Premembranes for Porogen-Derived Membranes and Thermal Decomposition of Porogens

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

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

SYNOPSIS

Various t-butyl and di-t-butyl esters, N-boc and di-N-boc amines, metal salts of N-boc amino acid, and glycerol–formic acid esters are potential porogens for porogen-derived membranes. Introduction of more than 20 such compounds into polysulfone or poly(vinyl chloride) films was studied. Transparency, IR spectra, changes in glass transition temperature, and differential scanning calorimetry were used to differentiate between molecular dispersion and formation of micro phases. The results show that for many of the studied additives more than 10% by weight can be practically molecularly dispersed in the polymers. The upper limit of porogen concentration in premembranes depends on characteristics of the polymer and of the porogen, on casting solvent composition, and on drying procedure. Metal salts of N-boc amino acids were found to be suitable heat-decomposable porogens. Their decomposition in premembranes proceeds in two stages, in the first of which 2 C_4H_8 + 2CO_2 are released per salt molecule. The metal complex formed goes through decarboxylation at a higher temperature. A heating procedure for completion of the first decomposition stage and for avoiding the second was determined.

INTRODUCTION

A new method for producing permeable polymeric membranes was described in a previous paper.[1] This method is based on inducing chemical decomposition in molecules ("porogens") 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 thus provide for affecting transport through chemical interaction.

The procedure for producing these porogen derived membranes (PDM) consists of:

a. Forming a uniform mass consisting of a polymer and at least one porogen [in case that an internal catalyst or precatalyst is used for decomposition[1], it is also added at this stage].
b. Shaping the obtained polymeric mass by any convenient technique such as extrusion, cal-
endering, or solvent casting to form a premembrane.
c. Inducing a chemical decomposition of the porogen in the premembrane.

The previous paper[1] illustrated the concept and the feasibility of membrane formation by the new method, using polysulfone as the polymer and di-N-boc-diamino hexane as the porogen. The present paper is devoted to preparation of premembranes and to thermal decomposition of porogens. Three polymers and about 20 porogens were studied. Subsequent papers will study the effects of polymer nature, porogen chemical properties and content, and preparation conditions on properties of the membrane formed.

EXPERIMENTAL

Materials

Materials used, their formulae, abbreviations, sources, and purity are summarized in Table I. Po-

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Table I Materials Used, Their Sources and Purity[a]

Name	Abbreviation	Formula	Source, Purity	MW
POLYMERS				
Poly(vinyl chloride)	PVC	$-(CH_2CHCl-)_n$	Electrochemical Ind., Epivil 46 vis. num. 136–140	
Polysulfone	PSF	$(-O-C_6H_4-SO_2-C_6H_4$ $-O-C_6H_4$ $-C(CH_3)_2-C_6H_4$	Union Carbide Udel 3500	
Nitrocellulose	NC		Usine de Bergerac, containing isopropanol	
POROGENS				
Di-*tert*-butyl oxalate	DTBO	$(tbu-O-C:O)_2$	Fluka, Perum	202
Di-*tert*-butyl dicarbonate	DTBDC	$(tbu-O-C:O-)_2O$	Fluka, 97%	218
Di-*tert*-butyl malonate	DTBM	$(tbu-O-C:O)_2CH_2$	Fluka, 98%	216
Butyl di-*tert*-butyl malonate	BDTBM	$(tbu-O-C:O)_2CH(CH_2)_3CH_3$		262
Di-*tert*-butyl adipate	DTBA	$(tbu-O-C:O)_2(CH_2)_4$		258
Di-*tert*-butyl sebasate	DTBS	$(tbu-O-C:O)_2(CH_2)_8$		314
Di-*tert*-butyl dodecane-dioate	DTBDD	$(tbu-O-C:O)_2(CH_2)_{10}$		342
Tert-butyl laurate	TBL	$tbu-O-C:O-(CH_2)_{10}CH_3$		256
Tert-butyl α-bromo laurate	TBABL	$tbu-O-C:O-CHBr$ $-(CH_2)_9CH_3$		336
Tertbutyl oleate	TBO	$tbu-O-C:O(CH_2)_7CH=$ $CH(CH_2)_9CH_3$		338
Di-*tert*-butyl terephthalate	DTBTF	$tbu-O-C:O-C_6H_4-C:$ $O-O-tbu$		278
Di-*N*-boc hydrazine	DBH	$(tbu-O-C:O-NH)_2$		232
1,2-Diboc diamino ethane	DBDAE	$(tbu-O-C:O-NH)_2(CH_2)_2$		260
1,4-Diboc diamino butane	DBDAB	$(tbu-O-C:O-NH)_2(CH_2)_4$		288
1,6-Diboc diamino hexane	DBDAH	$(tbu-O-C:O-NH)_2(CH_2)_6$		316
Mono boc hydrazine	BHd	$tbu-O-C:O-NH-NH_2$	Miles-Yeda	132
Mono boc amino butiric acid	BABA	$tbu-O-C:O-NH-(CH_2)_3$ $-COOH$	Miles-Yeda	203
Mono boc amino hexanoic acid	BAHA	$tbu-O-C-NH(CH_2)_5COOH$	Miles-Yeda	231
t-Butyl carbamate	TBC	$tbu-O-C:O-NH_2$	Aldrich, 98%	117
Mono boc amino butane	BAB	$tbu-O-C:O-NH-(CH_2)_3CH_3$	Miles-Yeda	173
Glycerol triformine	GTF	$CH_2(O-C:OH)CH(O-C:OH)$ $CH_2(O-C:OH)$		176

