Polyphosphazene-based gas separation membranes: Pushing the boundaries

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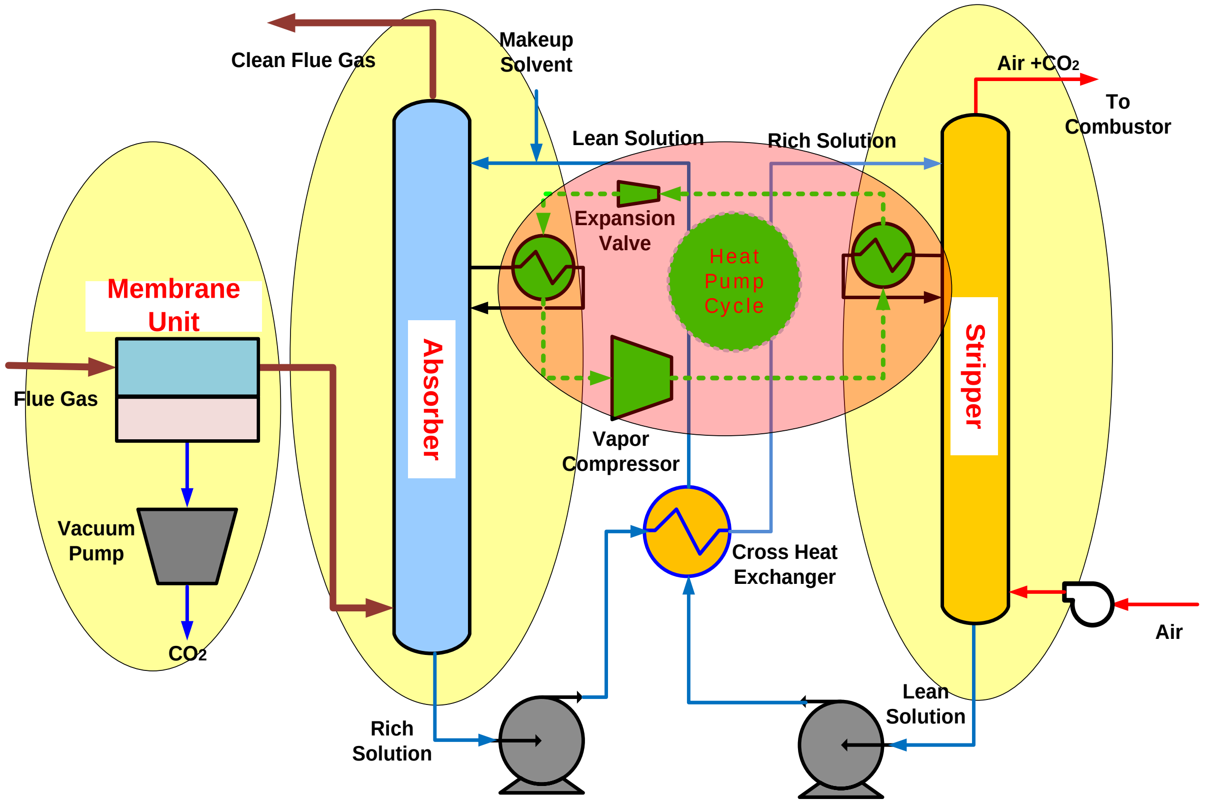
Membrane/Solvent Integrated Process

Advantages

- Tail-end technology which is easily used in retrofits
- No steam extraction is required
- Heat pump is seamlessly integrated into the cooling and heating of absorption/stripping process
- Operating pressure of the stripper will be very flexible depending on the low quality heat

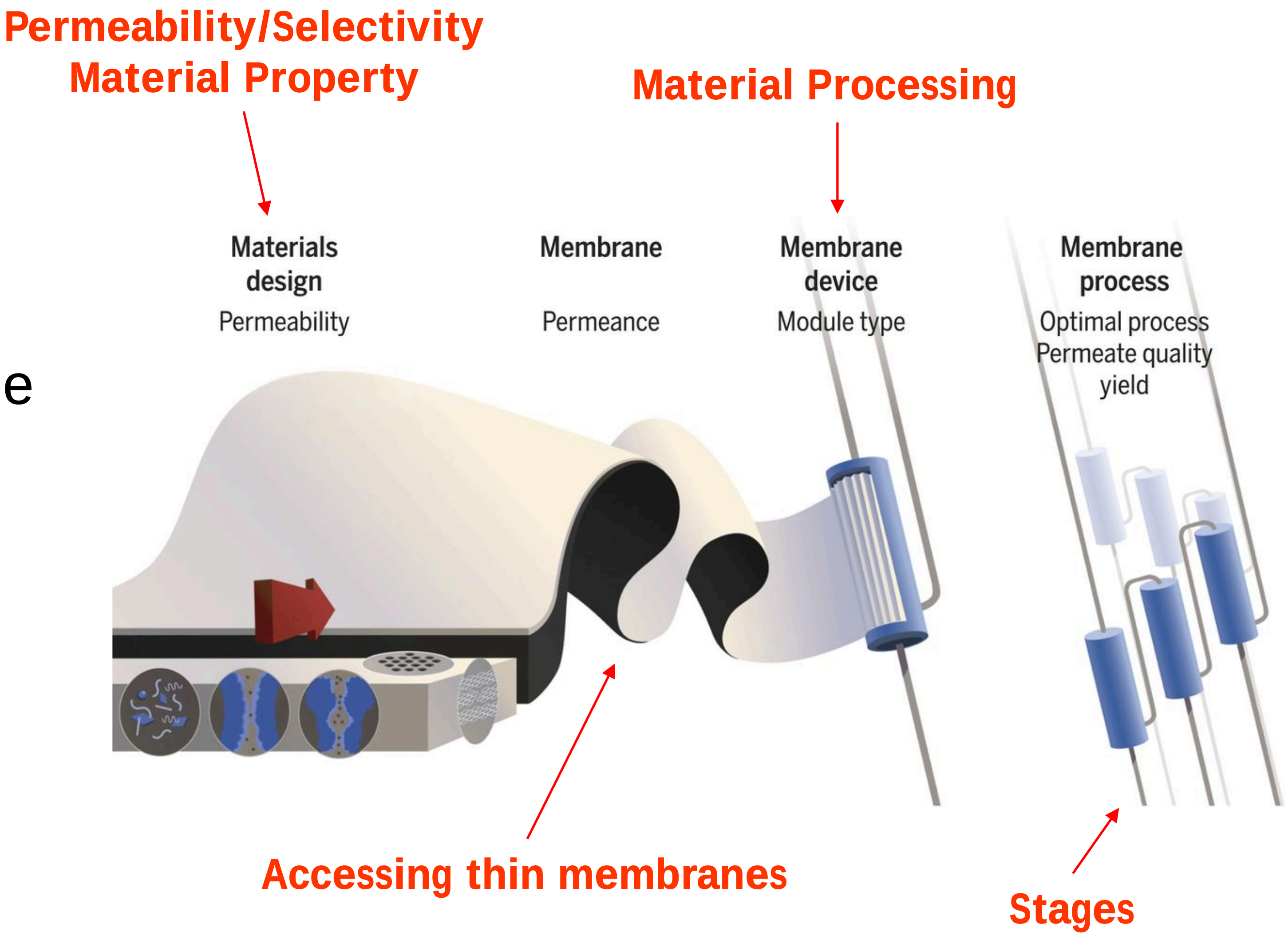
Disadvantage

- Capital cost could be intensive



Synthetic Membranes

- Used in variety of industrial, medical, and environmental applications.
  - desalination, dialysis, sterile filtration, food processing, dehydration
- Low energy requirements
- Compact design
- No moving parts and modular



Ho Bum Park et al. Science 2017;356:eaab0530

Membrane Terms

- Permeability is a *material* property: describes rate of permeation of a solute through a material, normalized by its thickness and the pressure driving force

