# *Ultrastructure of the Surface of a Polysulfone Ultrafiltration Membrane*

## INTRODUCTION

The first electron micrographs of an asymmetric polymeric membrane were published by Riley et al.[1,2] in 1964 and 1966 using a replica technique and the transmission electron microscope (TEM). The development of the scanning electron microscope (SEM) and its easier sample preparation techniques gave a further impetus to such investigations. Side views (cross sections) of flat sheet, anisotropic membranes[3–6] or hollow fibers[7,8] have also been published.

The surface structure of a flat sheet, ultrafiltration polysulfone membrane, i.e., the "skin" of the membrane, is its most critical part for it is there that the processed solution makes contact and separation of solution components occur. The skin has been photographed by the SEM[9] and TEM[6] but no pores were visible in these micrographs. Replica micrographs of some isolated cellulose acetate membranes have been published,[2] but the pore sizes calculated—of the order of 0.4 $\mu$m (4000 Å)—are larger than conventional ultrafiltration membranes,[10] which exhibit pores of 20–100 Å diam. This is too small for the conventional SEM, which has a limited resolution of 50–100 Å (for a perfect specimen and with excellent instrument conditions); photography becomes almost impossible at very high magnification and slow scanning rates.[5] The use of the TEM met with very little success because of the incompatibility of the polymers with the embedding media used.[11] Artifacts were inevitable using regular specimen preparation techniques.[6]

In this work, the ultrastructure of a flat sheet, anisotropic polysulfone membrane was studied and an estimate was made of the number and size of the pores on the membrane surface. It was hoped that this information would shed some light on the role of the membrane in the mechanism of fouling of ultrafiltration membranes by biological materials.[12]

## MATERIALS AND METHODS

A polysulfone membrane, provided by Millipore Corp. (Millipore Corp., Bedford, MA) was used in this study. The membrane is of the PTGC series with a nominal molecular weight limit of 10,000 daltons.

Pieces of the membrane were prepared for viewing by regular preparation methods.[12,13] The cured blocks were sectioned using glass knives on the LKB Ultratome III (LKB Produkter, Bromma, Sweden). The sections silver to gold, 500–1100 Å thick (according to Sorvall Microtome continuous interference color for thickness scale for thin sections, du Pont E-21685), were mounted on 400-mesh copper grids for viewing on the JEOL JEM 100 C TEM (JEOL Ltd. Tokyo, Japan), at 40–100 kV accelerating voltage.

For the replica micrographs, pieces of the membrane were air dried and coated with platinum at 300 Hz followed by carbon using the Balzers 301 freeze-etch unit (Balzers High-Vacuum Corp., Santa Ana, CA). The replica was peeled off the membrane using series of acetone–dimethylformamide (DMF) solutions in varying ratios to completely dissolve the membrane. The replica were washed in concentrated sulfuric acid for a few hours and viewed on the JEOL JEM 100 C TEM.

## RESULTS AND DISCUSSION

Preliminary studies on the PTGC membrane using the SEM at high magnification showed no visible structure on the membrane surface.[12] The TEM on the other hand, although having a higher

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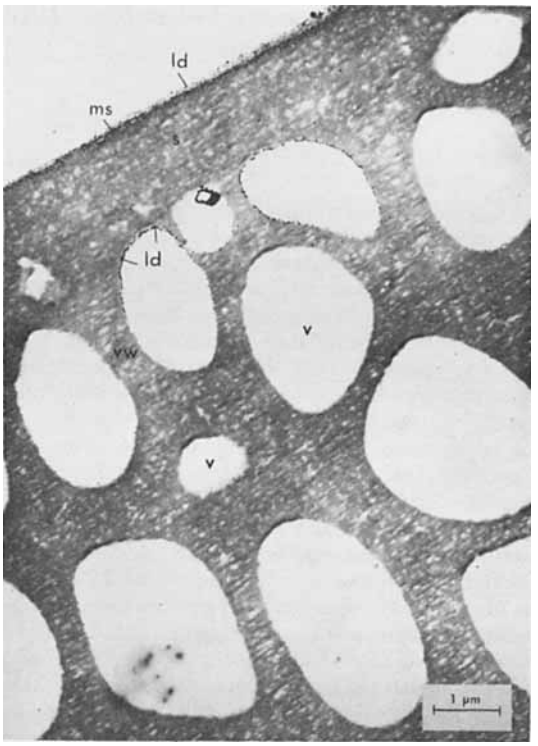