Table I (*Continued*)

Name	Abbreviation	Formula	Source, Purity	MW
Cu salt of N-boc glycine	CuGly	$(H_2C(tbu-OC:O-NH)COO)_2Cu$		411.5
Cu salt of N-boc valine	CuVal	$((CH_3)_2CHCH(tbu-OC:O-NH)COO)_2Cu$		495.5
Ni, Co, and Cu salts of N-boc phenylalanine	Ni/Co/ CuPhe	$(C_6H_5-CH_2-CH(tbu-OC:O-NH)COO)_2Cu$		587/587/591.5
Cu salt of N-boc tyrosine	CuTyr	$(HO-C_6H_4-CH_2CH(tbu-OC:O-NH)COO)_2Cu$		632.5
Cu salt of N-boc amino dodecanoic acid	CuDD	$(CH_3(CH_2)_9CH(tbu-OC:O-NH)COO)_2Cu$		691.5
Ni, Co, and Cu salts of N-boc lysine	Ni/Co/ CuLys	$(tbu-OC:O-NH)(CH_2)_4$ $CH(tbu-OC:O-NH)COO)_2Cu$		751/751/755.5
CATALYSTS AND PRECATALYSTS				
Methyl sufonic acid	MSA	CH_3SO_3H	Riedel, 98%	96
Oxalic acid	HOx	$(COOH)_2$	Baker/AR	90
Acetic-methyl sufonic anhydride	ASA	$CH_3SO_2-O-C-CH_3$		138
p-Toluene sulfonic acid	PTSA	$CH_3-C_4H_8-SO_3H$	Fluka/AR	172
SOLVENTS				
Tetra hydro furan	THF	C_4H_4O	Frutarom/AR	72
1,2-ethylene dichloride	DCE	CH_2ClCH_2Cl	Frutarom/AR	99
N-methyl 2 pyrrolidone	NMP	$CH_3N(CH_2)_3C:O$	Riedel, 99.5%	99
Cyclohexanone	CYC	$(CH_2)_5C:O$	Frutarom/CP	98
n-Butyl acetate	BA	$CH_3C:O-O-(CH_2)_3CH_3$	Frutarom	

ᵃ tbu = *tert*-butyl; materials prepared by Miles-Yeda and in our laboratory were characterized by NMR, IR, and elemental analysis.

rogens with no indication of source were prepared in our laboratory.

Methods

Premembranes were prepared by solvent casting. In order to limit contraction during drying and porogen decomposition (which frequently occur when premembranes are cast on flat surfaces), films were cast by dip coating small glass bottles (2.8 cm diameter, 6 cm high).