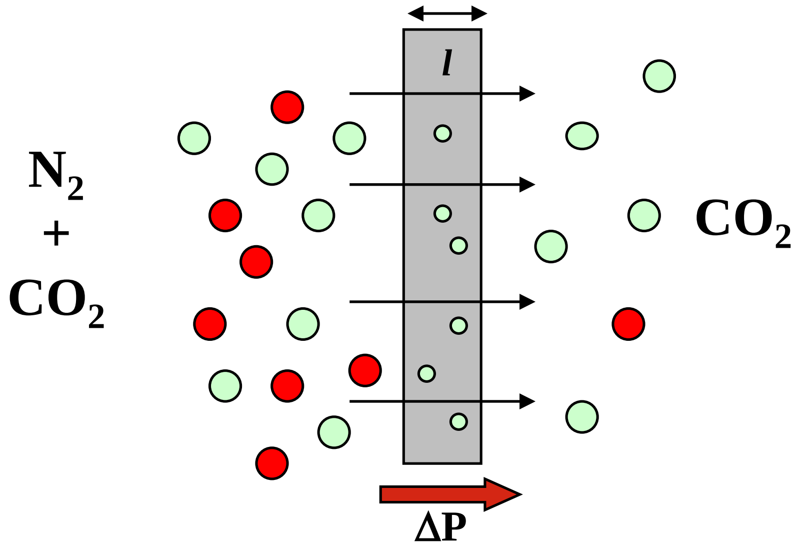
- Permeance is a *membrane* property: calculated as solute flux through the membrane normalized by the pressure driving force (but not thickness)

- Ideal selectivity describes the ratio of the permeabilities (or permeances) of two different permeating species through a membrane, and is a *material* property

- High membrane permeance is achieved by both material selection (high permeability) and membrane design (low thickness)

CO_2 Separation Using Membranes

- Mechanism of separation: **diffusion through a non-porous membrane**
- A pressure driven process - the **driving force** is the partial pressure difference of each gas in the feed and permeate.



– **Selective removal of fast permeating gases from slow permeating gases.**

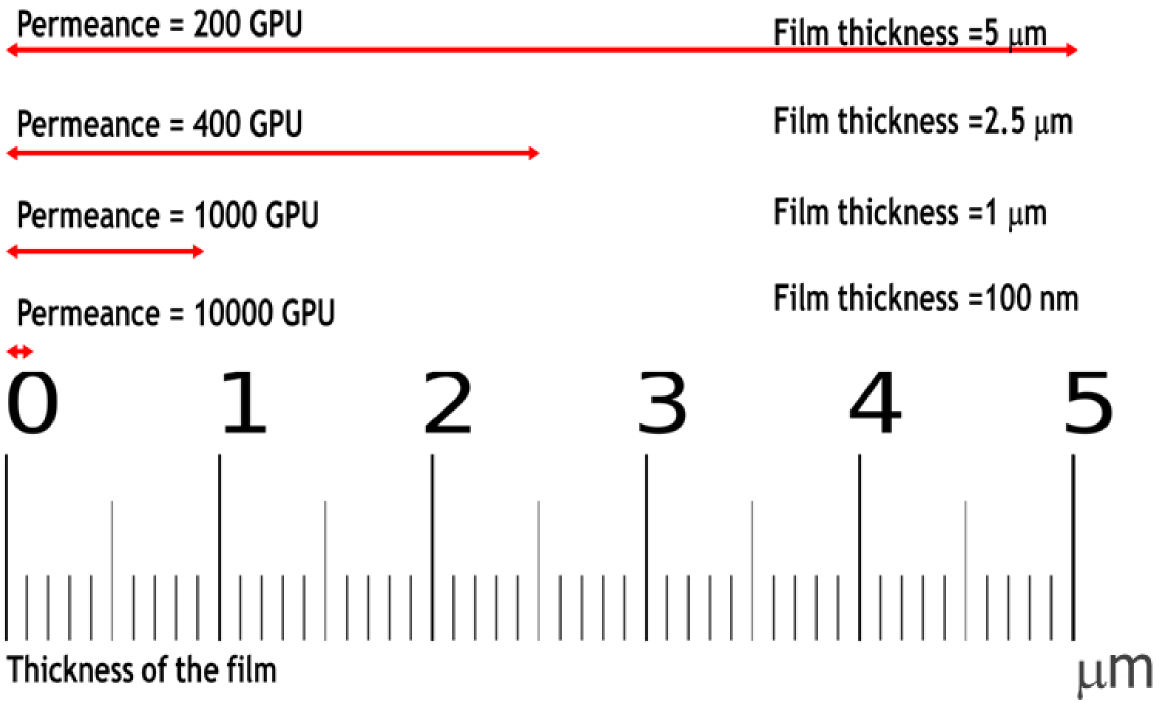
– **The solution-diffusion process can be approximated by Fick's law:**

$$J = \frac{P(p_1 - p_2)}{l}$$

$$P = D*S$$

- Selectivity - separation factor, α (typical selectivity for CO_2/N_2 is 20-45)
- Permeability = solubility (k) x diffusivity (D) (normalized over thickness)
- Either high selectivity or high permeability – Trade-off.

Permeance Vs. Permeability



- Current state-of-the-art fully commercialized membrane materials for CO_2/N_2 separations: 250 permeability with selectivity of 35-50.
- These are cast @ 100nm thickness, giving permeance of 2500 GPU.

The scale bar is in microns to illustrate permeability and permeance for a membrane material which as permeability of 1000 Barrers.

Mechanical Properties, Film Forming Ability

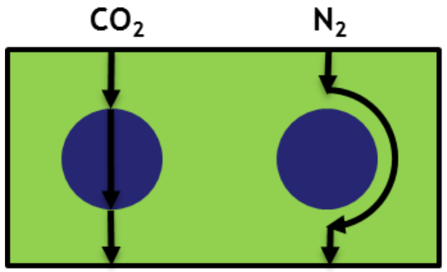
Membrane Material Advances

Needs

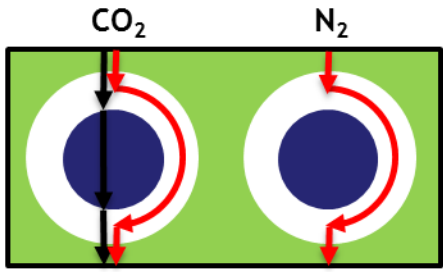
- More stable and robust membranes
  - Mechanically
  - Chemically
  - Thermally
- Higher permeability and selectivity
- Fundamental structure-property-processing relations needs to be incorporated.

- Various approaches to exceed the upper bound and access better performing membranes.
  - Surface modification
  - Phase separated polymer blends
  - Mixed-matrix membranes (MMMs)
    - Inorganic membranes (superior in performance but are difficult to make large thin films)
  - Supported ionic liquids
  - Facilitated transport

