MEMBRANE
TECHNOLOGY & RESEARCH

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
Video Meeting, August 16, 2021

Project Overview

- **Award Name:** Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture (DE-FE0031596)
- **Project Period:** June 1, 2018 – November 30, 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 of 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:** Commercial-scale composite membrane development, lab-scale module testing at MTR, bench-scale module test at NCCC

Current Status: - BP2 nearly completed
- BP3 Continuation Application underway

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Project Background

- MTR has developed the **PolarCap™** carbon capture process
- Key component is the highly permeable **Polaris™** membrane

- Higher permeance membranes will reduce cost of capture
- Higher selectivity, but lower permeance, membranes will reduce cost of capture, particularly in industrial capture where CO2 source may be available at elevated pressure

- Higher permeances are typically achieved by making composite membranes with thinner selective layers.

- Our previous work has established that the surface pore structure of the support membrane is a limiting factor for thin selective layers, because:

  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.

  CFD analysis has shown that the pore structure of the support changes the diffusion path in the selective top layer.

Project Objectives, Success Criteria

1. Produce Support Membranes with improved surface structures by
   1. Using block copolymers to create support membranes with isoporous surfaces
   2. Employ a dual-slot die casting technique to make “two-layer” support membranes

2. Demonstrate that these support membranes allow composite membranes to be produced with higher permeances

3. Investigate new selective materials to produce higher selectivity membranes

4. BP2 Success Criteria:
   1. Composite membranes prepared with CO_2 = 3,000 gpu and CO_2/N_2 = 20 (mixed gas)
   2. New selective materials demonstrated to have improved selectivity

5. 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

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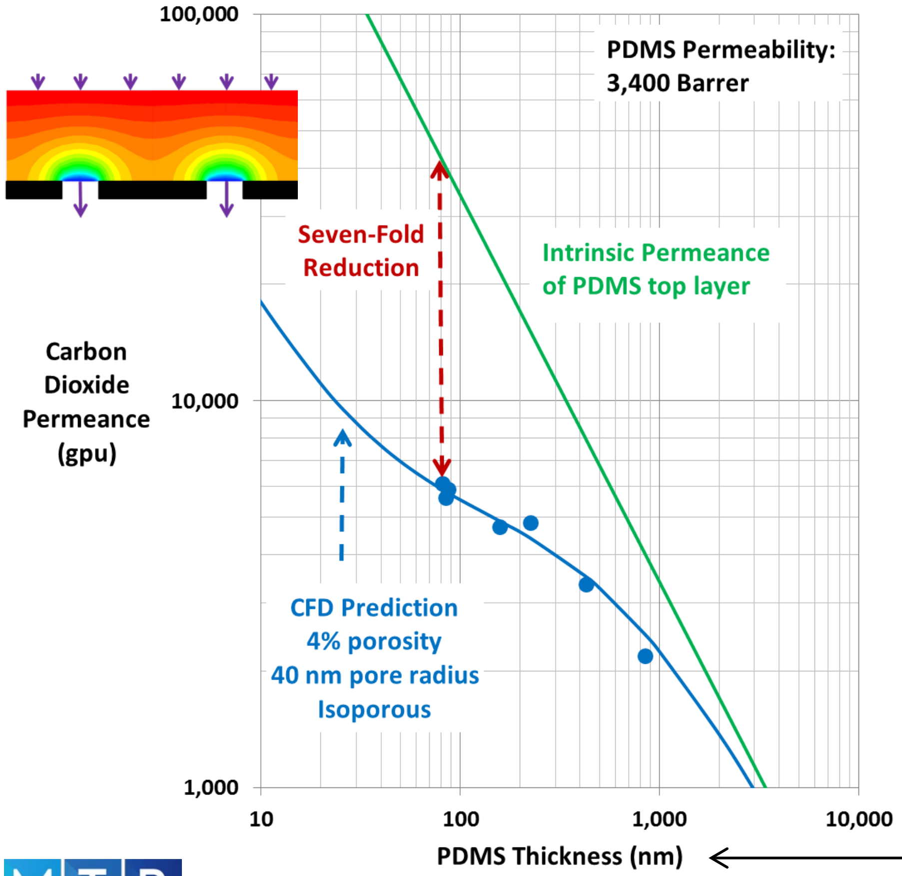
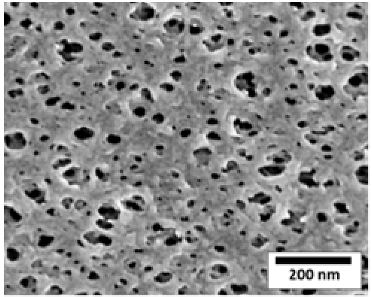
Effect of Support Membrane Surface

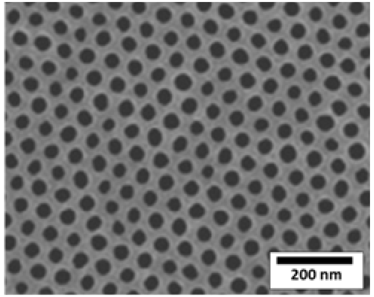


Computational Fluid Dynamics simulations show that non-uniform distribution of surface pores is a major contributor to the reduction in measured permeance. →

Isoporous membranes are ideal supports for composite membranes.

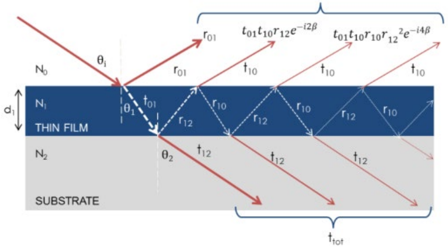


Surface of Conventional Support

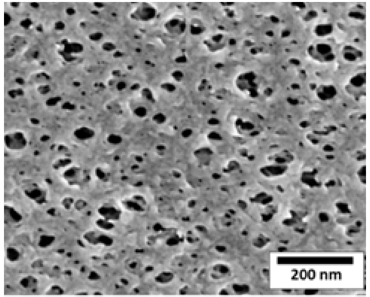


Surface of Isoporous Support

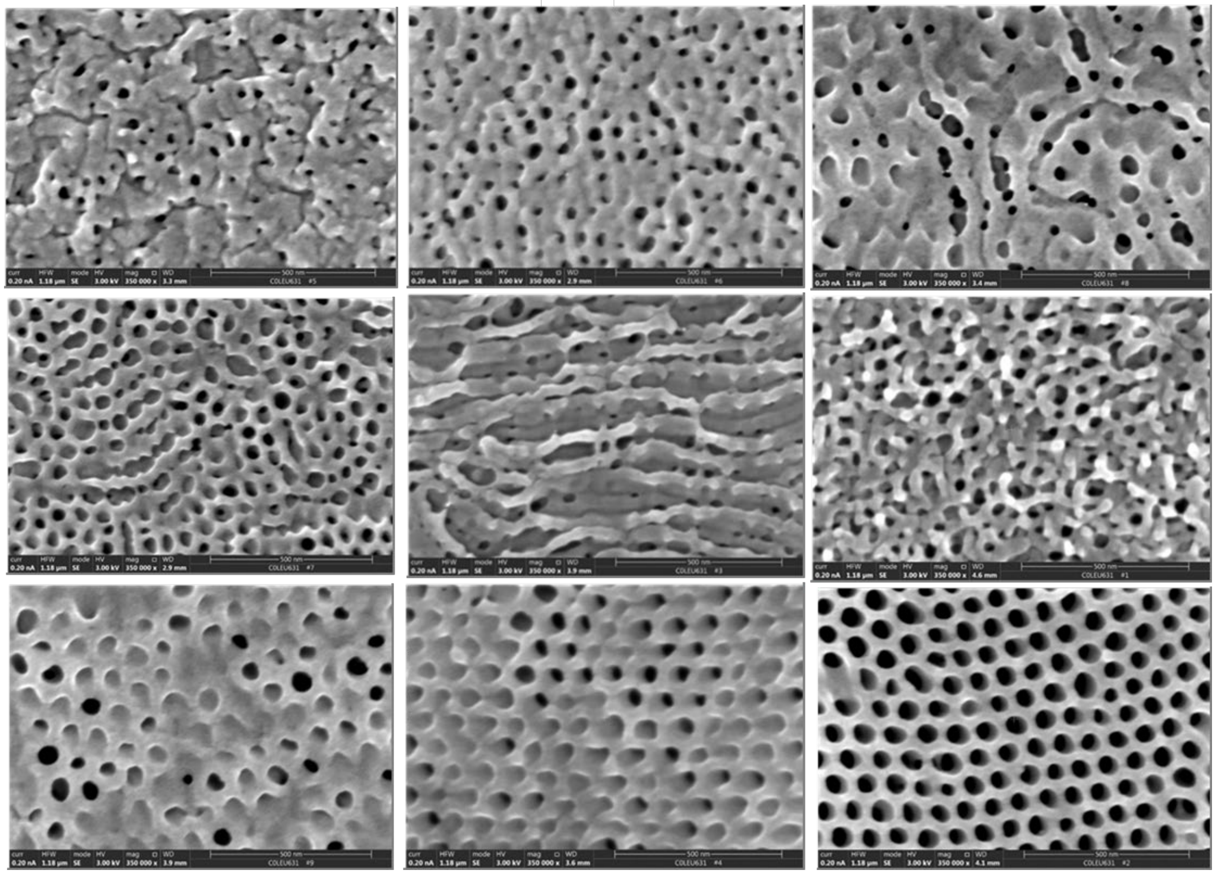
Ellipsometry



Variations in BCP surfaces obtained at MTR



Surface of Conventional Support

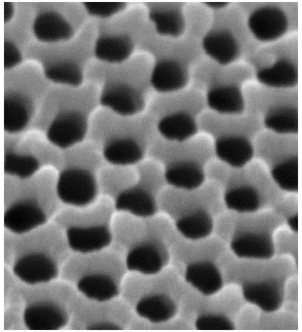


Conclusion:

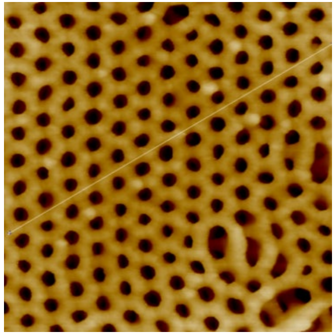
Reproducible preparation of isoporous surfaces on a large scale is difficult.

