required. This reagent may penetrate from the exterior of the polymeric mass (an external reagent) or may be present in the premembrane (an internal reagent). Internal reagents, introduced into premembranes by addition to the casting solution, should show some compatibility with the polymeric composition and should start decomposition reactions only when solvent evaporation is completed and when the premembrane assumes the desired

shape. A variation on this internal reagent concept consists of using an internal "precatalyst," a reagent that decomposes, generating the catalyst that induces porogen decomposition.

EXPERIMENTAL

Materials and procedures for premembrane casting and drying were described in previous articles.[1,2]

RESULTS AND DISCUSSION

Porogen Decomposition by an External Reagent

An external reagent, inducing porogen decomposition, should penetrate into the polymeric mass from a solution or from vapor in contact with the premembrane. Such penetration may be by dissolution in the polymeric mass, by permeation through pores formed by the reaction, or by a combination of both.

Concentrations and characteristics of reagent and porogen, polymer characteristics, and temperature are expected to affect the rate of porogen decomposition in the premembrane. Effects may be complex, due to the complexity of the matrix (polymer, porogen, volatile and nonvolatile decomposition products, reagent, internal surface) and due to extreme local changes during decomposition. The effects of various parameters were studied.

Premembranes were cast and dried using the methods described above.[1,2] For each composition, several film-bearing casting bottles were immersed in solutions of the reagents or were held in the vapor phase above a layer of the reagent solution. From time to time, a bottle was taken out, was rinsed with water, and the film was peeled off. The absorption of the carbonyl group in IR spectrum of the film was used as an indication of the degree of porogen decomposition.

Effect of Reagent Concentration

Nitrocellulose (NC) premembranes containing glycerol triformine (GTF), ($CH_2(O-C : OH)$-$CH(O-C : OH)CH_2(O-C : OH)$, as a porogen (NC/GTF, w/w ratio of 100/100) were immersed at room temperature in ammonia solutions. The effect of reagent concentration on the time required for near completion of porogen decomposition is shown in Figure 1.

Solutions of HBr, HI, HCl HF, and HNO_3 were studied as reagents for decomposition of porogens in polysulfone/ditertbutyl oxalate (tbu-O-C : O-C :
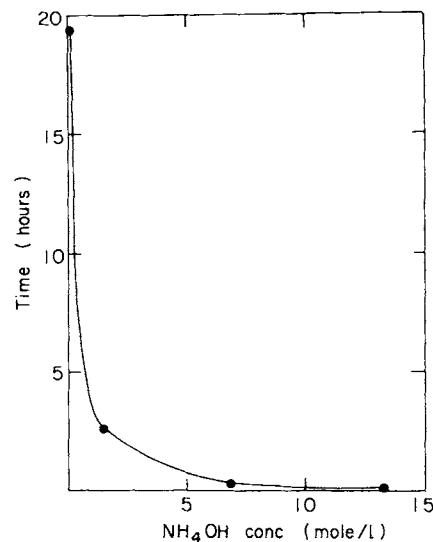

Figure 1. The effect of reagent (NH_4OH) concentration on the time required for complete decomposition of GTF in NC (porogen : polymer weight ratio of 1 : 1) at room temperature.

O-tbu), polyvinylchloride/ditertbutyl oxalate, and polysulfone/1,6 di-boc diamino hexane ((tbu-O-C : $O-NH_2)_2$ ($CH_2)_6$) premembranes (denoted PSF/DTBO, PVC/DTBO, and PSF/DBDAH, respectively). For each reagent, at least two concentrations were studied. Results are summarized in Table I.

Figure 1 and Table I bring out a strong dependence of decomposition rate on reagent concentration. The determining factor seems to be the water to reagent mol ratio. Decomposition rate is considerably enhanced when this ratio drops below 4. At this ratio, reagent activity strongly increases because of low hydration. (This is evidenced by solute partial vapor pressure: for 57% HI, H_2O : HI mol ratio of 5.4, it is 0.2 mmHg, while for 66% HI, H_2O : HI mol ratio of 3.7, it is 50 mmHg). The enhancement of decomposition rates, obtained with acids by the addition of their salts, is in accord with the foregoing explanation. Thus, for instance, the decomposition rate in 48% HBr solution saturated to LiBr is considerably higher than in salt-free 48% HBr solution.