Fig. 1. Transmission electron micrograph of a cross section in a PTGC membrane after lead citrate and $CO_2$ was permeated through it. ld, lead deposit; ms, membrane surface; s, skin; v, void; vw, void wall; final magnification, 8900×.

resolution of about 3.4 Å, required greater care during sample preparation. When very thin sections were used they tended to evaporate under the electron beam,[6] especially if the membrane had a void volume of 50–60% as the membrane used in this study probably had. Hence, rather thick sections of the order of 500–1100 Å had to be used. These samples, however, were too thick to reveal any pores in the "skin" of the membrane, since the sections themselves were over ten times thicker than the assumed pore size (Fig. 1). The fact that the membrane skin was porous was confirmed using an indirect approach. Lead citrate was filtered through the membrane, followed by carbon dioxide. The latter caused lead carbonate to precipitate and to appear as black spots in the TEM micrographs, as shown in Figure 1. Lead carbonate crystals (ld) can be seen spread over the surface of the membrane as black spots. Lead spots are also visible within the supporting structure of the membrane, confirming the assumption regarding the "spongy" formation. From this and other TEM micrographs,[13] we determined the thickness of the "skin" to be 0.1–0.2 μm.

To further confirm the existence of pores on the surface, the replica technique was used (Fig. 2). The pores appear to be quite uniform with regard to shape and diameter, ranging in size from 10 to 150 Å in diam. and numbering approximately $4 \times 10^{11}$ pores per $cm^2$ (calculated from the micrographs). From the pore size distribution (as determined from the micrographs) given in Table I, the mean pore size is 59.1 Å. The pores were estimated to occupy about 7–12% of the total membrane surface area. The big particles that can be seen on the surface are believed to be dust particles not removed by washing before shadowing, rather than "viruslike" particulates as suggested by Riley et al.[2]

The information from the micrographs can be used to predict water flux through the membrane using the Poiseuille model of flow through channels:

$$Q = \frac{R^4 \, \Delta P_T \, \pi}{8 \, \Delta x \, \mu}$$

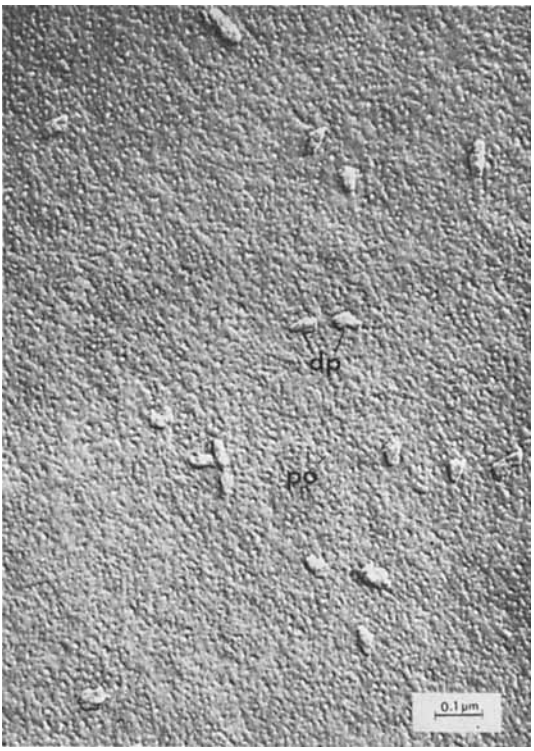


Fig. 2. Replica micrograph of PTGC membrane surface coated with platinum followed by carbon. dp, dirt particle; po, pore opening; final magnification, 67,500×.

TABLE I
Pore Size Distribution in PTGC membrane[a]

| Pore diameter (Å) | 10 | 20 | 42 | 63 | 83 | 104 | 125 | 146 |
|---|---|---|---|---|---|---|---|---|
| Distribution (%) | 0.9 | 4.2 | 33.9 | 42.3 | 12.0 | 4.7 | 1.5 | 0.5 |

[a] Estimated from Figure 2.

In this system, $R$ is the pore radius (29.55 Å), $\mu$ is the viscosity (0.55 cp), $\Delta x$ is the membrane thickness (0.1 $\mu$m), and $\Delta P_T$ is the transmembrane pressure (40 psig). The flux $Q$ was calculated as $1.5016 \times 10^{-13}$ ml/sec/pore or, assuming a pore distribution of $4 \times 10^{11}$ per cm$^2$ membrane surface area, flux is 2162.4 liter/m$^2$/hr. The experimental steady-state value obtained was 91.2 L/m$^2$/hr, indicating that this particular membrane has a tortuosity factor of 0.0422.

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