Isoporous Surface prepared at MTR

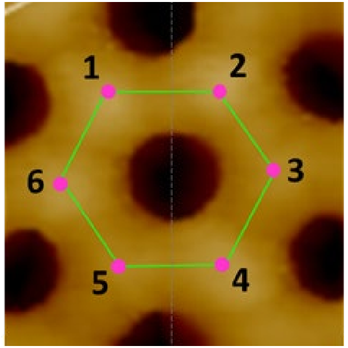
Scanning Electron Microscope

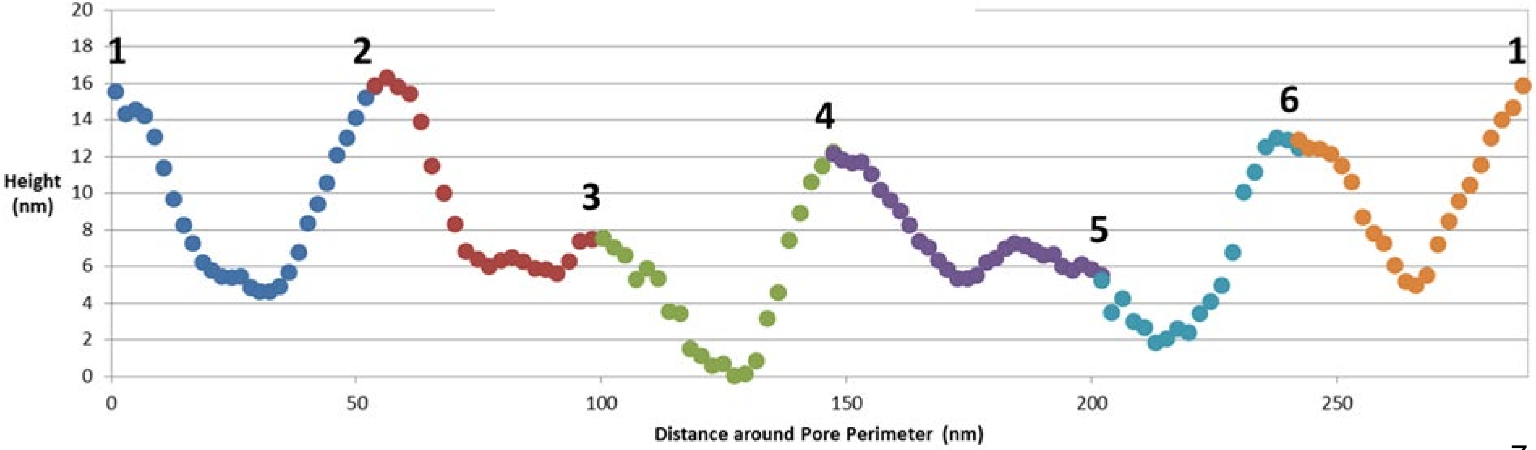


Atomic Force Microscope

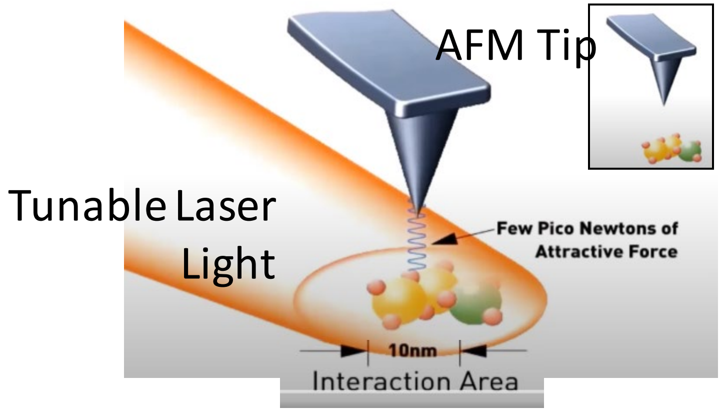


- Hypothesis in literature for mechanism of formation holds that the block copolymer in solution forms micelles that during formation assemble into an ordered structure
- The AFM profile shows that remnants of six micelles surround the pore at the surface
- Confirms the hypothesis that a pore is created by assemblies of six spherical micelles

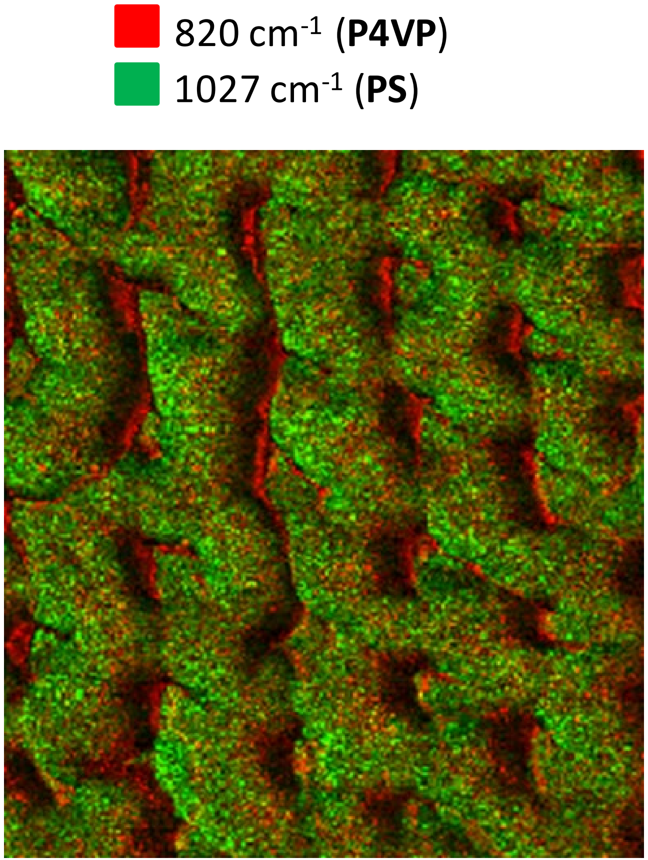




Nano-IR + PiFM reveals distribution of the Blocks



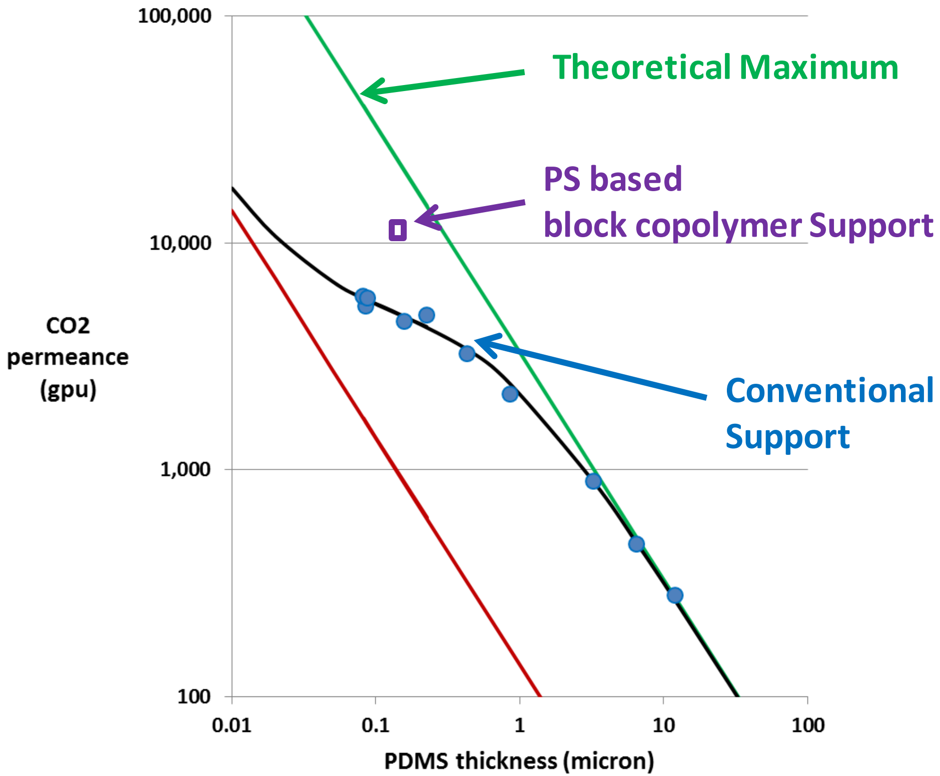
Nano-IR
+
PiFM



- Polystyrene (**PS**) forms the bulk of the support
- Polyvinylpyridine (**P4VP**) lines the pores, indicating that **P4VP** makes up the outer layer of the micelles
- Top surface shows traces of **P4VP** which is consistent with a top surface covered by a **P4VP** layer of about 5 nm thickness (Nano-IR depth penetration is about 20 nm)

PS based Block Copolymer (Polymer Source, Inc.)