Mixed Matrix Membranes



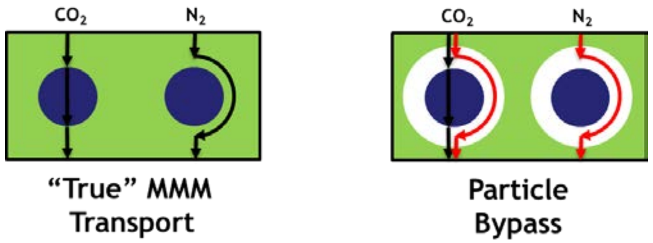
"True" MMM
Transport

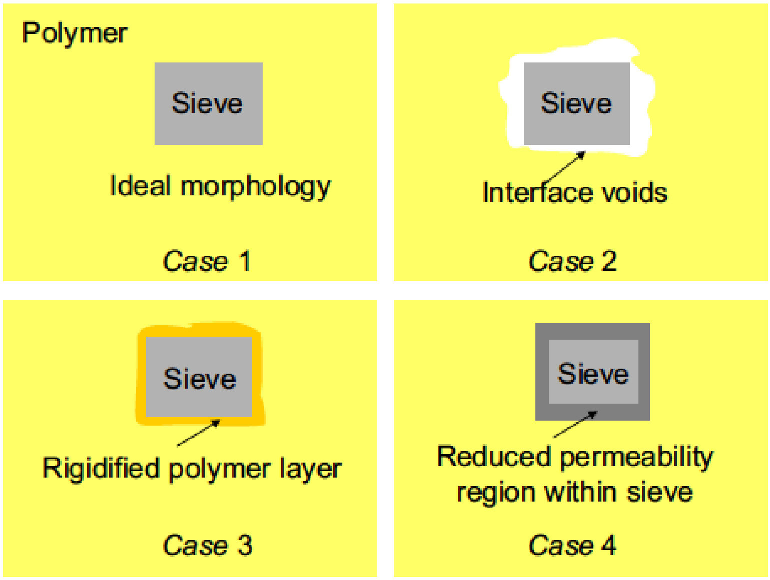


Particle
Bypass

The Trouble with Mixed Matrix Membranes

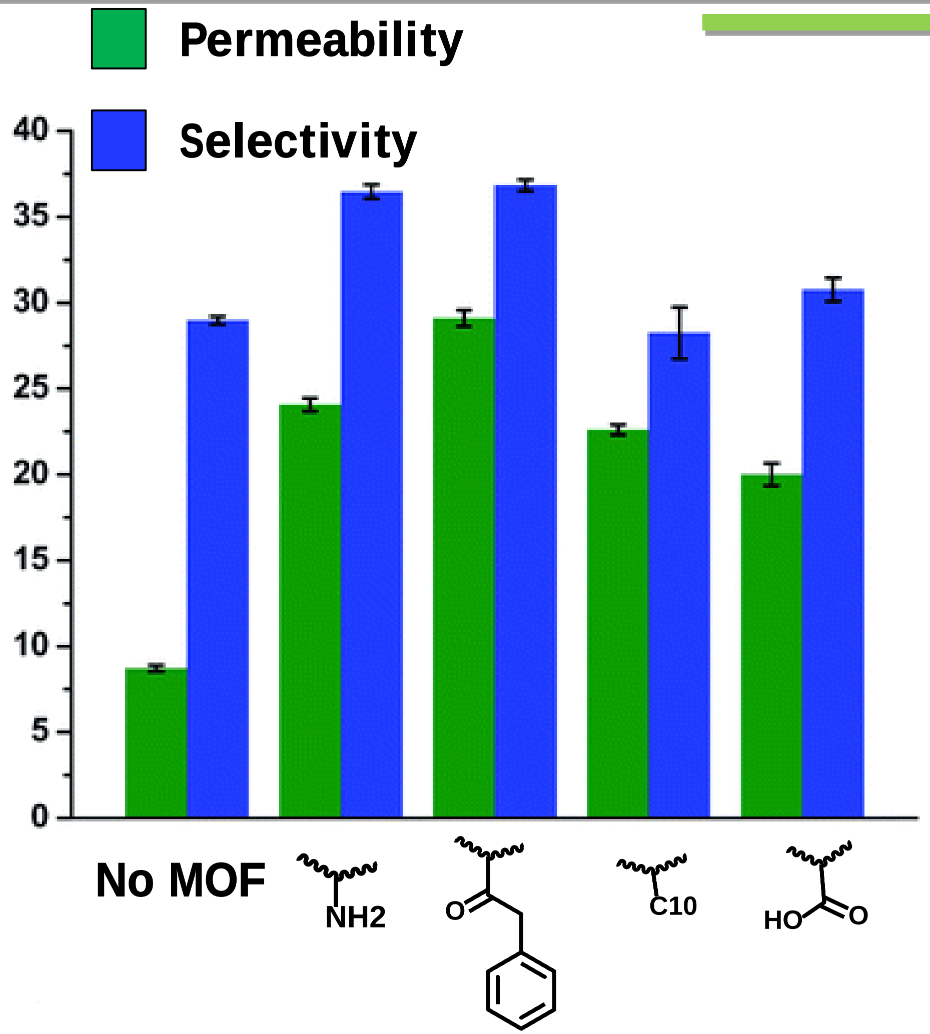
- Poor compatibility of the polymer and inorganic particles that leads to poor adhesion at the organic-inorganic interface.
- General trade-off between selectivity and permeability

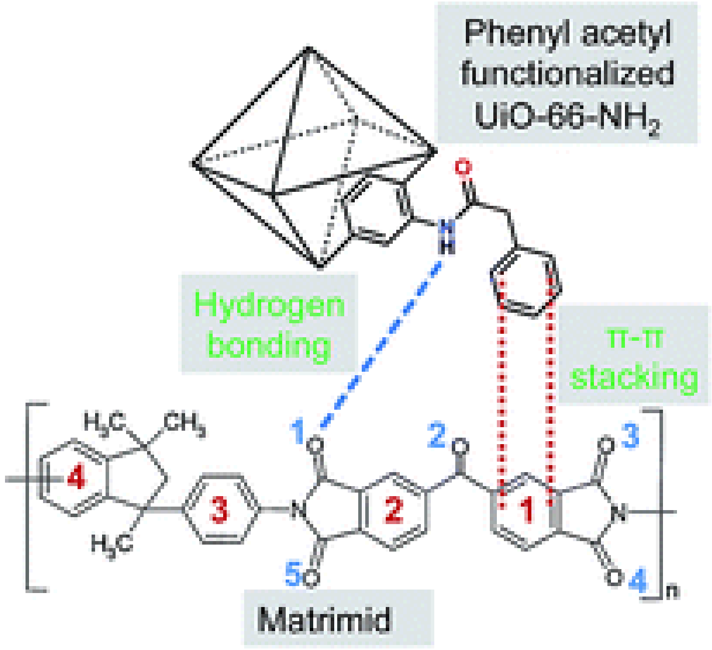




- Solutions:
  - Addition of interfacial agents
  - Surface modification of inorganic particles
  - Chemical modification of polymers
  - Use of flexible polymers

Insight

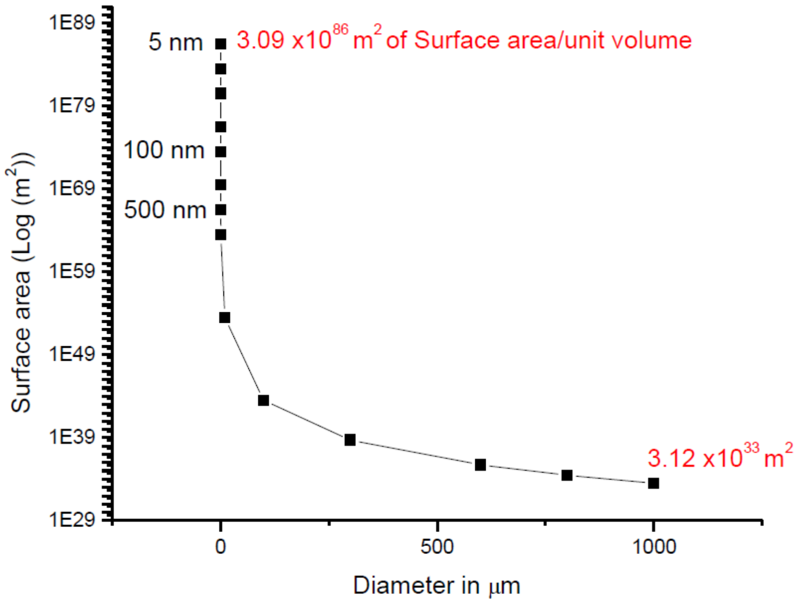


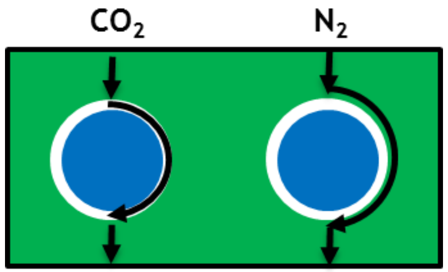


J. Mater. Chem. A, **2015**, *3*, 5014-5022
U.S. Patent Application number: 14/519,743

Interface

If you can't beat 'em, join 'em!

