

The Structure of the Effective Separating Layer of Asymmetric Hollow Fiber Membranes with Graded Density Skins

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Synopsis

The structure of the effective separating layer of an asymmetric polysulfone hollow fiber membrane with a graded density skin was studied by SEM, TEM, and osmium tetroxide vapor adsorption and compared to that of a bilayer asymmetric hollow fiber membrane prepared from a solvent/nonsolvent mixture. The studies revealed the presence of micropores which transverse the effective separating layer of the membrane with graded density skin. The structural units which constituted the effective separating layer of this membrane are less tightly packed and distorted than are the entities forming the effective separating layer of its congener prepared from the traditional solvent/nonsolvent mixture. These results indicate that the enhanced free volume in an asymmetric hollow fiber membrane with a graded density skin exists in the effective separating layer as well as in the membrane interior.

INTRODUCTION

In 1960, Loeb and Sourirajan invented the first integrally skinned membrane for desalination by phase inversion of cellulose acetate sols.¹ In the integrally skinned membrane, the skin and substructure are composed of the same material. The skin layer determines both the permeability and selectivity of the hollow fiber membrane, whereas the porous substructure functions as a physical support for the skin. Differences in density between the two layers are the result of interfacial forces and the fact that solvent loss occurs more rapidly from both the air-solution and coagulant-solution interfaces than from the solution interior.² Early electron microscopic investigators indicated that the very thin skin on top of the porous matrix was homogeneous.^{3,4} However, Schultz and Asunmaa discovered the presence of spherical nodules or "spheres" in the skins of cellulose acetate membranes which had been argon plasma etched,⁵ and Kesting subsequently found similar structures in the skins of dry-process membranes of cellulose acetate.^{6,7} These nodules, approximately 20 nm in diameter, have recently been shown to agglomerate into spherical nodule aggregates⁸ or micelles⁹ 40–80 nm in diameter. This morphology was earlier demonstrated to be general in integrally skinned membranes with the surface structure formed from closely packed micelles which are compressed and distorted.¹⁰ The skin is thus a denser form of the

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micellar structure which comprises the bulk of the membrane. Because the structure of the skin layer determines both the permeability and selectivity of an asymmetric membrane, the skin structure, and its correlation with membrane permeability have been the focus of extensive investigation.^{2,11} Oxygen plasma ablation studies on bilayer asymmetric membranes formed by classical phase inversion processes have shown that the effective separating layer is a small fraction of the thickness of the microscopically observable skin and that micropores and channels with dimensions below the limits of resolution of the scanning electron microscope exist in the skin below the effective separating layer.¹²⁻¹⁴

A new class of asymmetric hollow fiber membranes possessing graded density skins were discovered.¹⁵ These hollow fiber membranes are fabricated by spinning from Lewis acid : base complex solvents.¹⁵⁻¹⁸ The formation of a complex from the nonsolvent (Lewis acid) and the solvent (Lewis base) permits higher concentrations of nonsolvent to be included in the spinning dope than can be added with traditional solvent/nonsolvent mixtures. The rapid dissociation of the Lewis acid : base complex into smaller moieties accelerates the kinetics of the phase inversion process and facilitates the removal of the dissociated moieties from the nascent hollow fiber membranes. This rapid coagulation process is analogous to the rapid quenching of a polymer melt through its glass transition temperature to form a polymeric glass.

The accelerated kinetics of the sol-to-gel transition enhances the free volume of the resultant phase inversion membrane, which is reflected by an increase in the glass transition temperature readily seen during the first heat in differential scanning calorimetry.¹⁵ This elevated glass transition temperature is not equivalent to the increase in T_g as a result of superheating, which yields the " T_g overshoot" commonly observed in glassy polymers annealed below their glass transition temperatures.¹⁹⁻²¹ Sub- T_g annealing of polysulfone hollow fiber membranes prepared from Lewis acid : base solvent systems reveal a decline in the glass transition temperature and then a subsequent increase in T_g with increasing annealing times. Examination of the DSC scans of the annealed hollow fiber membranes shows the appearance of a sub- T_g endothermic peak which does not become superimposed on the T_g step to yield a " T_g overshoot" until the samples had been annealed for 166 h at 110°C.²¹ Therefore, the increase in free volume indicated by the DSC measurements reflects an increase in the spacing between the polymer chains forming the spherical nodules, which in turn constitute the nodule aggregates. Consequently, it is the assembly of the spherical nodules into nodule aggregates and the packing of these nodules aggregates which determine the structure of the effective separating layer of an asymmetric phase inversion membrane. It is the structure of the effective separating layer as well as the enhanced free volume in the nodules that comprise it that produces the multiple increases in gas transport rates with maintenance of selectivity which is observed in hollow fiber membranes prepared from Lewis acid : base solvent complexes over membranes prepared from the same polymer utilizing traditional solvent/nonsolvent mixtures.

Oxygen plasma ablation and scanning electron microscopy studies on these asymmetric membranes with graded density skins reveal profound structural

differences between them and asymmetric bilayer hollow fibers which are prepared from classical solvent/nonsolvent mixtures, such as formylpiperidine/formamide.¹⁷ Oxygen plasma etching has shown that the hollow fiber membranes spun from propionic acid : *N*-methylpyrrolidone complexes have thinner effective separating layers and thinner transition zones with a larger gradient of increase in pore size and porosity than do hollow fiber membranes spun from formylpiperidine/formamide, solvent/nonsolvent mixtures. Furthermore, the SEM photomicrographs reveal that the skin structure of the asymmetric hollow fiber membrane prepared from the Lewis acid : base complex is composed of aggregations of readily discernible spherical nodules, which become more densely packed as the outer surface layer is approached. Pores and channels are observed which diminish in size until their dimensions are below the limit of resolution of the SEM (4 nm). In contrast, the skins of the asymmetric hollow fiber membranes prepared from the classical solvent/nonsolvent mixtures indicate a much more monotonous structure, which results from the compression and distortion of the micellar structural units so that few voids appear.

It is the purpose of this paper to report additional insights gained on the structures of the effective separating layers of asymmetric hollow fiber membranes prepared from Lewis acid : base complexes and from classical solvent/nonsolvent mixtures by scanning electron microscopy and transmission electron microscopy. Surface replicas and cross sections of these hollow fiber membranes shadowed with gold/palladium are studied as well as cross sections of hollow fiber membranes treated with osmium tetroxide vapor.

EXPERIMENTAL

Polysulfone hollow fiber membranes prepared from propionic acid : *N*-methylpyrrolidone Lewis acid : Lewis base complex dopes and formylpiperidine/formamide solvent/nonsolvent dopes were prepared as discussed in the patent applications.¹⁵ In this discussion, a slash between the solvent and nonsolvent indicates that the pair is noncomplexed. A colon indicates complex formation. These samples were examined by means of a JEOL JSM-840 scanning electron microscope equipped with a Tracor 5500 energy dispersive spectrometer by C. J. Pellegrin. TEM observation of specimens were made by means of a JEOL 2000FX analytical electron microscope operating at 200 kV. Both surface replicas of the two fiber types were prepared in a Balzers evaporator. After dissolution of the underlying hollow fiber membrane with concentrated sulfuric acid, surface replicas were picked up on Formvacarbon electron microscope grids for viewing.