- Uncoated permeance of support is 162,000 gpu
- CO_2 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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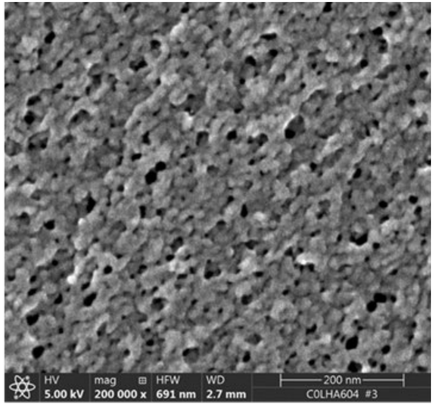
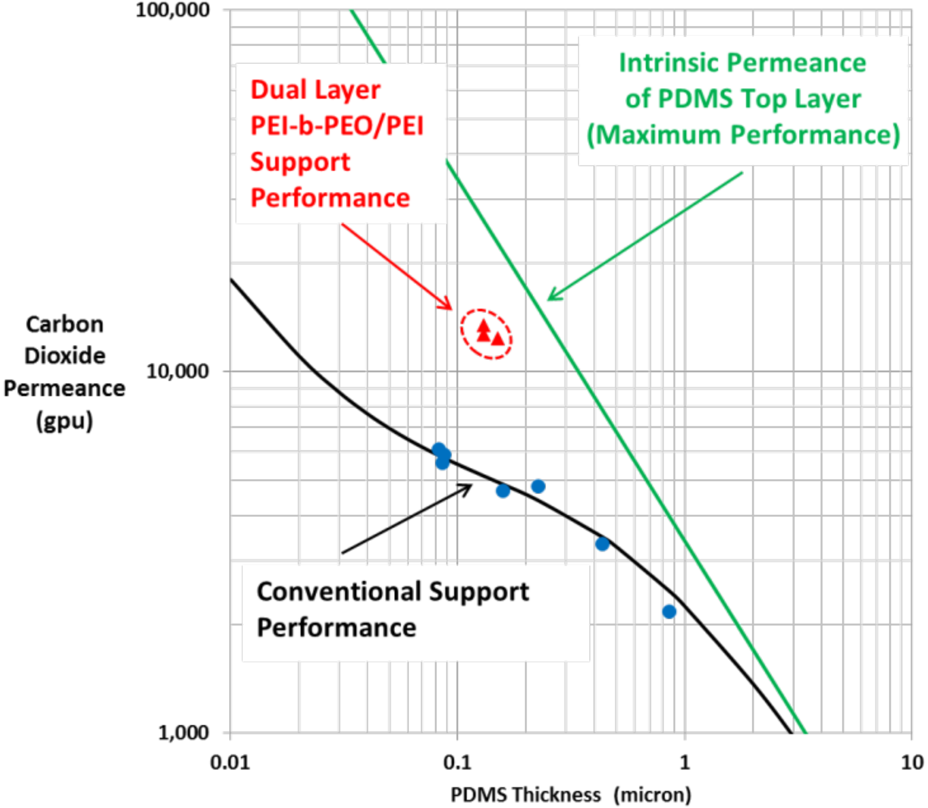
UT Austin Block Copolymer: Hand-Cast Support

- UT Austin developed an alternative approach to making block copolymers
- "Simplified block copolymer"
- Hand-cast dual layer supports with the **PEI-b-PEO block copolymer** as top layer
- Excellent support membranes, even though the surface is not truly isoporous:



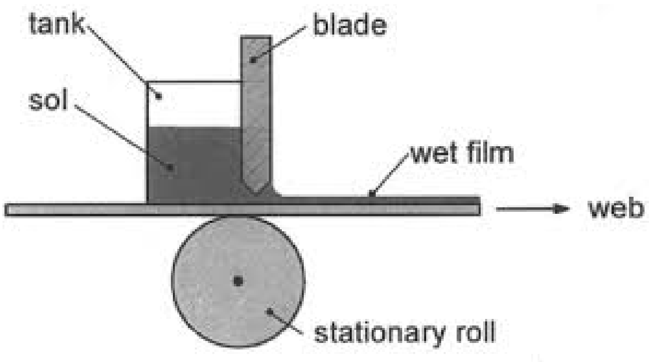
PEI-b-PEO block copolymer
N2 permeance = 95,000 gpu



Support Casting Techniques

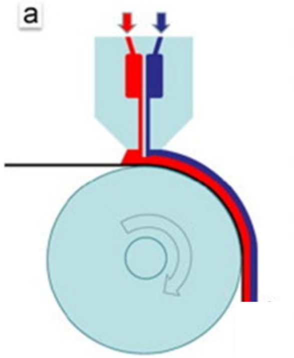
Blade Casting (conventional):

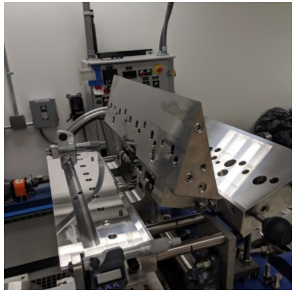
- Common method for membrane casting
- Simple equipment, simple operation
- Allows for deposition of only one layer

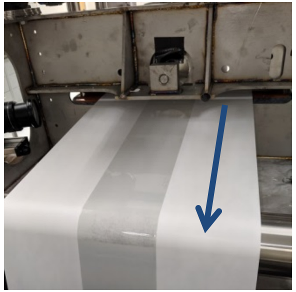


Slot Die Casting (this project):

- Possible to deposit multiple layers
- Better control of thicknesses
- More complicated, but used on large scale in many casting and coating operations







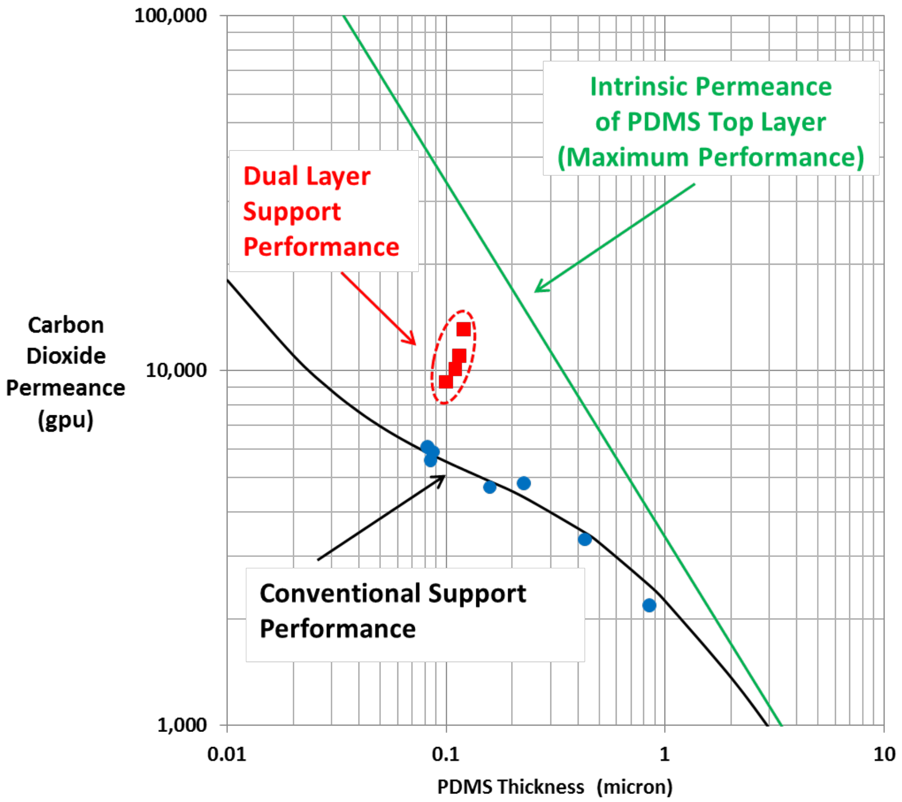
Conventional Polymer, Dual Slot Die

- **Dual Slot Die in stalled on MTR R&D casting machine**

- 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**

- Casting runs sufficiently long that Polaris coating runs can be made on MTR R&D coating machine.