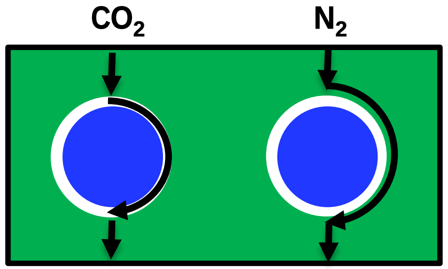


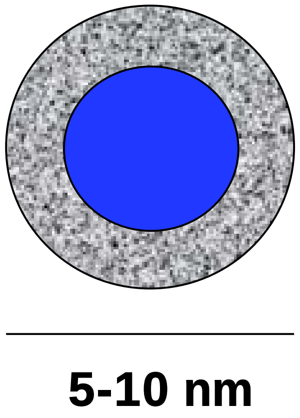


Interfacially-Controlled Envelope (ICE) Membranes

- Makes use of envelopment effects which have plagued mixed matrix membranes
- Diffusion phenomena determined by interactions with the particle and polymer surface
- Possibility of using simple nanoparticle fillers
- Advanced polymers allow an excellent starting point

Plan of Attack for Mixed Matrix Membranes



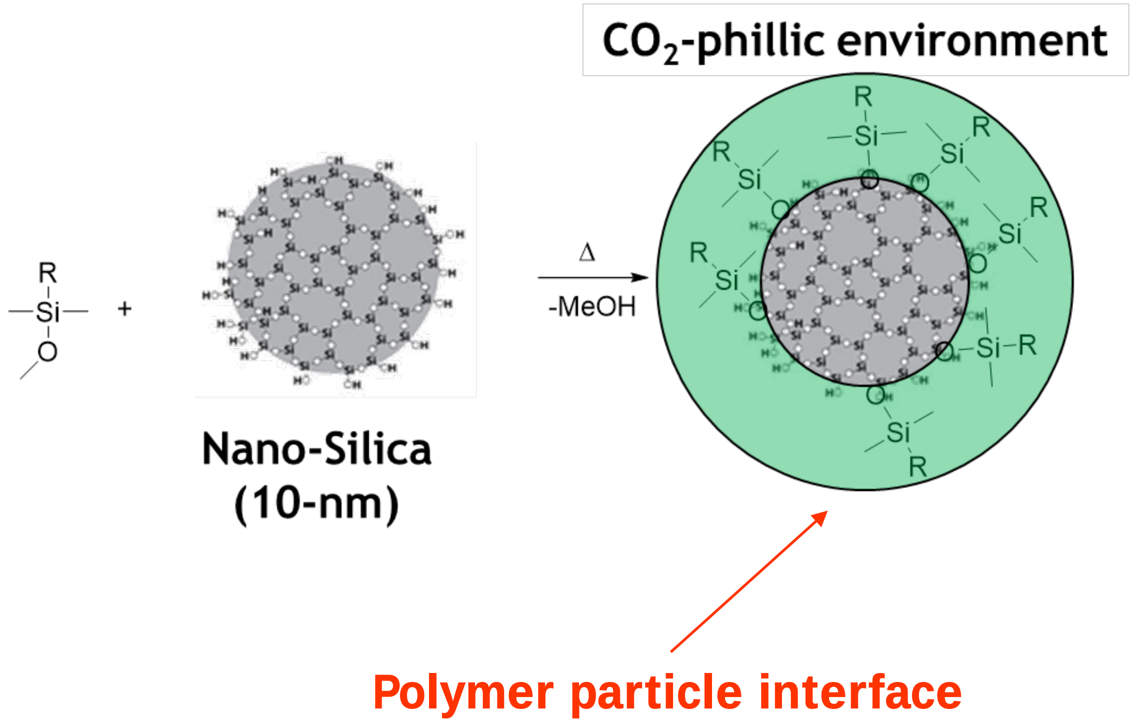


- Use simple nanoparticle fillers
- Surface modify the particles to tune optimal interactions with CO_2 and the polymer
- Employ an advanced polymer with good compatibility and CO_2 transport properties
- Create a membrane in which diffusion phenomena are determined by interactions with the particle and polymer surface

Surface Functionalized Nanoparticles

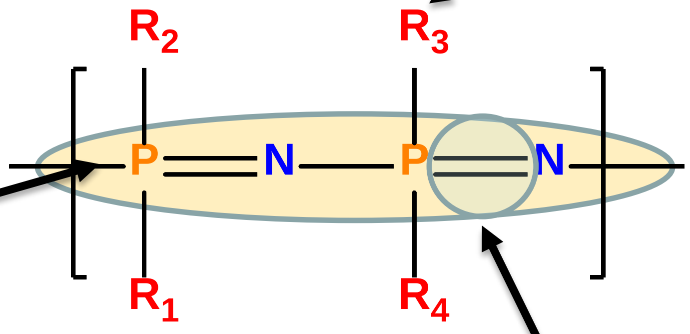
- Careful and detailed screening of the surface modifier was carried out.

- Nanoparticles have been synthesized @ 200g levels for 3 different loadings



Polymer of Choice

Macromolecular substitution



Ultra Flexible chains

High chain mobility

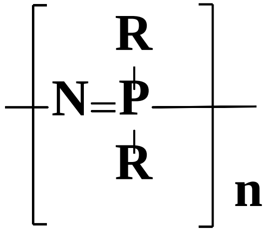
Improved gas solubility and diffusion

Excellent chemical and thermal stability

C-C =607Δ*Hf* kJ/mol vs.