Another set of hollow fiber membranes were exposed to vapors from a 4% osmium tetroxide solution for 1 h. Osmium tetroxide is absorbed into both semicrystalline and amorphous polymers and is often used to enhance the contrast for transmission electron microscopy.²² Therefore, it was believed that such a short exposure time might reveal structural differences between a membrane with a dense effective separating layer and one in which the effective separating layer is constituted of less tightly packed polymer aggregations. Subsequently, a gold/palladium layer was evaporated onto the hollow fibers' outer surfaces. The hollow fiber membranes were embedded in

Buehler epoxy, cut into 70 nm cross sections with a diamond knife, and viewed with no further staining in the TEM.

RESULTS AND DISCUSSION

Scanning electron micrographs of the outer edges of the polysulfone hollow fiber membranes prepared from the formylpiperidine/formamide solvent/nonsolvent mixture and the propionic acid : *N*-methylpyrrolidone Lewis acid : base complex solvent system are shown in Figures 1–4. The structural differences between these two types of fiber membranes are very apparent upon comparison of the figures.

The photomicrographs of the outer edge of a cross section of the hollow fiber membrane spun from the formylpiperidine/formamide mixture (Figs. 1 and 2) reveal a distinct boundary layer between the skin and supporting matrix. The skin appears to be relatively monotonous consisting of dense, tightly packed nodule aggregates. Close packing so distorts the micelles that their boundaries cannot be readily discerned.

Examination of Figures 3 and 4 reveals that nodular packing in the outer surface cross section of the hollow fiber membrane prepared from the propionic acid : *N*-methylpyrrolidone is less dense. Spherical nodule aggregates, indicative of less structural distortion and compression, can be identified in the outer surface layer. In addition, a more gradual transition from the outer surface to the supporting matrix is observed. Among these aggregations, voids

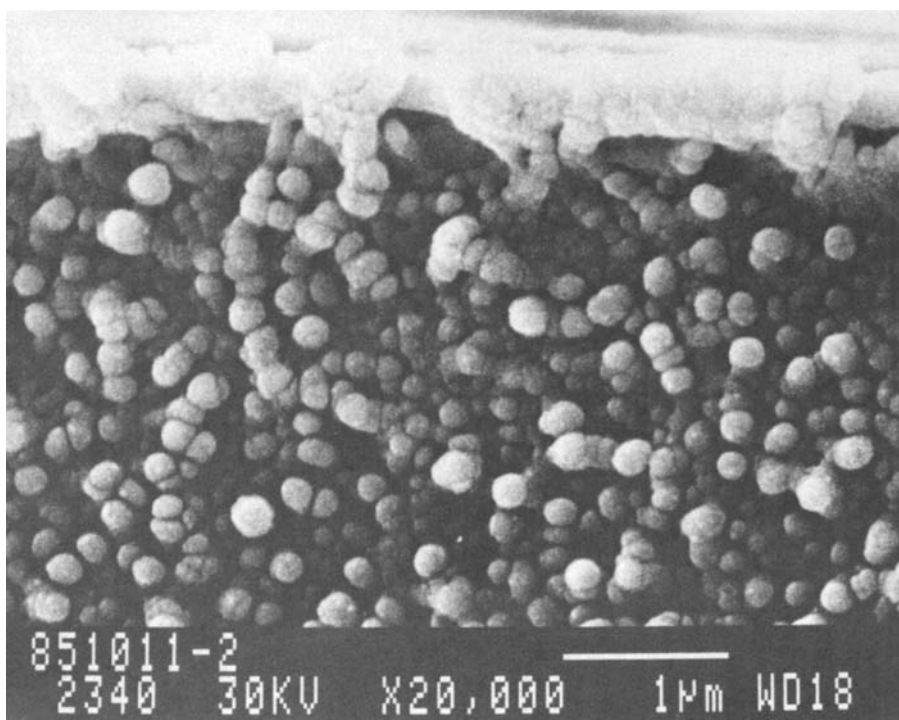


Fig. 1. Scanning electron micrograph of the outer edge of an asymmetric polysulfone hollow fiber membrane spun from formylpiperidine formamide at 20K magnification.

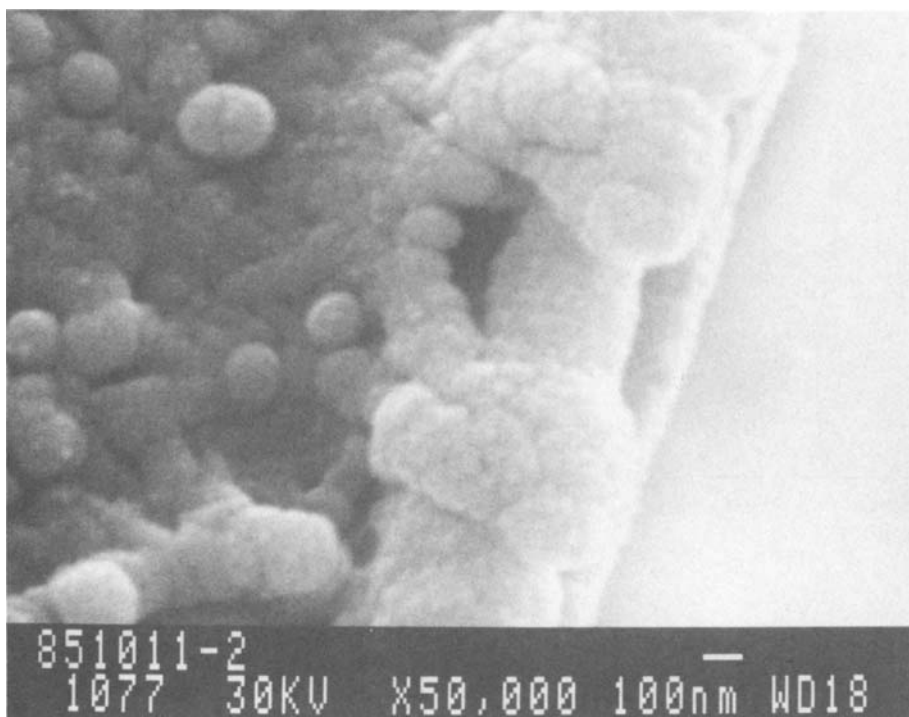


Fig. 2. Scanning electron micrograph of the outer edge of an asymmetric polysulfone hollow fiber membrane spun from formylpiperidine/formamide at 50K magnification.

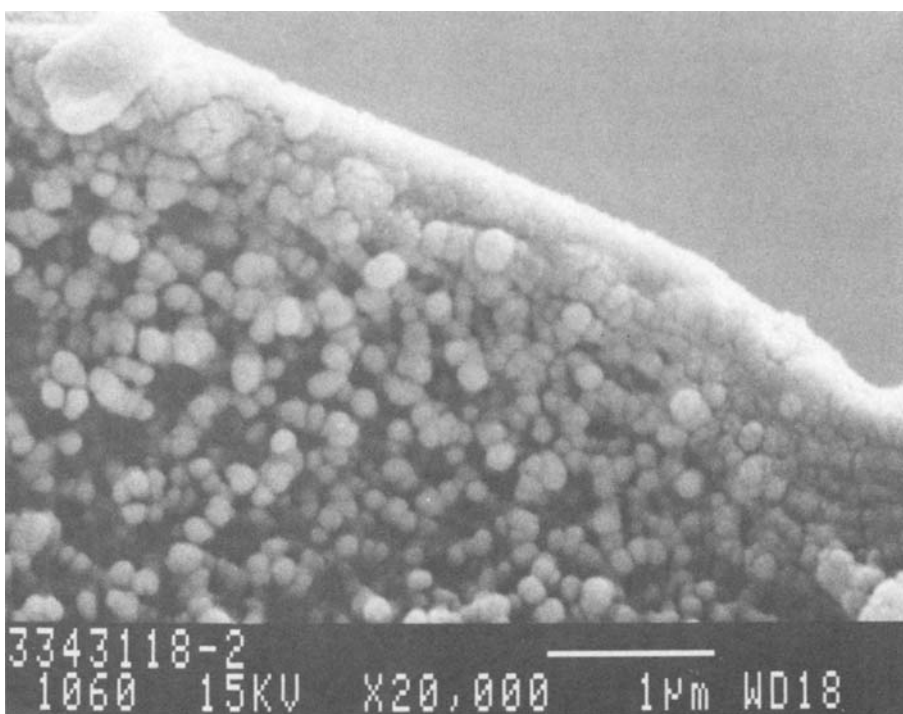


Fig. 3. Scanning electron micrograph of the outer edge of an asymmetric polysulfone hollow fiber membrane spun from propionic acid : *N*-methylpyrrolidone at 20K magnification.