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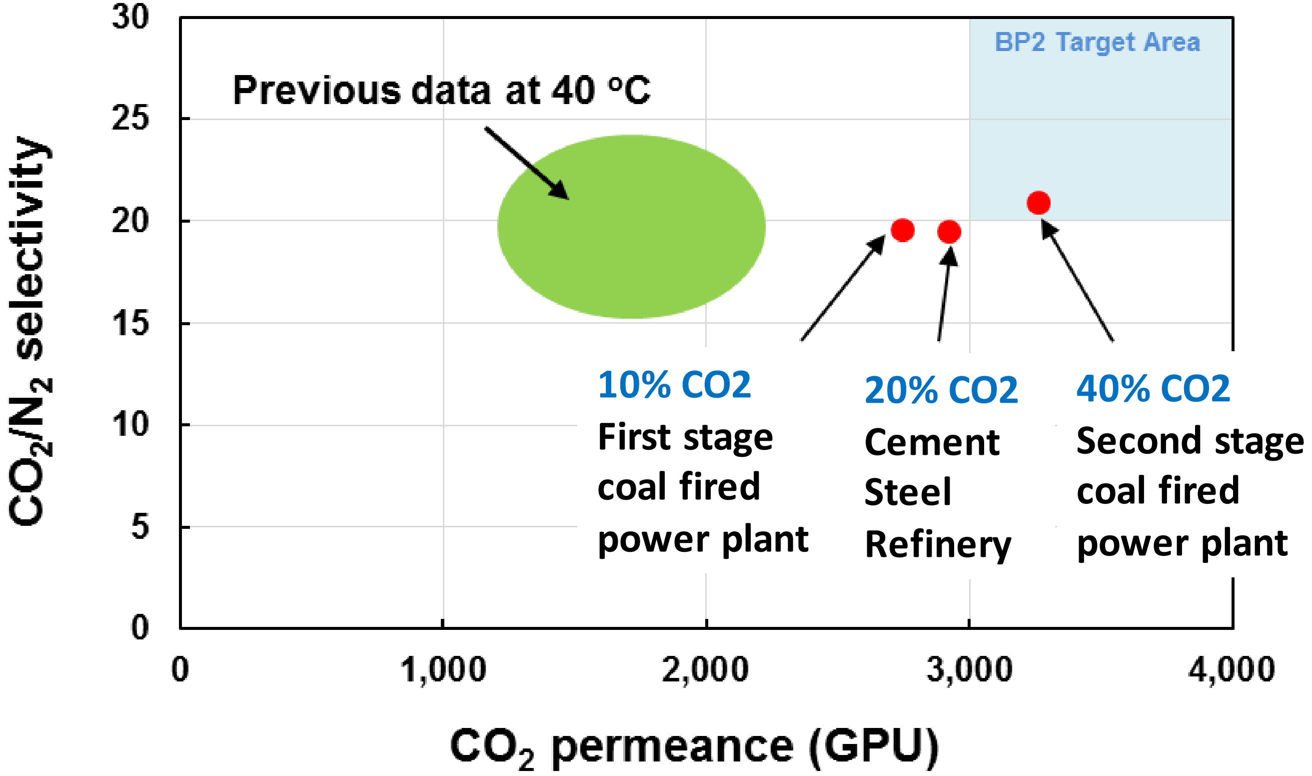
Current Best Polaris Membrane Performance



Membrane performance at 40C with dry CO2/N2 gas mixture.
Presence of water vapor increases permeances by 10 to 15%.

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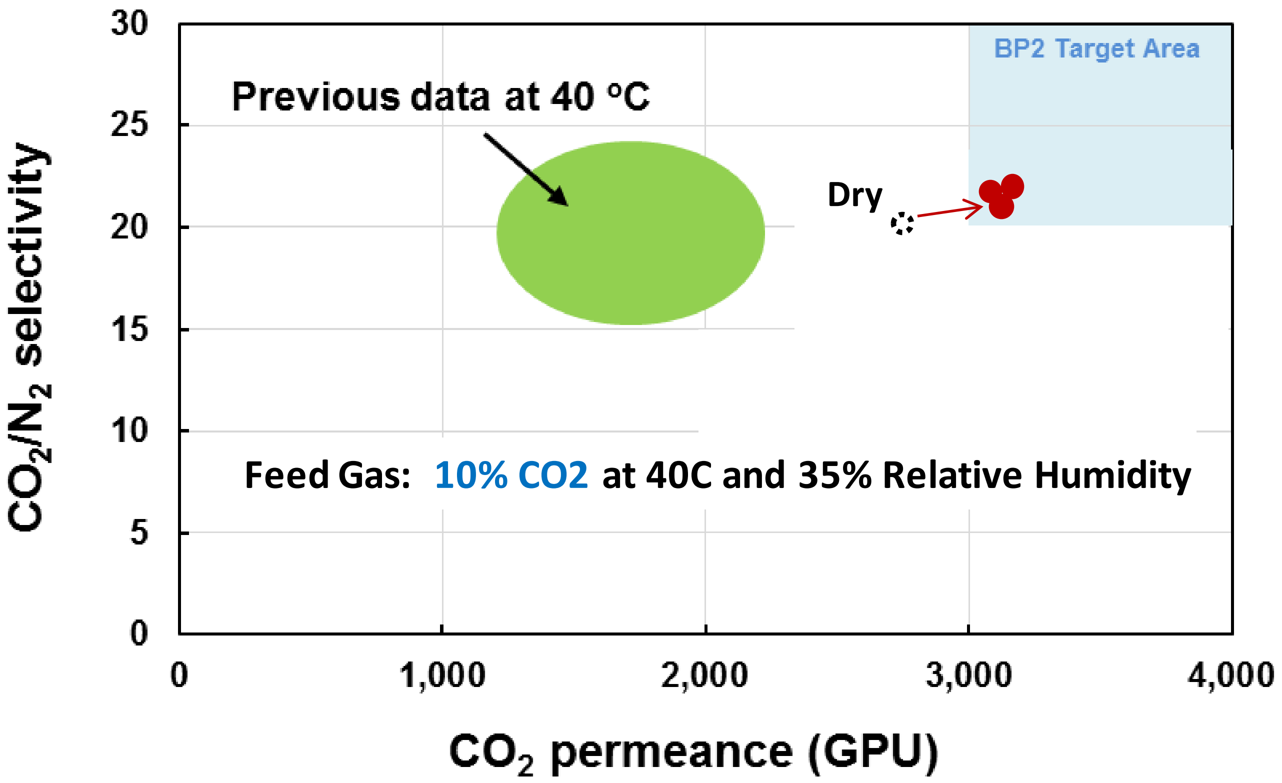
Polaris Performance with Wet Gas



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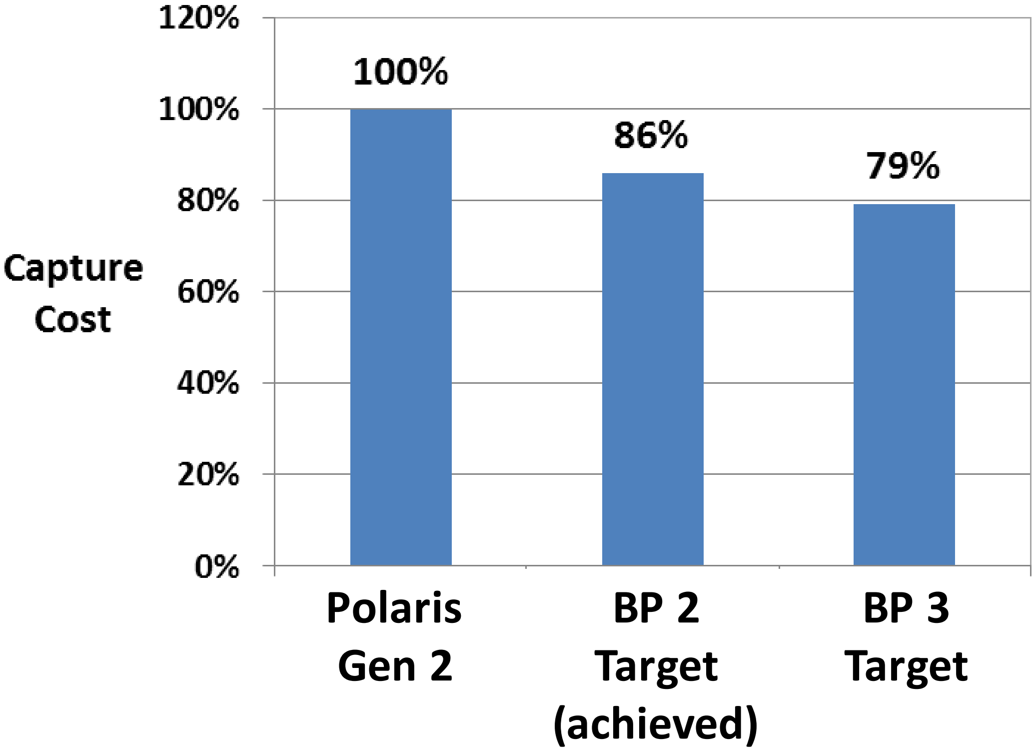
Effect of Membrane Improvement

Initial Techno-Economic Analysis:

- Effect of improved membrane.
- No optimization of operating pressures.



