Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture (DE-FE0031596)

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DOE NETL CO2 Capture Technology Project Review Meeting
Pittsburgh, August 18, 2022

Project Details

- **Award Name:** Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture (DE-FE0031596)
- **Project Period:** June 1, 2018 – May 31, 2022
- **Funding:** \$2,905,620 DOE; \$726,805 cost share (MTR and University of Buffalo)
- **DOE Project Manager:** Carl Laird
- **Participants:** Membrane Technology and Research, Inc., University at Buffalo, University of Texas at Austin
- **Project Objectives:**
  - Develop supports for composite membranes with highly regular surface pore structures that eliminate the restriction on diffusion in the selective layer that is present with current generation supports
  - Develop improved selective materials with higher permeance and/or higher selectivity compared to the current generation Polaris material
- **Project Plan:**
  - **BP1:** Lab-scale support development, screening of novel selective materials
  - **BP2:** Lab-scale support development, scale up of selective materials, composite membrane optimization
  - **BP3:** Continue lab-scale composite membrane development, lab-scale module testing at MTR, bench-scale module test at NCCC

Current Status: - BP3 is underway
- November 1, 2022: GO/NO GO for NCCC testing

Project Success Criteria, Activities

BP3 Success Criteria

1. Composite membranes prepared with CO_2 = 4,000 gpu and CO_2/N_2 = 25 (mixed gas)
2. Composite membranes prepared with CO_2 = 2,000 gpu and CO_2/N_2 = 50 (mixed gas)
3. Small modules tested at NCCC

Areas of Project Activities	
Support Membrane	Perfect block copolymers
	"Not so perfect" block copolymers
	Dual slot die casting technique
Selective Material	Macro-monomer → Polymer
	Polymer

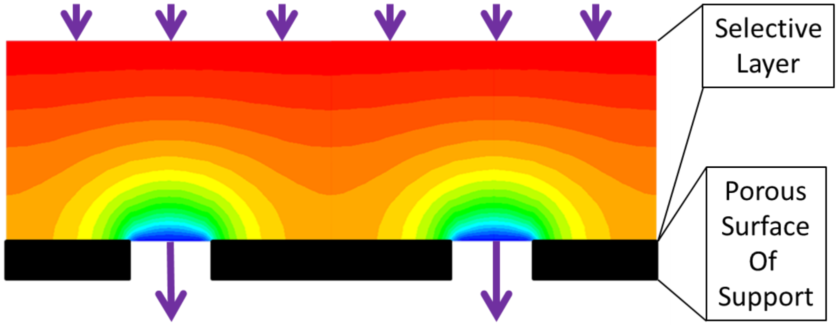
Support Membrane Background

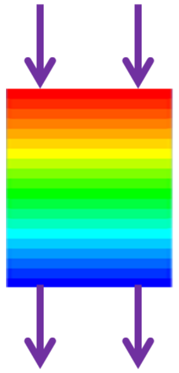
- Higher permeances are typically achieved by making composite membranes with thinner selective layers on top of a support membrane

- Experimental observation: Reducing the selective layer thickness by a factor of two **does not** increase the permeance by a factor of two, even though the support membrane has negligible resistance

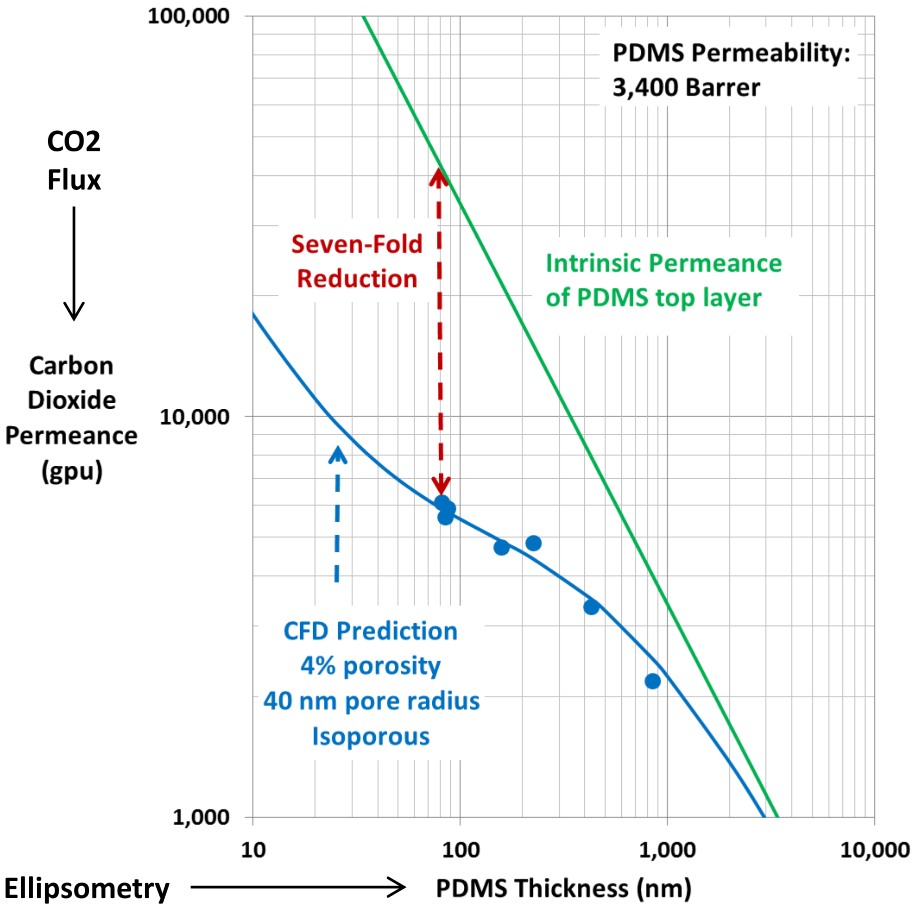
- Earlier work at MTR has established that the surface pore structure of the support membrane is a limiting factor

The Support Membrane Effect





Permeance is reduced because the non-porous area increases the average path length for diffusion.
In this example, reduction in permeance is three-fold.