P-N =617 Δ*Hf* kJ/mol

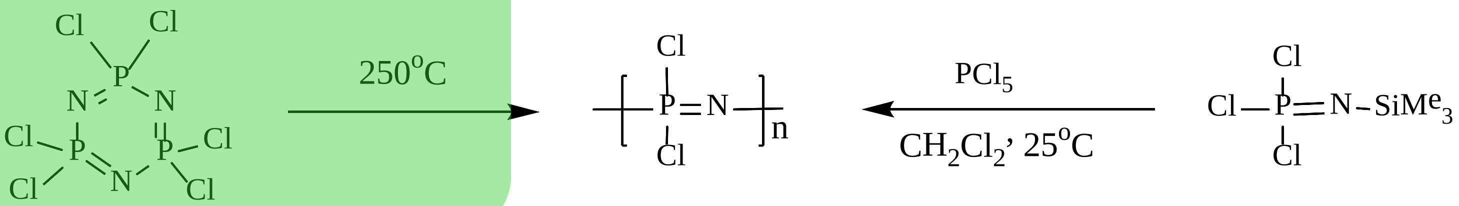
Polyphosphazenes



Organic-Inorganic Hybrid Polymeric System

Ring Opening Polymerization

Living Cationic Polymerization



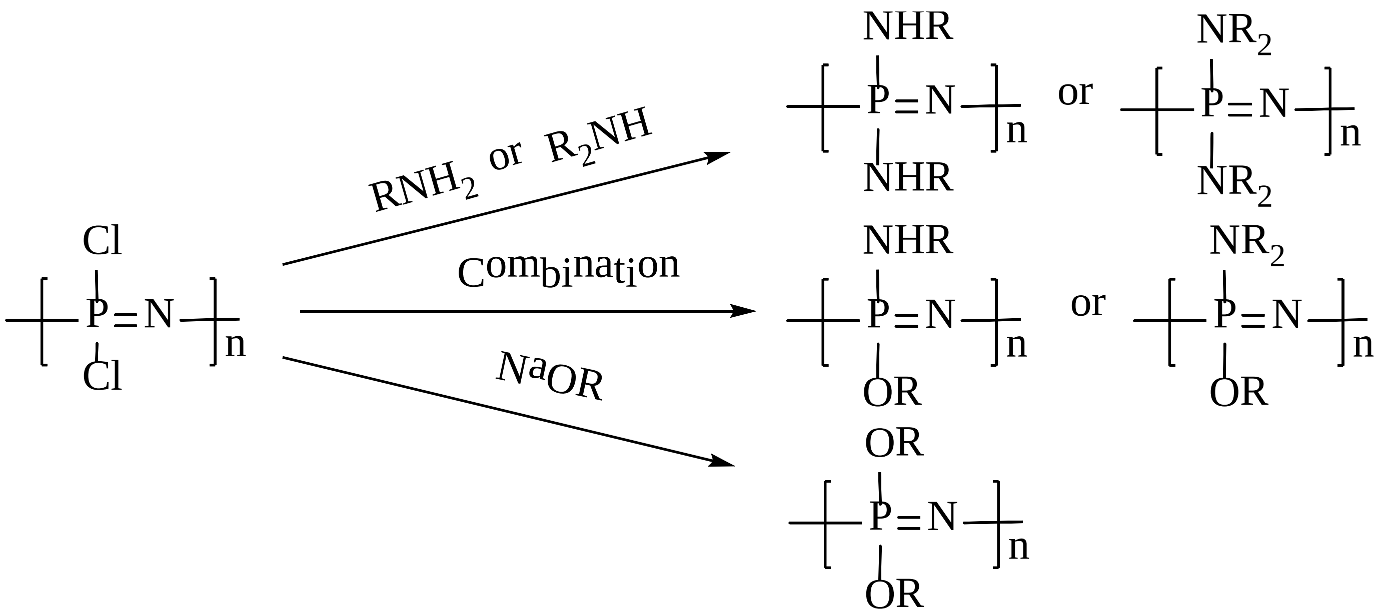
Poly(dichlorophosphazene)
Reactive Intermediate

- High Molecular Weight (MW)
- Relatively Large Scale Preparation
- Poor Molecular Weight Control
- Broad Poly-disperity (PD)
- No End-chain Modifications

- Relatively Lower MW
- Well-controlled MW and PD
- Room Temperature
- Small Scale Preparation
- End-chain Modifications

Polyphosphazenes

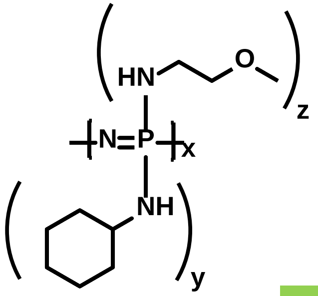
Macromolecular Substitution

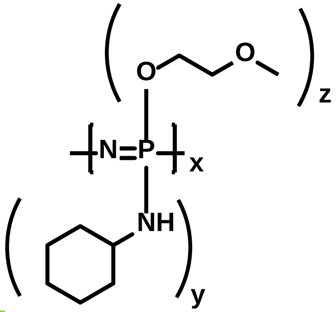


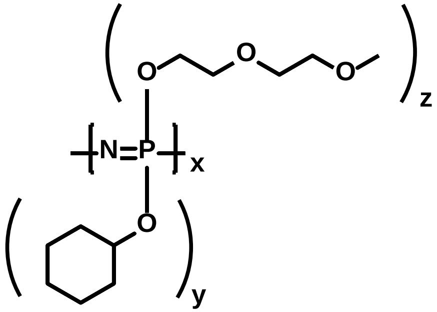
Library of Over 700 Different Polyphosphazenes

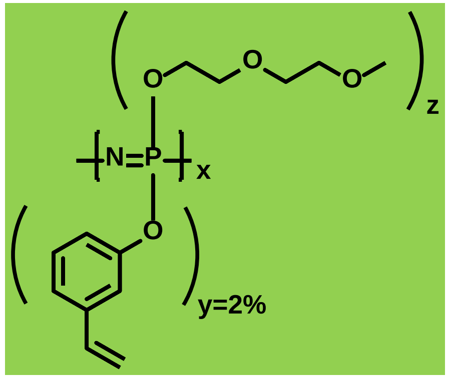
- **Synthetic Simplicity**: Nucleophilic Substitutions
- **Synthetic Tunability**: Homo-substitutions OR Mix-substitutions
- **Property Tunability**: Glass Transition Temperature, Solubility, Degradability, Hydrophobicity