Polaris Gen 2	BP 2 Target (achieved)	BP 3 Target
1,200 gpu	3,000 gpu	4,000 gpu
CO2/N2 = 25	CO2/N2 = 20	CO2/N2 = 25

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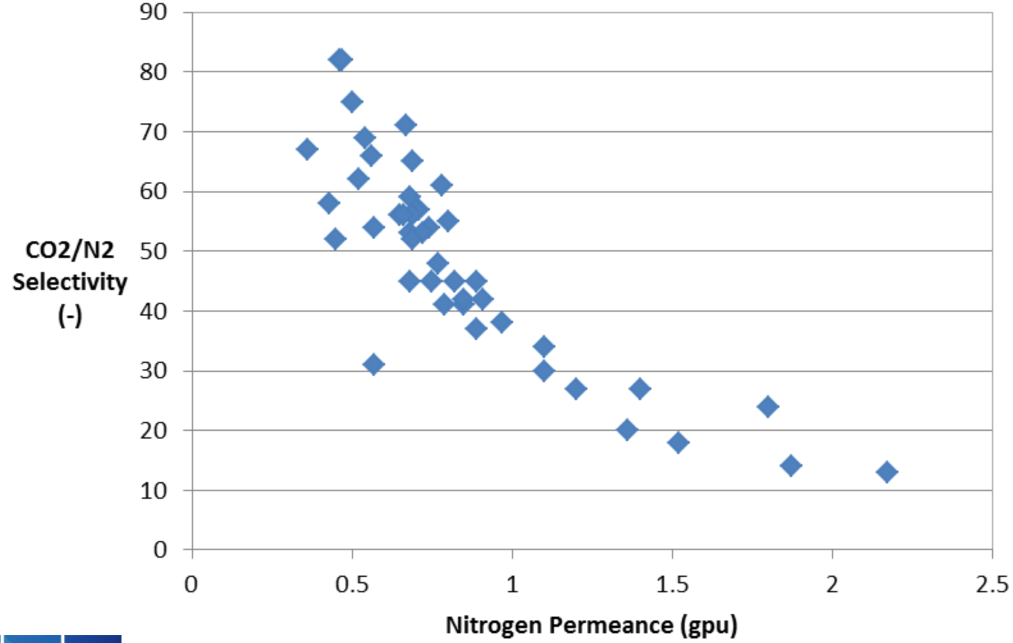
Novel Selective Materials

We confirmed that the novel materials made by the University of Buffalo have high selectivities, but also discovered that it is very difficult tailoring the MTR Polaris coating techniques to these new materials.



34 membranes
4 monomer batches

Difficulty in producing defect-free top layers → multiple coatings

The approach developed for BP3 is to combine the polymer synthesis and chemistry expertise of the University of Buffalo and UT Austin to solve this problem.

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Planned BP3 Activities

- Scale up PEI-b-PEO block copolymer manufacture to 1 kg scale (UT Austin)
- Synthesize alternative block copolymers (UT Austin)

- Install 40” wide dual slot die on MTR commercial casting machine
- Manufacture block copolymer based support membranes on commercial machine

- Prepare Polaris composite membranes on commercial coater
- Test Polaris membranes with pure gases and gas mixture

- Develop methods to turn the NYUB novel selective materials into suitable coating solutions (Buffalo and UT Austin)
- Prepare composite membranes with novel selective materials

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

- Build test system for small modules and operate at NCCC

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

Acknowledgements

- **U.S. Department of Energy**

  National Energy Technology Laboratory

  Carl Laird

- **University of Buffalo**

  Haiqing Lin

- **University of Texas at Austin**

  Nathaniel Lynd

Thank You

Questions?

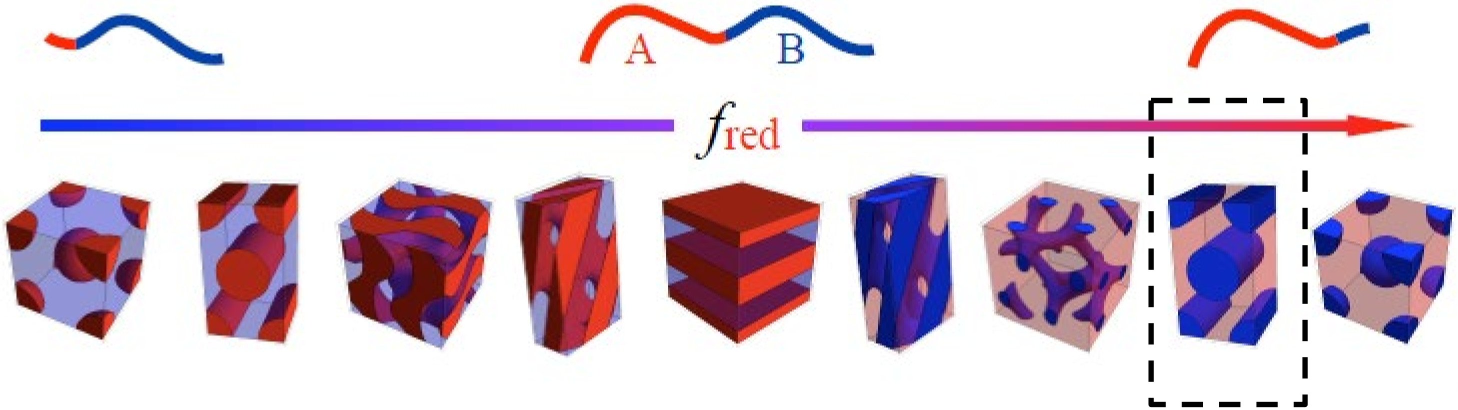
Extras

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.



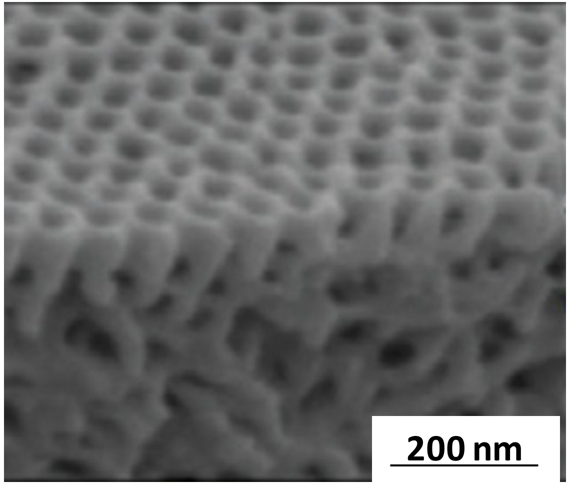
Desired morphology

Self Assembly → Isoporous

Asymmetric superstructure formed in a block copolymer via phase separation

KLAUS-VIKTOR PEINEMANN, VOLKER ABETZ* AND PETER F. W. SIMON
Institut für Polymerforschung, GKSS-Forschungszentrum Geesthacht GmbH, Max-Planck-Str. 1, 21502 Geesthacht, Germany
*e-mail: volker.abetz@gkss.de

(2007)



- Amphiphilic Block Copolymer in mixed solvent, evaporation step followed by immersion precipitation
- Block copolymers consist of two blocks, each block has a controlled molecular weight (mono disperse): Expensive

- Method creates top surface with highly ordered porous structure
- Literature working hypothesis is that the pores are formed via assembly of micelles, which have the majority blocks at the center and the minor block at the surface
- Structure below top layer has a “tendril” like structure, and is different from the porous structure in conventional porous supports

Nano-IR + PiFM

Nanoscale InfraRed Spectroscopy + Photo-induced Force Microscopy

- Atomic Force Microscopy scans the surface of the sample by measuring the attractive force between the AFM Tip and the sample

- A laser with variable wavelength is used to polarize the sample which increases the attraction with the AFM Tip.

- The degree of polarization depends on the laser frequency and the chemical nature of the sample, much like is seen in an FTIR spectra.