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Self Assembly of Perfect Block Copolymers

Asymmetric superstructure formed in a block copolymer via phase separation

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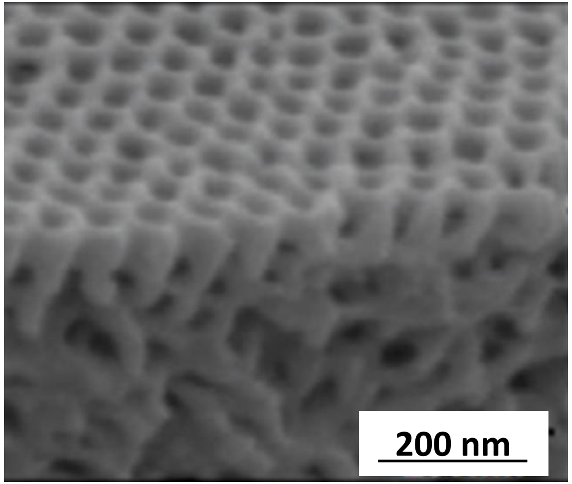
Institut für Polymerforschung, GKSS-Forschungszentrum Geesthacht GmbH, Max-Planck-Str. 1, 21502 Geesthacht, Germany
*e-mail: volker.abetz@gkss.de

(2007)



Block Copolymer consists of only two blocks

- One block is hydrophobic
- Second block is hydrophilic
- Each block has a controlled molecular weight (mono disperse)
- These polymers are expensive

Using block copolymers in the standard membrane phase separation process creates a top surface with a highly ordered pore structure, with a more random porous substructure below.

But only sometimes. This process is difficult to control.

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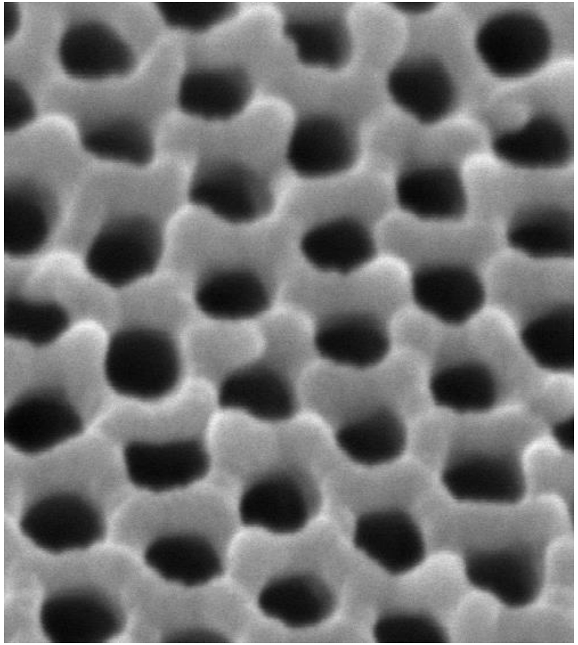
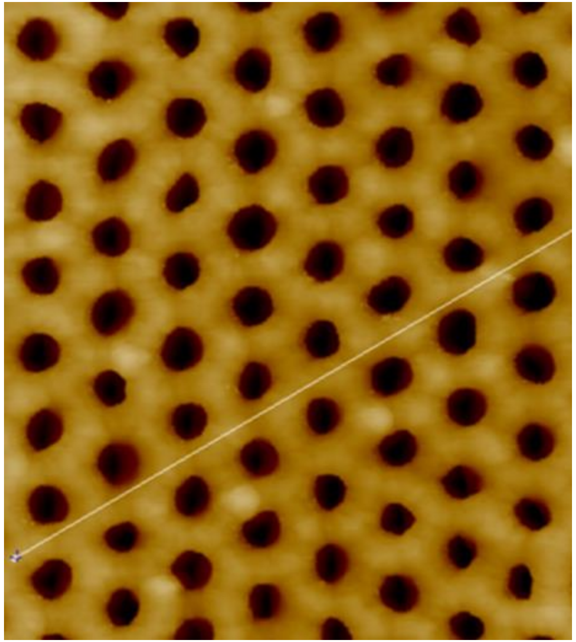
Analysis of Isoporous Surface

(PS-b-P4VP block copolymer)

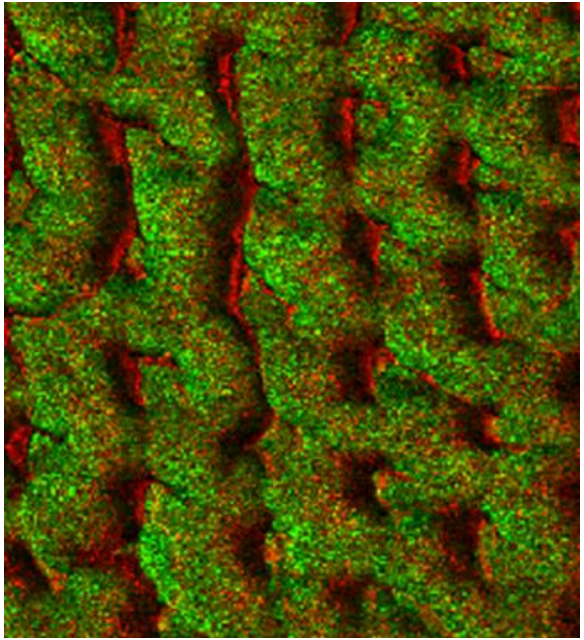
Scanning Electron Microscope



Atomic Force Microscope



Nano-InfraRed plus Atomic Force Microscope



820 cm^{-1} (P4VP)   1027 cm^{-1} (PS)

