Ultrafiltration (UF) is a separation method in which a solution containing macromolecular solutes is forced through a thin membrane[1,2]. The solvent passes through the membrane; the solutes are retained. The separation mechanism is normally at least partially physical: the small solvent molecules pass through the membrane's pores, while the larger solute molecules cannot do so. Such a porous membrane has a great potential market in water purification, where it can be used as a final step to remove viruses and other drinking water contaminants.

The key to ultrafiltration is the membrane, which should allow a large flux and show a sharp molecular weight cut-off. Many current UF membranes are made by phase inversion, in which a solution of membrane polymer is spread on a moving web, allowed to dry slightly, and then plunged into a bath of nonsolvent. The result is a tangle of polymer fibers like those shown at the left of Figure 1. By changing the process conditions, the size and packing of the fibers can be controlled. Not surprisingly, the flux can be adjusted without a lot of trouble, but realizing a sharp molecular weight cut-off is more challenging.

An alternative ultrafiltration membrane structure,[3,4] shown in the middle panel of Figure 1, begins with a thin, pore-free polycarbonate film. The film is then exposed to ionizing radiation, which weakens regions of the film. If the weakened film is then etched with caustic, it develops small near-cylindrical pores like those in the figure. Because the pores are nearly monodisperse, this membrane has a sharp molecular weight cut-off. However, because the pore density is low, the flux is usually dramatically lower than that of more conventional ultrafiltration membranes
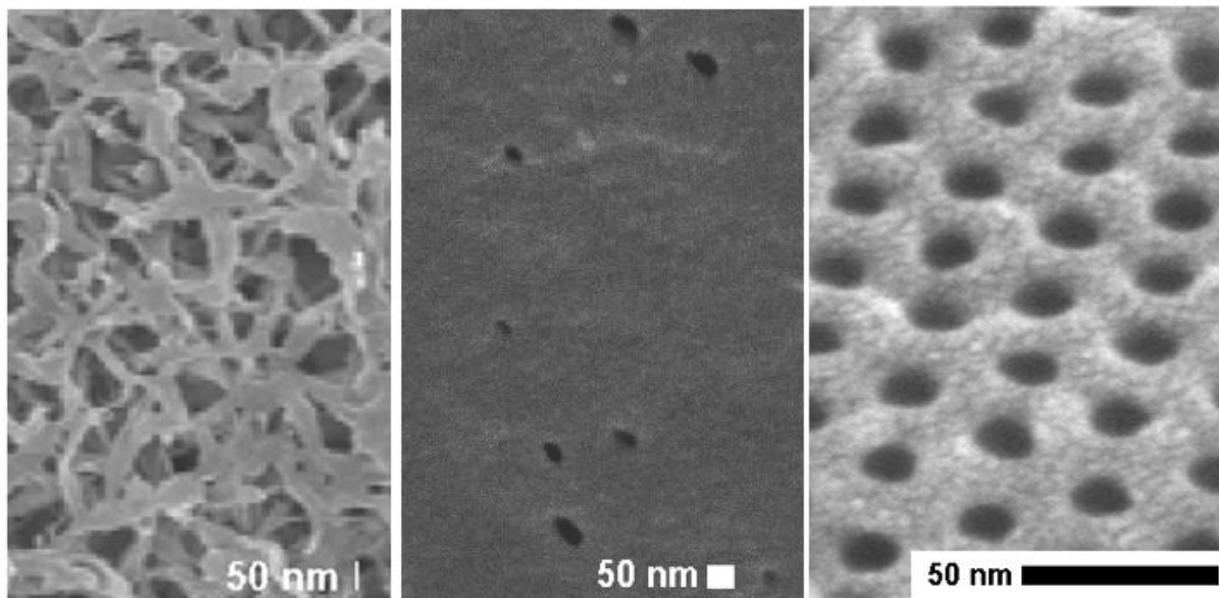
Figure 1. <u>Three Types of Membranes</u>. That on the left is a conventional ultrafiltration membrane formed by phase inversion, and that in the center is a track-etched polycarbonate film. The membrane on the left is that made here.

Recently, several groups have made membranes from block copolymer templates which have the potential of both high flux and sharp molecular weight cut-off,[5,6] and so have the promise of improved UF. The particular system studied here is typical of these efforts. It consists of a triblock copolymer of polylactide-poly(dimethylacrylamide)-polystyrene (PLA-PDMA-PS) as shown.
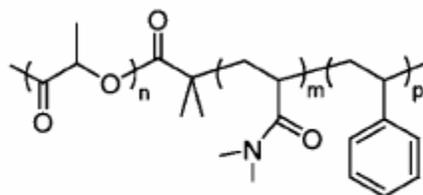
PLA-PDMA-PS

When their molecular weight and composition are within carefully specified limits these materials spontaneously self-assemble into cylinders[7-9] that can be aligned perpendicularly to the membrane surface. The PLA block forms the cylinders coated with a thin layer of PDMA in a surrounding PS continuum. After this structure is formed, the cylindrical block is removed by etching with a basic solution.

