

NOTES

The Morphology of Asymmetric Separation Membranes

This communication extends the micellar monolayer concept of reverse osmosis membrane surface layer morphology to a class of polyimide membranes. A dry, nongel polyimide membrane prepared by a method different from that used for previously discussed membranes has the same micellar structure and has permeation properties consistent with the proposed morphology.

INTRODUCTION

We have recently described a morphology of asymmetric reverse osmosis membranes¹ which considers the functional layer to be formed by a partly fused monolayer of deformed spheres supported by a randomly packed, less well-fused substrate of the same entities.² Gaps of 75–100 Å between spheres in the substrate offer a facile route for permeate, while the spheres in the functional monolayer are deformed and closely packed. The "micellar" morphology was found in polyamide-hydrazide,³ cellulose acetate,⁴ and polyamide membranes.

The previous discussion of asymmetry dealt only with wet membranes of the type used for aqueous separations.^{3,4} This paper describes a dry asymmetric polyimide membrane prepared by a procedure markedly different from the mixed solvent casting developed for polyamide-hydrazides and for cellulose acetate. The polyimide membranes were prepared by casting a 15-mil-thick layer of a 10% solution of the polyamic acid from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether. The cast films were immersed in a cyclizing solution composed of a tertiary amine and an acid anhydride in an inert hydrocarbon solvent. The cyclized film when dried has a glossy dense surface on a less dense substrate. This process is similar to mixed solvent casting in that the surface is developed by control over the process by which the polymer is forced out of solution, rather than by direct deposition of an ultrathin layer.

EXPERIMENTAL

Polyimide membranes were prepared from a 10% solution in dimethylacetamide of the polyamic acid from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether. The solution was cast to a thickness of 15 mils on a glass plate and immersed in a cyclizing bath. The bath, 1*M* triethylamine and 1*M* acetic anhydride in benzene, was held at room temperature for 15 min, then heated on a steam bath for 15 min. The film was washed with benzene and water, and air dried. The polyamic acid was essentially fully cyclized as shown by its infrared spectrum, determined by transmission from ground film in KBr and by attenuated total reflection on both sides of the membrane. The membrane was 1.7–1.8 mils thick. It consisted of a dense yellow layer on the air side of approximately 0.4 mil, supported on a spongy substrate.

Gas adsorption was measured with a Cahn vacuum microbalance. No H₂ or CH₄ adsorption to polyimides was found at room temperature under conditions which would be expected to detect one hydrogen per 10 polymer repeat groups.

Cross section electron micrographs were obtained on a Zeiss EM9S microscope by replication techniques discussed previously.¹ The figures are in the same sense as the original negatives and are best viewed as a rough "landscape" seen in glancing light.

Ion-etched surfaces were prepared by exposing the membrane to a corona discharge. Structure is occasionally visible without etching.⁴

Gas permeation data were obtained in a constant volume/variable pressure apparatus designed in our laboratory. Details of the equipment are described elsewhere.⁵ The data were obtained with separate gases at 115 psia and 30°C.

DISCUSSION

This discussion applies to what is generally referred to as the surface layer and the intermediate layer of an asymmetric membrane. In the present case, these two layers appear in the optical microscope as a clear homogeneous single layer supported by a much more porous, translucent substrate. The gross morphology of the substrate is controlled by the details of the casting procedure and, in the case of the polyimide, can vary widely from a fibrous mat to a sponge.

A cross section of the surface of the dense layer (Fig. 1) has an appearance nearly identical to that described earlier for wet membranes. The surface is composed of a "monolayer" of closely packed micelles supported by a more random substrate of disordered micelles. Gaps that appear in the surface monolayer, such as the one in the upper left-hand corner of Figure 1, are too few to represent the functional pores. The gaps are most likely defects which permit flow of the otherwise rejected species. In contrast, the micelles in the substrate are less well fused and 75–100 Å gaps, which offer relatively little impedence to the permeate, are seen.

It should be noted that the surface shown in Figure 1 was obtained by fracturing at -180°C a stack of membranes "potted" in nothing more reactive than distilled water. There thus appears to be little likelihood that the micellar structure can be an artifact of the sample preparation. This conclusion is confirmed by the appearance of the surface of the same membrane. Figure 2 depicts a surface which has been briefly ion etched to develop its topography by burning off the "glaze" which frequently makes a surface appear structureless. The "mounds" seen in this photograph have a center-to-center spacing of about 800 Å, the same dimension as the diameter of the micelles in Figure 1. This photograph was taken of a dry membrane which was treated and replicated in the absence of liquid or other potting materials. While similar surface photographs have been interpreted differently by others,^{5,7} the micellar monolayer structure is required by the cross section photographs.

