# UTILIZATION OF BLOCK COPOLYMERS AS ULTRAFILTRATION MEMBRANES.

<u>Background</u>.   Block copolymers offer a potential route to superior ultrafiltration membranes.  Such membranes are made of a polymer with two chemically distinct segments which self-assemble into a wide variety of structures[1].  Such nanometer-sized structures can include hexagonally packed cylinders of one component oriented perpendicularly to the surface of the membrane, if properly aligned[2].  When these cylinders are removed by selective etching, the resulting pores are closely packed and monodisperse.

Such membranes have shown promise for ultrafiltration[3,4].  These monodispersed pores should give high selectivity, and their close packing should allow high fluxes.  The membranes' flat surface suggests that fouling will be reduced. However, even starting to evaluate these possible advantages means that the cylinders in the self-assembled structure must be carefully oriented perpendicular to the membrane surface.  In this research, we avoid the formidable problem of alignment by using a bicontinuous network structure.  Where a "doubly reactive" block copolymer polynorbornenylethyl styrene-polylactide is used as a structural template during the crosslinking of dicyclopentadiene[5]. After crosslinking and subsequent etching with dilute base, the dicyclopentadiene membrane which remains has a nanoporous structure.  Such a membrane does have nearly monodisperse pores and so should give high selectivity.  Additionally, the membrane's pores are closely packed and so should be capable of high flux.

This research explores how much of the promise of these membranes is real.  We explore the details of the geometry by measuring the diffusion of a variety of gases across

these membranes.  We measure the degree of etching and wetting by determining the flow of water at various values of pH and ionic strength.  We demonstrate membrane selectivity by studying transport of a series of polyethylene glycols as well as mixtures of dextrans.  The research shows that the promise of these membranes is real, but it also identifies additional barriers which need to be overcome to realize practical value.

Results.  The experiments in this work are based on membranes 100 microns thick.  For gas diffusion experiments they are mounted in a diaphragm cell[6].  This cell consists of two compartments separated by a membrane.  The top, "donating" compartment initially contains gases at high pressure which diffuses across the membrane into the bottom, "receiving" compartment. The change in pressure is recorded a function of time, the results for a variety of gases are shown in Figure 1. The slope of the curves is used to calculate the effective diffusion coefficient for each gas. Table I presents the selectivities for the gases relative to helium diffusion.  Helium is chosen as the reference gas because it is not expected to interact with the solid membrane (Yang book). The experimental selectivities are within an average of 5 percent of those predicted demonstrating they have molecular weight dependence consistent with Knudsen diffusion, i.e. $\sqrt{1/\tilde{m}}$ [7].
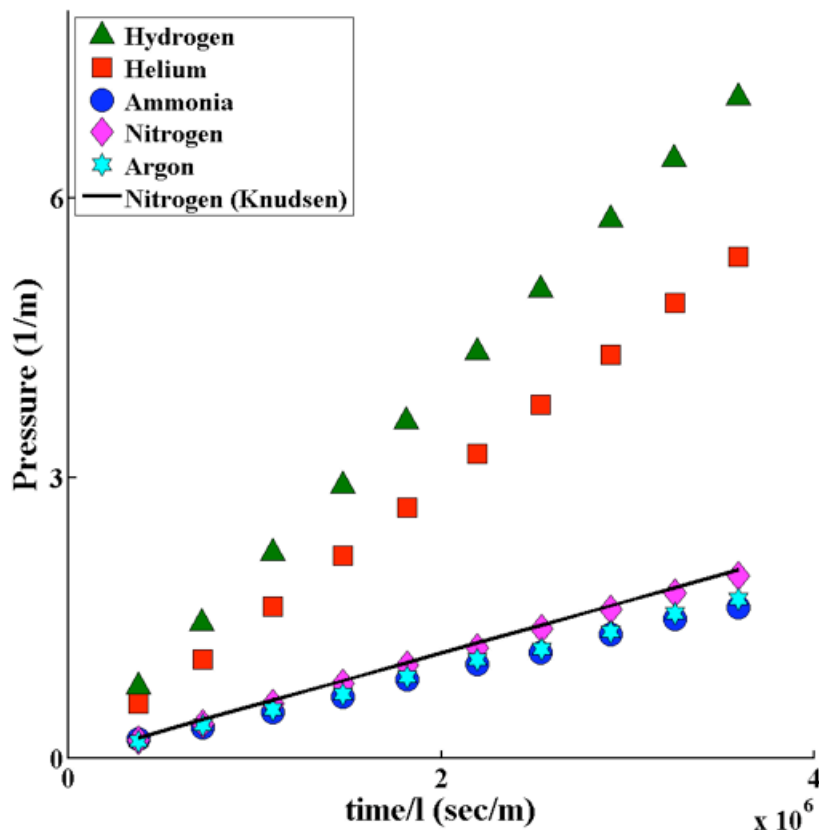
Figure 1: Gases Diffuse Across the Membrane by a Knudsen Mechanism. The slope of the experimental data is proportional to the gas permeability. Knudsen theory, shown for $N_2$ as a solid line, predicts a $\sqrt{\dfrac{1}{M}}$ dependence.