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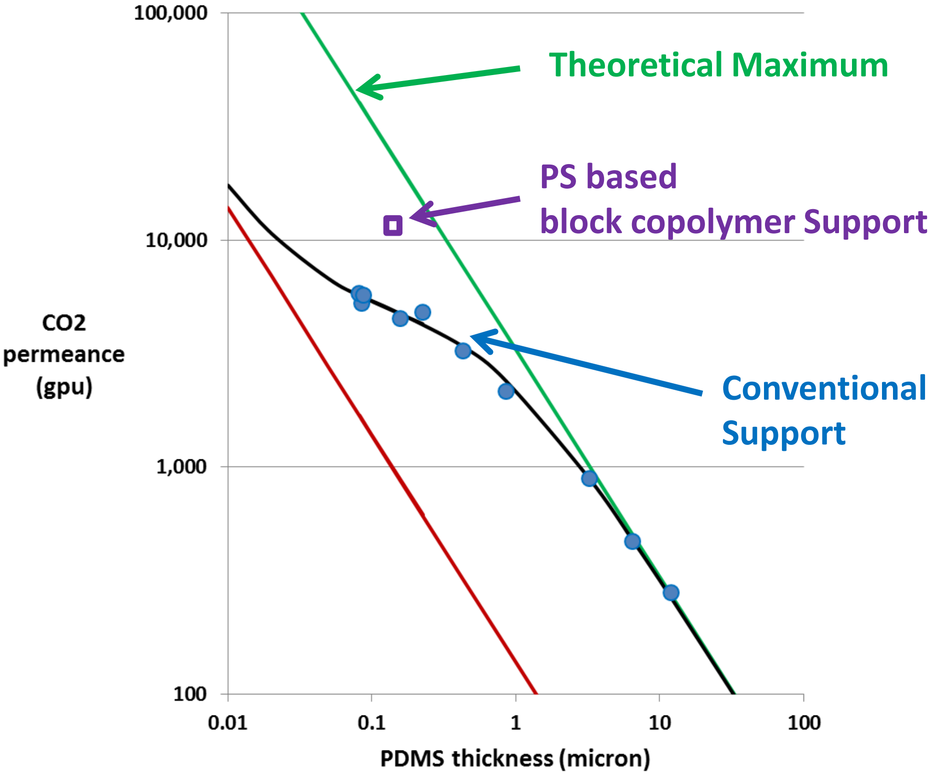
Support made from perfect block copolymer

- Permeance of uncoated support is 162,000 gpu
- CO2 permeance of PDMS coated support is 11,800 gpu
- PDMS thickness is 143 nm
- Sample too small to be coated with Polaris layer
- Confirms that a better surface results in an increase in permeance



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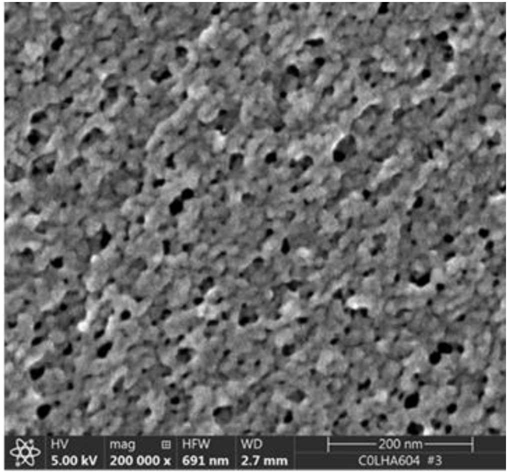
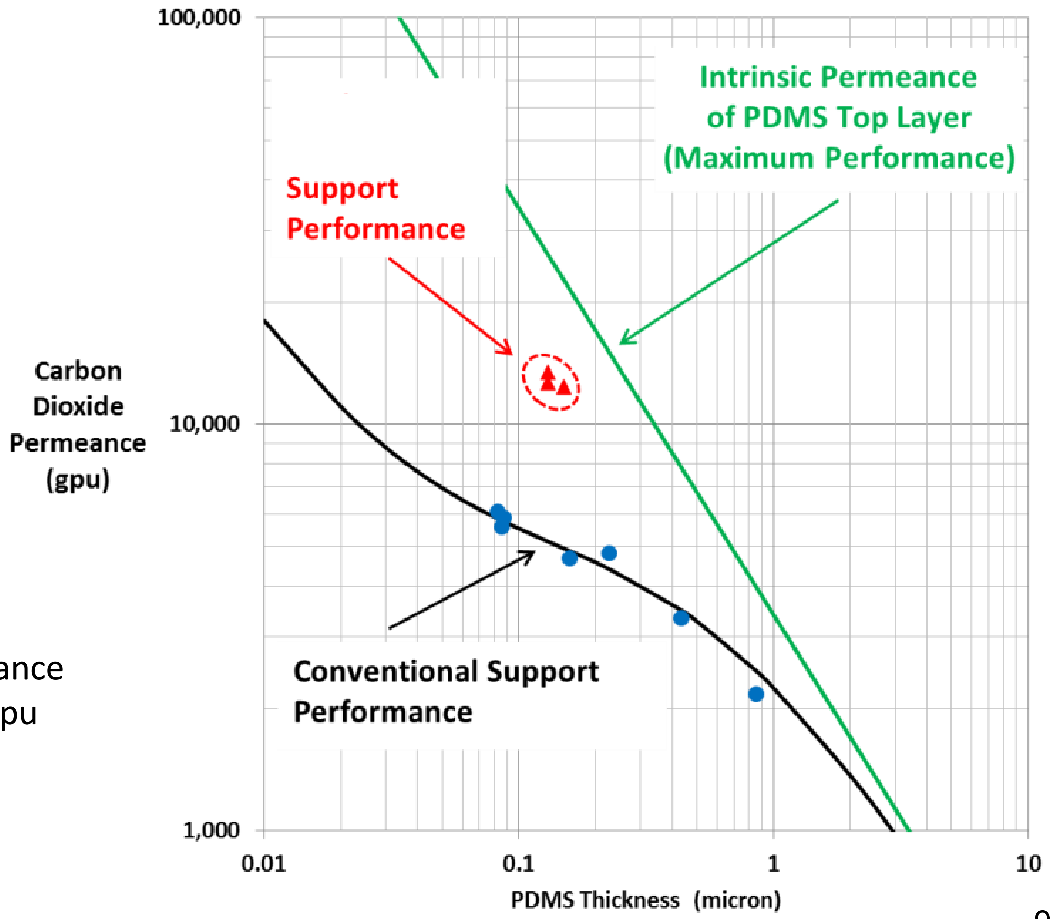
Support made from imperfect block copolymer