Characteristics of Acids as Decomposition Reagents

Premembranes, composed of PVC or polysulfone (PSF) as polymers and DTBO, DBDAH, ditertbutyl dicarbonate (tbu-O-C : O-O-C : O-O-tbu, DTBDC), or ditertbutyl dodecanedioate (tbu-O-C : O-$(CH_2)_{10}$-C : O-O-tbu, DTBDD) as porogens, were treated for porogen decomposition either in vapor

Table I   The Effect of Reagent Concentration on the Rate of Porogen Decomposition in Premembranes Still Attached to the Casting Bottle[a]

Premembrane Composition		PSF : DTBO = 100 : 15	PVC : DTBO = 100 : 15	PVC : DTBO = 100 : 30			PSF : DBDAH = 100 : 10		
Reagent	(c)	1 d	1 d	20 min	1 h	1 d	2 h	1 d	5 d
48% Hbr	4.9	2				2			
48% HBr + LiBr[b]		5				5			
57% HI	5.4	1	1			1			
66% HI	3.7	5	5			5			
37% HNO$_3$	6.0	1				1			
41% HNO$_3$	5.0	1				1			
44% HNO$_3$	4.5	1				1			
47% HNO$_3$	3.9	4				4			
50% NHO$_3$	3.5	5			1	5			
70% HNO$_3$	1.5			5					
21% HF	4.2								1
35% HF	2.1							2	5
48% HF	1.2						5		
27.7% HCl	5.3								3
30% HCl	4.7						3		
32% HCl	4.3						5		

[a] 1, 2, 3, 4, 5 stand for decompositions of $\leq$ 10, about 25%, about 50%, about 75%, and $\geq$ 90% respectively. All the experiments were performed at 25°C.
[b] Reagent formed by saturating 48% HBr solution with LiBr.
[c] H$_2$O: acid molar ration.
min, h, and d stand for minutes, hours, and days, respectively.

phase above concentrated HCl or HF solutions or by immersion at various temperatures in solutions of HF, HCl, HBr, HI, H$_2$SO$_4$, H$_3$PO$_4$, HNO$_3$, HClO$_4$, CH$_3$SO$_3$H, HCOOH, or CF$_3$COOH. The main observations were:

- Rates of decomposition by HCl were similar to those by HBr and by HI, but differ considerably from those by HF: decomposition of DBDAH in PSF premembranes by immersion in HF solution was considerably slower than in HCl solution (with similar H$_2$O : acid ratio and at the same temperature). Comparing activity of these acids in the vapor phase showed opposite results: decomposition of DTBDC in PVC premembranes is more rapid in the vapor phase above 48% HF (HF partial vapor pressure of 20 mmHg) than above 37% HCl (HCl partial vapor pressure of $\sim$ 200 mmHg).

- Comparing porogen decomposition rates, induced in premembranes by several acids, resulted in the following activity sequence:

$$HI \approx HBr \approx HCl \approx HNO_3$$
$$> H_2SO_4 \approx HClO_4 > H_3PO_4 \approx HF.$$

- Most organic acids show no activity. In cases where absorption of ester carbonyl disappeared from the IR spectra of the films (using CH$_3$SO$_3$H or CF$_3$COOH as reagents), it was not clear if decomposition took place in the film or if the porogen was leached out.

Differences in the activity of the examined acids may be due to differences in mechanisms of penetration, to a different mechanism of reaction with the porogen, and to decomposition products formed. As an example, parameters determining HF activity in porogen decomposition are discussed:

- Since it is a small molecule, HF penetrated more easily through dense films as also shown by its relatively high permeation rate through the membrane formed by its action on the porogen.

- In concentrated solutions, HF tends to form larger molecules, (HF)$_n$, due to strong H bonding, which also weakened the acidity. In the vapor phase, this phenomenon is less pronounced, which may explain the observed sequences of decomposition rates HF$_{vap}$ > HCl$_{vap}$, but HCl$_{aq}$ > HF$_{aq}$.

