Pore generation in asymmetric polymeric membranes

Correlation with solvent mobilities

J. P. Cohen Addad, P. Panine

Laboratoire de Spectrometrie Physique, Universite Joseph Fourier, Grenoble I,
B.P. 87, F-38402 St. Martin d'Heres Cedex, France

Summary

Analyzing videomicroscopy observations, this work deals with macrovoids detected through the skin of asymmetric polymeric membranes. The circle-like images of the macrovoids were found to form two-dimensional random patterns ; these were characterized from the mean distance, $\langle\lambda\rangle$, determined between nearest neighboring images. Starting from polyetherimide or polyacrylonitrile solutions, each solution cast as a film was immersed in a water bath, at room temperature ; $\langle\lambda\rangle$ was shortened either by increasing the solvent concentration in the casting solution or by decreasing the solvent concentration in the bath (non-solvent of the polymer). This study was based on the assumption that the formation of the macrovoid pattern may be correlated to the interface instability resulting from the current of solvent diffusing towards the bath and initiated by the immersion of the polymer solution. Master curves, involving $\langle\lambda\rangle$, the solvent concentrations in the polymeric solutions or in the bath and the solvent diffusion coefficients, measured prior to the immersion of the solution in the bath, were drawn. Diffusion coefficients were measured using a pulsed magnetic field gradient method.

I. Introduction

Polymeric skinned membranes are usually prepared by quickly immersing a polymer solution into a bath which is a non-solvent of the polymer ; the miscibility of the solvent with the non-solvent is supposed to be much higher than its miscibility with the polymer[1] . The immersion of the solution cast as a film yields a membrane with macrovoids filled with the non-solvent. The fundamental causes for the supposed instability resulting in the generation of macrovoids have been in question until now [1,2] . Recently, Smolders et al. pointed out that the formation of asymmetric membranes, prepared from an immersion-precipitation process, is mainly governed by the solvent mobility in the casting solution and the solvent affinity to the gelation bath [3] . More recently, the formation of macrovoids has been simulated on a lattice by a Monte Carlo diffusion process, taking both the solvent and the bath into consideration ; the model provided a strong evidence for the crucial role played by the molecular mobilities in the process of membrane formation [4] . However, considering the simulation approach, no strong experimental correlation has been established between molecular mobilities and the membrane morphologies. In this study, it is considered that the mechanism which originates the formation of macrovoids, implies a three-step process. i) Right after the immersion of the polymer solution, the diffusion of the solvent toward the non-solvent takes place and the interface between the solution and the bath undergoes an instability induced by the current of solvent. The interface subsequently ruptures and the instability results in the formation of holes through the interface permitting the rapid intrusion of the non-solvent into the casting solution. ii) This invasion gives rise to the growth of macrovoids or fingers below the interface. iii) Prior to the immersion process, the glass

transition temperature of the polymeric solution is lower than 300 K ; it is progressively raised when the solvent concentration in the casting solution decreases. The glass transition occurs at room temperature when the solvent concentration reaches an appropriate value ; the membrane structure is then frozen as a whole and can be conveniently characterized.

Using videomicroscopy in this study, macrovoids generated below the skin, were observed through the skin after completion of the process of membrane formation ; they were found to determine a pattern of circle-like images characterised by a mean spacing, $<\lambda>$, between nearest neighbors. Furthermore, the first step of the formation of macrovoids, was supposed to be due to the interface instability created by the fast onset of the solvent current going towards the bath. More precisely, it was considered that a "diffusional shock" occured during a very short time interval, right after the immersion of the casting solution into the bath. Assuming that this "diffusional shock" was governed by the initial solvent mobilities measured in the polymer solution or in the bath, prior to the immersion in the bath, attention was focused on the possible correlation existing between these solvent mobilities and the mean spacing between macrovoid images. In this work, videomicroscopy observations were associated with diffusion coefficient measurements to give evidence for a close relationship existing between the characteristic length, $<\lambda>$ and the solvent diffusion coefficients ; these two experimental approaches have not been yet applied to the understanding of the mechanism of macrovoid generation, except for two briefly reported preliminary investigations [5,6]. The analysis of the two dimensional pattern formed by macrovoid images is reported in Section III. The diffusion coefficients were obtained, using a pulse magnetic field gradient method [7] ; their dependence on the solvent concentrations either in the polymer solution or in the water bath is illustrated in Section IV. For the sake of generality, two polymer species were studied in addition to the two polyetherimides considered in the preliminary study [6]. Several solvents and non-solvents were used to make membranes.