Casting solutions were prepared by mixing, in desired proportions, a solution of a polymer and a solution of a porogen. Internal catalysts, if used, were added just before casting to minimize decomposition

in the casting solution. THF, NMP or DCE, and n-butyl acetate were established as satisfactory solvents for PVC, for PSF, and for NC premembranes, respectively. Films of thickness in the range of 5–10 μm were obtained from 7–9% PVC solutions in THF, from 16–18% PSF in NMP and from about 15% NC in butyl acetate.

Various methods were tested for drying the polymeric films in order to assure homogeneity and required thickness. Preferred procedures were determined. Bottles cast by dipping in PVC/THF solutions were immediately covered by a 100 mL beaker for 24 h and then transferred to a drying oven at 45°C for 24 h. Bottles bearing PSF/NMP films are introduced immediately after casting to a drying

oven at 100°C for 20 h. PSF/DCE films were dried similarly to PVC/THF films. NC/butyl acetate films were dried for 60 min in a desiccator with $CaCl_2$ and then in a drying oven at 45°C for 24 h.

Permeability measurements were performed as described in Ref. 1.

RESULTS AND DISCUSSION

Premembrane Preparation

PVC Films with No Porogen

Preliminary studies tested PVC films obtained from PVC/THF solutions with no porogen. Permeabilities of these films varied over a wide range—more than 2 orders of magnitude, reaching as high as 100 mmol/m^2 h in permeation from $4M$ HCl solution. PVC films cast from THF + 0.3% cyclohexanone were practically impermeable.

Comparing IR spectra of PVC films obtained from THF solutions to those obtained from THF + 0.3% cyclohexanone solutions (Fig. 1) shows that the first has three additional absorptions (910, 1060, and 2800 cm^{-1}). These absorptions appear also in IR spectra of PVC in the literature.[2] They seem to indicate residual solvent or additives used in solvent or in polymer manufacture.

Disappearance of these IR absorptions can be explained by the effect of cyclohexanone on the rate of solvent evaporation. THF is volatile (bp 64°C) and evaporates rapidly, resulting in inhomogeneous films with high permeabilities. It also leads to trapping of solvent microphases in the film. Cyclohexanone (bp 156°C) reduces the terminal rate of evaporation and acts a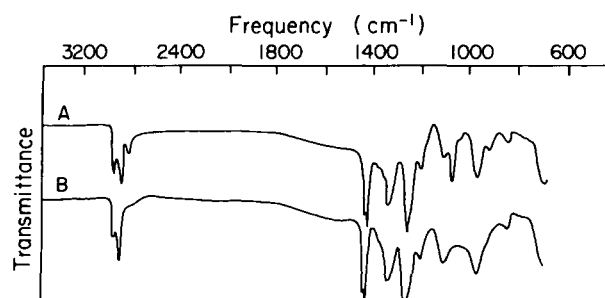s a plasticizer. It provides for regular diffusion of the solvent to the surface with the consequent formation of even, dense films free of gross defects.

Porogen Dispersion in Premembranes

Porogen-containing PVC premembranes cast from THF solutions form, as a rule, dense, defect-free films since the porogen has a plasticizing effect similar to that of cyclohexanone. Homogeneous molecular dispersion of porogens in the premembrane is required for homogeneous porosity formation on porogen decomposition. Most of the porogens have not been studied as plasticizers: Data as to their compatibility with polymers are not available. Upper limits of porogen content that still ensure homogeneous molecular dispersion were determined experimentally.

Films were cast from solutions of polymer in a chosen solvent containing also porogen in various polymer/porogen proportions. Transparency to daylight provided a quick and easy means for detecting microphases of porogen. Typical results for various porogens (and for some internal catalysts and precatalysts) are presented in Table II as $A < x < B$. A is the highest tested porogen content (in mg/100 mg polymer in casting solution) resulting in a premembrane transparent to daylight, while B is the lowest tested content resulting in an opaque film.

Transparency to daylight indicates that there are no microphases of porogen larger than visible light lowest wavelength (about 0.4 μm). For some polymer/porogen combinations homogeneity was also studied using instrumental methods:

a. Figure 2 shows decrease of glass transition temperature (T_g) of PSF premembranes with increasing content of diboc–diamine porogens. Larger molecules show stronger effects (compared on the same molar concentration basis). These results provide a strong indication of homogeneous dispersion up to concentrations of at least 0.3 mmol porogen per 1 g total composition. The upper limit seems higher (on a molar concentration basis) for the smaller molecules.

b. Differential scanning calorimeter (DSC) spectra of porogen-containing transparent premembranes show very little or no endothermic melting point peak, while opaque premembranes of same thickness show a considerable one at about 100°C (Fig. 3).

