The Development of Novel Nanoporous Membrane for Bioanalytical Chemistry

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Outline

- Motivation
- Mesoporous alumina membranes
- Chemistry and physics of acrylamide gels
- Characterization techniques
- Conclusions & future work

Bioanalytical Chemistry

What is Bioanalytical Chemistry?

The science of identifying specific biological organisms (i.e., bacteria, viruses, and toxins).

Applications

- Medical diagnosis (i.e., point-of-care and laboratory).
- Environmental monitoring (i.e., water, air, soil).
- Food and pharmaceutical production.

Current Trends

- Lab-on-a-chip

Nanoporous Membranes

Motivation

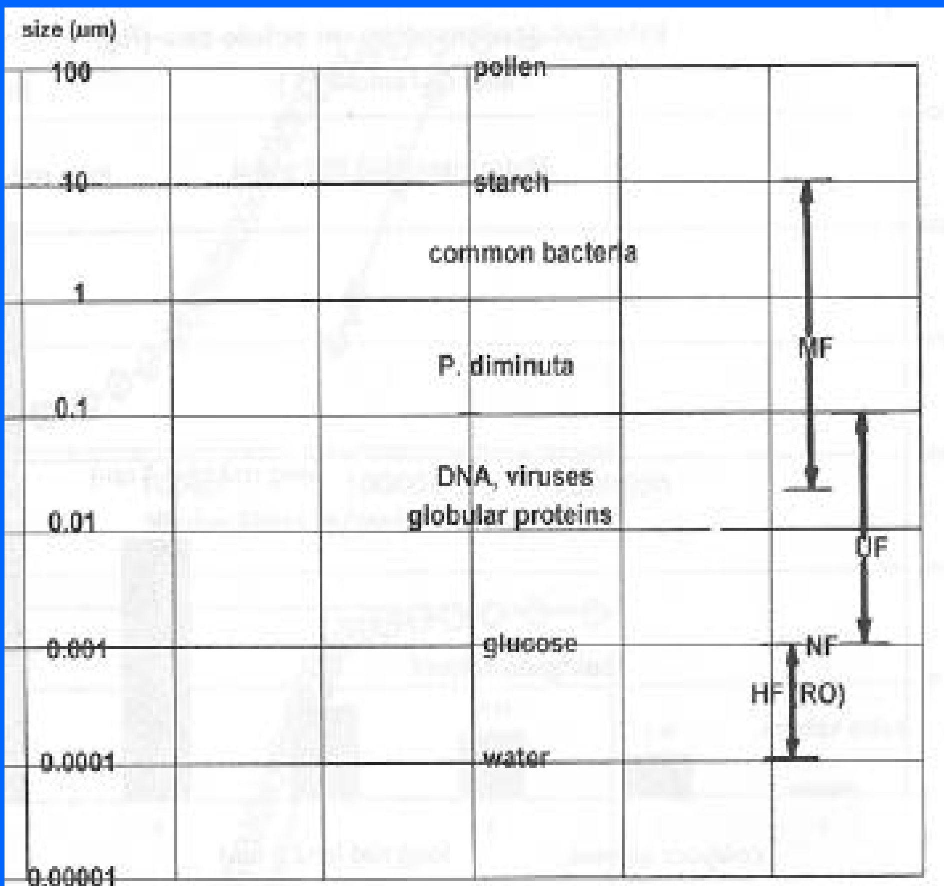
Bioanalytical samples typically are very dirty and there is a need for a technique that can quickly isolates molecules in the 1,000-30,000 Dalton molecular weight range.