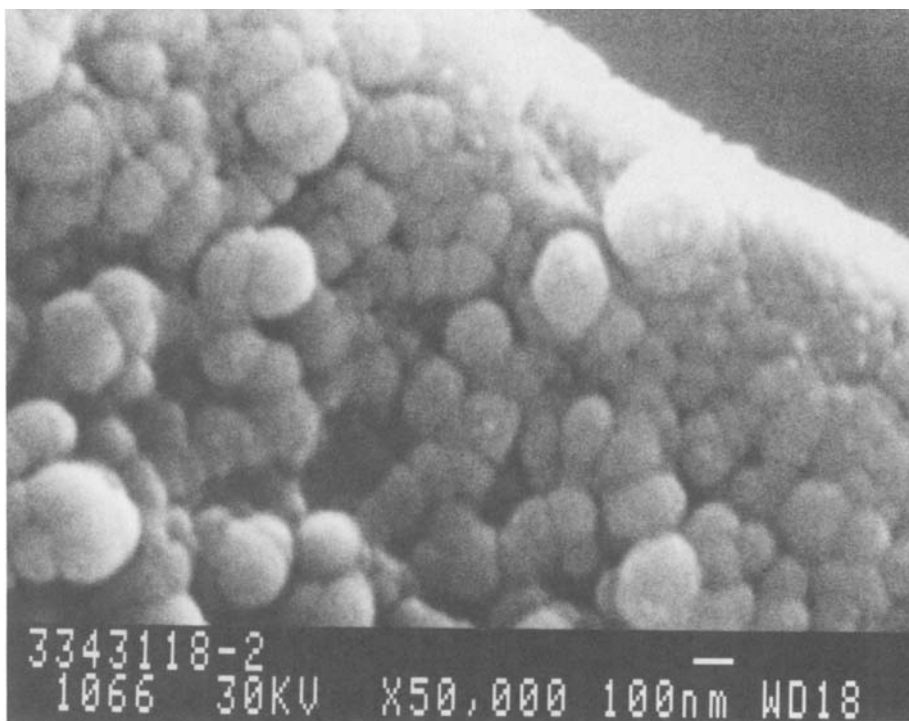


Fig. 4. Scanning electron micrograph of the outer edge of an asymmetric polysulfone hollow fiber membrane spun from propionic acid : *N*-methylpyrrolidone at 50K magnification.

can be seen which form channels which diminish in size until their dimensions are below the limit of resolution of the scanning electron microscope. Oxygen plasma ablation results indicate that these channels penetrate through to the surface of these hollow fiber membranes prepared from Lewis acid : base complex solvent systems but terminate below the effective separating layer of the hollow fiber membranes prepared from classical solvent/nonsolvent mixtures.¹⁷

Comparison of the scanning electron micrographs of the outer surfaces of these two types of hollow fiber membranes shows that they manifest different morphologies. The electron micrographs of the outer surface of the polysulfone hollow fiber membrane spun from the formylpiperidine/formamide solvent/nonsolvent mixture, shown in Figures 5 and 6, reveal a dense, tightly packed, grainy structure. These granules are at least an order-of-magnitude smaller than the nodule aggregates which reside below the skin, as seen in Figures 1–4. Examination of the interior spherical nodule aggregates in these figures indicates that they are also composed of smaller aggregations of polymer. Apparently, these smaller aggregates, which constitute the subsurface nodules, contribute to the grainy surface topography. The larger spherical nodule aggregates, which are formed by these smaller structures, are so compressed and distorted that any evidence of their existence or boundaries in the outer surface layer is obliterated. Inspection of surface photomicrographs of the hollow fiber membrane prepared from propionic acid : *N*-methylpyr-

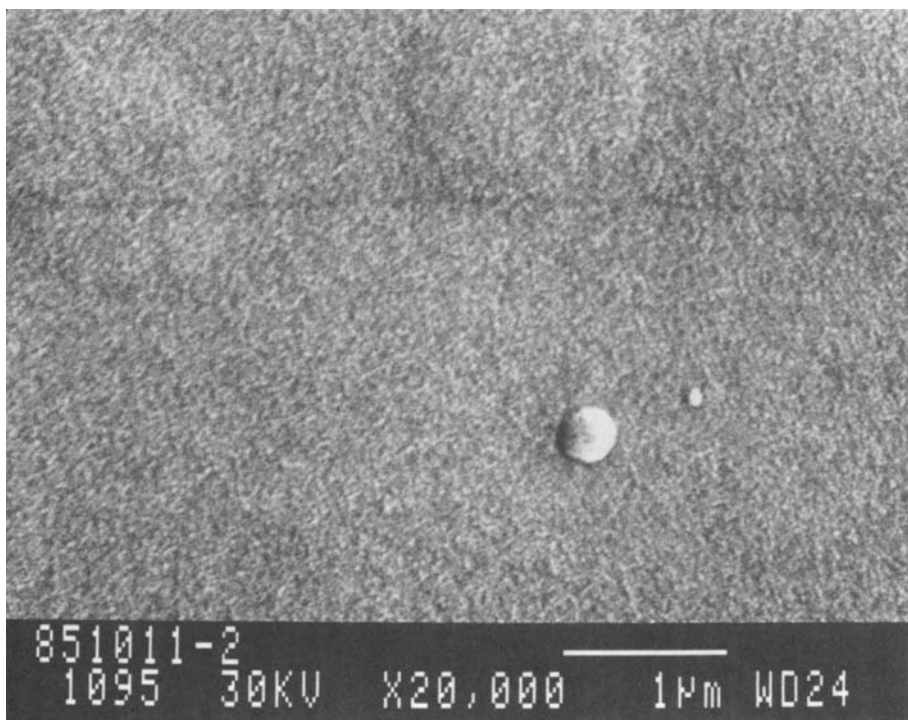


Fig. 5. Scanning electron micrograph of the outer surface of an asymmetric polysulfone hollow fiber membrane spun from formylpiperidine/formamide at 20K magnification.

rolidone, a Lewis acid : base solvent system (Figs. 7 and 8), also reveals the presence of these nodules, but they are not so tightly packed as are those seen the photomicrographs of the surfaces of the hollow fiber membranes prepared from the classical solvent/nonsolvent mixture. Many spherical nodule aggregates are observed in the surface of the hollow fiber membrane spun from the Lewis acid : base solvent system. In fact, these structures appear to be embedded into the surface at varying degrees. Some appear to almost entirely surrounded by surface material while others seem to be on the topmost layer of the surface. Where several of these nodular structures are evident, they appear to be lined in rows generally coinciding with the crests of the waves in the underlying or surrounding surface material, as seen in Figure 7. Furthermore, the diameters of these nodule aggregates appear to be equivalent to the widths of these waves. This structure suggests that the waves may be composed of rows of nodule aggregates in parallel arrays reminiscent of row nucleation and growth seen in semicrystalline polymers crystallizing under shear.²³⁻²⁵ However, they may simply result from imperfections in the spinnerette.