The result is a new ultrafiltration membrane like that shown on the right of Figure 1. The large concentration of pores (ca. 10^{11} cm^{-2}) means that this membrane will have a large flux: if we can make a 0.3 μm selective layer on a support, we can easily obtain fluxes similar to those achieved in phase inversion membranes. The monodisperse pores promise a much sharper molecular weight cut-off. A membrane like this could really represent a step change in the capability of ultrafiltration. Here we begin to measure the properties of nanoporous membranes made by etching block copolymers. We decided to start by measuring the diffusion of gases because the diffusion of gases is chemically simple. It is unaffected by solvation, by solute charge, or by polymer polarity. Also it provides a chance to see if the geometry of etched pores shown in the right panel of Figure 1 is really as simple as it looks. Later, we plan to study ultrafiltration across these porous membranes.

The measurements are made in the gas diffusion cell[10], shown in the inset of Figure 2, a well established technique for measuring gas transport. The cell consists of two compartments separated by the membrane. Receiving and donating compartment pressures are measured by electronic transducers and the temperature is monitored with a thermocouple. Typical data for nitrogen diffusion across the PS-PDMA-PLA triblock copolymer membranes are shown in Figure 2. The data are plotted as the logarithm of the ratio of pressure differences vs. time. The slope of this linear plot is proportional to the permeability: a larger slope means a larger

permeability. The slope for the unetched membrane is near zero because it has no pores, and diffusion through the polymer itself is so small. The slope of two different etched membranes is much larger and equal within 5 percent. We believe that this is typical of the reproducibility of our experiments.
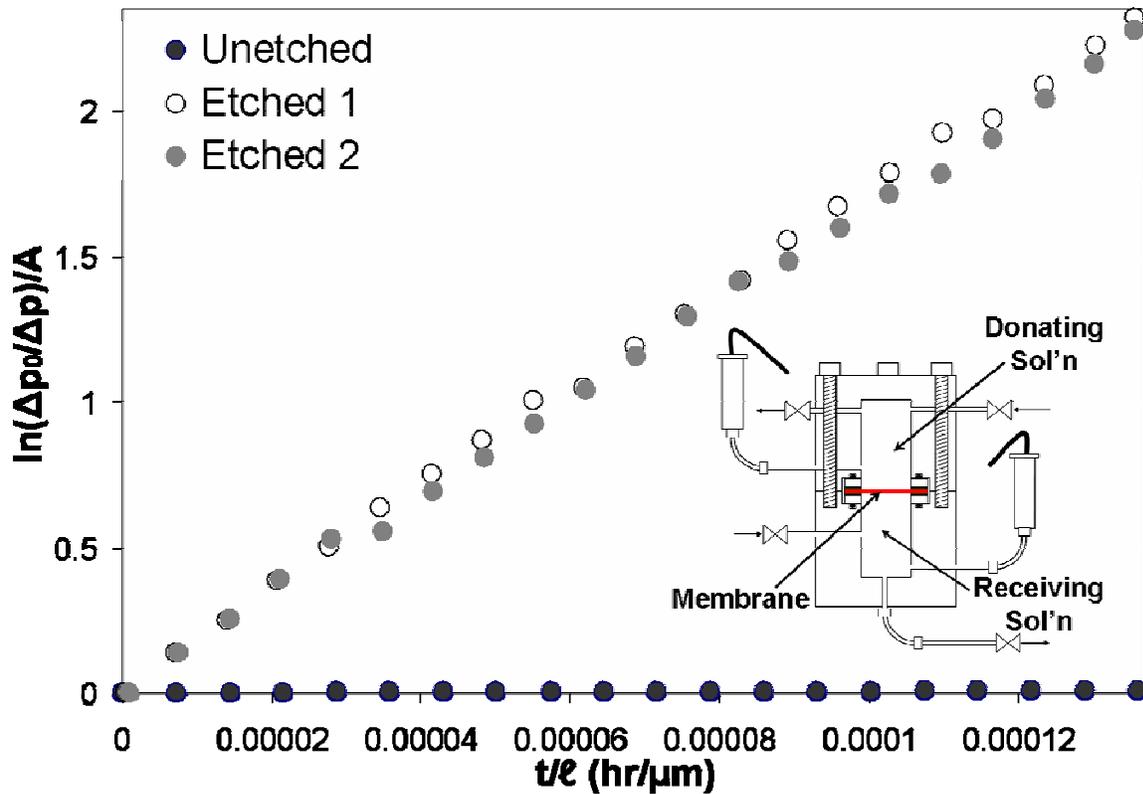
Figure 2. <u>Diffusion Data *vs*. Etching</u>. The pressure with time is reproducible for etched films, but very small for nonetched films.