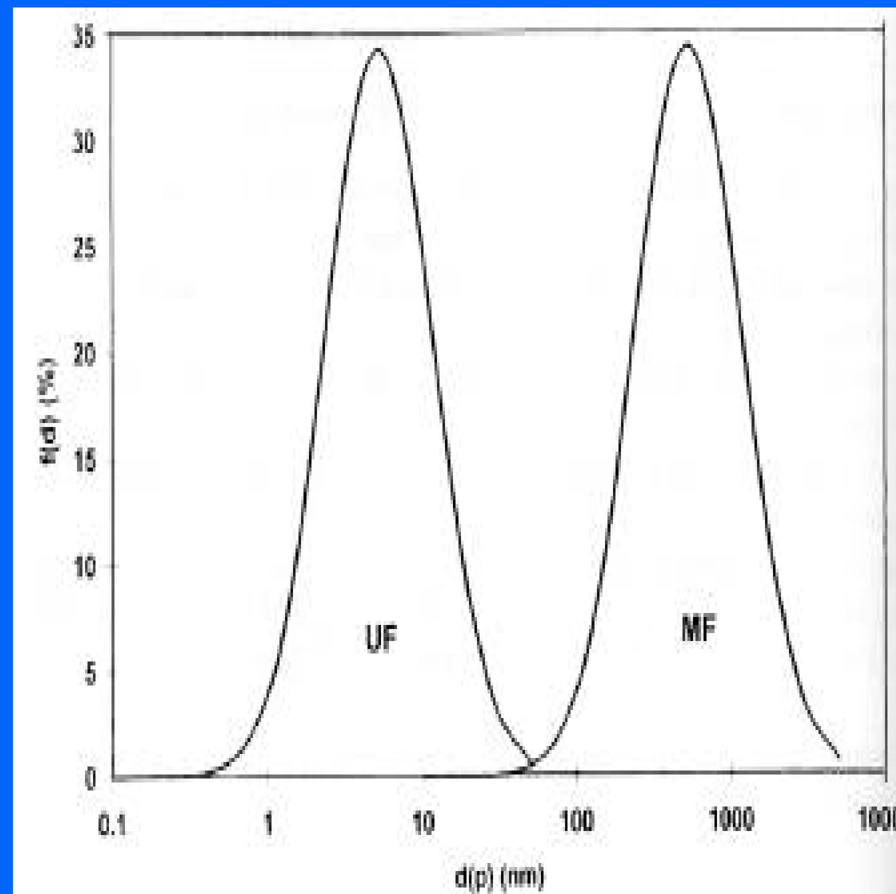
Approach:

- Synthesizing a novel nanoporous membrane for ultrafiltration.
- High density 1~ 2 nm nanometer sizes pores
- Thin film thickness of ~ 100 nm for high flux.
- High chemical and mechanical stability

Nanoporous Membranes

Current filtration technologies



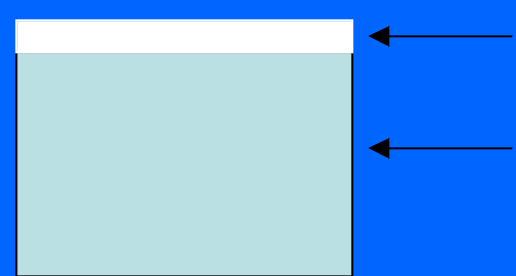


Source: L. J. Zeman, "Microfiltration and Ultrafiltration", pp. 13 & 182.

Novel Nanoporous Membrane

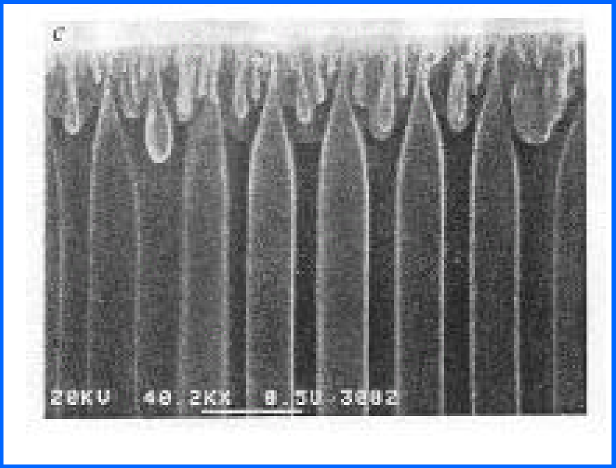
Approach:

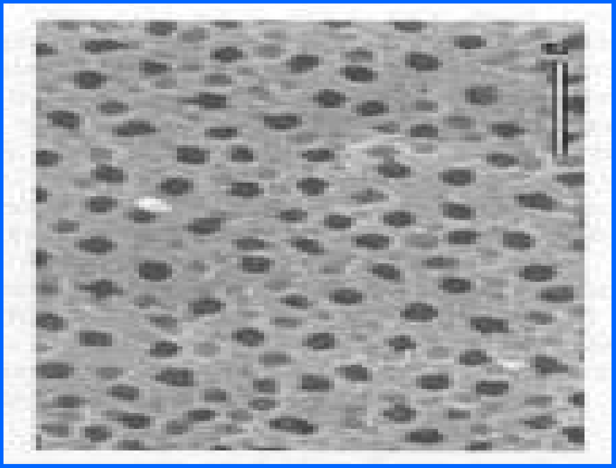
1. Start with a mesoporous alumina membrane with 20 nm pores.
2. Spin-coating a thin layer of polymeric monomer on an alumina membrane.
3. Cross-link the monomer to form a thin polymer film with 1-2 nm pores.



Alumina Membrane

1. Anodisc® alumina membranes have highly uniform pore size between 20-100 nm and high densities of pores.
2. They also have good thermal, chemical, and mechanical properties.
3. These membranes having a molecular weight cut-off of 30 ~ 60 kDa.





Source: N.T. Hovijitra, “Gas and Liquid Phase Permeability of Nanoporous Alumina Membranes”, unpublished, pp. 16 & 29

Polymer Membrane

Polyacryalmide Gel (PAG)

- The polymer has a well defined polymerization chemistry with a UV initiator.
- The monomer and initiator have a low viscosity and can be spin coated onto surfaces.
- The cross-linked polymer has a well defined pore size that can be tuned.
- Relatively chemically inert and mechanical stable for a polymer.

Novel Nanoporous Membrane

Free Radical Polymerization

General Reaction Scheme:

1. Initiation: $I \xrightarrow[\text{or heat}]{\text{UV light}} R\cdot$

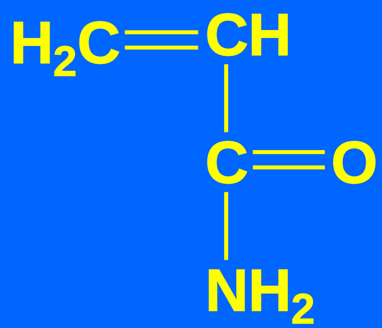
2. Addition $R\cdot + \text{Monomer} \longrightarrow P_N\cdot$

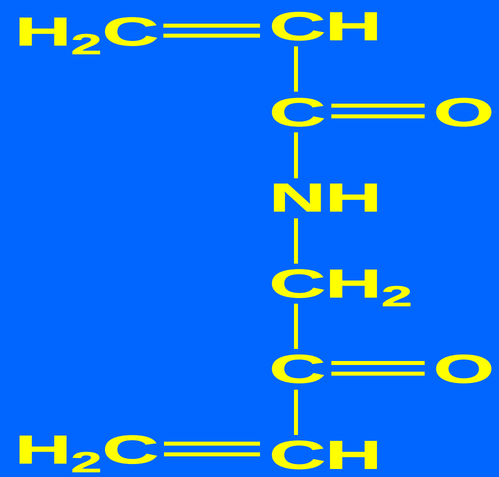
3. Propagation: $P_N\cdot + \text{Monomer} \longrightarrow P_{N+1}\cdot$