II. Experimental

The two polyetherimides were chosen because macrovoids can be conveniently detected, beneath the skin, from fluorescent reflection : Ultem 1000 (General Electric) and 6FDA-m-PDA in which protonated methyl groups are replaced with fluorinated methyl groups; the number-average molecular weight of Ultem is 10000 and the polydispersity index is 1.6. The good solvent was N-methyl-pyrrolidone (NMP). The polymers were dried at 150 °C, for 4 hours, before preparing solutions. NMP was dried over a 3 Å molecular sieve. The preparation of solutions was made at 60°C and their homogeneity was controlled visually. The two other polymers studied here were poorly fluorescent : polyacrylonitrile (PAN) and a statistical copolymer made of acrylonitrile and vinyl-acetate (8 %,w/w) (ANAV, Bayer). Macrovoids were detected beneath the membrane surface from reflection and transmission. The good solvent was dimethyl-formamide (DMF). Solutions were cast on a metallic plate (diameter : 3.5 cm and depth : 150 µm) at room temperature and quickly immersed in water (50 cm3). Membrane surfaces were observed, using a TC 654 EAX (Burle) video-camera, an IMT-2 Olympus microscope with a non-fluorescent objective 100Xoil (field depth : 1µm) and a video capture card Falcon . The image was analysed with a Digital Vision software; the resolution was 11.2 pixels per µm. The solvent diffusion coefficient was measured, using a CXP Bruker spectrometer operating at 60 MHz (proton) modified to carry out self-diffusion measurements (pulsed-field gradient technique [7]). The unit was calibrated with a sample of known diffusivity (water) giving field gradients, G , between 0 and 0.28 Tm-1. The data were all acquired with the same diffusion time parameters; the field gradient pulse separation, Δ, was set equal to 37 ms and the width of the field pulses, δ, was 6 ms. Diffusion coefficients of the solvent and of water were different enough to be easily discriminated from each other, applying a simple numerical analysis of data. The surface tension of the polymeric

solution in contact with air was measured using a Lauda Dr R. Wobser ring tensiometer, operating in the range 0 - 100 mN/m.

III. Two-dimensional pattern of macrovoids

Using video-microscopy, a typical two-dimensional pattern of images of macrovoids observed through the membrane skin, is illustrated in Fig. 1a. The picture was obtained from a solution of Ultem 1000 in NMP (NMP concentrations : 0.80 w/w in the polymer solution and 0.20 w/w in the water bath). The most striking feature concerns
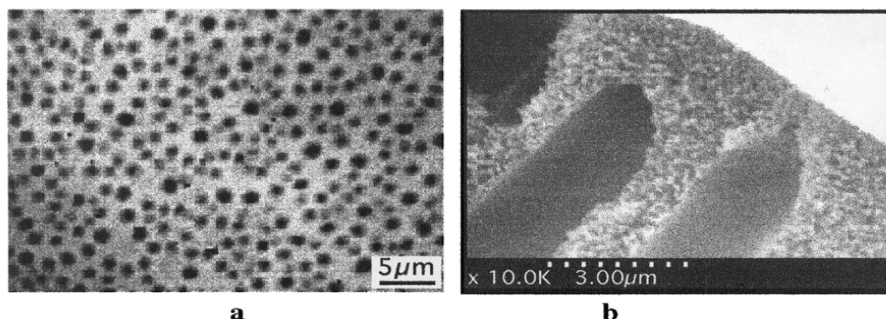

a   **b**

Fig. 1 - a) Top view of a polyetherimide membrane recorded from fluorescent reflection (field depth : 1μm). Ultem concentration in NMP : 20 % (w/w); solvent concentration in water : 20 % (w/w).
- b) Cross view of a polyetherimide membrane recorded from SEM. Ultem concentration : 16 % (w/w) and pure water.