Table II   Effect of Temperature on the Rate of Porogen Decomposition in PVC and PSF Premembranes Attached to Casting Bottles

Premembrane Composition	Decomposition Reagent	Decomposition Rates at		
		Low Temp	25°C	High Temp
PSF : DTBO = 100 : 15	37% HCl (vap)		4 h (3)	40°C, 2 h (5)
PSF : DTBO = 100 : 15	50% HNO$_3$	10°C, 1 d (1)	1 h (4)/ 1 d (5)	35°C, 40 min (5)/ 45°C, 15 min (4)
PVC : DTBO = 100 : 15	70% HNO$_3$		5 min (3)	35°C, 5 min (5)
PVC : DTBDC = 100 : 15	37% HCl	8°C, 3 d (5)		40°C, 2 h (5)
PVC : DTBDC = 100 : 15	48% HF (vap)	8°C, 2 d (5)		40°C, 5 h (5)
PVC : DTBDC = 100 : 15	70% HClO$_4$		70 h (1)	65°C, 30 min (4)
PSF : DTBDC = 100 : 15	70% HClO$_4$		21 h (1), 70 h (3)	65°C, 30 min (4)
PVC : DTBO : DTBDD = 100 : 1.3–13.3 : 6.7	70% HNO$_3$	−12°C, 15 d (5)		30°C, 2 h (5)

(vap) the premembrane bearing bottle was held in vapor phase above the solution. In all other cases it was immersed in the solution. (1), (2), (3), (4), and (5) stand for decomposition of ≤ 10%, about 25%, about 50%, about 75%, and ≥ 90%, respectively. (min) minute, (h) hour, (d) day. In cases of (5), the period is approximately the minimal required for full decomposition.

- As discussed above, hydration of the reagent molecule played an important role. Water penetration with HF was confirmed by decomposition products.

- Decomposition products brought out an additional difference: HF and HNO$_3$ acted solely as catalysts for porogen decomposition, while HCl HBr and HI also acted as reagents, being consumed in the reaction.

- Different decomposition products may lead to differences in initial pore formation, which in turn may affect reagent penetration rates.

Effects of Matrix Composition and of Temperature

Characteristics of porogen and of polymer, and their ratio in the premembrane, as well as temperature,

are basic determinants affecting porogen decomposition through: reaction rate, formation of volatile and nonvolatile decomposition products, extent of their diffusion out of the polymeric matrix, and fusion of small pores to form larger ones.

Decomposition rates increase with temperature elevation (see Table II), both in PVC premembranes (T_g only slightly above decomposition temperature) and in PSF premembranes ($T_g > 100$). These results are in accord with higher acid activities and with higher diffusion rates at higher temperatures. At temperatures approaching T_g, however, polymer fluidity increased too, which may have resulted in pore fusion, decrease of free volume, and, in turn, a decrease of porogen decomposition rates.

At conditions resulting in high decomposition rates, there was no pronounced difference between

Table III   The Effect of Polymer Nature on Decomposition Rate of Porogen in Premembrane[a]

Porogen	Polymer : Porogen Weight Ratio	Reagent	Treatment Temp.	Time	Degree of Decomposition	
					in PVC	in PSF
DTBDC	100 : 15	48% HBr	RT	21 h	10%	50%
DTBDC	100 : 15	48% HBr	RT	2 d	50%	100%
DTBO	100 : 15	70% HClO$_4$	RT	24 h	10%	40%
DTBO	100 : 15	70% HClO$_4$	RT	3 d	10%	70%
DTBDD	100 : 6.7	70% HNO$_3$	−12°C	4 d	Partial[b]	Complete
DTBDD	100 : 6.7	32% HCl[c]	RT	1 d	20%	30%

[a] The results here are for slow decompositions. In all cases but the last, the premembrane was attached to the casting bottle. (h) hour, (d) day.

[b] Complete porogen decomposition required about 15 days.

[c] The premembranes bearing bottle was held in the vapor phase above the solution. In all other cases is was immersed in the solution.

