Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

The Application of Scanning Electron Microscopy to Membrane Morphology

R. E. Resting[a]; M. Engdahl[a]; W. Stone Jr.[a]
[a] National Institute of Scientific Research, Los Angeles, California

To cite this Article Resting, R. E. , Engdahl, M. and Stone Jr., W.(1969) 'The Application of Scanning Electron Microscopy to Membrane Morphology', Journal of Macromolecular Science, Part A, 3: 1, 157 — 167
To link to this Article: DOI: 10.1080/10601326908053800
URL: http://dx.doi.org/10.1080/10601326908053800

J. MACROMOL. SCI.—CHEM., **A3**(1), pp. 157-167, Jan., 1969

The Application of Scanning Electron Microscopy to Membrane Morphology

R. E. KESTING, M. ENGDAHL, and W. STONE, Jr.

National Institute of Scientific Research
Los Angeles, California

INTRODUCTION

The efforts of the Office of Saline Water (U.S. Dept. of the Interior) to develop an economical means of desalination have catalyzed a general revival of interest in membrane separation processes. It is not surprising, therefore, that attempts are currently underway to reinvestigate those aspects of membrane separations which have not been definitively answered in the past. One key problem area has been a dearth of direct morphological evidence concerning the relationship between structure and function in semipermeable membranes. Neither optical nor electron microscopy has been very successful in elucidating the structure of semipermeable membranes; the former because of low resolution, and the latter because of the tedious sample preparation, the introduction of artifacts, and the interpretation of extremely flat images. Owing partially to these difficulties the functional approach has tended to predominate in the councils of membrane technologists. Very recently, however, a new investigative tool, scanning electron microscopy [1], has become available which promises to add substance to the field of membrane structure. The scanning electron microscope exhibits resolution midway between optical and standard electron microscopes and offers great advantages over both in ease of sample preparation and in image depth and quality. These advantages are all intrinsic to the nature of the scanning electron microscope, which utilizes back-scattered and secondary electrons over a wide range of angles to obtain a reflection image which is scanned and transmitted to an oscilloscope for photographing. In this paper, the application of scanning electron microscopy to such representative membrane problems as swelling, asymmetry, void size, pore size, rugosity, and the morphological changes attendant upon hydrolysis and deswelling will be considered together with some speculation as to its eventual application to liquid and nascent membranes.

EXPERIMENTAL

All of the illustrations contained herein are of membranes of the phase inversion type. Such membranes are fabricated from polymer solutions which are gelled either prior to or subsequent to their immersion in a suitable nonsolvent medium. The cellulose acetate membranes, details of which are described elsewhere, are of the Loeb-Sourirajan [2] type modified according to the procedure of Manjikian et al. [3]. Cellulose membranes were prepared by the deacetylation of acetate membranes with 0.4 M methanolic NaOH [4]. Both cellulose and cellulose acetate membranes were carefully desiccated after the prior inclusion of a solution of glycerol, 30% by weight, and a polyoxyethylenenonylphenol surfactant, Igepal CO-710, GAF, 5% by weight in water [5]. This procedure was necessary to prevent the structural collapse which otherwise occurs upon desiccation of water-swollen cellulosic membranes of the Loeb-Sourirajan type. Polycarbonate membranes were prepared from solutions of Lexan (General Electric) and were dried without the inclusion of the glycerol surfactant solution.

Dried membranes were cemented to copper stages and placed in a vacuum deposition chamber where they received a thin conductive gold coating. This procedure resulted in increased image clarity by eliminating charge accumulation. Artifact-free membrane cross sections were obtained from fresh edges prepared by splitting the membranes at liquid nitrogen temperatures. After coating, the samples were ready for insertion into the scanning electron microscope. Imbedding, microtoming, shadowing, and replication, all of which are necessary adjuncts to electron microscopy, are unnecessary in scanning electron microscopy. The elimination of these artifact-producing steps has resulted in such significant improvements in efficiency and image quality as to provide a broad practical basis for future studies of membrane structure.