the quasi-regular pattern formed by these images. Furthermore, the picture of membrane sections reveals oblong shapes of macrovoids ; the axis of quasi-axial symmetry of each cavity is perpendicular to the membrane skin (Fig. 1b). This type of pattern has been
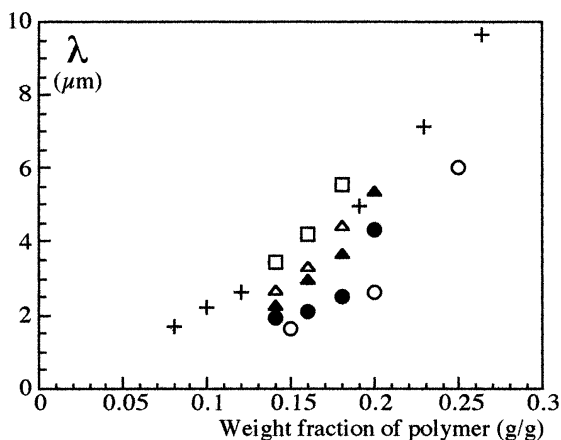

Fig. 2 Typical variations of the mean spacing length <λ> between neighboring circle-like images of macrovoids versus the polymer weight fraction. ANAV in DMF, DMF volume fractions in water : (●) 0, (▲) 0.2, (△) 0.4 and (□) 0.6. PAN/DMF, the bath is pure water : (+) and Ultem/NMP, the bath is pure water : (○).

already quantitatively characterized from the analysis of the ensemble of all quadrilaterals drawn from nearest neighbouring images.

The areas of quadrilaterals have been found to be proportional to their perimeters divided by 16 for comparison with lozenges ; the mean slope was equal to 0.85 (2 sin26°). The areas obeyed a log-normal probability distribution function 8 ; the area corresponding to the maximum amplitude of the distribution function was shown to shorten when the polymer concentration in the casting solution was decreased.

Considering one given image, the distances to the nearest neighbouring images were measured ; this procedure was then applied to all other images of the pattern to yield the mean value, $<\lambda>$, associated with a given pattern. The characteristic length, $<\lambda>$, was found to depend on both the initial solvent concentration, ϕ_s, in the casting solution and the initial concentration, ϕ_c, of solvent which may be added eventually to the bath, prior to the immersion (Fig. 2).

IV. Solvent diffusion coefficients

The self-diffusion coefficients of solvent and non-solvent molecules were measured quantitatively in order to correlate them with the mean spacing between macrovoid images.

IV. 1 Polymeric solutions

The concentration dependence of the diffusion coefficients of NMP in Ultem or in 6FDA-m-PDA solutions have been already reported elsewhere [6] ; the concentration dependence of the diffusion coefficients of DMF in PAN or in ANAV solutions is illustrated in Fig. 3. The solvent diffusion coefficient in the casting solution is called D_s , hereafter.
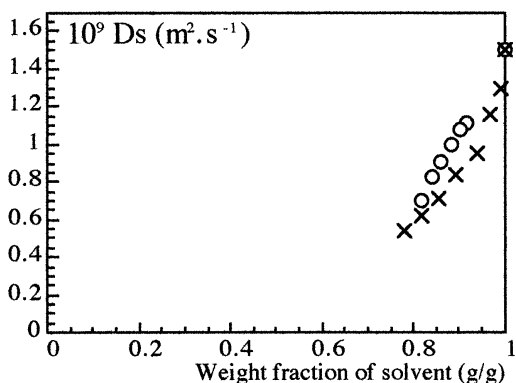
Fig.3 Self-diffusion coefficients of DMF in PAN (✕) and in ANAV (○) solutions.

IV.2 Nonsolvent solutions

In the case of DMF in the water bath, attention was focused on the possible effect of association of water with DMF molecules. Three series of measurements were performed in order to discriminate the self-diffusion processe of DMF molecules from that of water. The self-diffusion coefficient of protonated DMF, D_c^D, was first measured in deuterated water (Fig.4) ; the variations observed as a function of the volume fraction of solvent in water, exhibit a minimum which reflects an interaction between the two