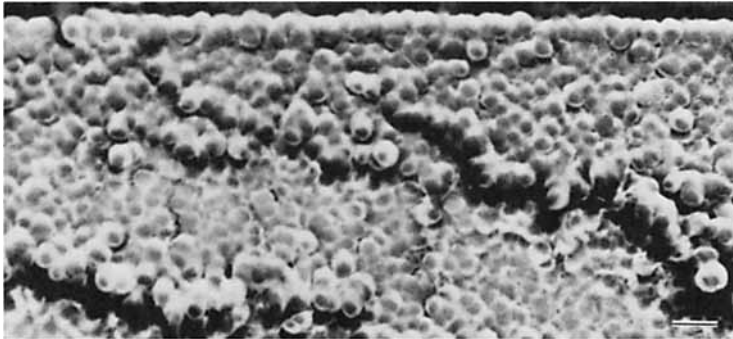


Fig. 1. Cross section of upper surface of asymmetric polyimide membrane. The bar represents 1000 Å.



Fig. 2. Upper surface of ion-etched polyimide membrane. The bar represents 1000 Å.

TABLE I
Effect of Gas Feed Direction on Flux^a

Flux direction	Flux ^c		Selectivity ^d
	H ₂	CH ₄	
Forward ^b	3100	27	110
Reverse	8200	3200	2.6
Forward	2700	25	110

^a Polyimide from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether.

^b The "forward" direction is that in which the gas pressure is applied to the dense surface of the membrane.

^c Flux in GTR units at 115 psia.

^d H₂ flux/CH₄ flux.

TABLE II
Effect of Flux Direction on Water Permeability^a

Pressure, psi	Flux, gal/sq ft/day	Flow direction
200	1.3	F ^b
200	1.3	R ^c
1000	6.0	F
1000	13	R
1500	13	F
1500	120	R ^d
1500	12	F

^a Fully aromatic polyamide prepared by a procedure reported previously.

^b Forward flow: pressure applied to surface layer.

^c Reverse flow: pressure applied to porous substrate.

^d Dye in water permeated in this case.

The gas permeation properties of these asymmetric polyimide membranes are related to the micellar structure. When the permeation of hydrogen and methane, two gases of considerably different molecular diameters, was tested on a typical asymmetric membrane by applying the feed gas to the dense layer side of the film at 115 psia, the relative rates shown in Table I were obtained giving a H₂/CH₄ selectivity of 112. When the gas was applied to the back side of the membrane, both hydrogen and methane permeation rates increased—hydrogen less than 3-fold and methane nearly 120-fold. The resultant selectivity was 2.8, the figure expected for capillary flow. The most reasonable interpretation of the data is that while the micellar units of the surface layer are well supported and therefore can withstand pressure from the top side, pressure from the back forces the micelles apart, stretching the poorly knit molecules between the micelles and opening pores. When pressure was returned to the front side of the same membrane, the permeation figures returned to those found originally.

The contrast between the forward and reverse data illustrates the difference between flow through the free volume (dynamic pores) and that through capillary pores. In this particular case neither hydrogen nor methane is selectively adsorbed by the membrane, which appears to function by "filtration." Uncertainty about the association of methane under conditions of permeation prevents us from ascribing an average size smaller than 4 Å (the approximate diameter of methane) to the free volume (i.e., dynamic pores). However, the dimension involved is one which permits hydrogen to pass but not methane. One can, of course, consider the membrane formation as the partial coalescing of micelles to form an "intersphere" void of 10 Å or less and then consider permeation to take place through this fixed pore. Such a concept seems difficult to define since it implies a channel between spheres each of which consists of amorphous coils of flexible chains having cross sections comparable to that of the supposed fixed pore.

While the preceding discussion has dealt with gas permeation through a dry membrane, the morphology presented requires similar behavior for water permeation through a wet mem-

brane. However, permeation rates of saline water in the reverse direction are made complex by concentration polarization.⁸ The effect of flow reversal on water flux is summarized for a low-flux polyamide membrane in Table II. The test solution was a dilute solution of dye in distilled water.

At relatively low pressure, the flux was identical in both directions. However, at 1000 psi, the reverse flux was twice the forward flux; and at 1500 psi, the reverse flux was ten times the forward flux and was completely reversible when the measurement was repeated in the forward direction. The dye was rejected in every case except in the reverse direction at 1500 psi. The high flux and the dye passage are both consistent with the concept of a micellar monolayer which is supported to pressure only in the forward direction.

One can also suggest that the micelles have deformed only slightly in fusing so as to leave voids. If, however, the voids are of 75 Å cross section, they would be visible in the electron micrographs. If they are of the order of 10 Å, the arguments discussed above apply equally to the wet membranes.

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C. W. ALEGRANTI*
D. G. PYE
H. H. HOEHN
MANUEL PANAR

Central Research Department
Experimental Station
E. I. du Pont de Nemours & Co.
Wilmington, Delaware 19898

* Current address: Universidade De Sao Paulo, Instituto De Quimica, Cidade Universitaria, Sao Paulo, Brasil.

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