Figure 1 IR spectra of PVC films obtained from THF solution (A) and from THF + 0.3% cyclohexanone solution (B).

Table II   Porogen, Internal Catalysts, and Precatalyst Dispersion in Premembranes[a]

	PSF/THF	PSF/DCE	PSF/NMP	PVC/THF
DTBO	15 < x < 20	15 < x < 20	Evap.	33 < x
DTBDC	10 < x < 15	18 < x < 20	Evap.	30 < x
DTBM	15 < x < 20	10 < x		
BDTBM	x < 10			
DTBA	12 < x < 15			50 < x
DTBS				
DTBDD	6.7 < x < 10	x < 6.7	6.7 < x < 13.4	25 < x
TBL	x < 10	x < 10	x < 10	10 < x
TBABL	x < 13	x < 13	x < 13	26 < x
TBO	x < 12.1	x < 12.1	x < 12.1	12.1 < x
DTBDF		35 < x		
GTF	15 < x < 20			15 < x < 16
DBHd			12.5 < x < 15	
DBDAE			12.5 < x < 15	
DBDAB			12.5 < x < 15	
DBDAH		x < 10	15 < x < 20	
CuVal			2–3 < x < 5	15 < x
Cu Phe		x < 5	10 < x < 25	5 < x
Ni Phe	2 < x < 3	3–4 < x < 5	8–9 < x < 10	
MSA	0.5 < x < 1			0.5 < x < 1
HOx	0.5 < x < 1			0.5 < x < 1
NBS	1 < x < 2			2 < x < 4
ASA			0.5 < x < 1	

[a] The results are presented as $A < x < B$, where A is the highest tested porogen content (in mg/100 mg polymer, in the casting solution) that still results in premembranes transparent to daylight and B is the lowest tested porogen content (same basis) that resulted in premembranes opaque to daylight.

Transparent premembranes thus do not contain aggregates of porogen molecules of thermodynamically significant sizes and number.

c. IR spectra of transparent PVC and PSF premembranes containing DTBO as porogen are shown in Figure 4. The carbonyl absorption is affected by the polymer, indicating that a considerable proportion of porogen molecules
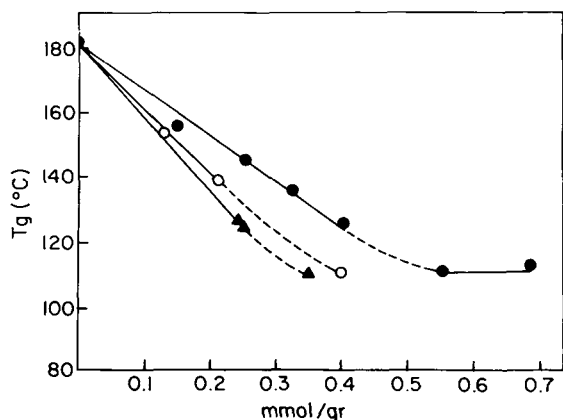

Figure 2   The effect of porogen concentration (mmol/gr composition) on T_g of PSF premembrane: (●) DBH; (O) DBDAB; (▲) DBDAH.
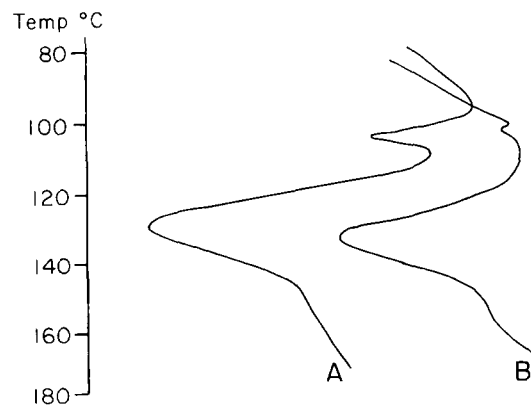