molecular species. The self-diffusion coefficient of protonated water, D_c^w, was then measured in deuterated DMF. Finally, the self-diffusion coefficients of protonated water, (D_c^{WH}) and protonated DMF molecules, (D_c^H), were derived from the sharp numerical analysis of the total proton relaxation curve observed as a whole (Fig.4) ; D^D was found to be close to D_c^H while D_c^{WH} was found to be slightly higher than D_c^w. The effect of deuteriation on the water molecule diffusion is slightly stronger than on the DMF diffusion. The concentration dependence of the self-diffusion coefficient of NMP in water has been reported elsewhere [6].
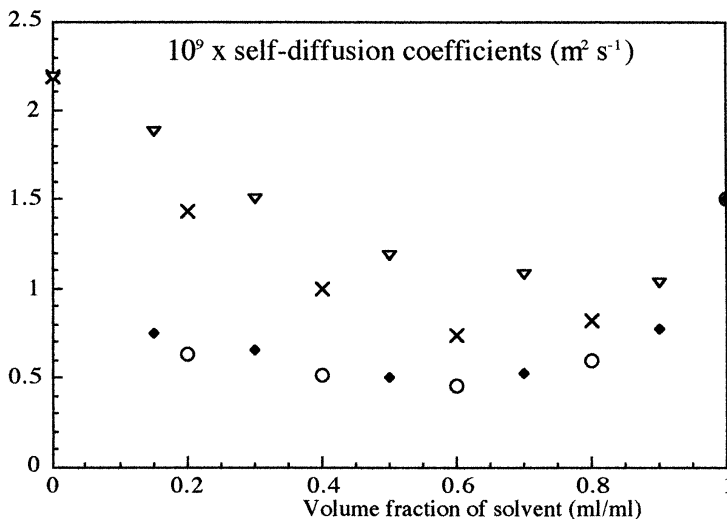

Fig.4 Self-diffusion coefficients measured as a function of the volume fraction of DMF, ϕ_c, in water. Self-diffusion coefficient of protonated DMF in deuterated water : ○ ; self-diffusion coefficient of protonated water in deuterated DMF : ✕. Self-diffusion coefficients of protonated water (∇) and protonated DMF (◆), derived from the total proton relaxation curve.

V. Analysis of patterns of macrovoid images

The following analysis is proposed to serve as a guide for correlating the mean spacing between macrovoid images with the diffusion coefficients of the solvent. Several features are taken into consideration. i) The mean image spacing, <λ>, ranges from about 1 to 10 μm ; it is predetermined by the concentrations of solvent in the polymeric solution, on the one hand and in the bath, on the other hand. It is thus governed by the initial conditions chosen to make a membrane. ii) Due to the immiscibility of the bath and the polymer, the interface between the polymeric solution and the nonsolvent is well defined at any time provided polymer chains can overlap. No membrane can be formed when the polymeric concentration is lower than the concentration of overlap of the chains. iii) The observed pattern of images (Fig.1) is similar, except for the space scale, to the pattern of drops formed from the Rayleigh-Taylor hydrodynamic instability of a viscous liquid film deposited on a plane surface and whose the interface with air is submitted to the weight of the fluid. For this gravitational instability, the mean spacing, μ, between

drops is expressed as $\mu = (4\pi^2\gamma/\Delta\rho \; g)^{1/2}$; with usual values of the surface tension γ (5×10^{-2} N/m) and of the density difference $\Delta\rho$ between the two studied fluids (10^3 kg/m3), μ is about 10^{-2}m (g is the gravity)[9]. For macrovoids, $\langle\lambda\rangle$ is about 10^{-5} m and the macrovoid formation is independent of gravity.

Here, a formal analogy with the gravitational instability is proposed ; the pressure gradient, as represented by the product $g\Delta\rho$, is replaced with the derivative of the current of solvent Js toward the nonsolvent. The expression of the current of solvent, J_s (x,t), toward the bath, is obtained from the simplified description of the molecular diffusion from a semi-infinite medium (x > o) representing the polymeric solution toward a semi-infinite medium (x < o) representing the nonsolvent ; this purely entropic description is well known when it is established from a continuity condition which applies to the current, for x = o at any time. The current is expressed as

$$J_S(x,t) \;=\; -(\phi_S - \phi_C) \; \sqrt{D_S}/(1+\sqrt{D_S/D_c^H}) \; \exp(-\frac{x^2}{4D_S t})/\sqrt{4\pi t} \tag{1}$$

for x > o; ϕS and $D S$ are the concentration and the diffusion coefficient of the solvent in the casting solution, respectively while D_c^H is the diffusion coefficient of the solvent (NMP or DMF) measured as a function of its initial concentration, ϕ_c, in the bath. The numerical value of D^H, corresponding to $\phi_c = 0$, was extrapolated from the plot of D_c^H versus ϕ_c. The time derivative of the solvent current, at x= 0, is written as

$$\frac{dJ_S}{dt} \;=\; [(\phi_S - \phi_C))/(1+\sqrt{D_S/D_c^H})] \, D_S^2 \, [\frac{1}{2D_S t}]^{3/2}/\sqrt{2\pi} \tag{2}$$