Table IV The Effect of Porogen Nature on Decomposition Rate[a]

Porogen	Polymer	Polymer : Porogen Weight Ratio	70% HNO₃ 12°C	70% HNO₃ 10 m	32% HCl 30°C 1 h	32% HCl 30°C 2 h	32% HCl 30°C 6 h	HCl Vap above 32° HCl RT 1 h	HCl Vap above 32° HCl RT 2 h	HCl Vap above 32° HCl RT 6 h	HCl Vap above 32° HCl RT 1 d
DTBO	PVC	100 : 14.0	< 10			≤ 5	~ 25		≤ 5	≤ 5	~ 35
DTBDC	PVC	100 : 15.0	~ 15			≤ 5	~ 70		≤ 5	~ 5	> 95
DTBDD	PVC	100 : 23.5	~ 80			~ 35	~ 85		~ 20	~ 30	> 95
DTBDD	PVC	100 : 13.1									~ 50
DTBDD	PVC	100 : 16.0									~ 25
BAHA	PVC	100 : 16.0	> 90		> 95	> 95		> 95			
DBDAH	PVC	100 : 21.7	> 90			> 95		> 95			

Porogen	Polymer	Polymer : Porogen Weight Ratio	50% NHO₃ 30°C 3 m	50% NHO₃ 30°C 10 m	50% NHO₃ 30°C 30 m	50% NHO₃ 30°C 60 m	50% NHO₃ 30°C 120 m	HCl Vap above 32% HCl RT 60 m	HCl Vap above 32% HCl RT 205 m	HCl Vap above 32% HCl RT 5 h	HCl Vap above 32% HCl RT 1 h	HCl Vap above 32% HCl RT 2 d
DTBO	PSF	100 : 11.5	< 5			~ 30	~ 70	< 5		< 5	~ 5	~ 50
DTBDC	PSF	100 : 12.4	< 5			~ 75	~ 90	~ 10		~ 40	~ 80	≥ 95
DTBDD	PSF	100 : 6.7	< 5			~ 40	~ 85	~ 5		≤ 5	~ 30	~ 50
BAHA	PSF	100 : 18.0	~ 5	~ 40	> 90			~ 45	> 95			
DBDAH	PSF	100 : 13.6	~ 10	~ 50	> 90			~ 45	~ 85	~ 95		

[a] Premembranes were detached from casting bottles prior to contact with decomposition inducing reagent. All PVC premembranes (solvent: THF) were 9–10 μm thick. First three PSF premembranes (solvent: THF) were 14 μm thick and the others (solvent: NMP) were 9–10 μm thick.

PVC and PSF. For slow decompositions however, rates in PSF were higher (see Table III). These results can be explained by the higher rigidity of PSF, which may slow reagent penetration, but allows for more stable free volume. Penetration through porosity, as it forms with porogen decomposition, is thereby enhanced.

Results for DTBDD in Table IV and for ditertbutyl terephthalate (tbu-O-C : O-C₆H₄-C : O-O-tbu, DTBTF) in Figure 2 indicated increasing porogen decomposition rate with increasing porogen concentration. This effect was more pronounced for the PSF premembranes. These results can be explained by the two contradicting effects of porogen content. High porogen molar concentrations resulted in larger initial free volumes, which enhanced reagent penetration. However, as decomposition was not completed instantaneously, the plasticizing effect of higher content of undecomposed porogen allowed fluidity to counteract free volume formation and thereby slowed decomposition. This second effect was obviously weaker in PSF than in PVC.

Ditertbutyl oxalate (DTBO), ditertbutyl dicarbonate (DTBDC), ditertbutyl dodecanedioate (DTBDD), di-boc diamino hexane (DBDAH),