The smaller nodules which form the nodule aggregates are shown in Figure 8. Assemblies of the aggregates were seen to separate under exposure to the electron beam, those constituting the surface of the polysulfone hollow fiber membrane spun from *N*-formylpiperidine/formamide. The higher stability of these samples to the electron beam suggests that its constituent structural

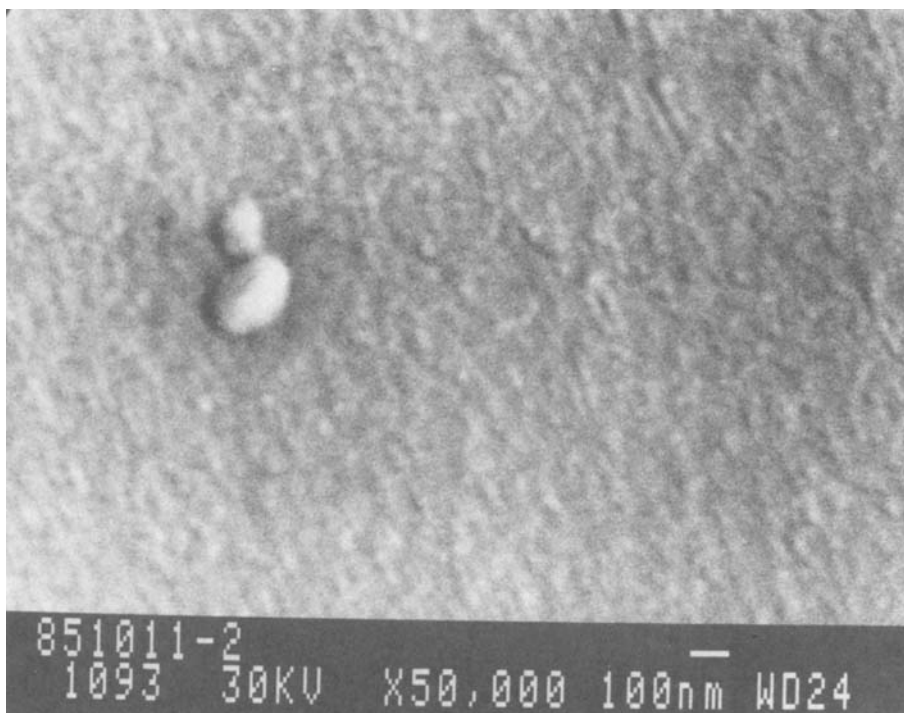


Fig. 6. Scanning electron micrograph of the outer surface of a polysulfone hollow fiber membrane spun from formylpiperidine/formamide at 50K magnification.

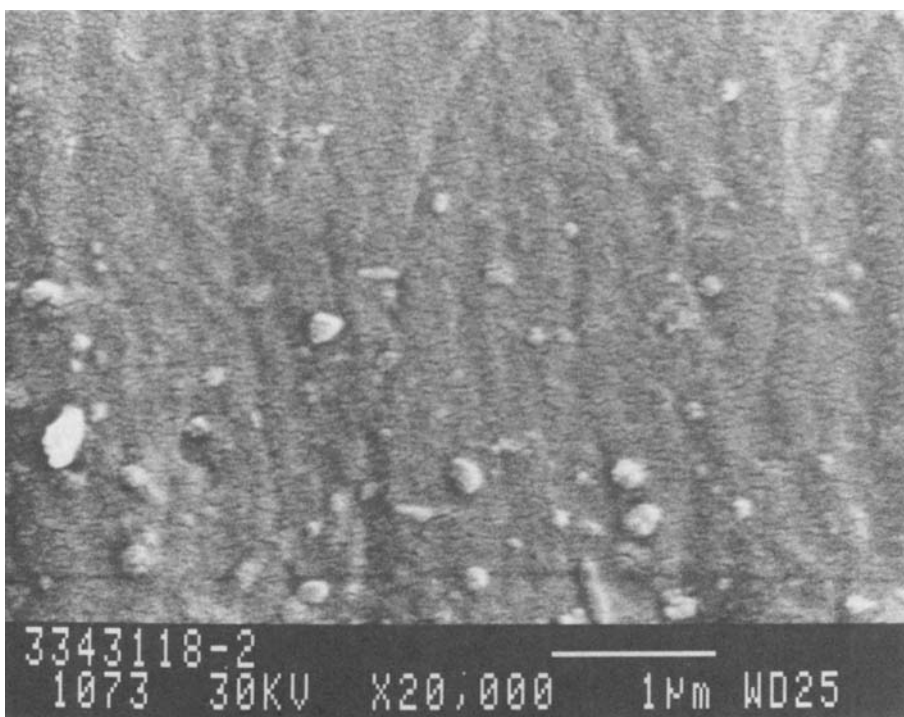


Fig. 7. Scanning electron micrograph of the outer surface of a polysulfone hollow fiber membrane spun from propionic acid : *N*-methylpyrrolidone at 20K magnification.

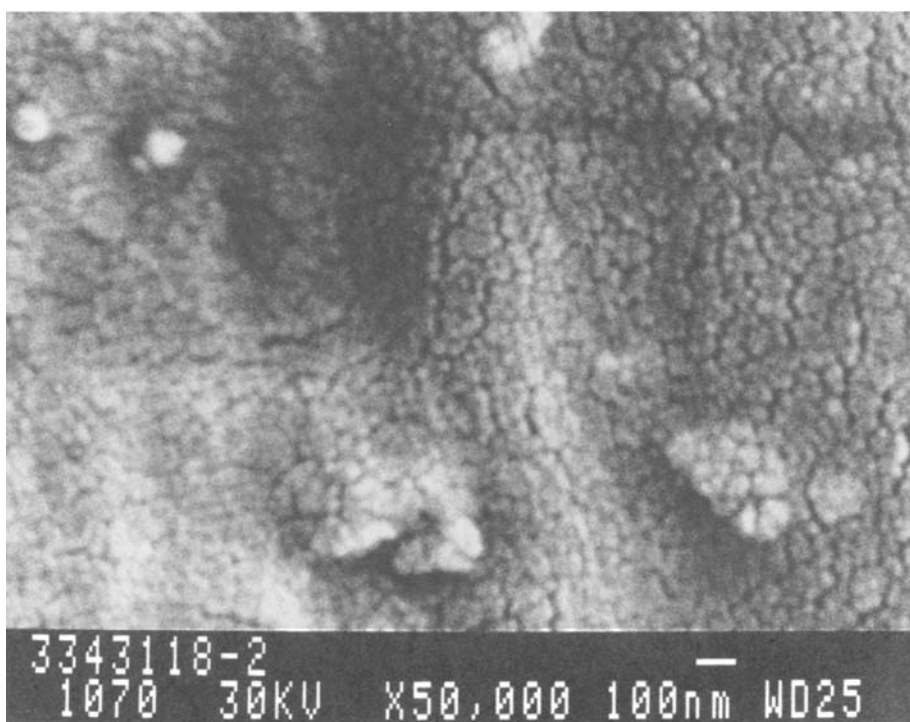


Fig. 8. Scanning electron micrograph of the outer surface of a polysulfone hollow fiber membrane spun from propionic acid: *N*-methylpyrrolidone at 50K magnification.

units are more tightly packed and fused, and its microscopically observable skin is thicker and denser.