- Block copolymer made by UT Austin by attaching a hydrophilic block to a widely used hydrophobic polymer

- Excellent support membrane, even though the surface is not truly isoporous:



N2 permeance = 95,000 gpu



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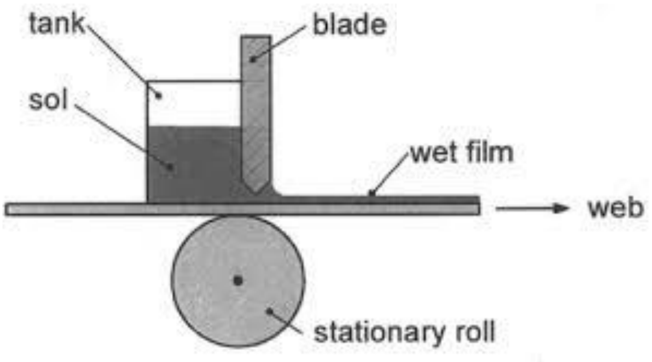
Dual Slot Die Casting

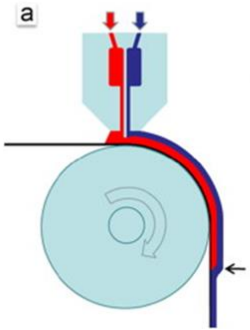
Blade Casting (traditional):

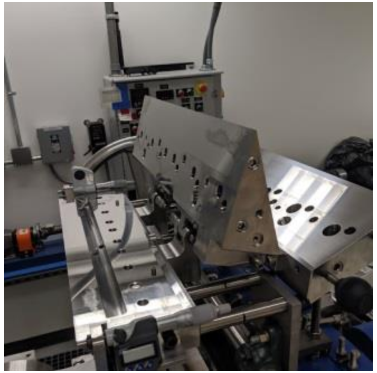
- Common method for membrane casting
- Simple equipment, simple operation
- Allows for deposition of only one layer

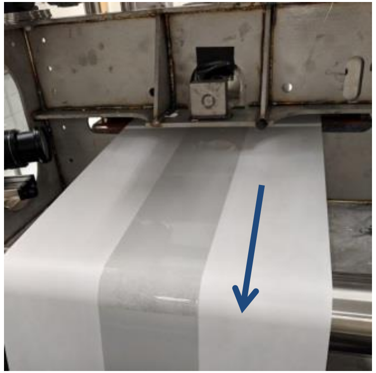


Slot Die Casting (this project):

- Allows deposition multiple layers
- Better control of thicknesses
- More complicated, but used on large scale in many industrial film operations



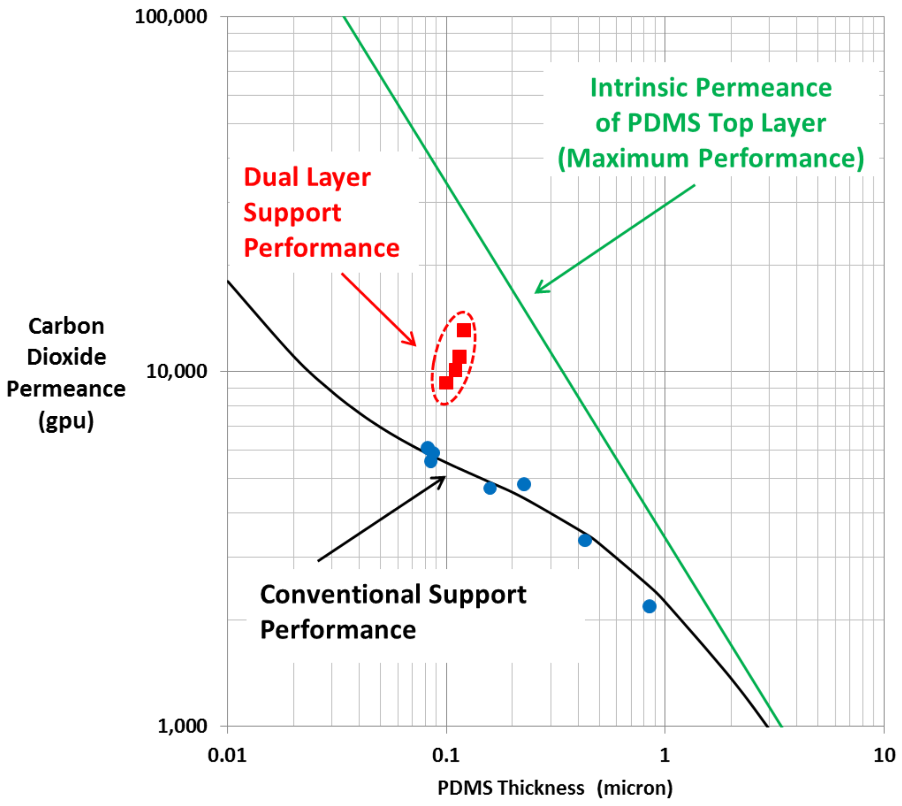




Support made with Dual Slot Die

- Advantage of Dual Slot Die is that the top and bottom layers can be made with different casting solution formulations
- This allows optimization of top layer for surface properties
- And allows optimization of the bottom layer for mechanical strength