tertbutyl laurate (tbu-O-C : O-(CH₂)₁₀CH₃, TBL), tertbutyl oleate (tbu-O-C : O(CH₂)₆CH=CH (CH₂)₈CH₃, TBO) and mono-boc amino hexanoic acid (tbu-O-C-NH(CH₂)₅COOH BAHA) were used as porogens in PVC or PSF premembranes. The effects of porogen chemical nature on decomposition rate was studied. Some of the results are
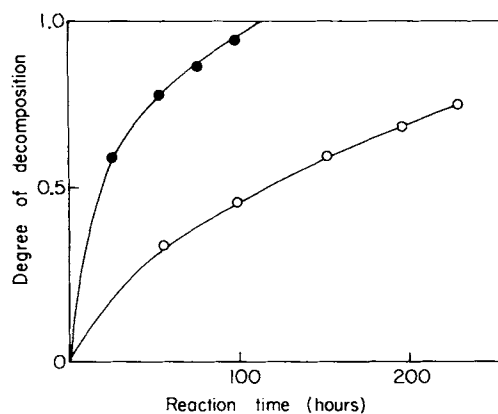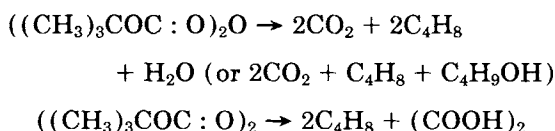

Figure 2. Decomposition of DTBTF in PSF by contact with HCl vapors. (○) 0.72 mmol porogen per g composition, (●) 0.94 mmol porogen per g composition.

summarized in Table IV. The main observations were:

- On similar molar concentration basis, decomposition of larger molecules were somewhat more rapid. This was probably due to easier diffusion of the reagent—larger porogen molecules have stronger plasticizing effects (see Fig. 2 in Ref. 2).

- Di-N-boc diamino hexane decomposed more rapidly than the t-butyl esters, possible reasons: (a) bonds in the N-boc group are very sensitive to acidity, (b) the amine hydrochloride formed assists in H^+ penetration (assisted transport), (c) on decomposition of N-boc group C_4H_8 + CO_2 were formed (compared to C_4H_8 for t-butyl esters)—formation of relatively larger initial free volume.

- Ditertbutyl dicarbonate decomposed more rapidly than DTBO, probably due to larger free volume formation:

$$((CH_3)_3COC : O)_2O \rightarrow 2CO_2 + 2C_4H_8$$
$$+ H_2O \text{ (or } 2CO_2 + C_4H_8 + C_4H_9OH)$$
$$((CH_3)_3COC : O)_2 \rightarrow 2C_4H_8 + (COOH)_2$$

- Oxalic acid, formed on DTBO decomposition, tended to retention in the polymeric matrix (see the following article).

- N-boc-6-aminohexanoic acid decomposed more rapidly than any other porogen studied. Fast decomposition rates were attained, even in relatively dilute acid solutions. The effect of the carboxylic group was not clear. Possible explanations were: (a) action as an internal catalyst (although it is a weak acid), (b) assistance of H^+ penetration and (c) stabilization of the amine group formed on N-boc group decomposition.

Decomposition by Internal Catalysts

Strong acids with small molecules were expected to act as internal catalysts when dissolved in the premembrane. However, such acids were not compatible as a rule with polymeric matrices. The concentrations of internal catalysts that still allow for transparent films (0.05 mmol/g polymer), are low as compared with porogen concentrations (0.2–1.2 mmol/g polymer).

Transparent films were made from casting solutions containing PVC, DTBDC or DTBO, and methyl sulfonic acid (MSA), with oxalic acid or p-
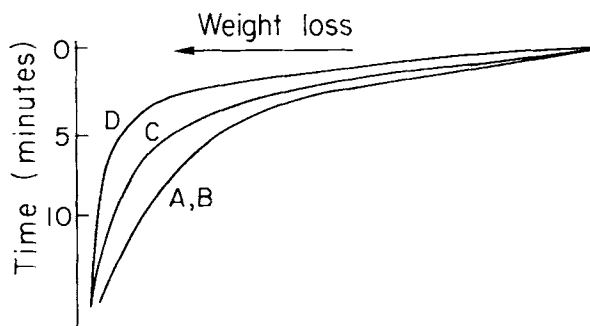

Figure 3. The effect of internal catalyst: weight losses at 100°C as a function of time. (A) PVC : DTBDC (w/w ratio 100 : 30), (B) PVC : DTBDC : PTSA (100 : 30 : 0.8), (C) PVC : DTBDC : MSA (100 : 30 : 0.4), (D) PVC : DTBDC : MSA (100 : 30 : 4).

toluene sulfonic acid (PTSA) as prospective internal catalysts.[1] No decomposition was observed in the casting solution and very little, if any, during drying at 45°C.