Polymer Screening

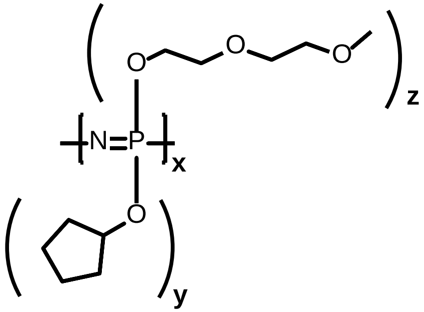


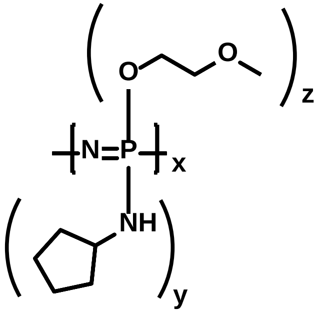


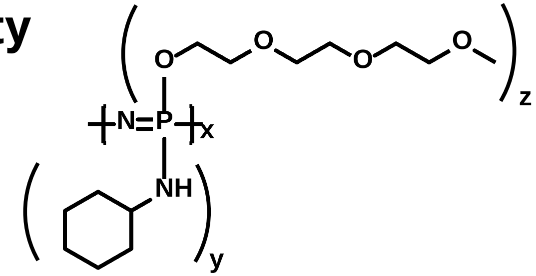




250 Barrers
62 Selectivity





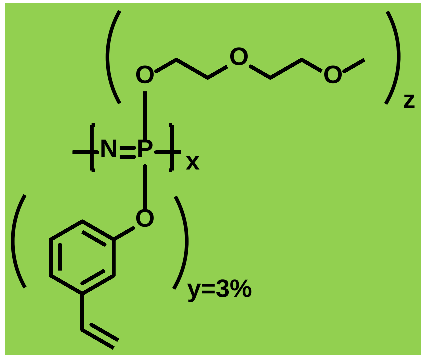


J. Mem. Sci., **2001**, *186*, 249-256

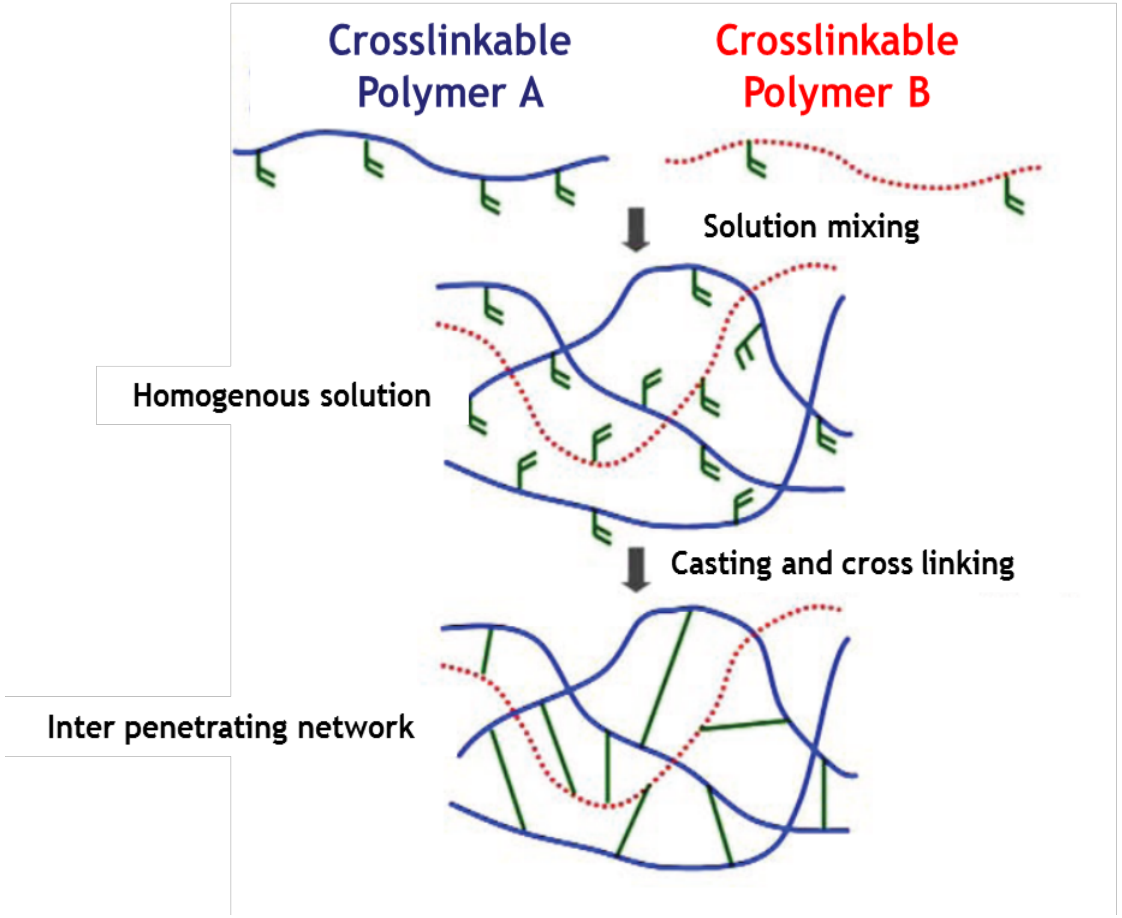
Material Optimization

Challenges

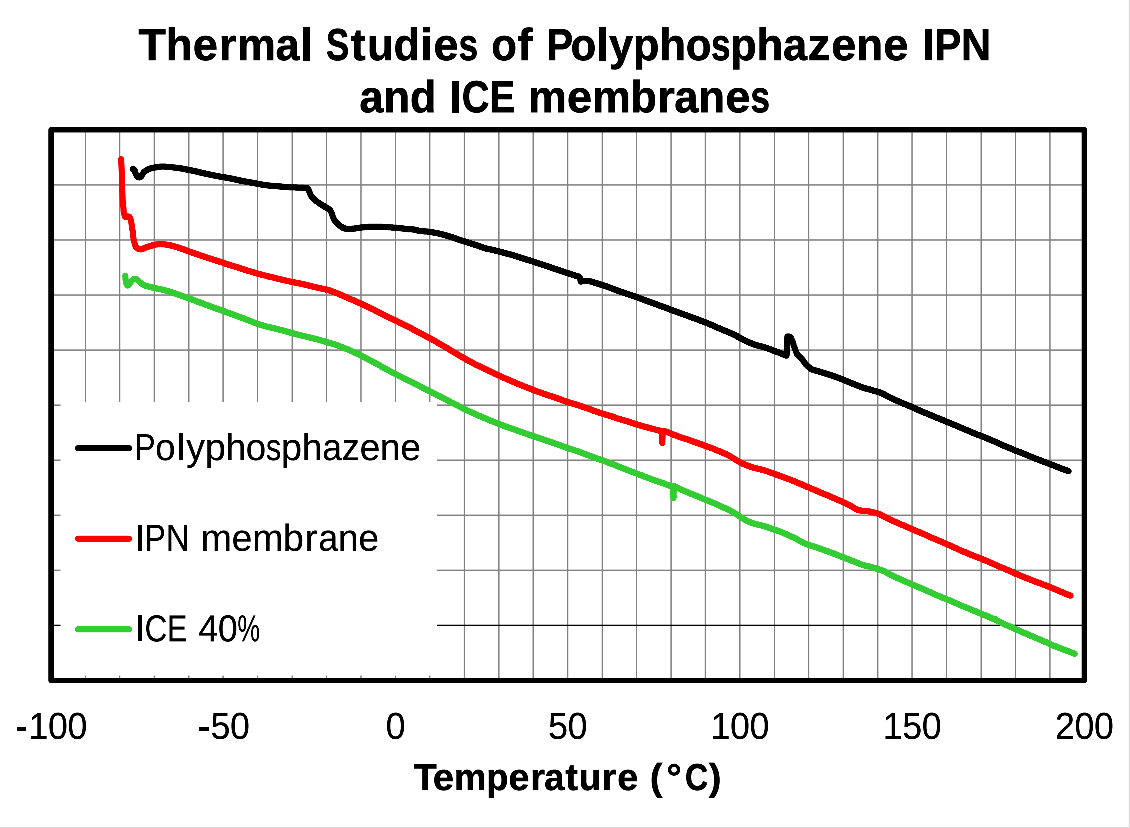
- Not a film former
- Sticky
- Does not have required mechanical properties

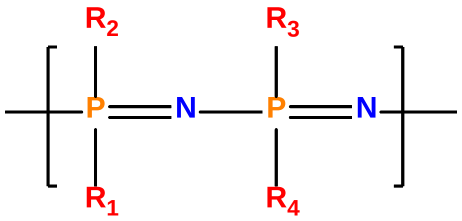


Solution = Inter Penetrating Networks (IPN)



Glass Transition Studies



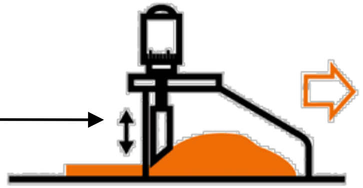


- Difference T_g of uncrosslinked Polyphoshazene vs. IPN is observed
- Minor difference is observed between IPN vs. ICE membranes in T_g studies.
  - Effect of extremely chain mobility
- 30 compositions of ICE membranes have been evaluated for their thermal properties.
  - Long-term stability test are on going.