- **Dual Slot Die produces a better support, even with conventional polymers**



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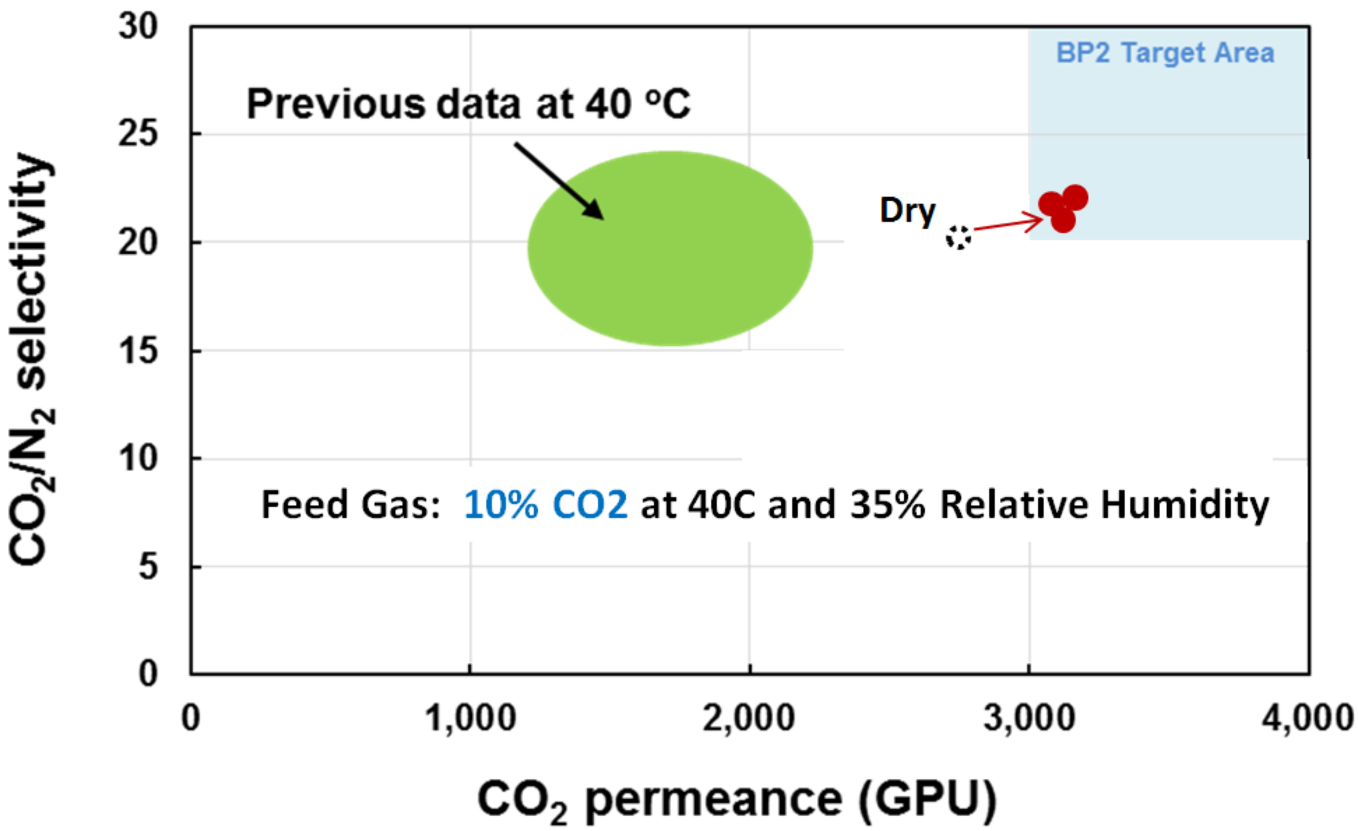
Current Best Polaris Membrane Performance