EXPERIMENTAL RESULTS AND DISCUSSION

The Role of Swelling Agents in Multicomponent Phase Inversion Sols

The most significant advance in membrane technology within the past decade has been the development by Loeb and Sourirajan of a highly asymmetric membrane of secondary cellulose acetate for desalination in the process of reverse osmosis [2]. This membrane was produced by adding an aqueous solution of magnesium perchlorate to an acetonic solution of the polymer. Subsequently, Manjikian et al. [3] replaced the aqueous magnesium perchlorate with formamide and achieved substantially identical results. Although

Kesting [6] established that such additives functioned as swelling agents, thereby increasing void volume and decreasing resistance to material transport, it was not until the advent of scanning electron microscopy that the effects of swelling on membrane morphology [5] became evident (Fig. 1). Membranes prepared from a formamide-free solution of cellulose acetate in acetone were dense films free of voids (Fig. 1A). Those prepared from a 10 mole % solution of formamide possessed a small number of large, thick-walled, but widely spaced voids which were closed cell in nature (Fig. 1B). As the concentration of formamide exceeded about 20 mole % (Fig. 1C), closed cells were superseded by smaller and

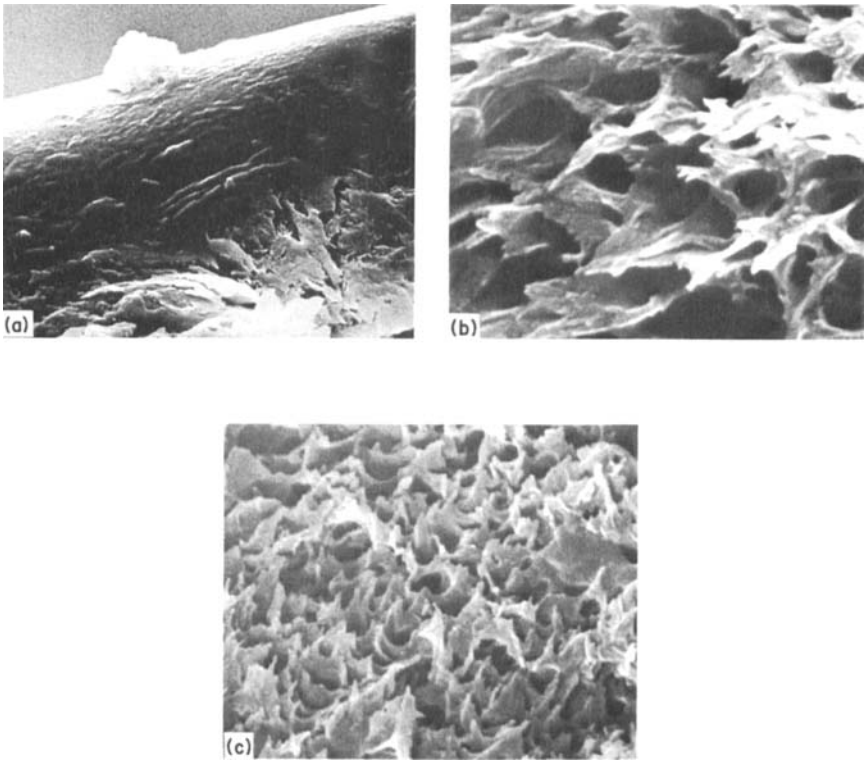

Fig. 1. Cross sections of cellulose acetate membranes prepared from acetonic solutions containing varying concentrations of formamide: (A) 0, (B) 10, and (C) 50 mole %.

more numerous open cells. The definitive nature of the scanning electron photomicrographs formed the basis for an interpretation of the dependence of membrane morphology upon swelling agent concentration [5]. This hypothesis related membrane structure to the appearance or nonappearance of a phase inversion within its sol precursors. In the absence of swelling agent, solvent loss went to completion without the formation of a second phase, and dense impermeable films resulted (Fig. 1A). Where swelling agent concentration was low, separation of droplets of excess swelling agent was postponed to a later stage in the desolvation process, by which time droplet size and the thickness of the layer of polymer molecules surrounding these droplets were increased, thereby accounting for the large closed cells (Fig. 1B). Where swelling agent concentration was high, on the other hand, phase separation occurred at an early stage in the desolvation process, so that droplets of the disperse phase were small, numerous, and, because of the large total surface area, thin-walled (Fig. 1C). Desolvation of the latter sols led to the formation of open-celled membranes in which the only resistance to material transport was that offered by the dense skin layer.

MEMBRANE ASYMMETRY

It has long been recognized that the gel structure at that surface of the membrane which is first exposed to the gelation medium differs considerably from that in the interior of the membrane. This phenomenon is not unique and, in fact, a closely analogous situation is encountered for the case of the skin-core structures of viscose rayon filaments [7]. Asymmetry in membrane structure results both because of the more rapid desolvation which occurs at the interface between the polymer solution and the gelation medium, and because of differences between interfacial and bulk forces [5]. Membranes of the Loeb-Sourirajan type [2] are so asymmetric that they can be considered as being composed of two distinct layers: the surface or "active" layer, which is a dense, ultrathin, effective resistance to solute transport, and the porous substructure, which acts merely as a support. The great advantage of such a bilayered structure is the maintenance of the high degree of permselectivity possessed by dense films while simultaneously attaining the high rates of material transport characteristic of more swollen membranes.