4. Termination: $P_N\cdot + P_M\cdot \longrightarrow P_{N+M}$

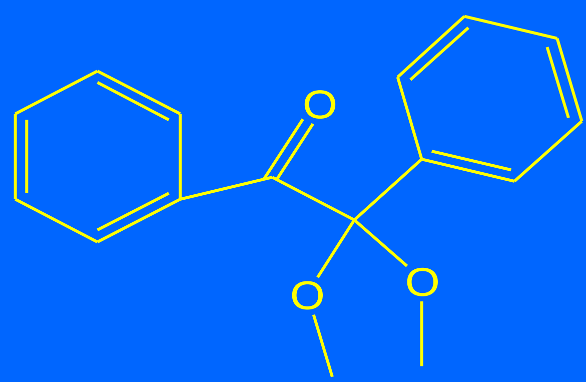
Polyacrylamide Chemistry

Monomers: Acrylamide and N,N'-Methylenebisacrylamide

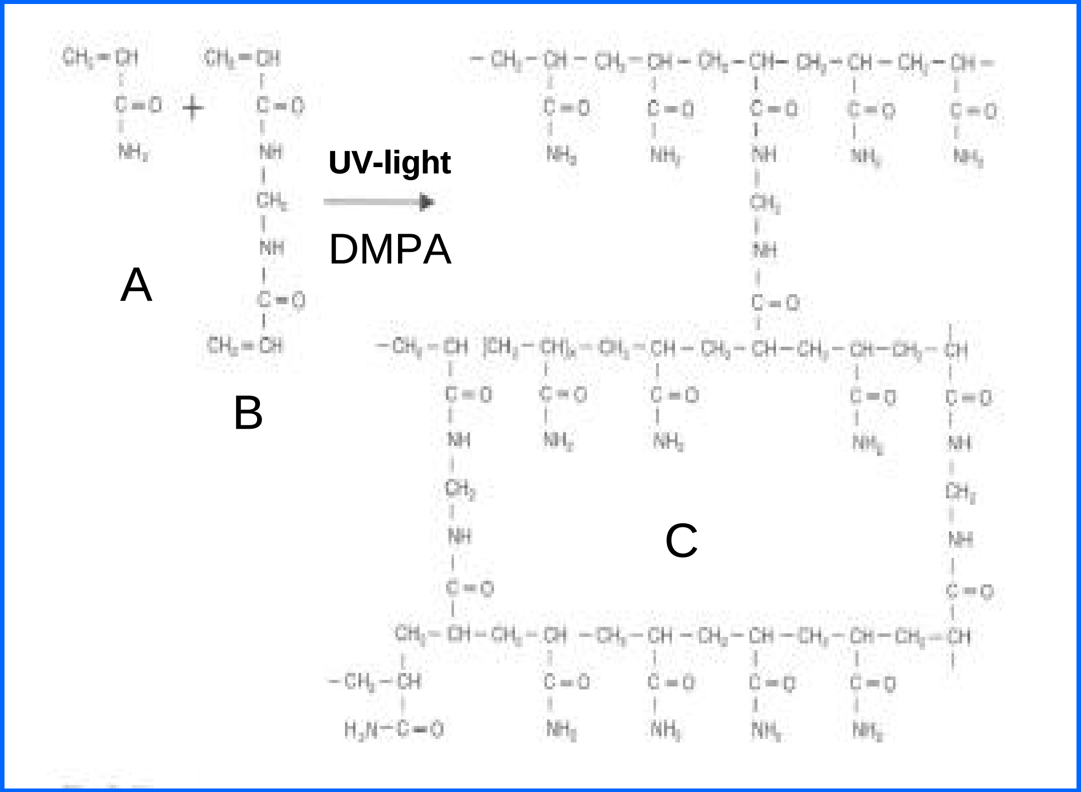




UV-initiator: 2, 2-Dimethoxy-2-phenyl Acetophenone (DMPA).