Selectivity and permeance increase with increasing CO2 concentration

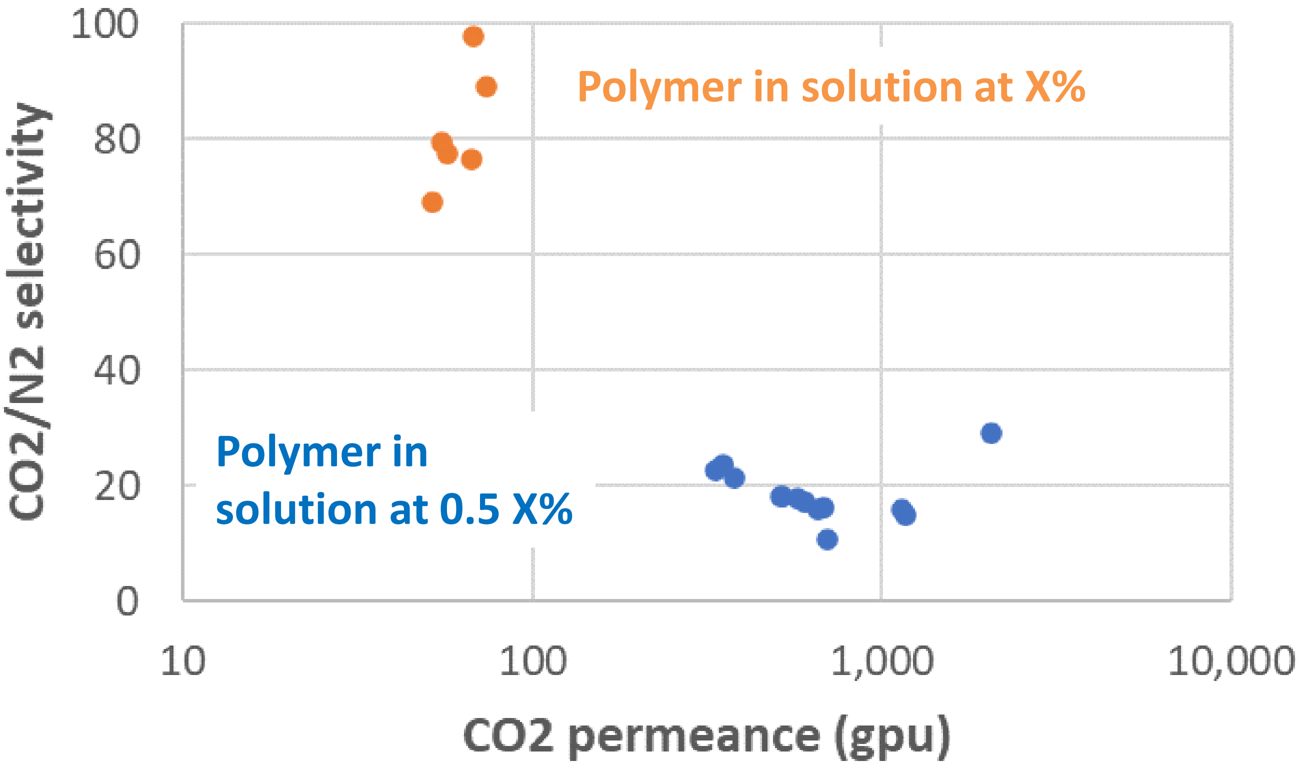
Selectivity increases and permeance decreases with decreasing temperature

Novel Selective Materials

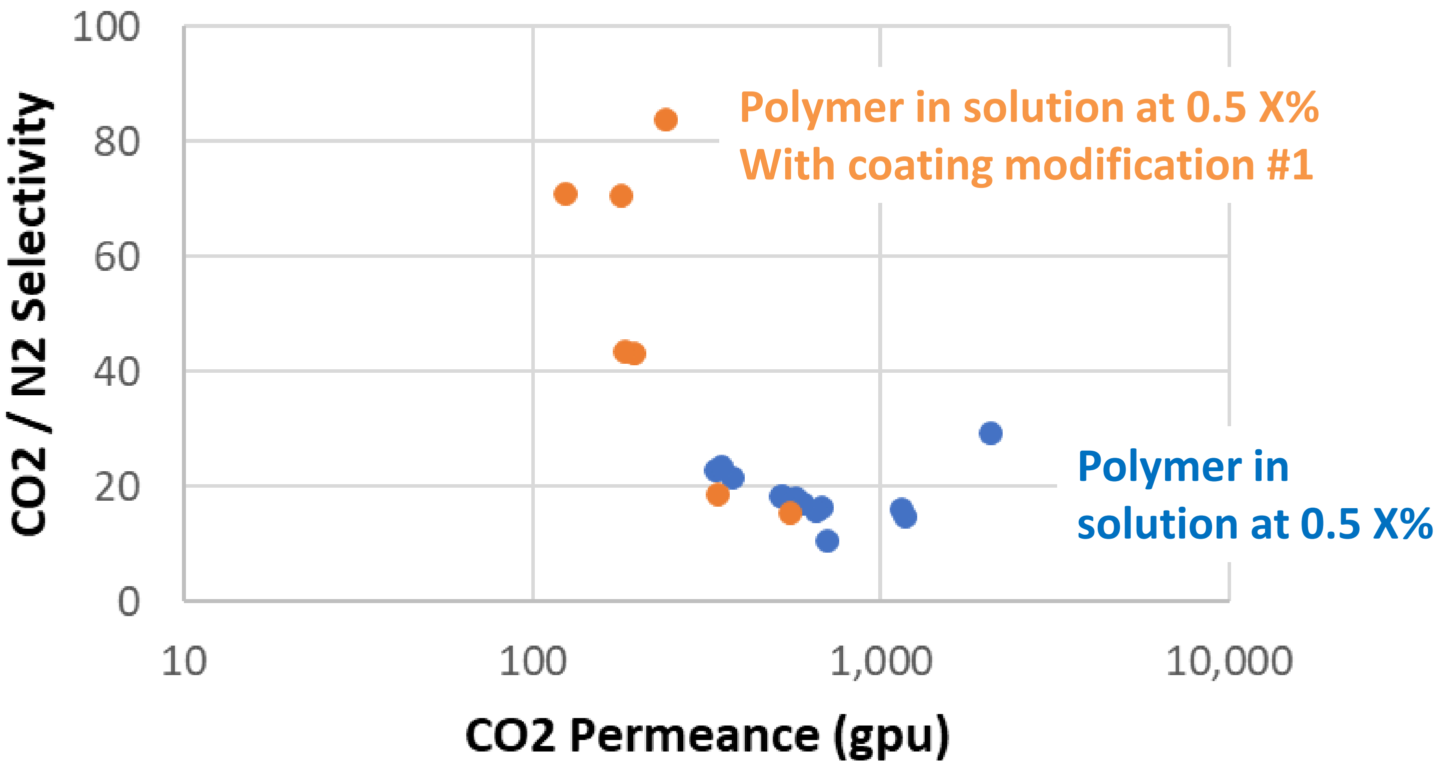
Party	Role
U Buffalo	Polymer preparation: Reversible addition–fragmentation chain-transfer polymerization (RAFT)
U Texas	Polymer preparation: Two different pathways to macro-monomers, followed by free radical polymerization
MTR	Preparation of support membranes Preparation of composite membranes Pure gas testing Gas mixture testing

In the first months of BP3, MTR has worked exclusively with polymers provided by the University at Buffalo.