Figure 3   DSC spectra of PSF/DBDAH premembranes with w/w ratios of 100/17 [(A) opaque] and 100/10 [(B) transparent].
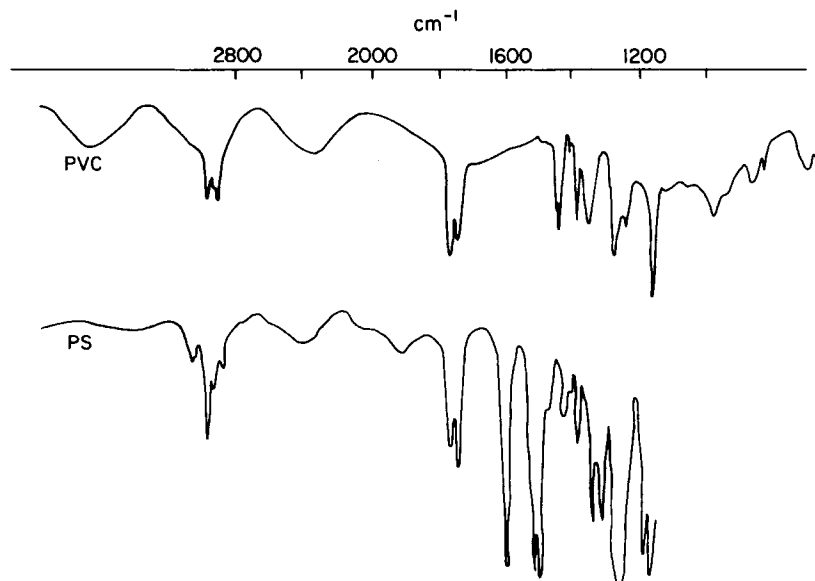
Figure 4   IR spectra of DTBO containing PVC and PSF premembranes.

are surrounded by polymer chains rather than by other porogen molecules.

d. Another indication of film homogeneity is provided by IR interference fringes. As they appear only when the membrane surfaces are parallel, they will not appear for all homogeneous membranes. However, if a film shows interference fringes, it is dense and homogeneous. IR interference fringes appear in spectra of DTBO containing PVC and PSF premembranes (Fig. 4) and in spectra of transparent PVC/DTBDD film (Fig. 5B).

They are absent in spectra of opaque PVC/ DTBDD films (Fig. 5A). IR interference fringes appear in spectra of transparent PSF/ DBDAH premembranes w/w ratio of 100/ 10 cast from NMP, but are absent in spectra of films having similar total composition cast from DCE (opaque).

e. An absorption at 3350 cm^{-1} appears in spectra of DBDAH and of opaque PSF films containing it as a porogen in high proportions. It is absent in spectra of transparent PSF/ DBDAH film (see Fig. 1 in Ref. 1).
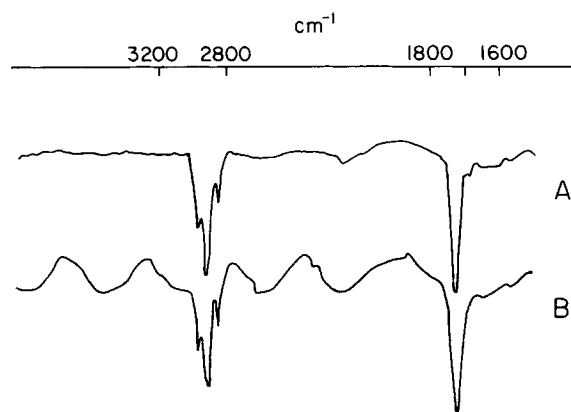

Figure 5   IR spectra of opaque (A) and of transparent (B) PVC–DTBDD premembranes.

These results confirm that homogeneous molecular dispersions of porogens in polymer are attainable. Good agreement with transparency to daylight is observed. Assuming that porogen/polymer ratios in premembranes approximate those in casting solution, Table II indicates the upper concentration limits for molecular, homogeneous dispersion of porogens.

Using a model described in Ref. 1, the minimal distance between porogen molecules in homogeneous premembrane was calculated as a function of porogen molecular weight and concentration. The results in Table II for the highest porogen content still resulting in homogeneous premembranes, correspond to distances of about 6 °A and about 3 °A for PSF and PVC films, respectively.