Premembranes, containing an internal catalyst, were examined thermogravimetrically. They were compared to premembranes with no internal catalyst in order to determine porogen decomposition at higher temperatures.

Results for PVC : DTBDC and PVC : DTBO systems (Figs. 3 and 4) showed that the presence of MSA affects weight loss. Assuming that it does not affect porogen evaporation, these results indicated that MSA acts as an internal catalyst and induces DTBDC and DTBO decomposition in the premembranes. No such effect was observed with p-toluene sulfonic acid (PTSA) (0.8% w/w) or oxalic acid (0.5% or 1% w/w) as internal catalysts.

The action of MSA as an internal catalyst was confirmed by a thermogravimetric experiment, in which a film with PVC : DTBO weight ratio of 100 : 15 and 1% MSA (opaque film) was held at 65°C for 20 min. It lost 4.3% of its weight. Comparing IR spectra of the film before heating and after shows that, while the C–O–C absorption at 1150 cm^{-1} decreased, there was no significant decrease in the carbonyl absorption. Thus, weight loss was mainly due to decomposition of the DTBO to give oxalic acid (and not due to evaporation).

PVC or PSF premembranes, containing di t-butyl sebacate (DTBS) or di t-butyl terephthalate (DTBTF) and relatively large MSA concentrations (2–7%, 0.12–0.5 mol per mol of porogen) were kept in an oven at 52°C. The resulting film was dissolved in THF and porogen decomposition was determined by titration. The main results were: (a) porogens
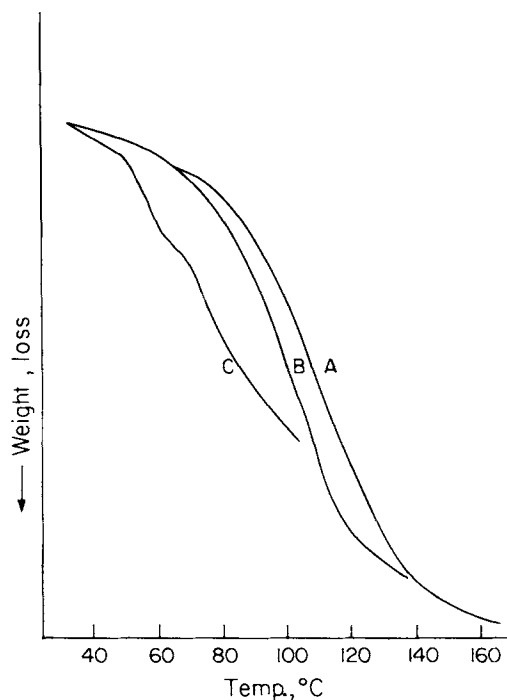
Figure 4. The effect of internal catalyst: weight losses as a function of temperature. (A) PVC : DTBO (w/w ratio 100 : 15), (B) PVC : DTBO : MSA (100 : 15 : 0.5), (C) PVC : DTBO : MSA (100 : 15 : 1).

were decomposed at this relatively low temperature, (b) decomposition in PVC films approached completion in these conditions while in PSF films completion was not attained, (c) decomposition increased with internal catalyst concentration, (d) decomposition increased with porogen concentration, the effect being stronger in PVC.

For catalysis of porogen decomposition, a direct contact between the catalyst and the porogen was required. In films with homogeneously dispersed low concentration catalyst (porogen: catalyst equivalent ratios of 8 : 1 to 40 : 1) this direct contact can be reached only by catalyst migration in the polymeric matrix. Our results indicated that such migration occurred only at a temperature of about, or higher than, the T_g of the whole system. In films with higher MSA concentrations, the mechanism was different, as indicated by considerable decomposition at 52°C, even in PSF premembranes with T_g of above 100°C. These films were opaque and contained microphases induced by the noncompatible MSA. It seems that porogen, "dissolved" in these microphases, was decomposed at 52°C due to direct contact with the catalyst. The rest of the porogen (which is molecularly dispersed in the polymeric matrix) was not affected.