Transmission electron micrographs of gold/palladium replicas of the outer surfaces of the two hollow fiber membranes were obtained. Unfortunately, the grain size of the Au/Pd replica (5–10 nm) is too coarse to convey fine detail as seen in Figure 9. However, the transmission electron micrographs of the cross sections of the hollow fiber membranes exposed to osmium tetroxide vapors and subsequently coated with an Au/Pd prior to embedding and sectioning are more informative. Figures 10 and 12 are photomicrographs of the cross-sectioned outer surface layer of a cross section of the hollow fiber membrane spun from formylpiperidine/formamide, and Figures 11 and 13 are comparable photomicrographs from the cross section of the Lewis acid:base spun congener. The surface texture can be inferred by examining the contours of the metal layer evaporated on the fiber surface. A flat surface is represented by a dense narrow band of metal particles while a convoluted surface is represented by a diffuse wide band of particles. As observed in Figures 11 and 13, the hollow fiber membranes spun from the Lewis acid:base complex have convoluted metal coatings while those prepared from the solvent/nonsolvent mixture have flatter, more smooth metal coating, as shown in Figures 10 and 12. The osmium tetroxide vapor treatment reveals dramatic differences in the surface structure of these two classes of asymmetric hollow fiber membranes.

One hour's exposure to osmium tetroxide is sufficient to visibly darken the interior structure of the hollow fiber membrane with graded density skin, but

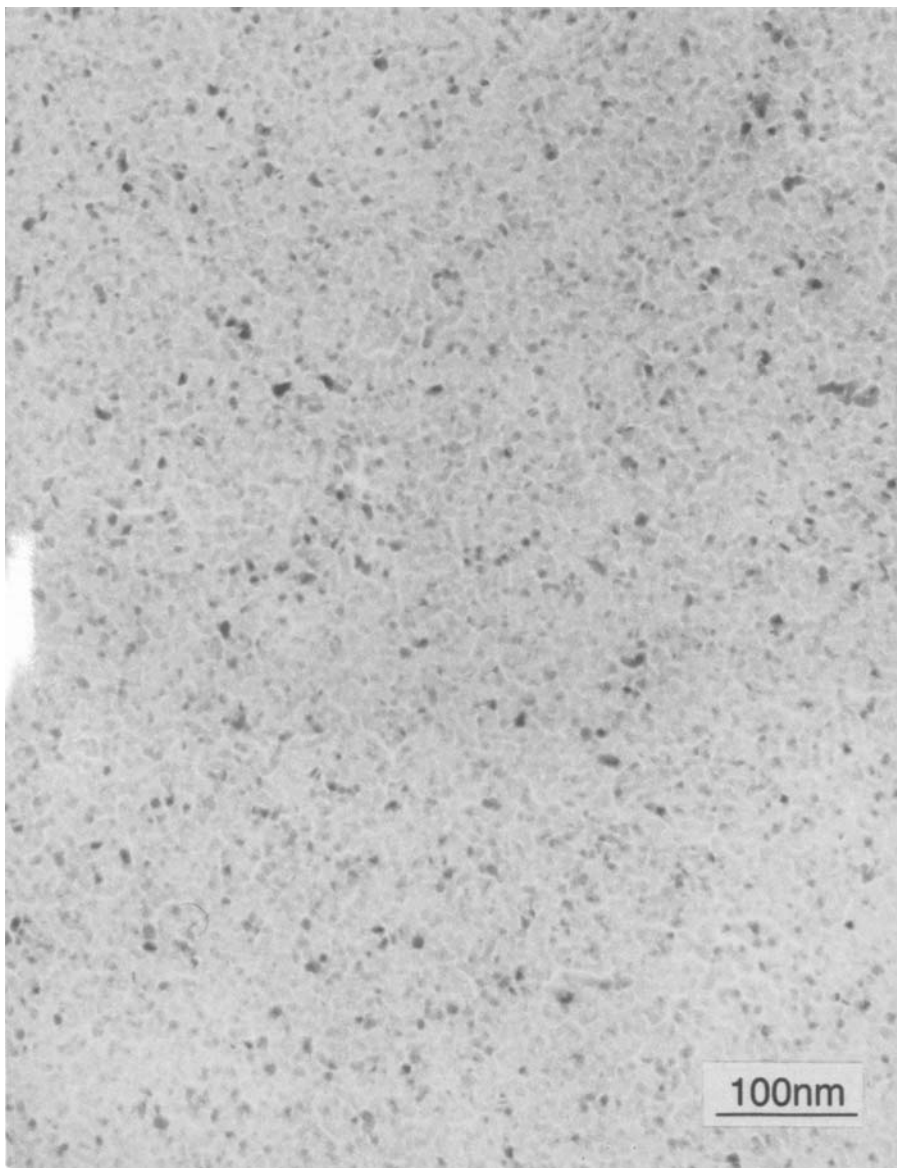


Fig. 9. Transmission electron micrograph of a gold palladium replica of the outer surface of a polysulfone hollow fiber membrane spun from formylpiperidine/formamide.

the interior matrix of the classical bilayer hollow fiber membrane prepared from the solvent/nonsolvent mixture remains unchanged. Electron dispersion spectroscopy measurements on the polysulfone hollow fiber membrane spun from formylpiperidine/formamide reveals a strong sulfur peak and negligible osmium tetroxide in the matrix, as shown in Figure 14. However, sufficient osmium tetroxide traversed the effective separating layer of the polysulfone hollow fiber membrane prepared from the Lewis acid : base solvent system to obscure completely the sulfur response after its absorption into the interior