As expected, internal catalysts being small polar molecules, show very low compatibility in the polymers. Somewhat higher compatibility is shown by salts of N-boc amino acids while t-butylesters and N-boc amines are quite compatible. Diesters of smaller molecules (DTBDC, DTBO, DTBM) show higher compatibility in PSF than DTBDD on both molar concentration and weight percent basis. This is probably due to higher ester/CH_2 ratio.

In most cases, maximal proportions of dispersed porogen in PVC are higher than in PSF. This is in agreement with the higher cohesive forces between PSF chains (molar cohesive energies of 25710 and 4440 cal/mol for PSF and PVC, respectively[3]).

The effect of solvent on porogen dispersion indicates that this phenomenon is more complicated than just the solubility of the porogen in the polymer. Low solubility of the porogen in the solvent may lead to its separation during solvent evaporation and thus to porogen content lower than porogen solubility in the polymer. Higher contents may result from supersaturation and depend on viscosity of the polymeric matrix at the drying temperature.

Thermal Decomposition of Porogens

Porogen decomposition by heating has the inherent virtue of eliminating the need for external reagent penetration into the premembrane. Suitable porogens should be stable at the drying temperature, but should decompose while the polymer is still stable and preferably under the T_g of the premembrane.

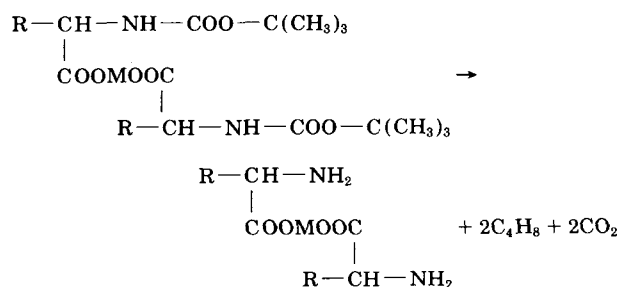### Thermal Decomposition of N-Boc Amino Acids and Their Salts

Salts of N-boc amino acids were examined as thermally decomposable porogens. Their decomposition is expected to leave metal complexes (or metal oxides) in the membrane formed. Thermal decomposition of such salts (and of the corresponding N-boc amino acids) was thermogravimetrically studied. Heating rates, temperatures of maxima rates of weight loss, and weight losses (as percent of total porogen weight), are summarized in Table III.

Results in Table III divide the tested porogens into two groups according to temperature of maximal

Table III   Thermogravimetric Analysis of N-Boc Amino Acids and Their Salts

Tested Compound	MW	Heating Rate (°C/min)	Weight Loss % of Total Porogen Content	Temperature of First Maxima in Weight Loss Rate (°C)
N-boc dodecanoic				
Acid	314	10	54	195
Cu salt	692	5	30	140
Co salt	687	5	22	145
N-boc valine				
Acid	216	10	66	175
Cu salt	497	2	61	170
N-boc glycine				
Cu salt	412	5	50	165
N-boc tyrosine				
Cu salt	624	5	32	135
N-boc phenyl alanine				
Cu salt	592	4	62	230
Ni salt	587	5	51	220
Co salt	587	5	34	199
N-boc lysine				
Cu salt	756	5	65	203
Ni salt	751	5	44	251
Co salt	751	5	41	191

decomposition rate (T_d). In the first group, showing lower T_d, weight loss agrees with release of two C_4H_8 and two CO_2 molecules per salt molecule, probably according to

$$R—CH—NH—COO—C(CH_3)_3$$
$$|$$
$$COOMOOC \quad\quad\quad\quad \rightarrow$$
$$|$$
$$R—CH—NH—COO—C(CH_3)_3$$

$$R—CH—NH_2$$
$$|$$
$$COOMOOC \quad\quad + 2C_4H_8 + 2CO_2$$
$$|$$
$$R—CH—NH_2$$

Porogens of this group show an additional decomposition at a higher temperature. For porogens of the second group (higher T_d) there is only one decomposition stage with weight loss higher than expected for $2C_4H_8 + 2CO_2$ elimination. Decarboxylation of the salt of amino acid takes place.