The step functions used to describe the initial distributions of the concentration of solvent leads to an unspecified value of the derivative of J_s when $t\longrightarrow 0$. The order of magnitude of D_s is actually 10^{-10} m^2/s with a jump equal to about 3 Å; this corresponds to a mean time interval between two molecular jumps equal to about 10^{-9} s.; it is considered that Gaussian character of the diffusion process (Smoluchovski limit) takes place after about 20 jumps [10]. Consequently, the relevant time origin to is about equal to 2 10^{-8} s and the solvent current derivative is expressed as

$$\frac{dJ_S}{dt}(t \longrightarrow t_0) \approx [(\phi_S - \phi_C)/(1+\sqrt{D_S/D_c^H})] \; \frac{D_S^2}{\langle b^2\rangle^{3/2}} \tag{3}$$

where $\langle b^2\rangle \approx 2 \; D_s t_0 \approx 400$ Å^2. Correspondingly, the threshold of instability which determines the mean spacing between macrovoid images is given by the equation

$$\langle \lambda \rangle (\gamma)^{-1/2} \; [(\phi_S - \phi_C)/(1+\sqrt{D_S/D_c^H})]^{1/2} \, \langle b^2\rangle^{-3/4} D_s \approx \kappa \tag{4}$$

κ is a simple numerical constant of order unity [9]. It is worth noting that the order of magnitude of the mean spacing $\langle\lambda\rangle$ calculated from Eq.4 is 2µm, with $\gamma = 5 \; 10$-2 N/m, $\phi_s - \phi_c \approx 0.5 \; 10^3$ kg/m^3, $\langle b^2\rangle \approx 4 \; 10^{-18}$ m^2 and $D_s \approx 2 \; 10^{-10}$ m^2/s ; this order of magnitude is in agreement with experimental values. For convenience, variations of $\lambda^* = \langle \lambda \rangle [(\phi_s - \phi_c)/(1+\sqrt{D_S/D^H_c})^{1/2}$ are plotted as a function of D_s^{-1} in Fig. 5 ; solvent concentrations ϕ_s and ϕ_c are reported in the Figure caption. All experimental points were found to lie on straight lines and each straight line was associated with a given polymer

species ; linear correlation coefficients were better than 0.99. $\langle\lambda\rangle$ is a decreasing function of the increased concentration of solvent in the polymeric solution.

The property of superposition of straight lines drawn as a function of the inverse of the solvent diffusion coefficient in the polymeric solution is crucial (Fig.5). It is considered that it gives a strong evidence for the diffusional origin of the macrovoid generation process ; the superposition is mainly due to the factor $(\phi_s - \phi_c)^{1/2}$; however, the smooth variation of the factor $(1+(D_s/D_c^H)^{1/2})$ brings a small contribution, too. The intersection of each straight line with the D_s^{-1} axis is close to $1/D_s^*$; D_s^* corresponds to the concentration of chain overlap. The limiting value $1/D_s \longrightarrow 0$ has no physical meaning ; consequently, the threshold of instability is written in order to satisfy the condition $\lambda = 0$
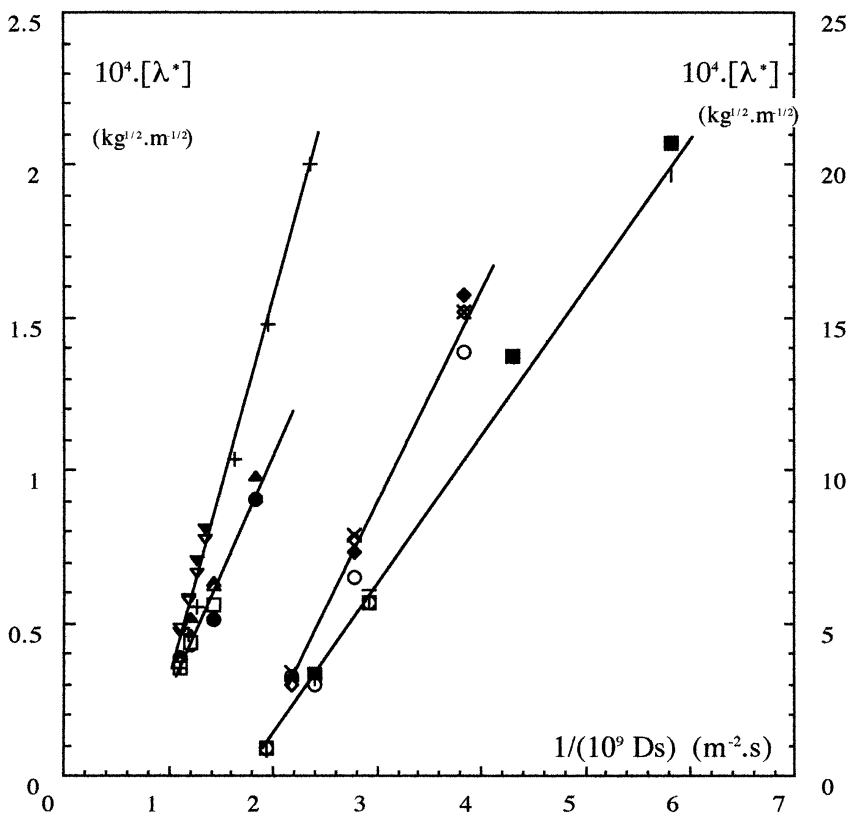