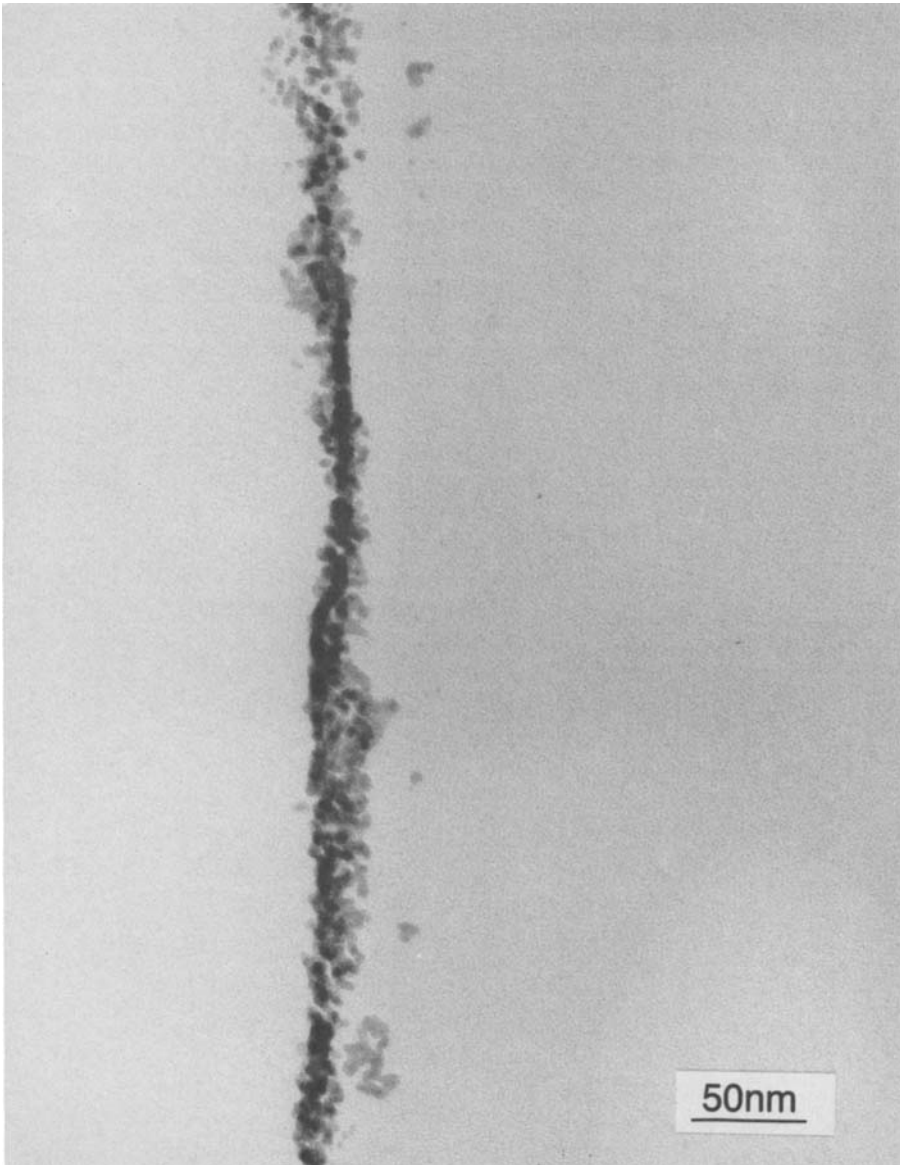


Fig. 10. Transmission electron micrograph of the outer edge of an ultrathin cross section of a polysulfone hollow fiber membrane spun from formylpiperidine/formamide on which a gold/palladium surface layer was deposited, 238K magnification.

matrix material. Instead of a strong sulfur response, osmium is detected, as seen in Figure 15. These results indicate that micropores, which are below the limits of resolution of the scanning electron microscope, penetrate through the effective separating layer to the surface of an asymmetric membrane with a graded density skin and that these micropores have radii which are greater than the van der Waals' radius of osmium tetroxide. Osmium tetroxide is a tetrahedral molecule with a van der Waals' radius of 3.3 Å.²⁶ The results of the oxygen plasma ablation studies indicate that micropores below the limits

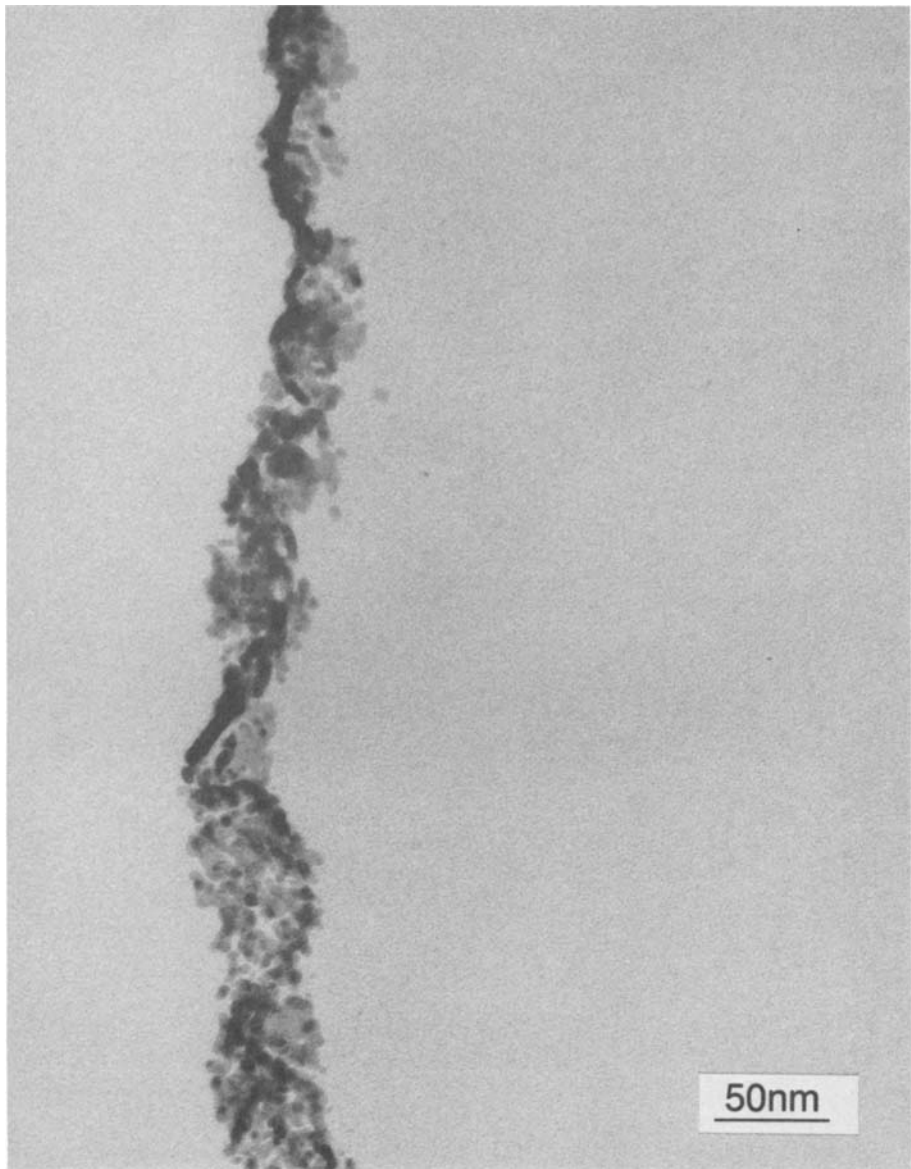


Fig. 11. Transmission electron micrograph of the outer edge of an ultrathin cross section of a polysulfone hollow fiber membrane spun from propionic acid : *N*-methylpyrrolidone on which a gold/palladium surface layer was deposited, 238K magnification.

of resolution of the electron microscope also exist in the microscopically observable skins of classical bilayer membranes but terminate below the effective separating layer.¹²⁻¹⁴ These osmium tetroxide vapor results support this model of the skin structure of asymmetric bilayer membranes. If any micropores extend through the effective separating layer of a classical bilayer membrane, these micropores have radii less than the van der Waals' radius of osmium tetroxide.