Results in Table III show that, for salts of N-boc phenyl alanine and for salts of N-boc lysine, temperature of maximal decomposition rate changes

with the cation (M). The effect of M may result from stabilization of the decomposition product due to complexation.

Thermal Decomposition of N-Boc Amino Acid Salts in Premembranes

Salts of N-boc amino acids considered as porogens for thermal decomposition should be compatible enough to provide for relatively high concentration in the premembrane. Cobalt salt of N-boc phenylalanine (CoPhe) was thus chosen for PSF and copper salt of N-boc valine (CuVal) for PVC. In addition, for formation of a reactive metal ion complex in the membrane, decomposition should be limited to the first decomposition stage (release of $2C_4H_8 + 2CO_2$ per salt molecule).

Studies of Premembranes Detached from Casting Bottles. PSF/CoPhe (w/w ratio of 100/10) premembranes were cast from NMP solution and dried in the method described above. The films obtained were peeled off the casting bottles and studied thermogravimetrically. At a heating rate of
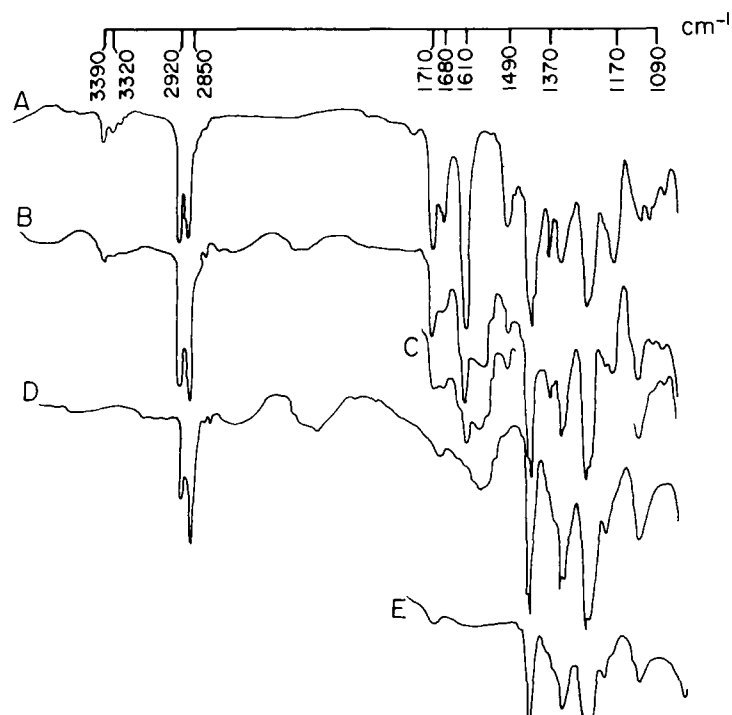

Figure 6 IR spectra of PVC-CuVal premembrane (PVC : porogen weight ratio of 100 : 25) at various stages of porogen thermal decomposition: (A) prior to heating; (B) and (C) after partial decomposition, (D) after the first stage of decomposition (release of $2C_4H_8$ and $2CO_2$ per porogen molecule); (E) after the second stage (decarboxylatin).

1°C/min, maximal rate of decomposition was observed at 230°C. Weight loss was 3.35% of total premembrane weight, corresponding to release of $2C_4H_2$ + $2CO_2$ per porogen molecule. Another film of similar composition was heated to 180°C at a rate of 5°C/min and held at this temperature for 120 min. The weight loss, 1.3% of the total weight of the film, indicates that at 180°C decomposition in the premembrane is very slow.

Porogen decomposition in PVC/CuVal (w/w ratio of 100/25) premembrane was followed by IR spectra. Of the main absorptions (Fig. 6A), the following correspond to the porogen: carbonyl of the amide group (1680, 1710 cm^{-1}), carbonyl of the carboxylate (1610 cm^{-1}), N—H of the C—O—NH—R amide group (1490 cm^{-1} shifted to 1600 cm^{-1}) in C—O—NH_2), $C(CH_3)_3$—O group (1170, 1370 cm^{-1}), and C–N (1090 cm^{-1}). In the first stage of decomposition the N to carboxylic C and the O to C_4H_9 bonds are opened. As a result, the corresponding absorptions disappear from the IR spectrum and the carbonyl absorption is shifted, probably due to Cu–amine complex formation. Spectrum 6D is obtained. (Spectra 6B and 6C are intermediate stages.) In the second stage decarboxylation seems to take place as the carbonyl IR absorption disappears (spectrum 6E).