Mechanism of UV-Initiator free radical polymerization for PAG



A : Acrylamide

B: N,N'-Methylenebisacrylamide

C: PAG

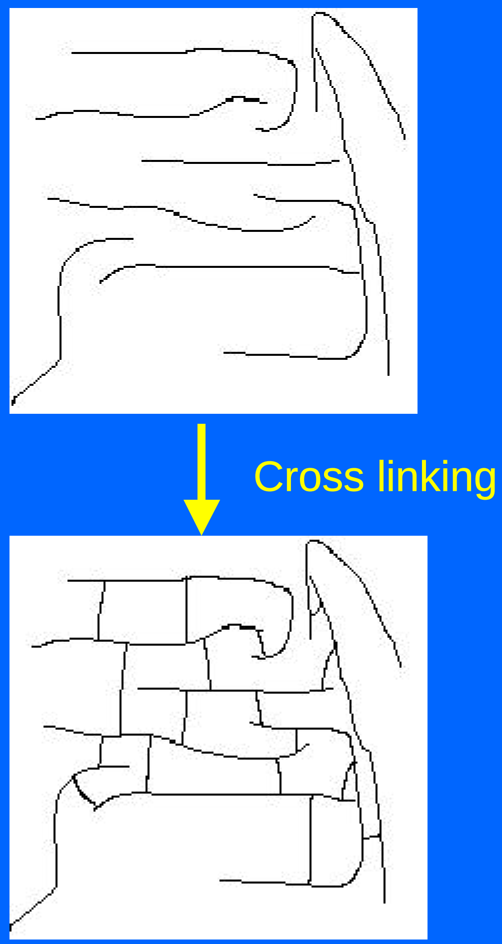
Development of Nanoporous Membrane

Cross Linking

1. A polymer’s properties can be tailored to the desired need by cross linking.

2. Cross linking creates bonds between different polymer molecules

3. Cross linking will give polymer a higher mechanical sustainability.



Cross linking process of a polymer

PAG Pore Size

The pore size of PAG is the function of the 2 variables:

I. Concentration of PAG, T

II. Degree of cross-linking, C

$$T = \frac{(a+b)*100}{V} \, [\%] \quad ;$$

$$C = \frac{b*100}{(a+b)} \, [\%] \, ,$$

Where,

a: Mass of acrylamide,

b: Mass of N,N'-Methylenebisacrylamide,

V: Volume of gelling solution.

PAG Pore Size

1. The pore size decreases when C remains constant and T increases. ***So we want to increase the concentration of monomer.***

2. When T remains constant and C increases, the pore size follows a parabolic function: the minimum being at C = 4 ~ 5 %.

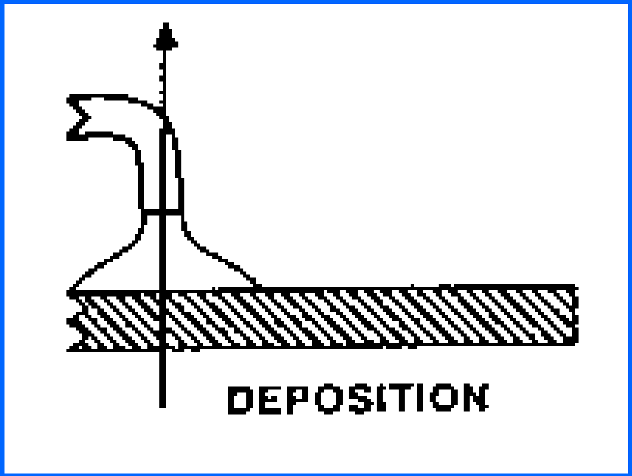
Source: R. Westermeier. “Electrophoresis in Practice”, 2nd Edition, pp. 18.