- Sample area is about 10 nm by 10 nm
- Laser penetrates sample by about 20 nm

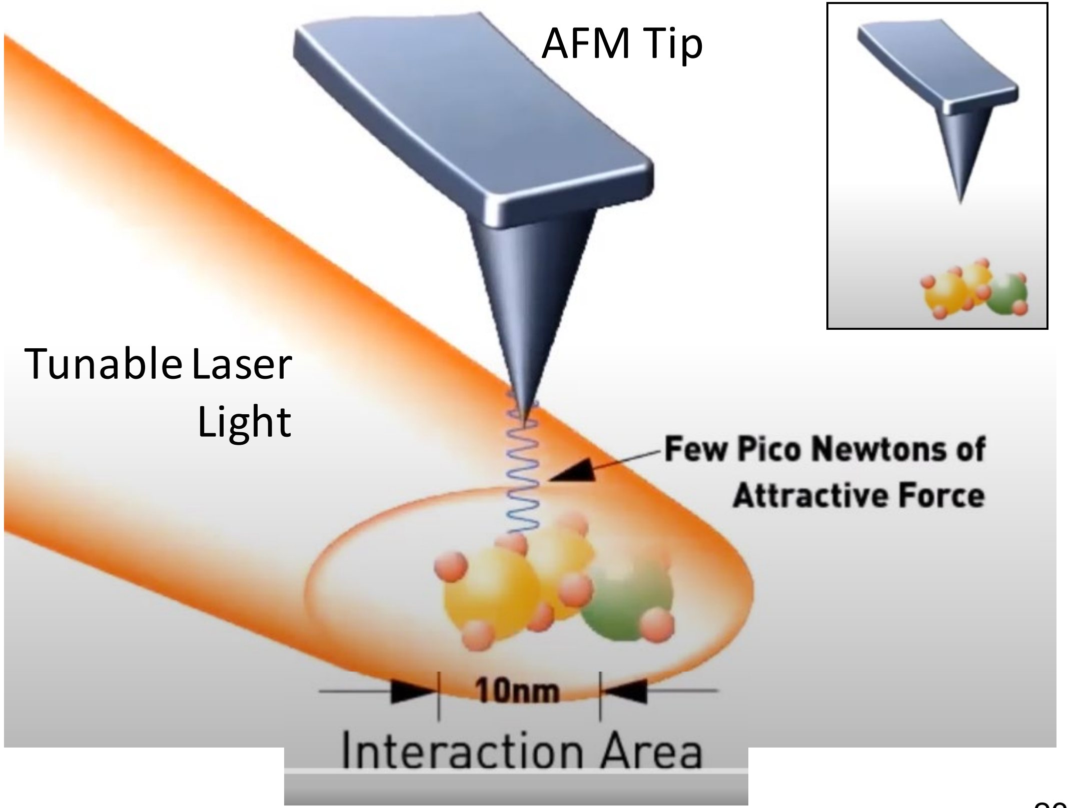


Image courtesy of
Molecular Vista, San Jose, CA
www.molecularvista.com

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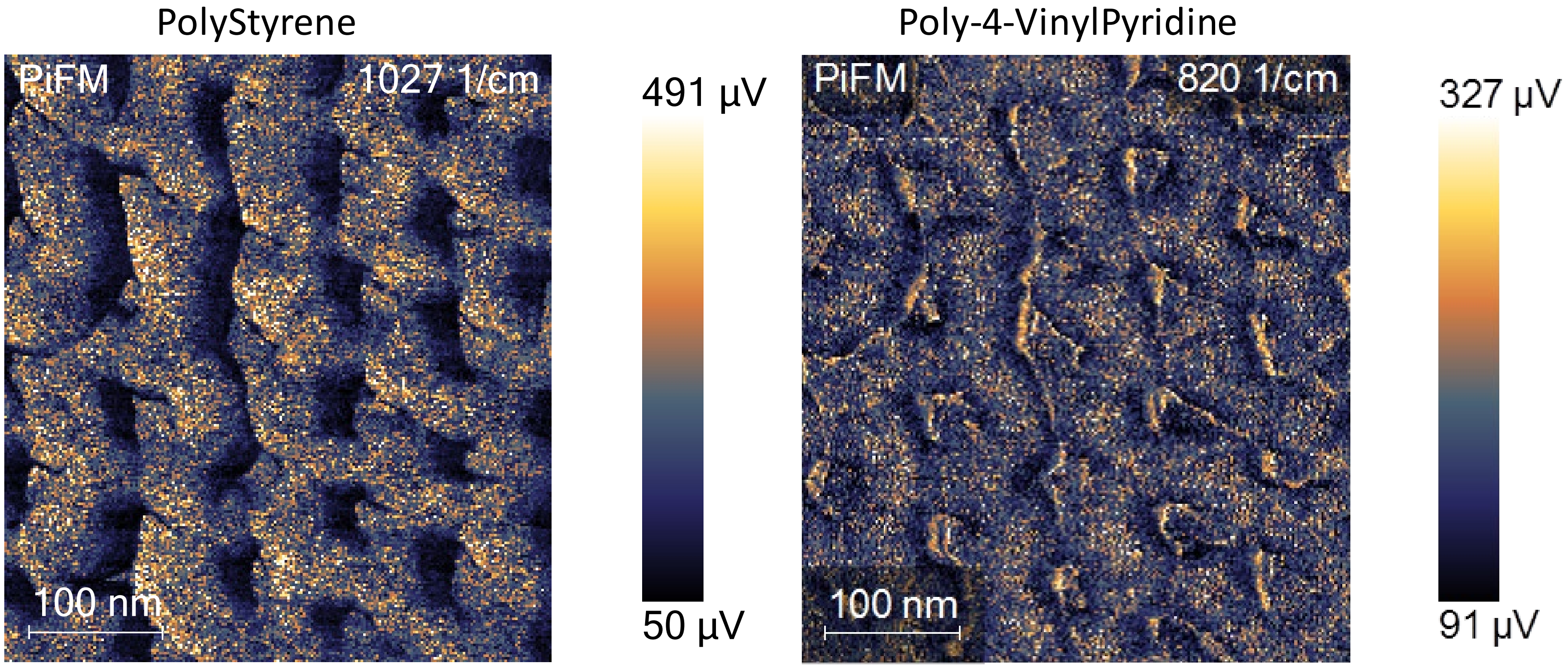
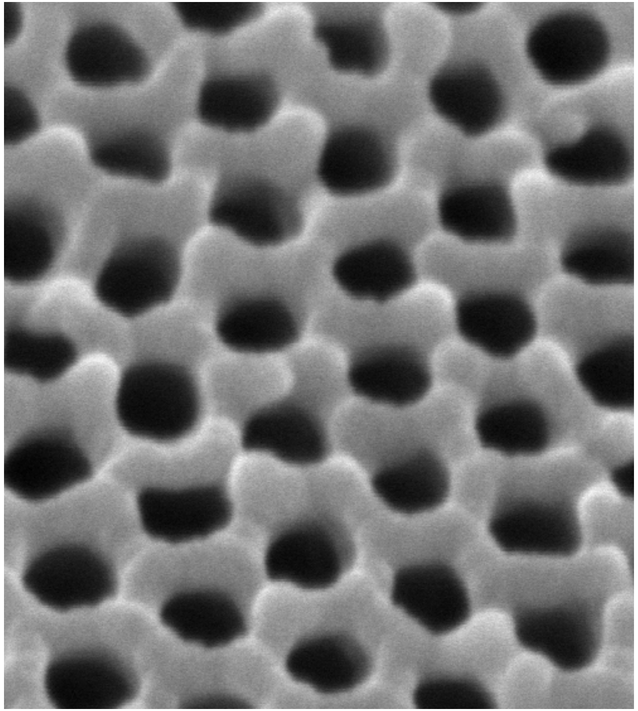
PS-b-P4VP block copolymer: PS and P4VP areas



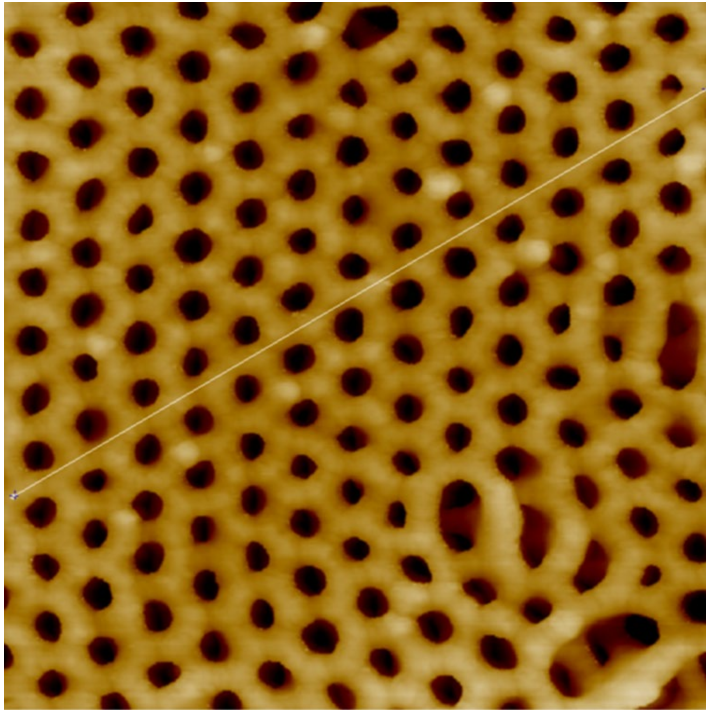
Looking into the pore openings: No polystyrene, all poly-4-vinylpyridine
In between pores: Mostly polystyrene, but also some poly-4-vinylpyridine

Isoporous Surface prepared at MTR with PS based block copolymer (Polymer Source)