The extent of the active layer in reverse osmosis membranes has been a matter of dispute. Riley et al. [8] have cited a value of 0.25 μ and Kesting et al. [9] a value of about 4 μ. Trudelle and Nicholas [10] have recently reinvestigated this problem utilizing differences in refractive index to distinguish between surface and

substructure layers. They concluded that the water content increased steadily from the surface inward, probably very quickly in the surface region, and more slowly, but not negligibly, in the deeper regions. Scanning electron microscopy is helping to resolve this controversy. It has already been established, e.g., that the skin layer of polycarbonate membranes is several microns in depth (Fig. 2). A dense layer several microns thick, perhaps corresponding to the active layer, has also been observed in reverse osmosis membranes (Fig. 3).

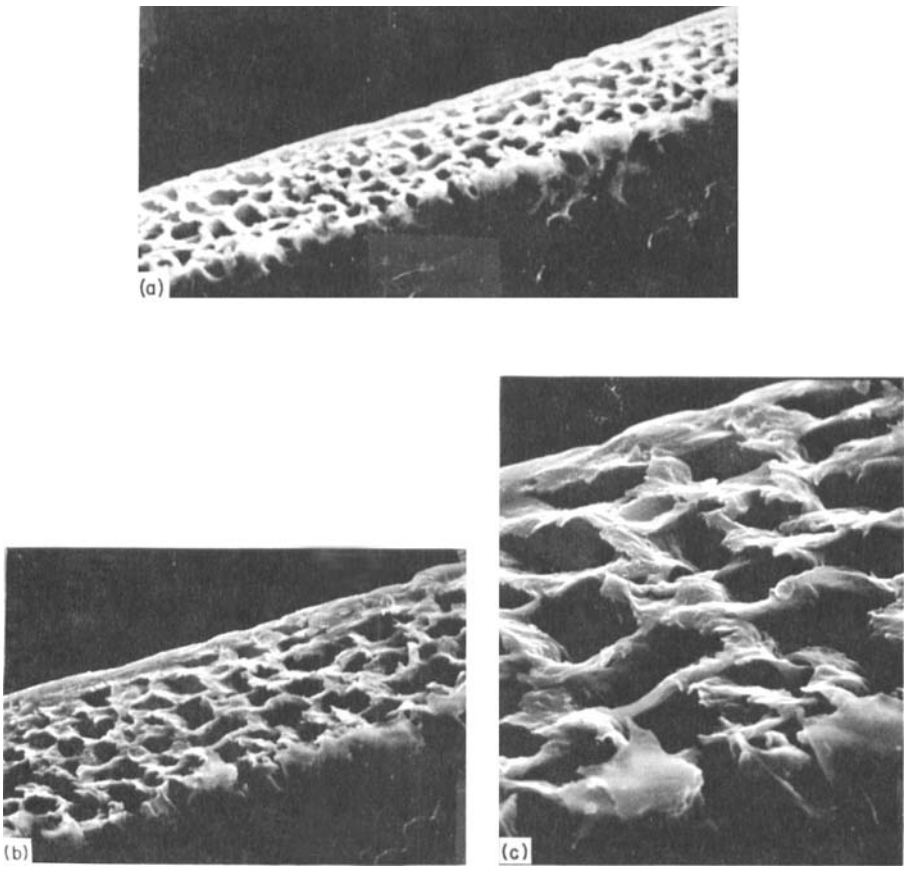

Fig. 2. Cross sections of a polycarbonate membrane: (A) × 450, (B) × 700, and (C) × 1800.