The mechanism of gas diffusion in small pores depends on the Knudsen number,[11] i.e., the ratio of the mean-free path to the pore diameter. When the mean-free path is much smaller than the pore size, the Knudsen number is small and diffusion is the result of random collisions between different molecules. When this occurs the diffusion coefficient can be calculated using the Chapman-Enskog equation from kinetic theory. The situation when the mean-free path is

much larger than the pore diameter is different. Now, when the Knudsen number is large, diffusion is the result of collisions between the diffusing gas and the walls of the pores. Knudsen theory can be used to predict the diffusion coefficient. The predictions made by these theories are used as a comparison for our experimental diffusion results.

The transport mechanism in these membranes is Knudsen diffusion, as shown by the summary of results in Table I. The upper part of this table gives the results for the PS-PDMA-PLA etched block copolymer membranes, and the lower part is for the track-etched membranes studied as a benchmark. The organization of the results within these two parts is the same. The first column gives diffusing gas, and the second column gives the experimentally determined diffusion coefficient. The next two columns give the diffusion coefficients calculated from Knudsen and kinetic theories, respectively. The last two columns give the membrane selectivities relative to helium found from experiment and calculated for Knudsen diffusion.

The results in Table I show conclusively that transport through the pores etched in the block copolymer occurs by Knudsen diffusion. The measured coefficients are within 5 percent of those calculated from the Knudsen mechanism. They are about six times smaller than the values expected from kinetic theory. This is expected because estimates of the mean-free path of these gases average about ten times larger than the pores themselves. In addition, the selectivities measured relative to helium are close to those calculated from Equation 2. They are a function only of the inverse square root of the molecular weight and are not dependent on factors like the collision diameter, which alter kinetic theory estimations. Finally, the experiments with the track-etched membranes used as a benchmark give very similar results, justifying our procedure.

Table I. <u>Experimental and Predicted Diffusion Coefficients for Etched PS-PDMA-PLA Block Copolymer Membranes and for Commercial Track-Etched Polycarbonate Membranes</u>. Diffusion coefficients are given in cm^2/s.

PS-PDMA-PLA

Gas	D (Experimental)[a]	D (Knudsen)[b]	D (Kinetic Theory)	Experimental α	Predicted α
He	0.051	0.051	1.12	1.00	1.00
N_2	0.019	0.019	0.135	2.59	2.65
O_2	0.017	0.018	0.137	2.90	2.83
Ar	0.017	0.016	0.122	3.08	3.16

Poretics

Gas	D (Experimental)[a]	D (Knudsen)[b]	D (Kinetic Theory)	Experimental α_{He}	Predicted α_{He}
He	0.128	0.124	1.12	1.00	1.00
Ar	0.040	0.039	0.122	3.21	3.16

[a] Assuming void fraction $\varepsilon = 0.26$
[b] Assuming 13.7 nm pores
[c] Assuming void fraction $\varepsilon = 0.006$
[d] Assuming 29.5 nm pores