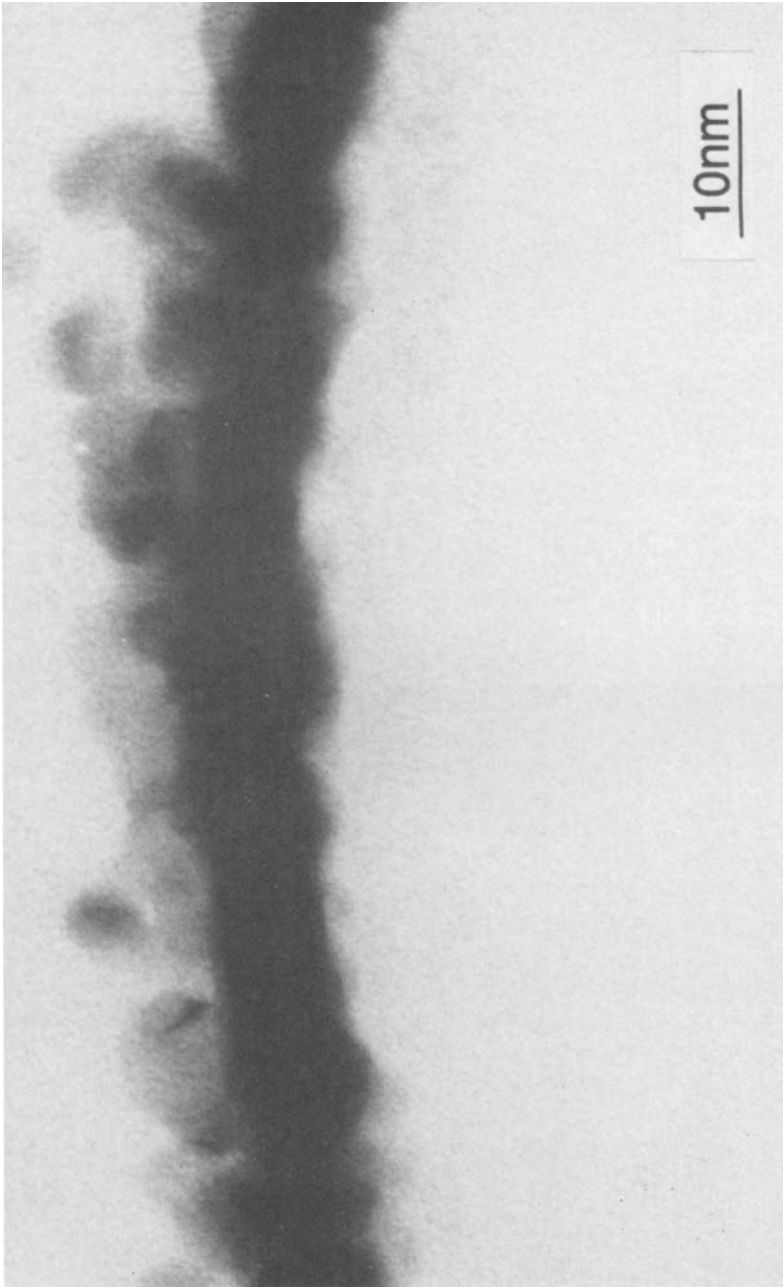


Fig. 12. Transmission electron micrograph of the outer edge of an ultrathin cross section of a polysulfone hollow fiber membrane spun from formylpiperidine/formamide on which a gold/palladium surface layer was deposited, 1148K magnification.

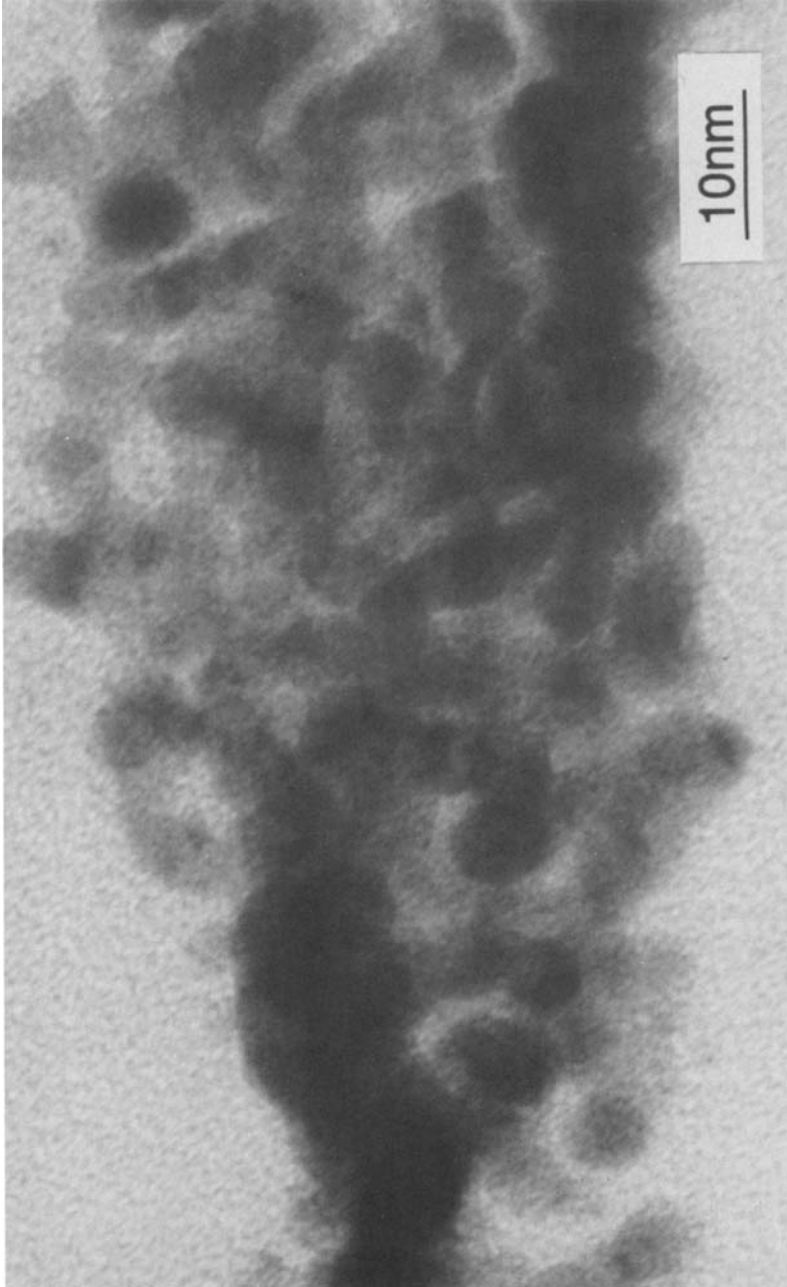


Fig. 13. Transmission electron micrograph of the outer edge of an ultrathin cross section of a polysulfone hollow fiber membrane spun from propionic acid : *N*-methylpyrrolidone on which a gold/palladium surface layer was deposited, 1148K magnification.

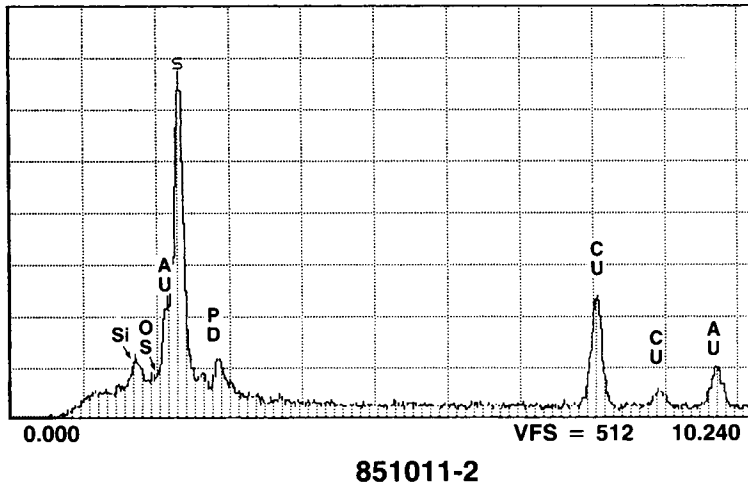


Fig. 14. Electron dispersion spectrogram of interior of a polysulfone hollow fiber spun from formylpiperidine/formamide after 1-h exposure to osmium tetroxide vapor.