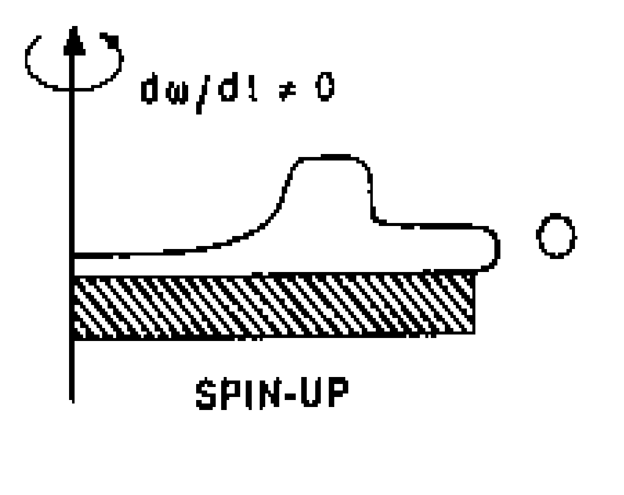
Spin Coating

1. The deposition, an excessive amount of fluid is dispensed onto a substrate.

2. In the spin up stage, the substrate is accelerated.

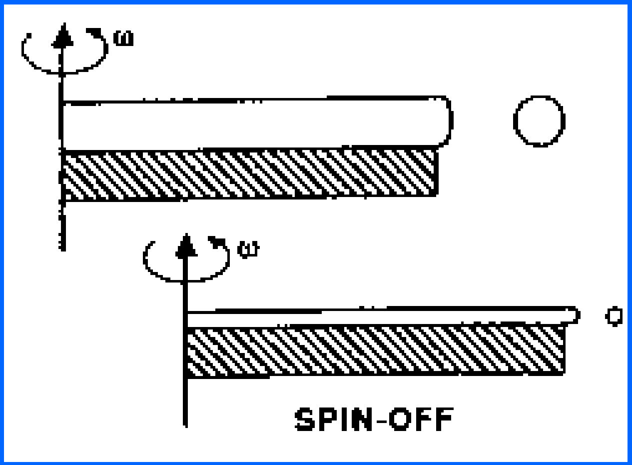
- As rotational forces are transferred, a wave fronts are flowed to the substrate edge, leaving a uniform layer behind.





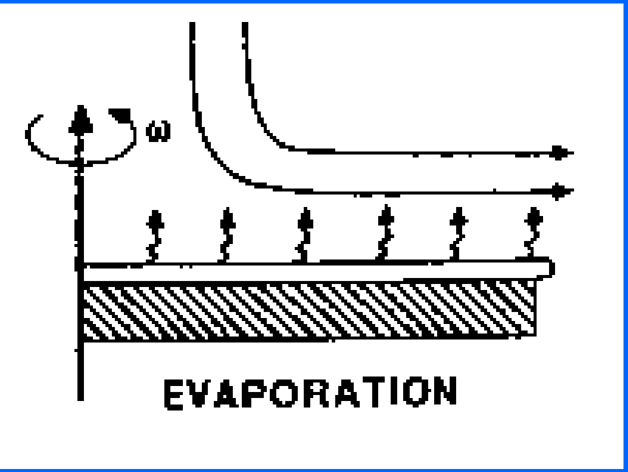
Spin Coating

3. The spin off stage - the excess fluid is flung off the substrate surface.



- The fluid is being thinned by centrifugal forces.

4. Evaporation is the complex process where the excess fluid is absorbed into the atmosphere.



Spin Coating

$$H = \frac{K\,C^{=}\,\_^{=}}{\omega^{-}}$$

- The thickness (H) of the film is mainly depending on the concentration (c), the intrinsic viscosity (_), and the angular speed (ω) of the fluids.

Where, K = the calibration constant of spin coater,

_,_,_ = various exponential factors.