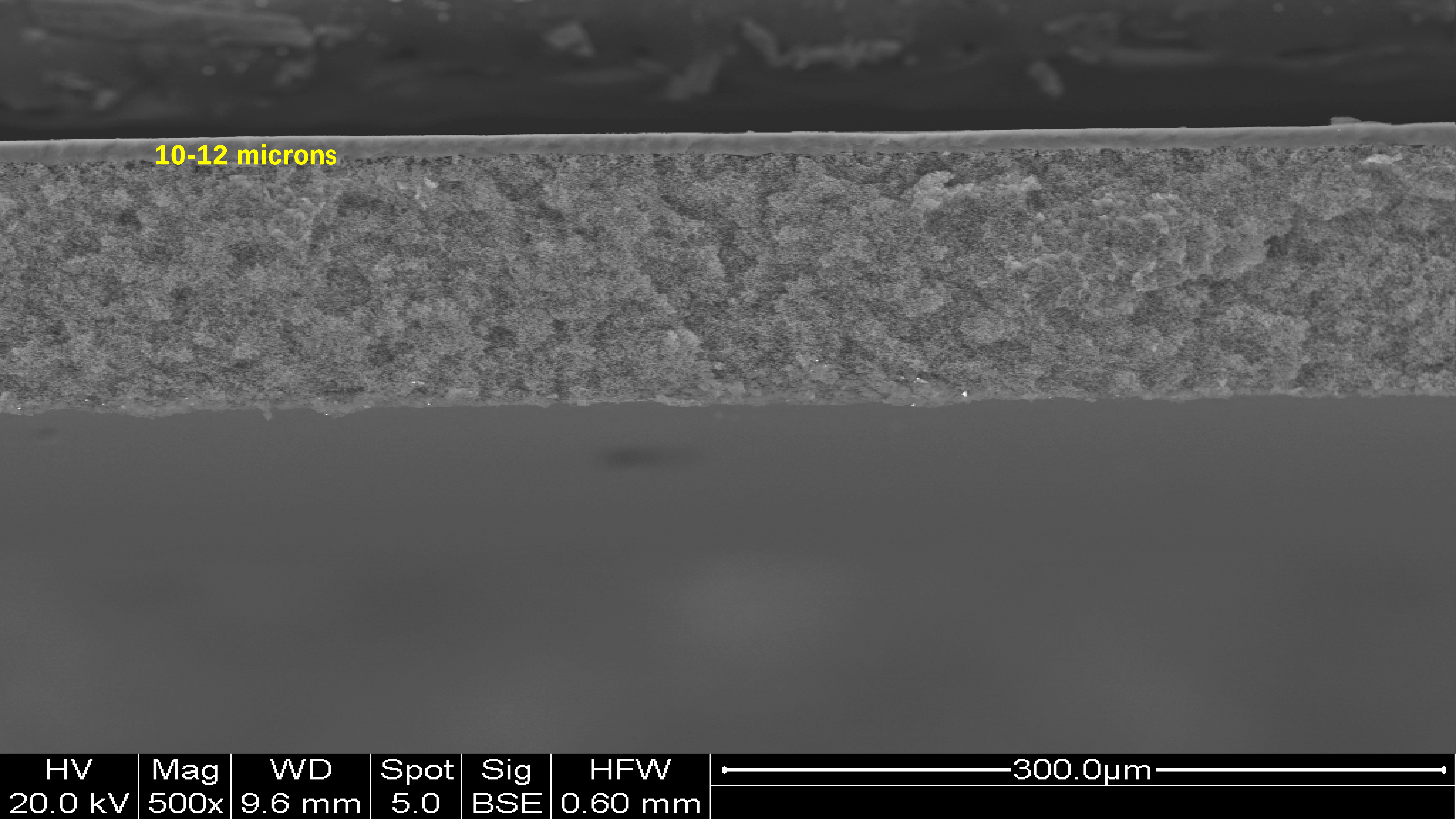
Membrane Casting

Screening is done using films cast by hand

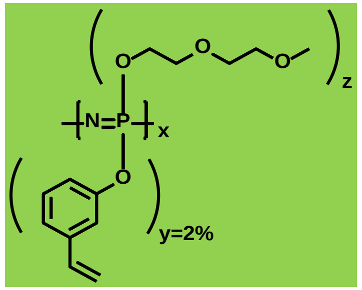
Knife



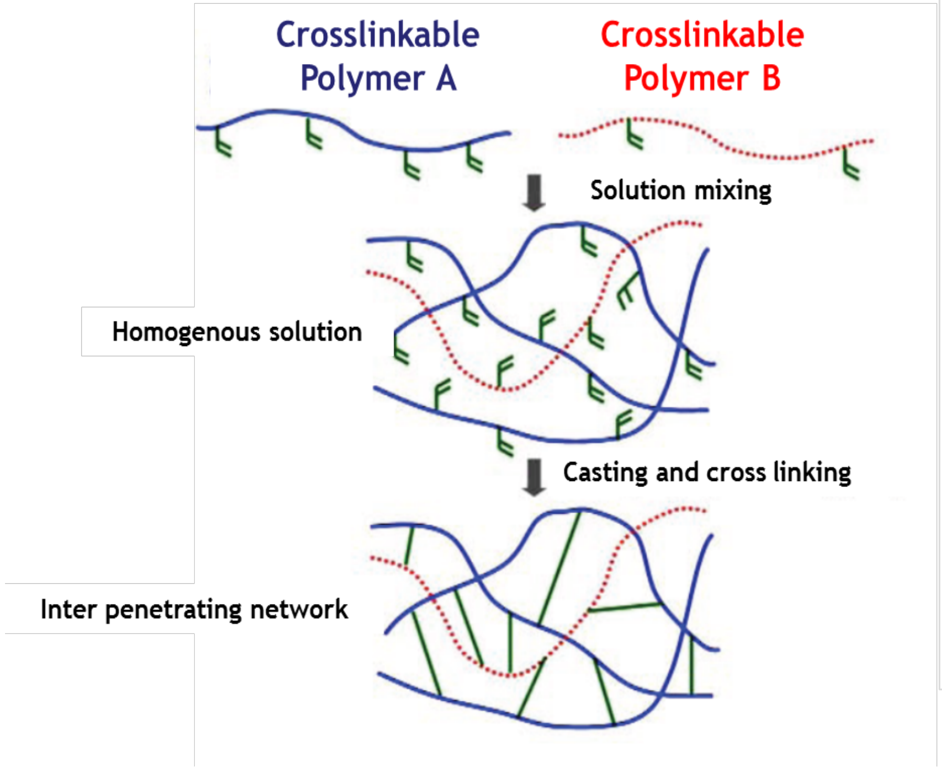
Polymer dope

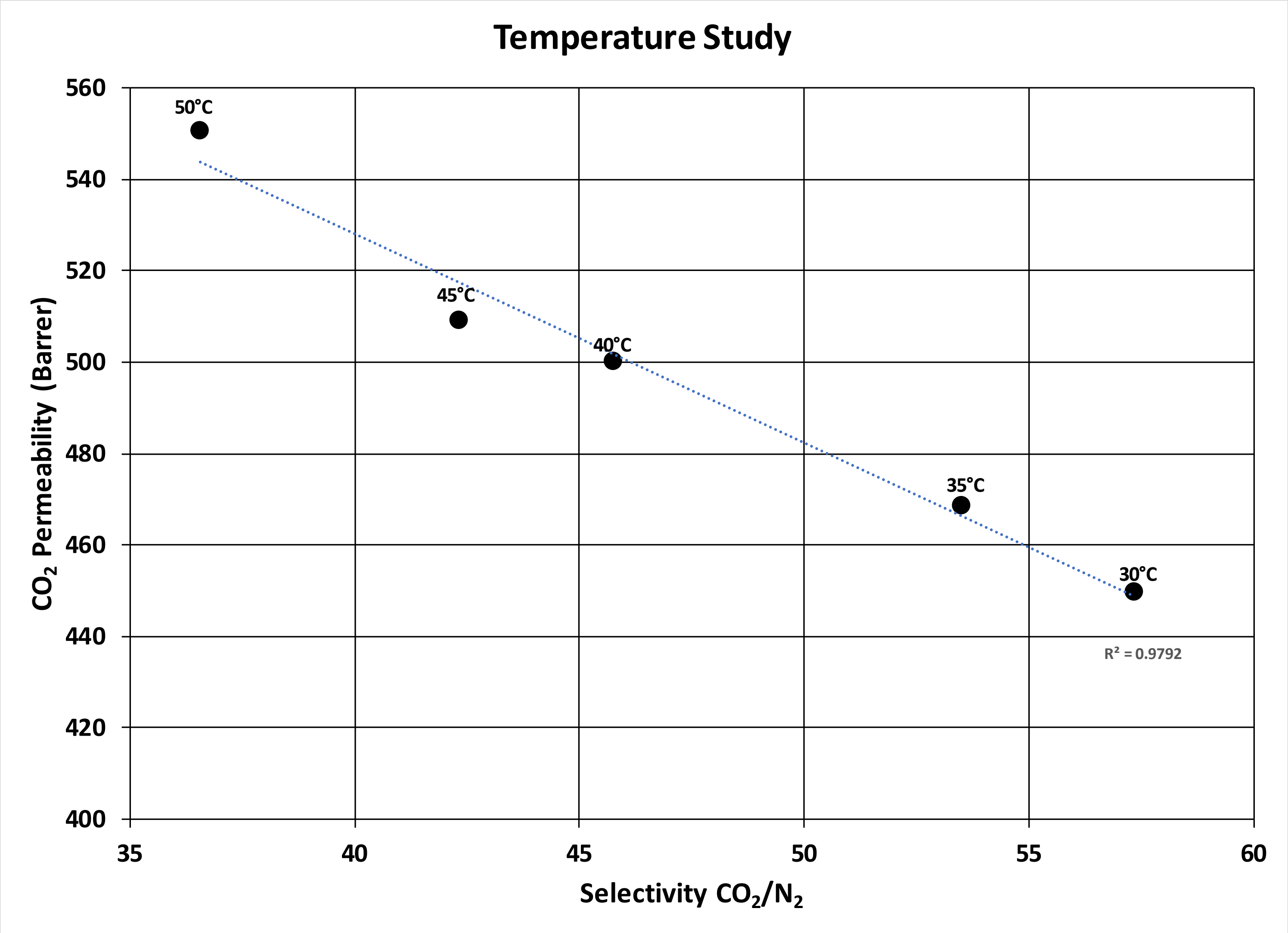

10-12 microns
HV
20.0 kV
Mag
500x
WD
9.6 mm
Spot
5.0
Sig
BSE
HFW
0.60 mm
300.0μm

Polymer Membrane Results



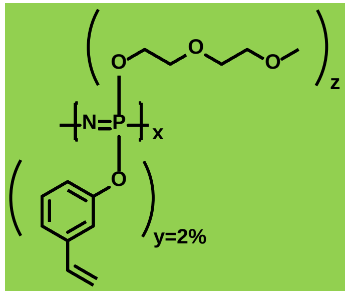
250 Barrers
62 Selectivity





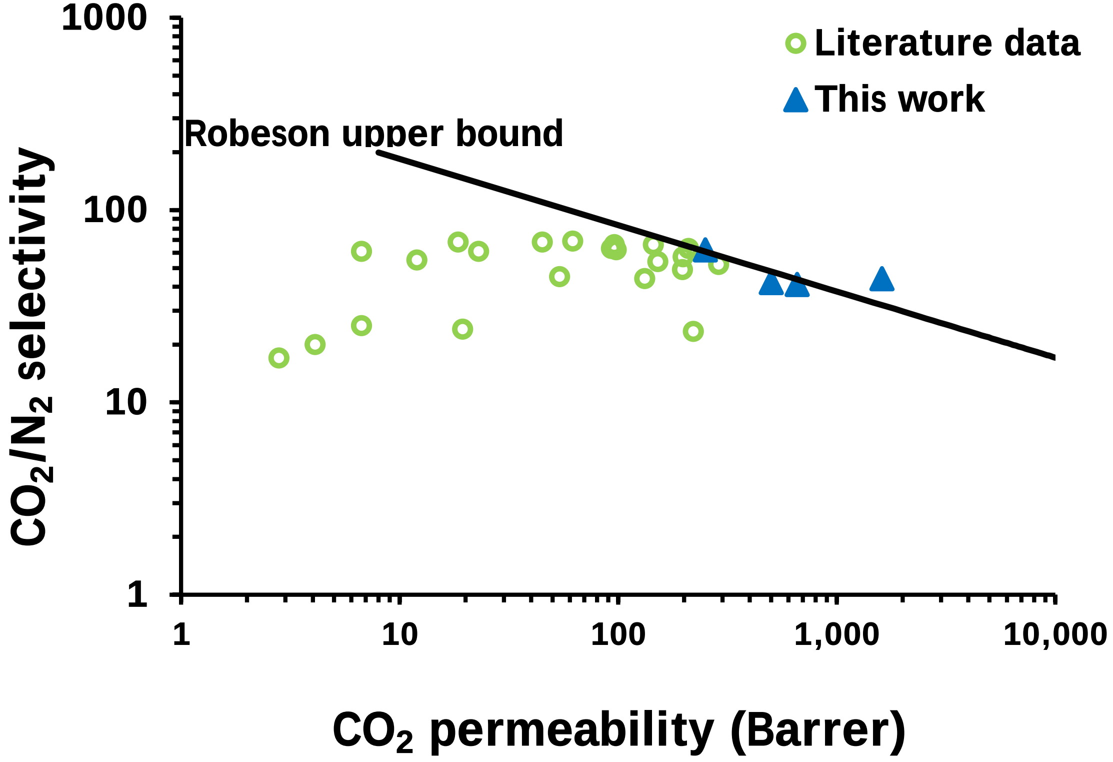
Membrane Performance

%wt. Loading of Nanoparticles	Cast number	Characterization	Membrane results	
			Permeability	Selectivity
30% unmodified particles	LS-01-45A	Turned into a gel with white precipitates (not useable)	N/A	N/A
10% surface modified 10 nm particles	LIS-01-41 A	SEM, TGA, DSC, Membrane testing	659	41
20% surface modified 10 nm particles	LS-01-51 B*	Membrane testing	675-1025	20-33
40% surface modified 10 nm particles	LIS-01-41 B, LIS-01-43	SEM, TGA, DSC, membrane testing	1609	44