Porogen decomposition in these films was also followed by changes of film's color and by UV + VIS spectra. The premembrane is green. After the first stage of decomposition it changes to greenish yellow and after the second to brown. Prior to decomposition the UV + VIS spectrum of the film shows absorptions at 200, 235, 260, and 710 nm. As decomposition proceeds, these absorptions decrease or disappear and absorptions at 210 and 280 nm appear. These changes were not analyzed, but it is clear that they are related to changes in Cu^{2+} coordinations.

Thermal decomposition of porogen in PVC/CuVal premembrane was also studied thermogravimetrically. At a heating rate of 1°C/min the first stage of decomposition starts at 135°C and reaches a maxima at 158°C. The weight loss, 8.3% of the film, agrees with the first stage of decomposition ($2C_4H_8$ + $2CO_2$ per porogen molecule). The second stage starts right after the first, with probably some overlap.

Study of Films Attached to the Casting Bottles. Another set of experiments, with PVC/CuVal premembranes (w/w ratio of 100/25) studied thermal decomposition of the porogen in films still attached to the casting bottle (in order to reduce shrinkage at these high temperatures). A procedure

was sought for completion of the first decomposition stage and avoiding the second.

In preliminary experiments, the bottles with the films attached to them were heated in a tubular electric oven. On heating at 150°C the required decomposition was attained, but very slowly. At 180 and 200°C, the first stage is completed in 5 and 2 min, respectively, before the second stage starts. However, under our experimental conditions decomposition was not homogeneous.

Bottles bearing premembranes were immersed in silicone oil at 183°C. (The volume of oil—500 mL— was such that temperature drop due to immersion was about 2°C). After 4 min in hot oil, the bottles were taken out of the oil and after an additional 50 s they were immersed in petrol ether for cooling and for oil removal. The resulting films were homogeneous and their IR spectra and color indicated that the first stage of decomposition was completed. No indication of starting of the second stage was observed. Thus, by a fast and precise heating-cooling sequence, thermal porogen decomposition may be controlled.

The films obtained were tested by applying 54 mm Hg pressure of nitrogen in a device described in Ref. 1. Permeation rates were 0.5–2.2 mL/min. In a similar test practically no nitrogen permeation was measured through premembranes prior to porogen decomposition.

CONCLUSIONS

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. The results of the above described study show that these molecules can be homogeneously and practically molecularly dispersed in PVC and PSF to form premembranes. The upper limit of porogen concentration depends on characteristics of the polymer and porogen as well as on solvent used for casting and on drying procedure and temperature.

Metal salts of N-boc amino acids provide suitable porogens for thermal decomposition. Temperature of decomposition is, however, considerably higher than T_g of PVC and is about the T_g of PSF. Decomposition proceeds in two stages. In the first, $2C_4H_8$ + $2CO_2$ molecules are released per porogen molecule to form metal complexes of the corresponding amino acids. In a second stage decarboxylation takes place. Heating procedure for completion of first decom-

position stage and avoiding the second was established.

Data obtained in this study seems of interest to several fields beyond formation of porogen derived membranes:

— It shows how compatibility of additives with polymers is affected by polymer and additive properties and by parameters of matrix formation (e.g., solvent and drying procedure on solvent casting). Most of the tested additives (porogens) have plasticizing effect.
— A method is provided for molecular dispersion in polymer of incompatible metal complexes.
— Better understanding is gained as to thermal properties of polymeric matrix with changing amounts of plasticizer and as to thermal de- composition of molecules dispersed in this matrix.

REFERENCES

1. A. Baniel, A. Eyal, D. Edelstein, K. Hajdu, B. Hazan, Y. Ilan, and E. Zamir, *J. Memb. Sci.,* **54,** 271 (1990).
2. Charles J. Pouchert, *The Aldrich Library of Infrared Spectra, Edition II,* Aldrich Chemical Company.
3. W. Wrasidlo, *Adv. Polym. Sci.,* **13,** 47 (1974).