Table 1: Summary of Gas Diffusion Data.

| Solute | $D_{eff}$ | $\alpha_{exp}$ | $\alpha_{Kn}$ |
|--------|-----------|----------------|---------------|
| $H_2$ | 0.0184 | 0.84 | 0.71 |
| He | 0.0154 | 1.00 | 1.00 |
| $NH_3$ | 0.0043 | 3.58 | 2.06 |
| $N_2$ | 0.0055 | 2.80 | 2.66 |
| Ar | 0.0047 | 3.27 | 3.15 |

Liquid flow measurements were made using an Amicon stirred cell set up. A pressure head was applied using compressed nitrogen and the mass of permeating

solution recorded as a function of time. The slope of these plots were used to calculate the flux through the membrane at a given pressure drop. The flux, in m$^3$ per m$^2$ second, is plotted in Figure 2 *vs* the pressure drop, in kPa. A linear relation as expected from the Hagen-Poiseuille relationship is observed. The fluxes are small, around $1 \cdot 10^{-6}$ m$^3$/m$^2$ sec (4 gal/ft$^2$ day) at a pressure drop of 30 kPa. However, if the membrane thicknesses were decreased from 100 μm to 0.1 μm and the pressure drop was increased to 200 kPa, the flux would be $1.4 \cdot 10^{-2}$ m$^3$/m$^2$ sec (28,000 gal/ft$^2$ day). These experiments do not show these high fluxes, though they do suggest the potential of these membranes.
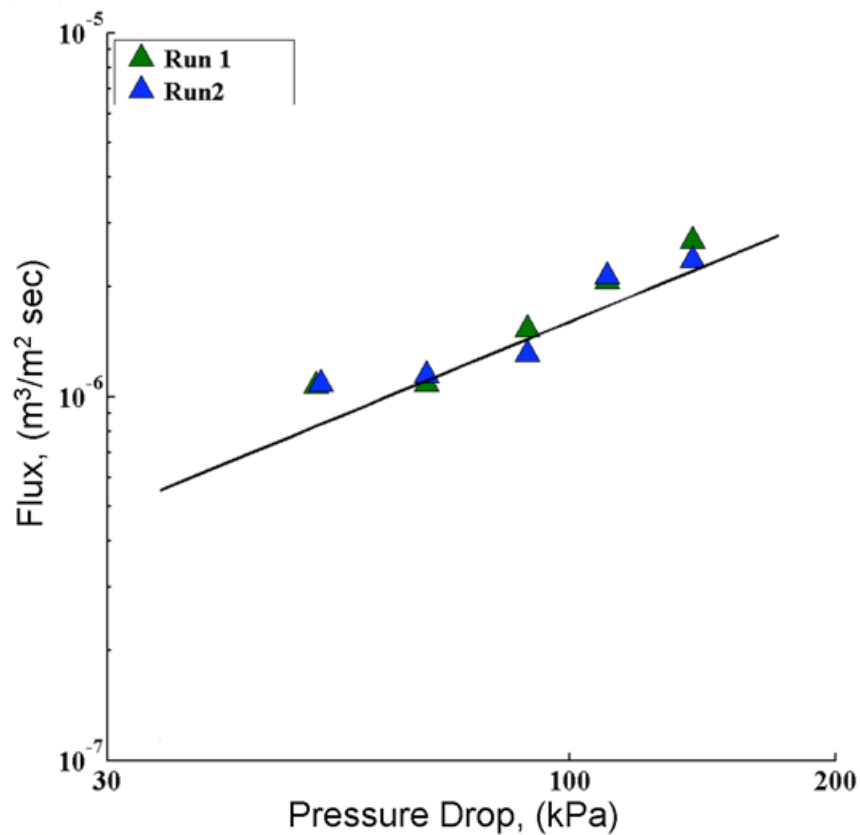


Figure 5:  Water Flux is Proportional to Pressure Drop. Experimentally observed fluxes are compared to a theoretical prediction based on a pore diameter of 14.2 nm and a tortuosity of 1.56.