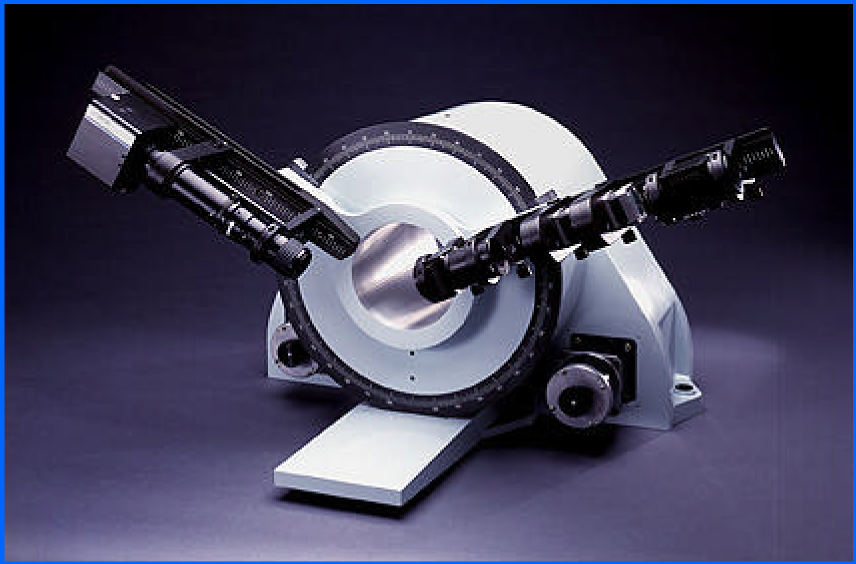
Spin-coating of PAG

1. Mixture of 30% PAG solution with 10 wt% DMPA is spin-coated on a substrate.
2. Spin speed of 3000 revolutions per minute (rpm) for 30 seconds.
3. The sample is exposed to UV light for one minute.
4. Soaking in deionized distilled water (dd-H_2O) for 24 hours.

Characterization: Ellipsometry

Ellipsometry

- An optical technique that uses polarized light to probe the dielectric properties of a sample.
- Its common application for the analysis of very thin films.



Beaglehole Instruments: Imaging Ellipsometry.

Ellipsometry

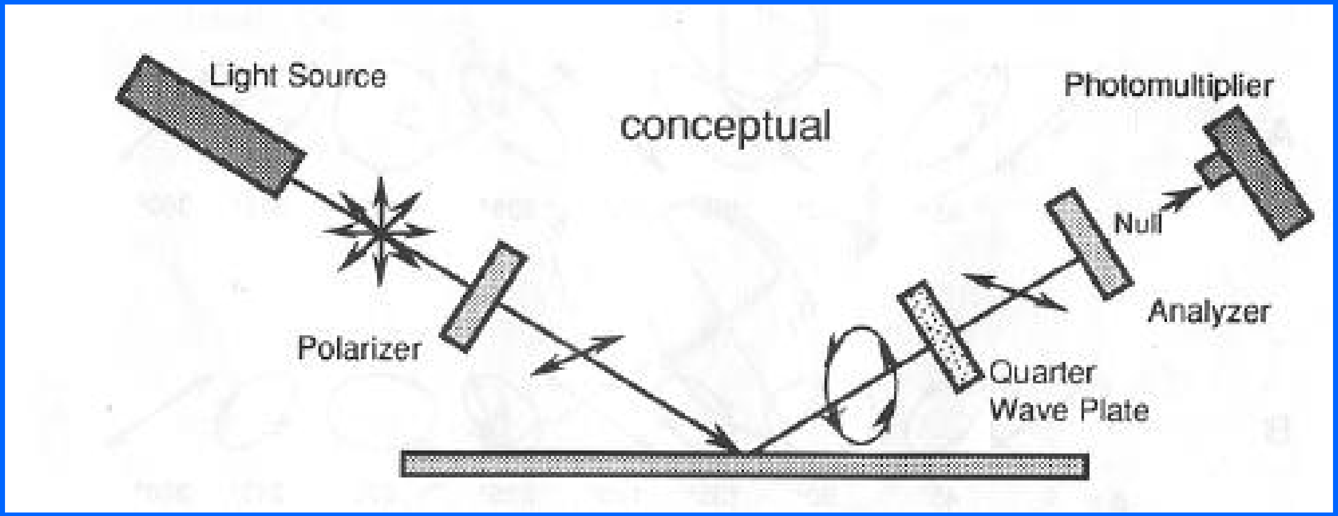


Figure 5. Conceptual mechanism of Ellisopmetry.