Composite Membranes with Novel Material



Coating Procedure Optimization



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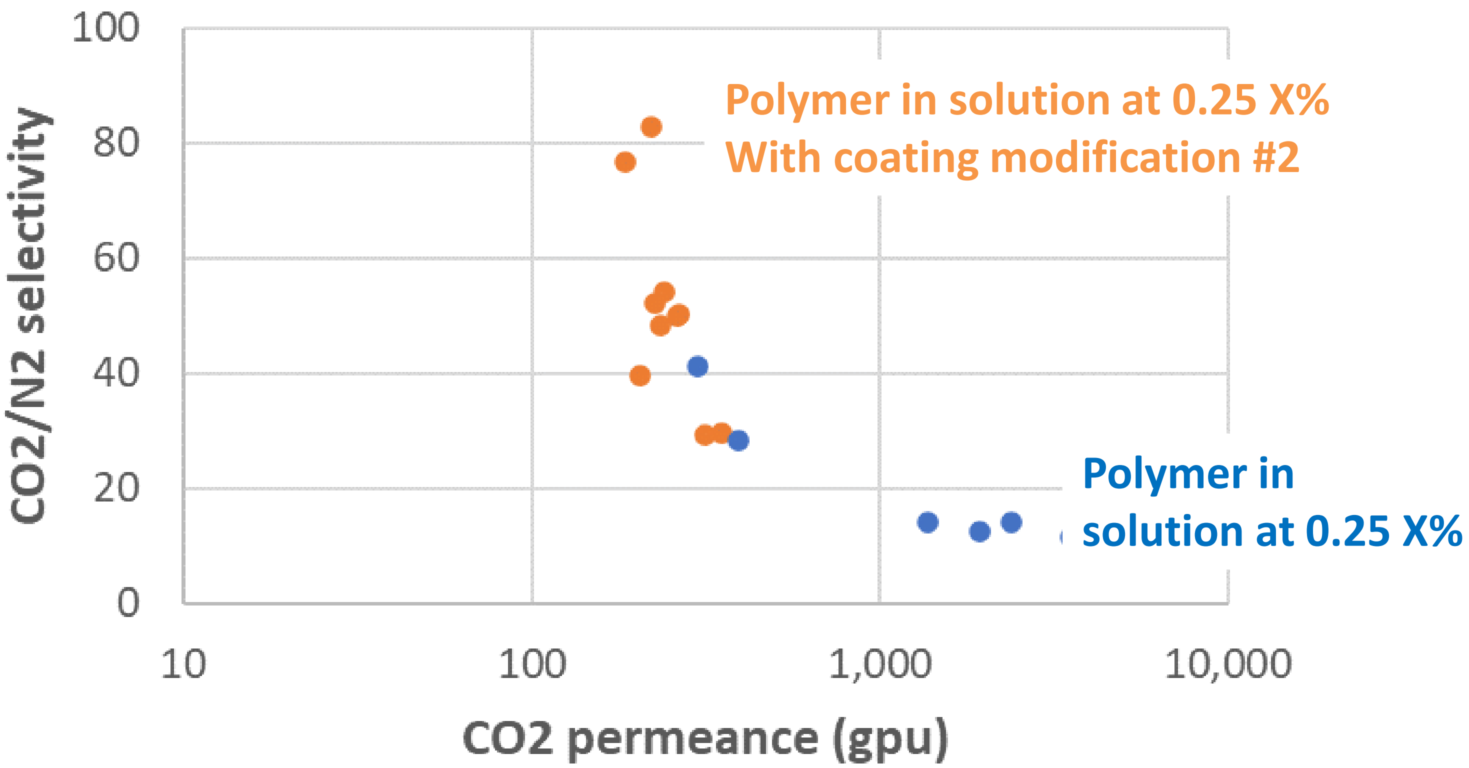

Future BP3 Activities

- Continue work on support membranes

- Continue optimization of composite membranes
  - Optimize coating modifications 1 and 2, separately and in combination
  - Investigate blends of the novel material with the standard Polaris formulation
- Test membranes with pure gases and gas mixture

- Prepare lab-scale modules with improved composite membranes
- Test modules with pure gases and gas mixture

- Design small module test system for NCCC (tabletop system)
- Test at NCCC in first/second quarter of 2023 (depends on GO/NO GO decision)

- Perform Techno-Economic Analysis, Technology Gap Analysis and EH&S Risk Analysis