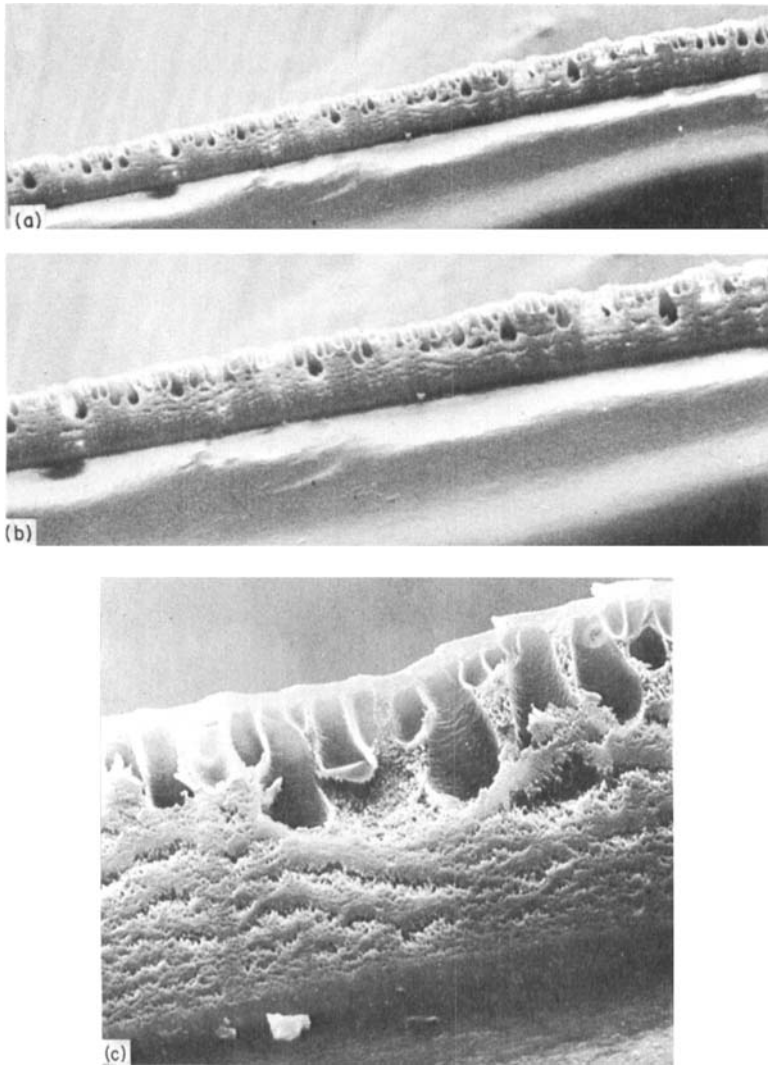

Fig. 3. Cross section of an asymmetric cellulose acetate reverse osmosis membrane: (A) × 80, (B) × 160, (C) × 300.

The greater reflectivity and hydrophobicity of a membrane's skin as compared with its substructure layer is apparent from even a cursory visual examination. The morphological basis for this, as evidenced from scanning electron photomicrographs, is the greater pore frequency and increased rugosity of the bottom surface (Figs. 4 and 5). It is apparent that the more extensive application of scanning electron microscopy to membrane structure would put the calculation of pore size and pore size distribution on a far more satisfactory basis than is possible with the current indirect methods.

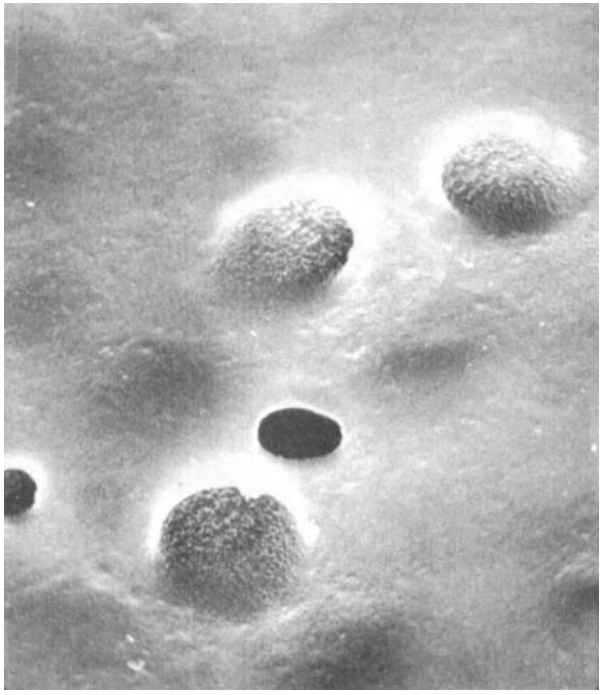

Fig. 4. Skin (top) surface of polycarbonate membrane (× 2700).