Source: H. G. Tompkins, “A User’s Guide to Ellipsometry”, pp.26

- Ellipsometry can yield information about the layers, through the analysis of the polarization state of the light that is reflected,

Characterization: Permeability

$$\text{Permeability} = \frac{\text{flow rate}}{\text{pressure}}$$

Characterization:

I. Physical Properties:

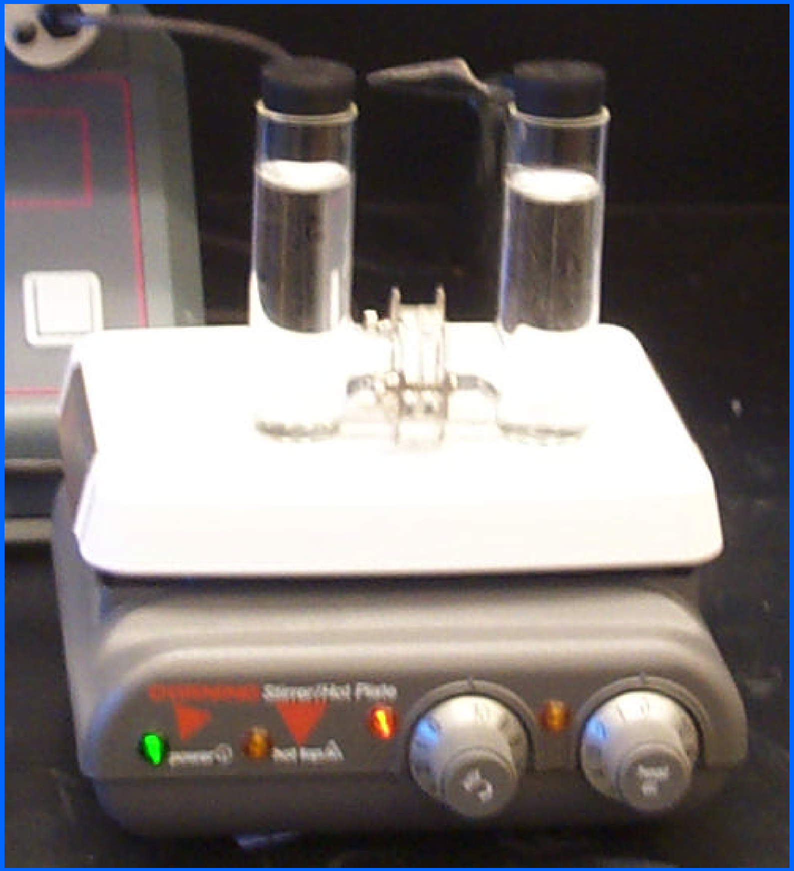
- Measurement on the flow rate in liquid/gas.
- Measurement on the permeability in liquid/gas.

Liquid/Gas flow rate measure equipment.

Courtesy by Norman T. Hovijitra.

Characterization: Diffusion Cell

- Diffusion Cell - common techniques to measure the molecular weight cut-off of a membrane.
- There is an existence of concentration gradient between two cells (tubes).
- Measuring the changes of the concentration gives information of the molecular weight cut-off.



Diffusion Cell

Novel Nanoporous Membrane

Future work :

1. Characterization:
   - Ellipsometry on measuring the thickness.
   - Permeability.
   - Diffusion Cell on molecular weight cut-off.
   - Atomic Force Microscope (AFM) imaging on the nanoporous membrane and characterization of mechanical properties.

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