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Acknowledgements

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- University at Buffalo

  Haiqing Lin

- University of Texas at Austin

  Nathaniel Lynd

Thank You

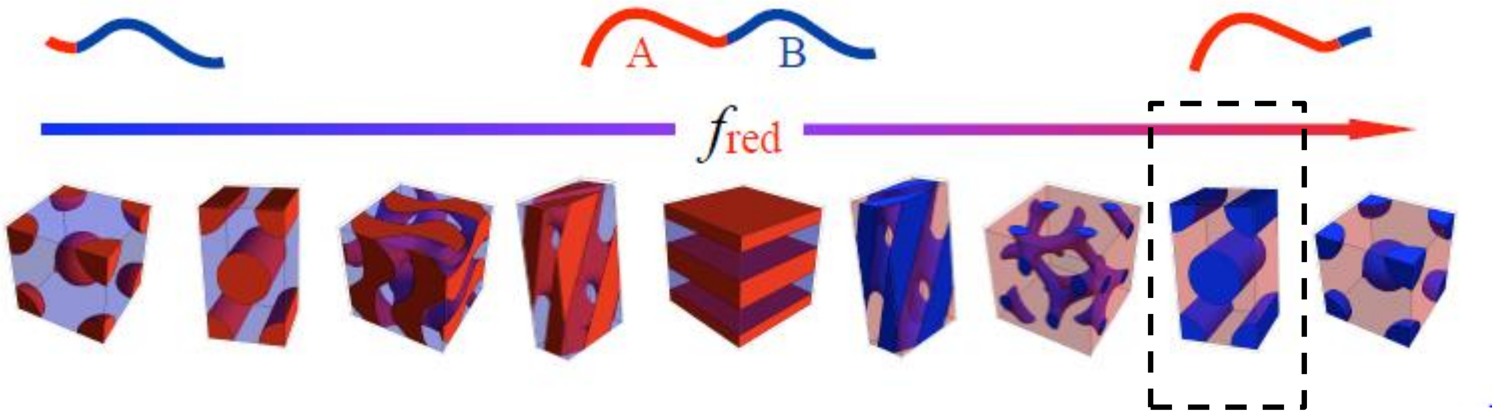
Questions?

Self Assembly

Amphiphilic block copolymer: A is hydrophobic, B is hydrophilic.

Separately A and B are not compatible, but in the block copolymer they are connected.

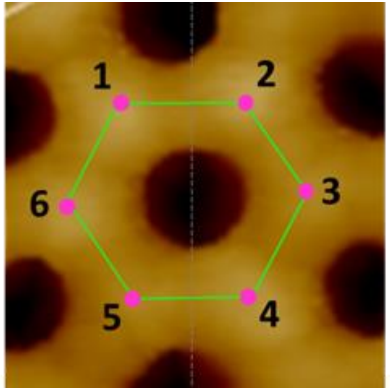
This leads to assembly into a range of different morphologies, depending on composition.



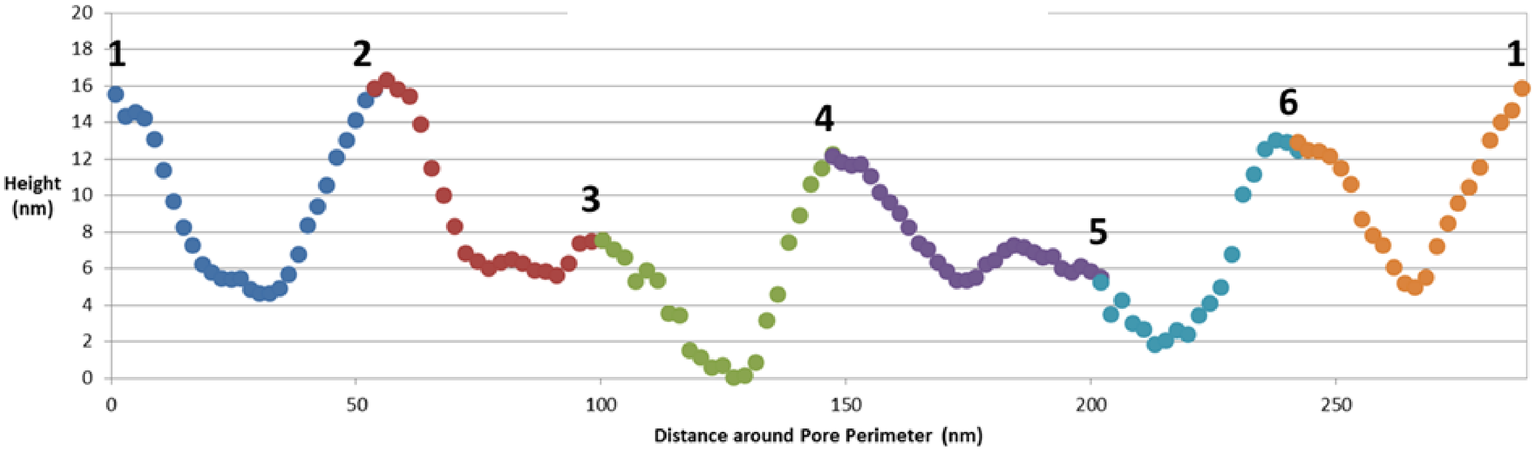
Desired morphology

Height Profile around the Pore

- Confirms the hypothesis that a pore is created by assemblies of six spherical micelles
- The remnants of six micelles surround the pore at the surface and the profile reveals that the spheres have not been completely flattened

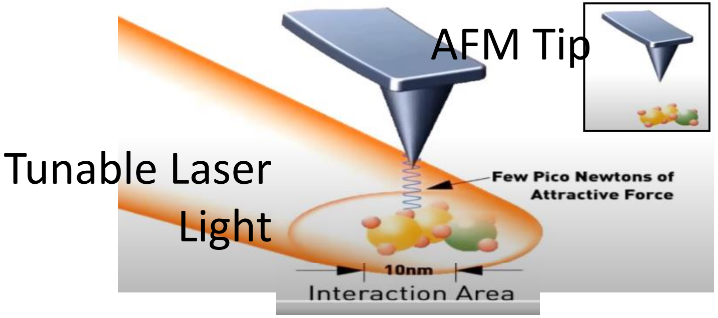


Atomic Force Microscope



Nano-IR + PiFM reveals distribution of the Blocks

- Polystyrene forms the bulk of the support
- Polyvinylpyridine lines the pores
- Top surface shows traces of polyvinylpyridine which is consistent with a top surface covered by a polyvinylpyridine layer of about 5 nm thickness (Nano-IR depth penetration is about 20 nm)



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Nano-IR