60% surface modified 10 nm particles	LIS-01-51A*	TGA, DSC, Membrane testing	250-400	25-30



60% loading

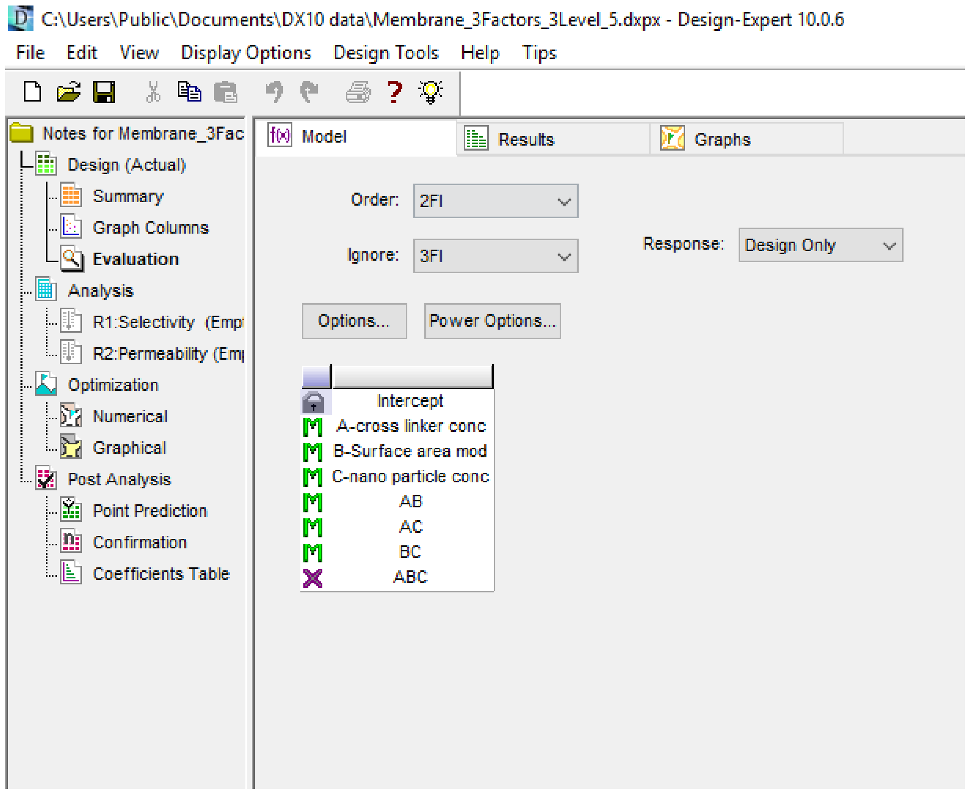
Membrane Performance



- Membrane of half a micron would yield permeance of 3200 GPU with a selectivity of 44 for CO_2/N_2 separation.
- Work is being performed to convert these materials properties into membranes – Open for collaborations
- Module design– Open for collaborations and joint research.

Design of Experiments Matrix

- Further optimization of membrane composition Design of Experiments
  - Optimized surface modification of the nanoparticles
  - Optimized concentration of nanoparticles
  - Optimized level of crosslinking
- 30 composition done
- DSC studies complete
  - Minor differences in T_g
  - Structure-property relationship is being carried out
- Performance testing in Progress.



Using statistical analytical tools to optimize membrane composition

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