Both types of membranes are rendered into membranes suitable for gas separations by a proprietary coating procedure.²⁷ A highly permeable, nonselective coating is placed on an asymmetric membrane to plug the pores and defects in the membrane and render transport through the underlying membrane predominant. The structural model being advanced here suggest that the coating procedure primarily plugs defects in the effective separating layer of classical bilayer asymmetric membranes but serves to obstruct both defects and micropores in the membranes with graded density skins.

The existence of micropores in the effective separating layer of the hollow fiber membranes with graded density supports the conclusions derived from the oxygen plasma ablation, scanning electron microscopy, and transmission

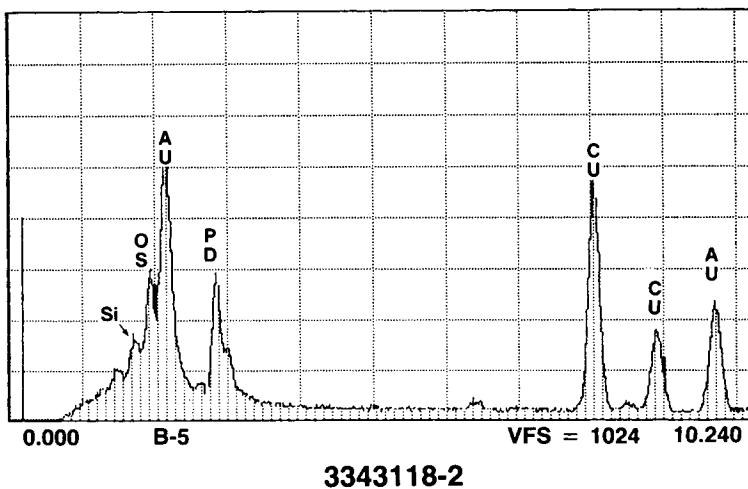


Fig. 15. Electron dispersion spectrogram of interior of a polysulfone hollow fiber membrane spun from propionic acid : *N*-methylpyrrolidone after 1-h exposure to osmium tetroxide vapor.

electron microscopy investigations, i.e., the nodule aggregates and the nodules which form them are less tightly packed than those constituting the structure of the effective separating layer of a classical asymmetric membrane formed by phase inversion from a traditional solvent/nonsolvent mixture. Because these structural units exhibit less compression and distortion than their congeners in the surface of a classical asymmetric hollow fiber membrane, the nodule aggregates constituting the effective separating layer of the hollow fiber membrane spun from the Lewis acid : base complex solvent system more nearly resemble in their structure those in the interior of the membrane than those composing the effective separating layer of the hollow fiber membrane prepared from the *N*-formylpiperidine/formamide mixture.

The differential scanning calorimetry studies which yielded elevated glass transition temperatures on the initial thermal scan for hollow fiber membranes prepared from Lewis acid : base complex solvent systems were obtained using the entire hollow fiber membrane.^{15,19-21} These results only demonstrate that the free volume of the bulk membrane is higher than that of an asymmetric membrane prepared from a traditional solvent/nonsolvent mixture. However, the material forming the microscopically observable skin is only a minute fraction of the amount of polymer in the asymmetric hollow fiber membrane. Furthermore, the effective separating layer constitutes only a minor portion of the microscopically observable skin. Therefore, it was concluded *a priori* that the enhanced free volume of asymmetric membrane with a graded density skin persists through the microscopically observable skin into the effective separating layer. The structure and morphology of the effective separating layer as revealed by these SEM, TEM, and osmium tetroxide vapor studies support the validity of this reasoning. If it were possible to measure the glass transition temperature of the polymer material forming the effective separating layers of these two classes of membranes, the glass transition temperature of this layer for the membrane with graded density skin would not be significantly less than that exhibited by the entire asymmetric membrane. Furthermore, it is speculated that the glass transition temperature of the effective separating layer of a comparable asymmetric membrane prepared for a traditional solvent/nonsolvent mixture would exhibit a much lower glass transition temperature than the material from the membrane interior provided solvent removal is complete from both. This lower glass transition temperature would result from the reduction in free volume in the effective separating layer due to the tight packing of its constituent structural units leading to their ultimate compression and distortion. Therefore, if the glass transition temperatures of only the effective separating layers of these two classes of membranes could be measured, it is predicted that their free volume differences as indicated by the glass transition temperature on the initial thermal scan would be greater than those implied solely from measurement of the bulk hollow fiber membrane thermal properties.

The profound differences between the effective separating layers of these two classes of asymmetric membranes is strongly influenced by the differences in their coagulation rates. The asymmetric membrane with a graded density skin is formed from a solvent system containing a Lewis acid and a Lewis base. Many Lewis bases (such as *N*-formylpiperidine, dimethylacetamide,

N-methylpyrrolidone, and dimethylformamide) can be complexed with a spectrum of Lewis acids (such as acetic acid, propionic acid, butyric acid, or isobutyric acid) to obtain similar results with a wide variety of polymers. In this investigation, the Lewis acid is propionic acid, a nonsolvent for polysulfone. *N*-methylpyrrolidone, the Lewis base, is a solvent for the polymer. Together they form a Lewis acid : Lewis base complex permitting much higher concentrations of nonsolvent to be incorporated into the spinning dope than can be achieved using a noncomplexing nonsolvent in a traditional solvent/nonsolvent mixture, i.e., formylpiperidine/formamide. The Lewis acid : base complex, also a solvent for the polymer, dissociates on contact with water into its constituent moieties accelerating the kinetics of the phase inversion process. The kinetics of the sol-to-gel transition are so accelerated that the final structure is fixed before compaction and distortion of the constituent structural units can occur. Therefore, the enhanced free volume in the effective separating layer of asymmetric membranes with graded density skins results from restricting the available time in which the polymer molecules can approach equilibrium by undergoing further packing and/or conformational rearrangement in a process analogous to rapid quenching of a polymer melt in contrast to slow cooling and fixing the structure of the effective separating layer before the tight packing and concomitant compression and distortion of the structural units can occur.

CONCLUSIONS

The structure of the effective separating layer of an asymmetric membrane with a graded density skin differs from that of a bilayer asymmetric membrane. Although both structures are composed of nodule aggregates formed from smaller polymer nodules, the structural units forming the effective separating layer of the asymmetric membrane prepared from the Lewis acid : base complex are less tightly packed and distorted than those constituting the effective separating layer of the bilayer congener. Consequently, its component structural unit possess higher free volume and microporosity. Osmium tetroxide vapor penetration studies indicate that these micropores, which have dimensions below the limits of resolution of the scanning electron microscope, traverse the effective separating layer with radii greater than the van der Waals' radius of osmium tetroxide (3.3 Å). In contrast, the microporosity in the denser skin structure of the asymmetric membranes formed from traditional solvent/nonsolvent mixtures terminates below the effective separating layer, which is composed of tightly packed, compressed, and distorted structural entities.

The structural differences between these two effective separating layers is derived from the differences in their kinetics of coagulation. Utilization of a Lewis acid : base complex permits incorporation of higher concentrations of nonsolvent into the solvent system than can be obtained with traditional solvent/nonsolvent mixtures. The Lewis base solvent sequesters the Lewis acid nonsolvent by formation of a complex, which then dissociates into its component moieties upon contact with water accelerating the kinetics of the coagulation process. Therefore, the enhanced free volume in the effective separating layer of asymmetric membranes with graded density skins results

from restricting the available time in which the polymer molecules can approach equilibrium by undergoing further packing/or conformational rearrangement and fixing the structure of the effective separating layer before tight packing and concomitant compression and distortion of its component structural units can occur.

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