Hexagonally packed right cylinders would give a higher flux but they are difficult to align. Because the bicontinuous structure used here is isotropic, it requires no special

alignment. The price paid is the lower flux and the less well-defined pore structure. These results of the gas diffusion and liquid flow show that the membranes have reproducible pores, which span the membrane thickness.

The ultrafiltration experiments begin to explore the practical value of these membranes. A series of experiments were made with a mixed feed of dextrans. These experiments, performed at GE Osmonics, imitate quality control studies carried out industrially[8]. In experiments like these, all solutes are fed simultaneously, and the flux of each out of the membrane is determined using SEC with refractive index. The ratio of the appropriate peak areas from the RI detector output is used to calculate the rejection curves shown in Figure 3.
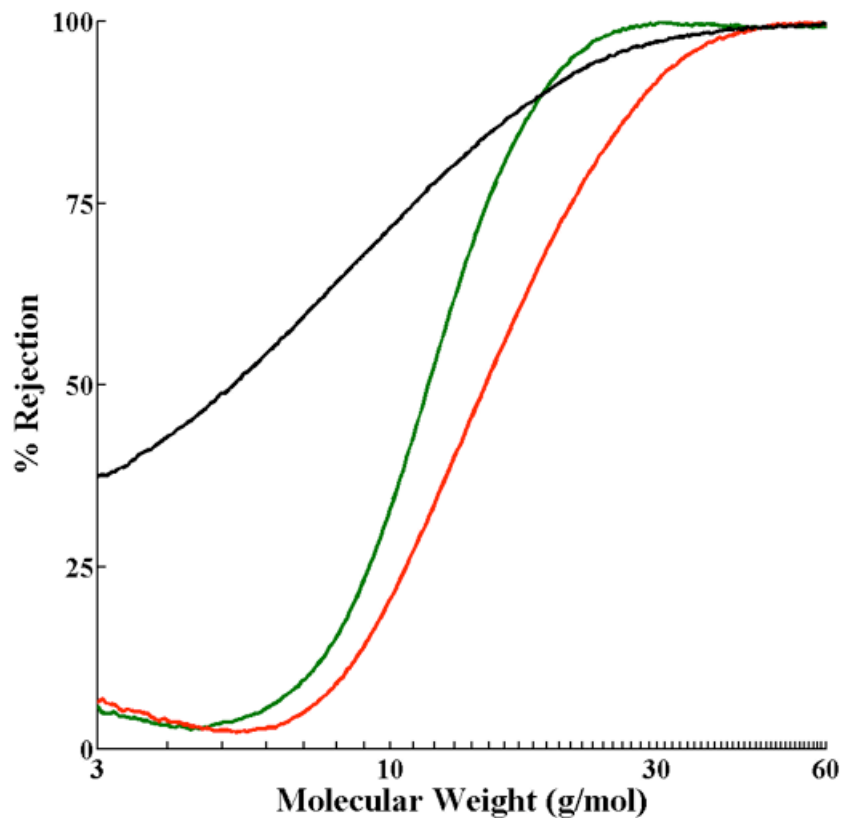


Figure 3.   <u>PDCPD Membranes Show a Sharper MWCO Than a Membrane Made by Phase Inversion</u>. The green (32 kDa) and red (65 kDa) lines are rejection

curves for the membranes developed in this work.  The black line is the rejection curve for a representative phase inversion membrane.

We would like these curves to be step functions with no rejection until a critical molecular weight and then complete rejection above this critical weight.  However, this is inconsistent with the underlying theory of Brenner and Bungay[9], where the rejection is gentler because of altered free volume and drag of the solute within the pores.  Even though step functions are not possible the results in Figure 3 are encouraging.  The data for two membranes based on etched, self-assembled, block copolymer-based membranes show a sharper rejection than those of the commercial membrane.  Moreover, the data for a membrane with a 32 kD chain reassuringly show a cut-off at lower molecular weight for a 65 kD chain.  This suggests that block copolymer membrane properties can be further tuned to perform a specific desired separation.  These membranes show promise as ultrafilters.  The sharp rejection curves demonstrate the membranes are able to perform separations better than current technologies.  The flux data suggest that if thin films can be made these membranes will be comparable to current membranes.  The final area that must be explored is the tendency of theses membranes to foul during operation.  These studies have begun and seem promising.

Reference.

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