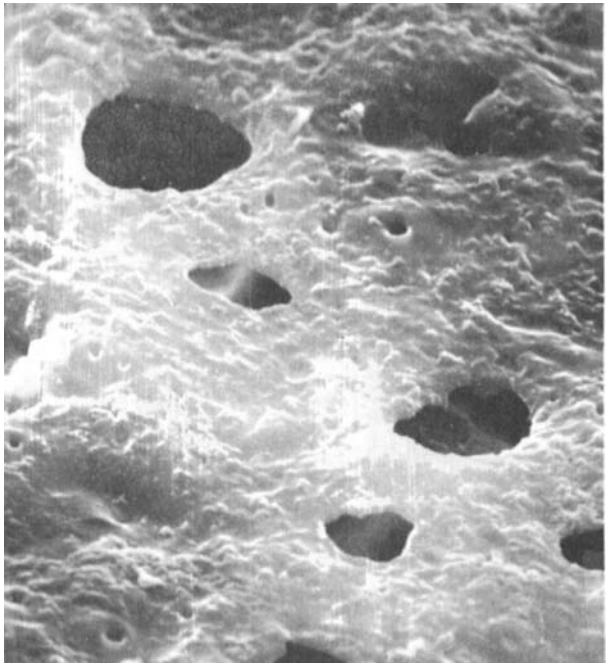

Fig. 5. Bottom surface of polycarbonate membrane (× 2700).

Chemical and Physical Modifications of Membrane Structure

The deesterification of membranes of cellulose acetate and cellulose nitrate to produce those of pure cellulose has frequently been effected where the chemical inertness of the latter and the ease of fabrication of the former are desired. Until recently, the morphological changes accompanying deesterification were strictly a matter of speculation. Now, however, it has become apparent that deesterification, at least with 0.4 M methanolic NaOH [4], does not greatly alter the original gel structure (Figs. 6 and 7). If, however, desiccation is effected in the absence of glycerol and surfactants, deswelling results in the appearance of a dense, high resistance film (Fig. 8). It will also be of interest to employ this tool in studying the nature of the structural changes attendant upon chemical cross-linking or physical deswelling induced by heat and pressurization.

Structural Irregularities

The nature of structural irregularities, to whose random appearance may be attributed irreproducibility of permeation data, is of great importance to membrane technology. Helmcke [11] has attributed these defects to the emergence, after the onset of gelation, of droplets of solvent and air through the dense skin at the surface of the membrane. Solvent droplets appear in the substructure during gelation. Their density is lower than that of the surrounding solution so that they eventually rise to the skin layer, which subsequently dwells and dissolves as the solvent concentration increases. After the emergence of the solvent, membrane skin will reform but usually in a somewhat less orderly fashion than found in the original homogeneous structure.

Helmcke [11] observed the presence of large, irregular voids within the membrane substructure and suggested that such voids represented emptied pockets of desolvating liquid (Fig. 9). He further suggested, but did not observe, a structural relationship between these voids and surface irregularities. It is felt that scanning electron microscopy will prove of great value in elucidating the nature and origin of structural irregularities, thereby contributing materially to improvements in membrane permselectivity.

Nascent and Liquid Membranes

It appears probable that scanning electron microscopy will be useful not only in the study of gel membranes but also in investigations of their sol precursors, i.e., the nascent membranes existing prior to gelation. Rapid quenching of sol structures by immersion in liquid nitrogen, followed by lyophilization, should produce

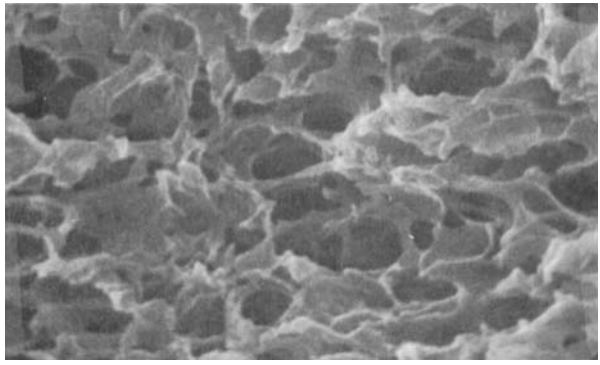

Fig. 6. Cross section of cellulose acetate reverse osmosis membrane (× 9000).

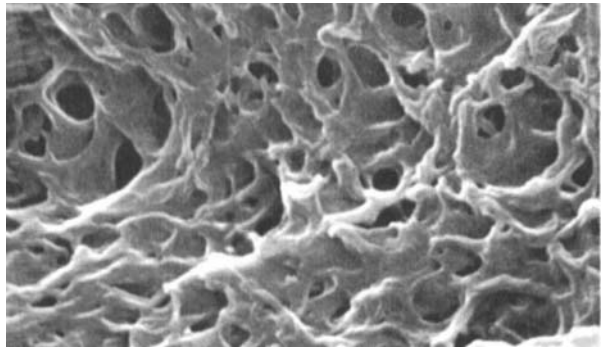

Fig. 7. Cross section of deacetylated cellulose acetate membrane (× 9000).