Scanning Electron Microscope

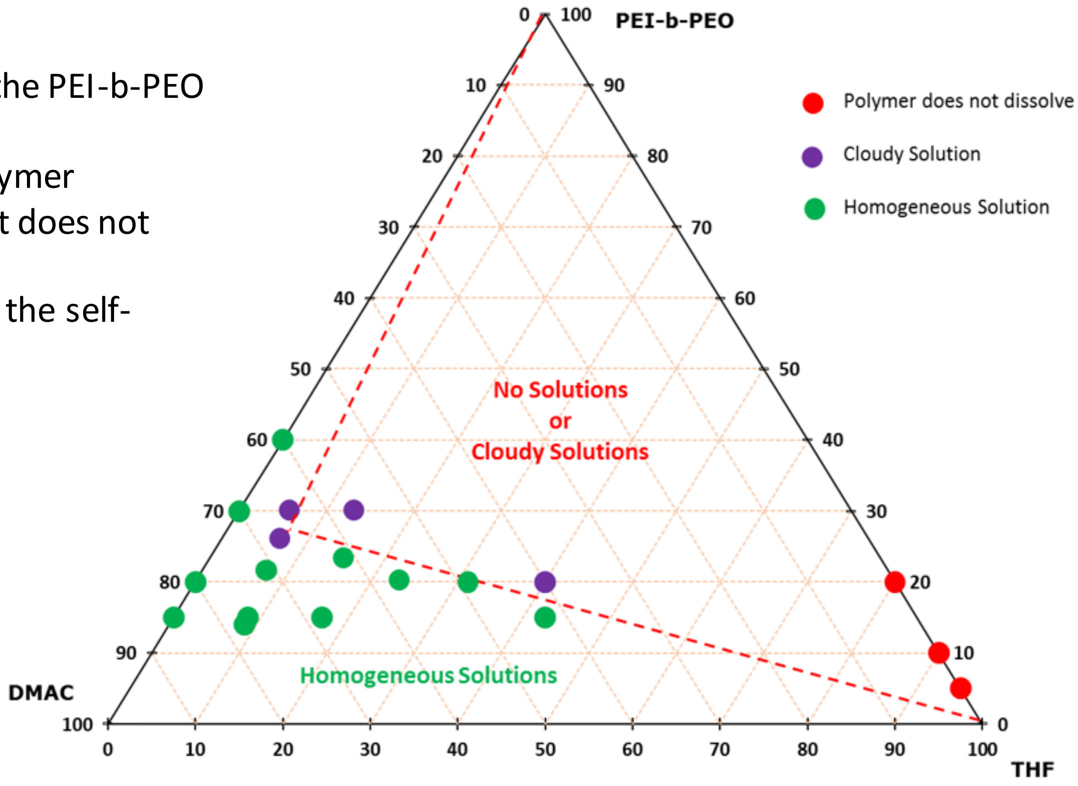


Atomic Force Microscope



Solvent System for PEI-b-PEO

- Developed solvent systems that dissolved the PEI-b-PEO block copolymer
- DMAc is a good solvent for the block copolymer
- THF is a good solvent for the PEO block, but does not dissolve the block copolymer
- Small amounts of THF are used to facilitate the self-assembly of the PEO blocks



- Successfully produced a porous support in hand casting experiments
- Uncoated support has permeance of 68,000 gpu.
- Pore radius is 38 nm

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Structure of the Project

Self Assembly of
Block Copolymers
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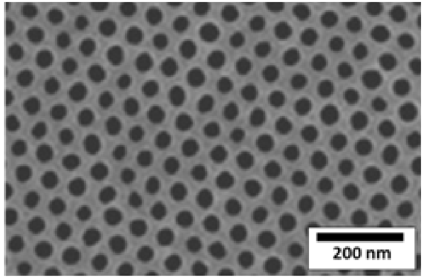
Synthesis Novel
Block Copolymers
UT Austin

Improved
Support Membranes



Dual Slot Die
Casting Technique
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Synthesis Novel
Selective Materials
NYU Buffalo

Existing Polaris
Selective Material
MTR

Polaris Carbon Capture
Composite Membranes
**With Improved
Permeance**

Polaris Carbon Capture
Composite Membranes
**With Improved
Selectivity**

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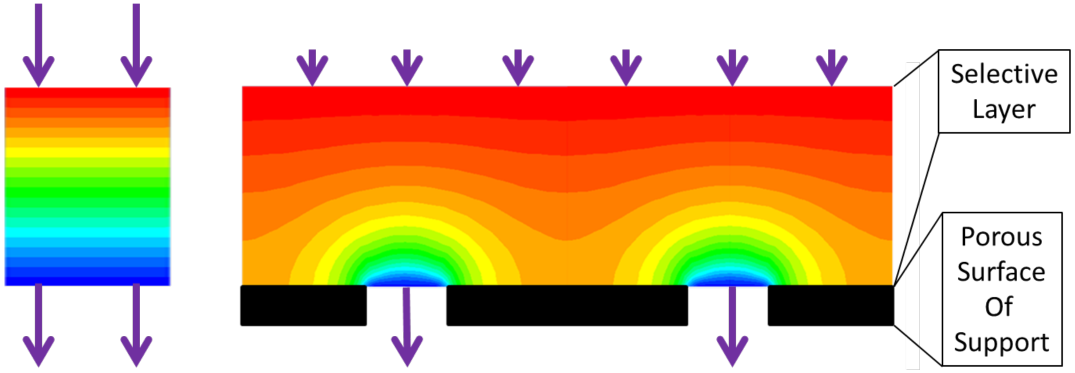
Computational Fluid Dynamics



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

CFD results for uniform pore distribution are very accurately correlated by:

$$\psi(\phi,\tau) = \frac{\phi + 1.6 \cdot N_R^{1.1}}{1 + 1.6 \cdot N_R^{1.1}} \quad \text{where} \quad N_R = \frac{\phi \cdot \tau}{1 - \phi}$$

Top Layer Thickness/ Pore Radius

Wijmans and Hao (2015)

Permeance Reduction

Porosity

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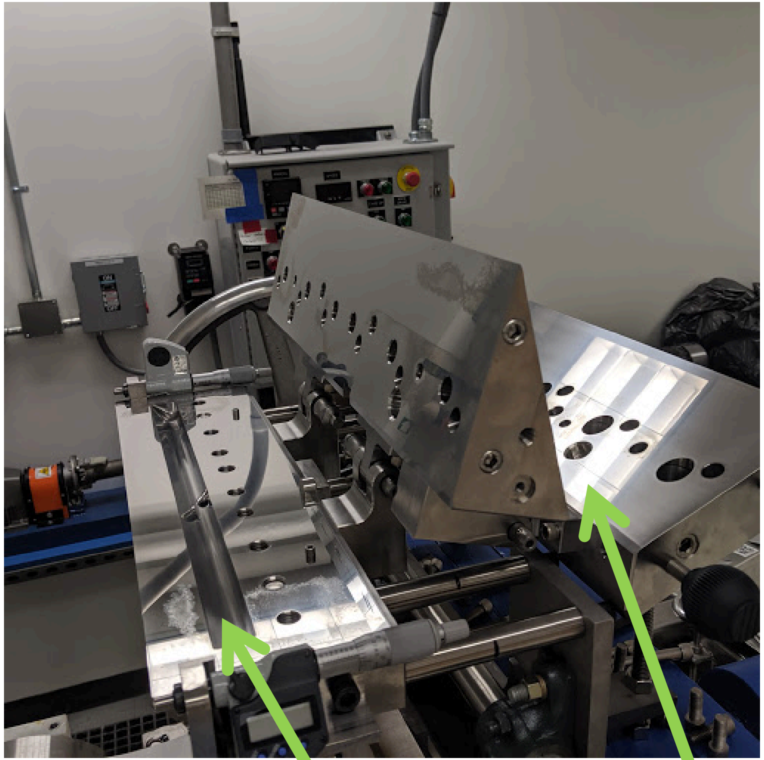
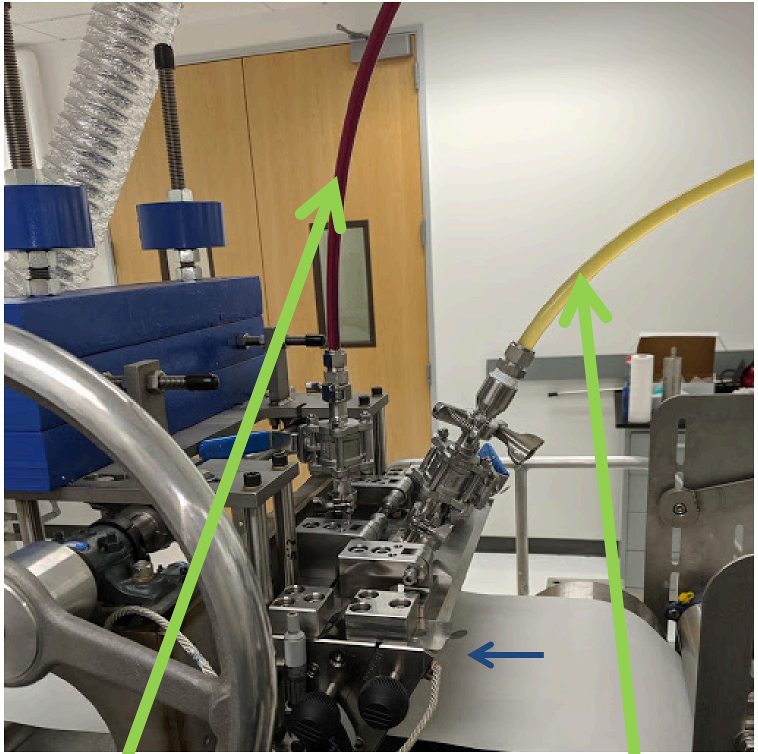
Slot Die Casting