Table V Porogen Decomposition, Determined by TGA of PVC : DTBDD : ASA Films at Elevated Temperatures

PVC : DTBDD Weight Ratio	PVC : ASA Weight Ratio		
	100 : 0.5	100 : 1	100 : 3
100 : 6.7	CD (98°C)	CD (80°C)	
100 : 13.4	80% D	CD (105°C)	CD (70°C)

(D) Decomposition, (CD) (Substantially) Complete Decomposition (decomposition of ≥ 90%). The temperature of maximum rate of weight loss in the TGA is given in parentheses.

Decomposition by a Precatalyst

A mixed anhydride of acetic acid and methyl sulfonic acid (ASA)[1] was selected as a precatalyst. Weight losses were observed in thermogravimetric analysis (TGA) of PVC/DTBDD/ASA films at elevated temperatures (Table V). DTBDD is not volatile at these temperatures, weight losses therefore indicate porogen decomposition. More complete decompositions, and at lower temperatures, are obtained at higher ASA : porogen ratios. Such porogen decomposition was observed for premembranes dried at room temperature after casting, but not for those dried at 45°C. Other films, with similar compositions, were dried at room temperature and then were introduced to an oven at 45°C for prolonged periods (24–144 hours). Their IR spectra after this treatment show porogen decomposition. Here again, more complete decomposition is obtained at higher ASA : DTBDD ratios (Table VI).

PSF : DTBDD : ASA=100 : 6.7 : 0.5 cast from n-methyl pyrrolidone (NMP) solution, and dried overnight at 100°C, show decomposition of the porogen. The film obtained was not homogeneous.

The primary results of experiments studying ASA as an internal precatalysts are, therefore:

Table VI Porogen Decomposition, Determined by IR Spectra, of PVC : DTBDD : ASA Films Kept at 45°C for Various Periods

PVC : DTBDD Weight Ratio	PVC : ASA Weight Ratio		
	100 : 0.5	100 : 1	100 : 3
100 : 6.7	90% D (72 h)	CD (24 h)	CD (24 h)
100 : 13.4	ND (144 h)	ND (24 h)	CD (24 h)

(D) Decomposition, (CD) (Substantially) Complete Decomposition, (ND) (Substantially) No Decomposition. In parentheses: Period at 45°C.

1. The observed compatibility of ASA is not better than that of MSA.
2. Full decomposition of DTBDD can be obtained at relatively low temperatures.
3. Porogen decomposition seems to require the presence of a residual solvent.
4. Decomposition rate increases with ASA content.

The catalyst, MSA, is obtained by hydrolysis of ASA. It is not clear at what stage of the experiment this hydrolysis takes place. The possibility of hydrolysis prior to or during casting cannot be ruled out. This may also explain the low compatibility observed for ASA.

In these experiments, an acid catalyzed porogen decomposition by an internal reagent was observed at relatively low temperature in films that did not show phase separation. A reagent is formed, acting as a catalyst (the porogen to ASA ratio is 10–20 : 1), that can migrate in the polymeric mass. This migration at relatively low temperatures is probably due to the presence of residual solvent. It seems that in both PVC and PSF films, the decomposition temperature was above T_g (lowered by solvent presence).

As in the case of an internal catalyst, further studies are required.

CONCLUSIONS

The variety of porogens decomposable by acid catalysts is wide. Results show that substantially complete decomposition of porogen molecules, molecularly dispersed in the polymeric matrix, is attainable. The decomposition rate is affected by a combination of parameters, determined by characteristics of polymer, porogen and reagent, polymer/porogen ratio, reagent concentration, and temperature. Porogen decomposition can be completed in several hours at ambient.

The concept of decomposition by an internal catalyst, such as MSA, was also proven valid. Implementation in practice is, however, not straightforward. The same is true also for internal precatalysts.

In addition to direct relevance to the new method of membrane formation, the study described in this article provides better understanding of phenomena of general interest, such as:

- Transport of mineral acids and organic acids through changing polymeric matrices: (i) effects of polymer nature, (ii) effects of nature and amount of plasticizers, (iii) effects of nature of penetrating molecules, and (iv) effects of temperature.
- Chemical reaction (decomposition) of compounds molecularly dispersed in a polymeric matrix.
- Study of polymeric matrices under extreme local changes, resulting from decomposition of plasticizers to small, noncompatible molecules.

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