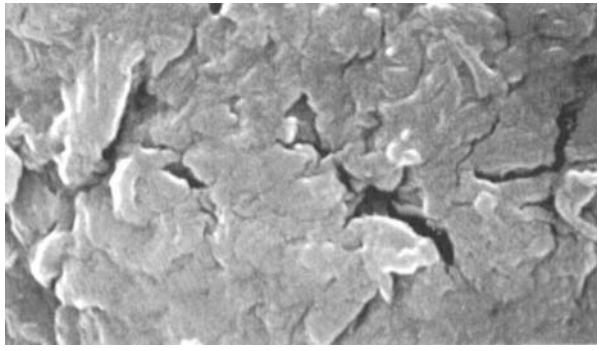

Fig. 8. Cross section of deacetylated cellulose acetate membrane irreversibly deswelled (× 9000).

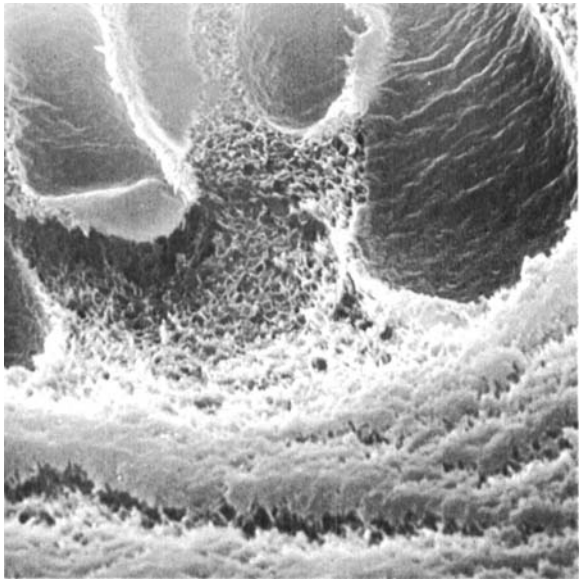

Fig. 9. Cross section of cellulose acetate membrane showing structural details in the voids (× 1200).

solution "ghosts," an analysis of which would contribute greatly to our understanding and control of the gelation process itself. In like manner, the recently discovered liquid membranes [12], which form spontaneously as a result of the surfactant capacities of various polymeric feed additives, should also be amenable to study with this technique.

While this descriptive paper has enumerated several areas related to membrane structure which have already been at least cursorily investigated by scanning electron microscopy, its future widespread application should greatly facilitate the practical and theoretical development of all membrane separation processes.

ACKNOWLEDGMENT

The authors wish to thank Mr. Al Yost of JEOLCO for his kindness in arranging the use of the JSM-2 scanning electron microscope.

REFERENCES

[1] S. Kimoto, *On a Scanning Electron Microscope, JEOLCO Publ. SM-67013*, Tokyo, October 1967.

[2] S. Loeb and G. Sourirajan, *UCLA Dept. Eng. Rept. 60-60*, 1961.

[3] S. Manjikian, S. Loeb, and L. McCutcheon, paper presented at 1st Intern. Symp. Water Desalination, Washington, D.C., October 3-9, 1965.
[4] R. Kesting, U.S. Pat. 3, 290, 286 (1966).
[5] R. Kesting and A. Menefee, *Kolloid Z. Z. Polymere*, in press.
[6] R. Kesting, *J. Appl. Polymer Sci.*, **9**, 663 (1965).
[7] P. H. Hermans, *Textiles Res. J.*, **20**, 553 (1950).
[8] R. Riley, J. Gardner, and U. Merten, *Science*, **143**, 801 (1964).
[9] R. Kesting, M. Barsh, and A. Vincent, *J. Appl. Polymer Sci.*, **9**, 1873 (1965).
[10] Y. Trudelle and L. Nicholas, paper presented at Membrane Symp., Paris, February 1-3, 1967.
[11] J. G. Helmcke, *Kolloid Z.*, **135**, 101 (1954).
[12] R. Kesting, W. Subcasky, and J. Paton, *J. Colloid Interface Sci.*, 28, 156 (1968).

Accepted by editor October 30, 1967
Received for publication August 29, 1968