Fig. 5 Variations of the λ^* parameter versus the inverse of the solvent diffusion coefficient in polymeric solutions for several solvent volume fractions in the water bath. Ultem/NMP : (○) 0 , (◆) 0.2 , (◇) 0.4 and (✕) 0.6 ; 6FDA-m-PDA /NMP : (■) 0, (○) 0.25 , (|) 0.35 and (−) 0.50. PAN/DMF : (+) 0, (▼) 0.2 and (▽) 0.4 ; ANAV/DMF : (●) 0, (▲) 0.2, (△) 0.4 and (◻) 0.6.

when $\phi = \phi_s^*$; ϕ_s^* the limiting value corresponding to the formation of membranes:

$$(\lambda+\lambda^*)[((\phi_s-\phi_c)/(1+\sqrt{D_s/D_c^H})\gamma]^{1/2} = \frac{\kappa}{D_s} \text{ and } \lambda^*[(\phi_s^*-\phi_c)(1+\sqrt{D_s^*/D_c^H})\gamma]^{1/2} = \frac{\kappa}{D_s^*} \quad (5)$$

The surface tension of the polymeric solution, in contact with air, was measured in the concentration range used to make films ; it was found to be negligible (3.8 to 4 10^{-2} N/m). Finally, the glass transition of the studied polymer solutions occured around 300K, for $\phi_s \approx 0.7$ g/g ; consequently, the diffusional instability was rapidly stopped by the glass transition induced by the decrease of solvent concentration following the immersion into the bath.

VI. Conclusion

It has been long known that the formation of macrovoids in membranes, prepared from a ternary polymeric solution, can be avoided by choosing a solvent-nonsolvent pair with a low tendency of mixing with each other or by increasing the polymer concentration in the casting solution or by adding solvent to the coagulation bath [11,12]. In addition to miscibility properties, the molecular dynamics of the solvent and of the bath are also involved in the process of membrane formation. The entropic description of dynamic properties proposed in this work accounts for the analysis of observed data; however, it may be worth noting that the description of other systems may require the use of chemical potentials of the solvent in the polymeric solutions or in the bath [13]. The interface of the polymeric solution with the bath consists of two miscible liquids and a polymer highly insoluble in water ; this calls for the following comment. There is no interface between two miscible liquids ; however, during the immersion process of the solution, the polymer does not diffuse in water which is a non-solvent; this ensures the existence of an interface. It must be noted that a gravitational instability has been quantitatively predicted by Brochard-Wyart and De Gennes [14,15] when the two liquids have different viscosities. The system studied here can be differentiated from two miscible liquids because of the presence of the polymer. There exists a polymer-solvent surface with a cohesion which is well defined as long as chains can overlap. In dilute solutions, the presence of polymer at the solution surface is not continuous and no membrane can be made.

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