The results in Table I begin to realize the promise of etched block copolymer membranes for fast ultrafiltration with sharp molecular weight cut-off. However, the predicted values of Knudsen diffusion coefficients are based on a pore diameter of 13.7 nm, somewhat less than the value of 16.8 nm found from both electron microscopy and SAXS. We explored this discrepancy via experiment as well, by measuring flow of water liquid through the etched pores. A membrane is clamped into the diaphragm cell shown inset of Figure 3. This cell consists of two compartments separated by the membrane. The donating compartment is attached to a large reservoir and the receiving compartment is connected to a precision bore capillary. The large reservoir is completely filled with pure water, while the capillary is partly filled. Because the water height in the reservoir is greater than that in the capillary, a hydrostatic pressure difference drives the flow through the membrane. The fluid velocity is laminar and described by the Hagen-Poiseuille law because the pores are so small. The results are shown in Figure 3, where the data plotted as the logarithm of the ratio of height difference are linear in time. The average pore diameter as calculated from the slope in Figure 3 is 13.0 nm, in close agreement with the diffusion results.
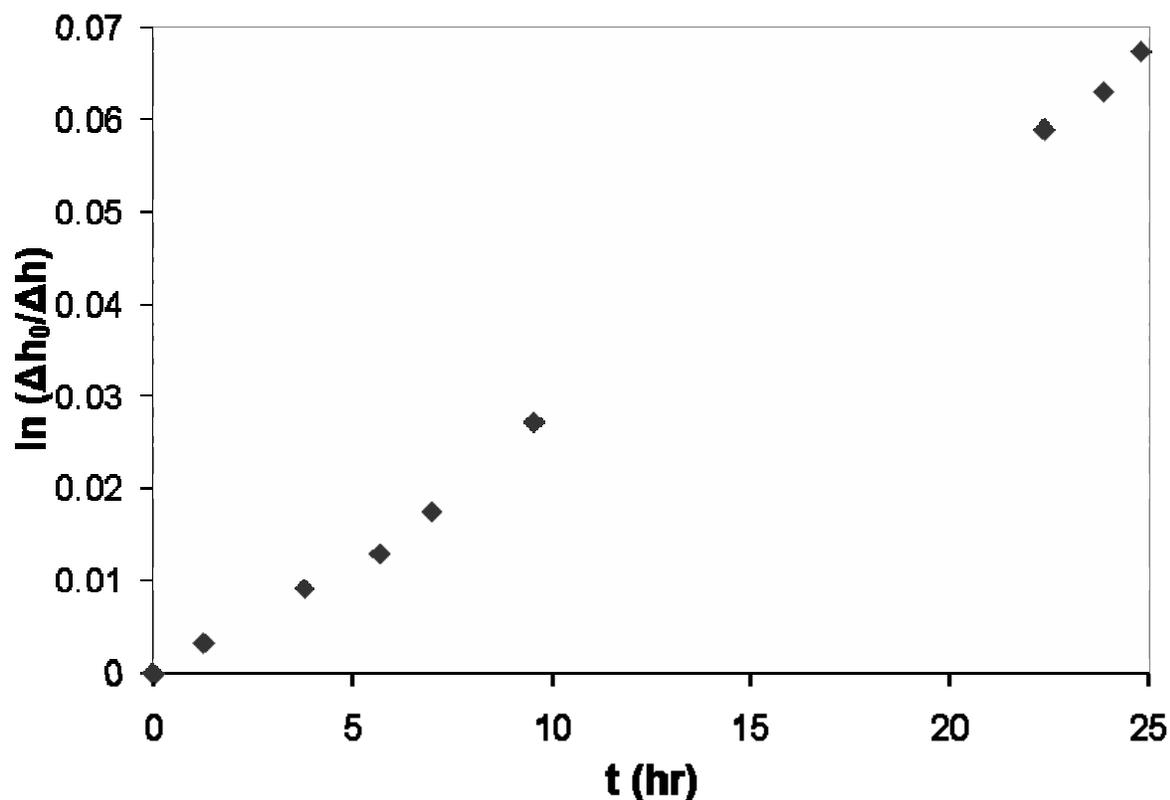
Figure 3. Liquid Water Flow Through Nanoetched Pores. The solid line is based on a pore
diameter of 13 nm, close to the value of 13.7 nm found from the data in Table I.

The results given above begin to realize the promise of ultrafiltration membranes based

on etched block copolymers. The diffusion coefficients that are observed are consistent with

those expected for Knudsen diffusion. The close agreement between theory and experiment

implies that the pore geometry we have obtained is close to that of right circular cylinders with

an aspect ratio of over 100,000:1. Any branching or constrictions in the pores would mean that

the agreement between theory and experiment would be weaker. At the same time, the diffusion

data are consistent with a large body of earlier literature that explores whether these simple

theories of membrane transport are valid for very small pores.[12-14] Our data, which seem reliable,

do support these simple theories, both for gases and liquids.[11,14] The nearly monodisperse pores

within these films should give sharp molecular weight cut-offs like those observed using track-etched membranes.

Finally, we turn to the two steps which must come next in the development of these materials as ultrafiltration membranes. First, we must show that these new nanopores do, in fact, show the sharp molecular weight cut-off which we expect. The second step needed to develop these materials is much more demanding: we must develop an easier method to align these nanopores in thin films. This alignment method must be suitable for large scale manufacture of these new ultrafiltration membranes. Our current alignment method uses shear alignment,[15-17] followed by slicing the resulting polymer monolith into short lengths and gluing these together to make a membrane. This is completely unsuitable for large-scale production. An alternative which we will probably pursue, uses a block copolymer which self-assembles into a bicontinuous "gyroid" structure.[18] This new structure will require no special methods for alignment, but it may plug extremely easily. We look forward to these future efforts to see if the huge potential of these new ultrafiltration membranes can continue to be realized.

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