Slot Two

Slot One



Top Layer Solution

Bottom Layer Solution

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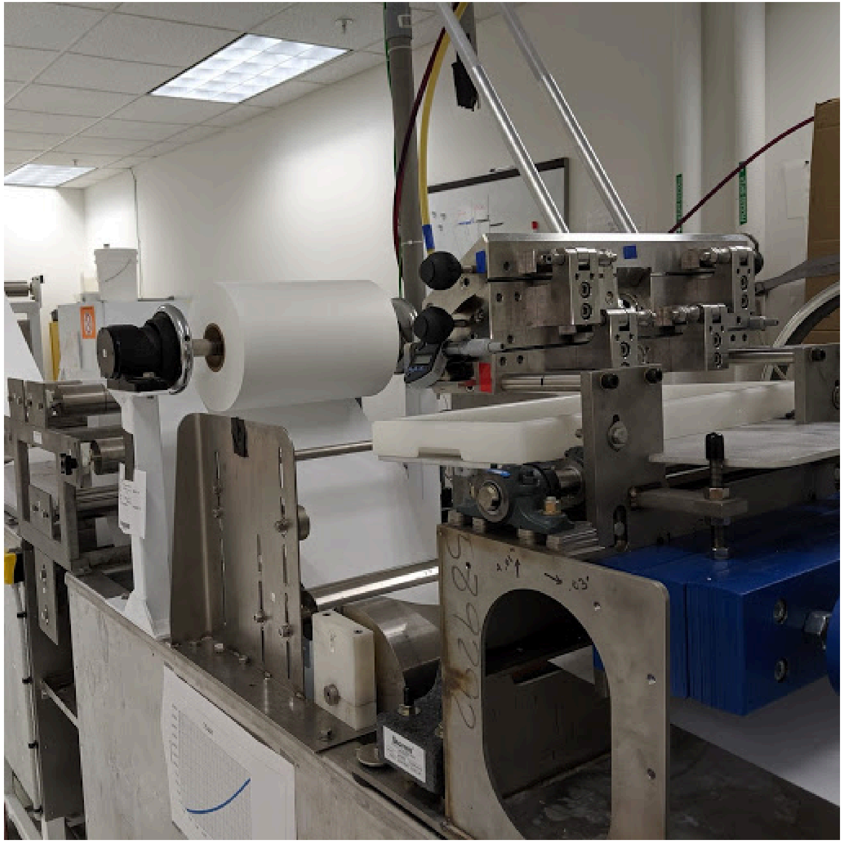
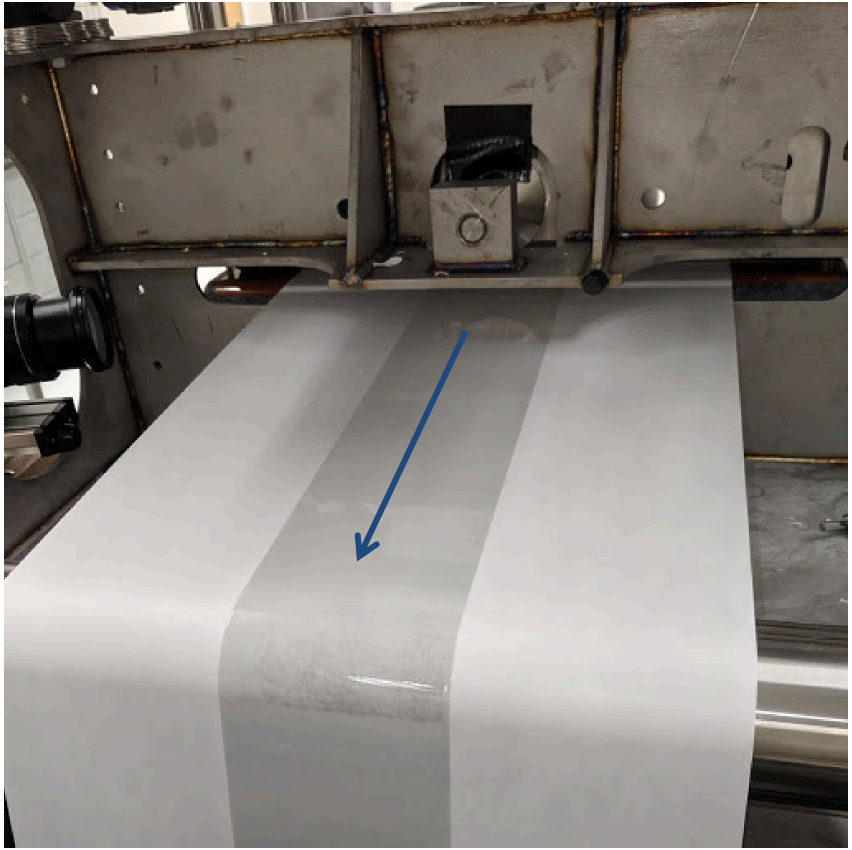
Slot Die Casting



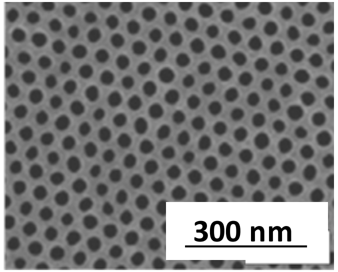


Alternative to "Perfect" Block Copolymers

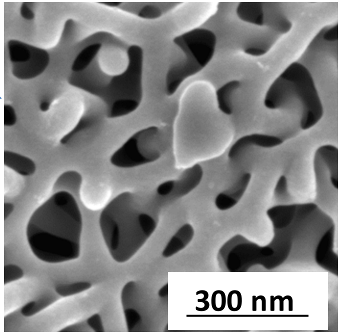
The perfect block copolymer, very expensive,
A and B are monodisperse in molecular weight:

A B

Perfect Conditions



Less Perfect Conditions



Start with Polyetherimide, commercially available engineering polymer, polydisperse:
(Prof. Lynd, UT Austin)

A

The polymer chains have two different end groups, but these are distributed randomly. Attaching a block B to the polymer thus will create a mixture of three different configurations.

50%	A B
25%	B A B
25%	A

BP2 subcontract with UT Austin ($30,000)

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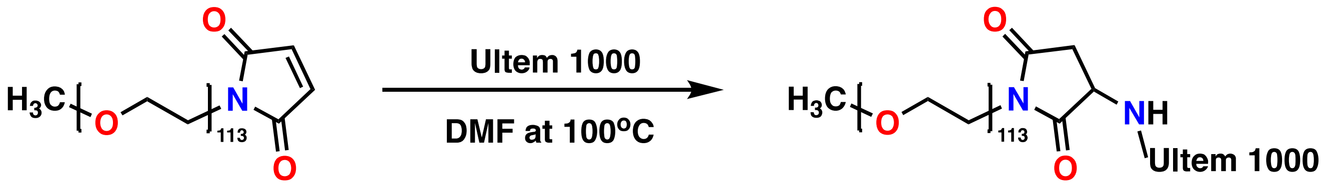
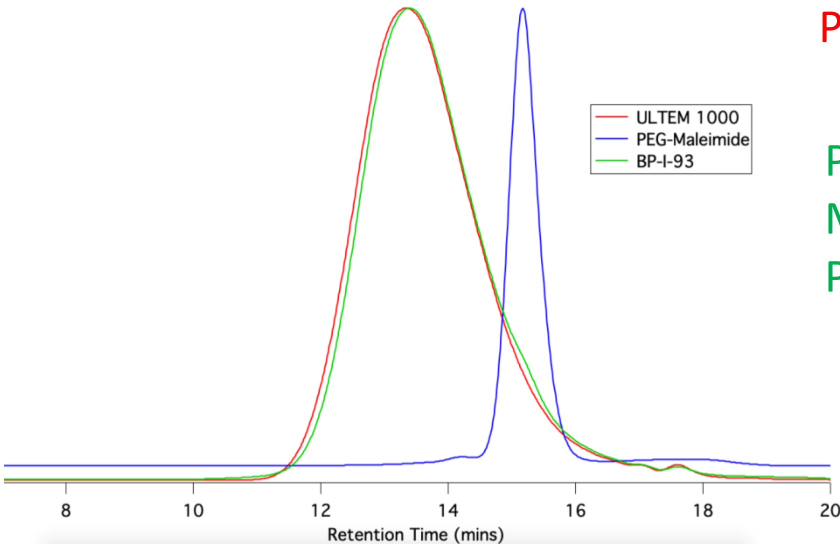
UT Austin block copolymer

The approach is to attach a Poly-ethylene-oxide block (M=5k) to the commercially available engineering polymer Ultem 1000 (poly-ether-imide):



- About 50 grams of this material has been delivered to MTR
- UT Austin will scale up to 1 kg range

- UT Austin has provided MTR with samples based on 2k and 10k PEO.



Ultem 1000
M_n = 18.1k
PDI = 2.0

Product
Mn = 24.1k
PDI = 1.6

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Two Layer Approach: Dual Slot Die

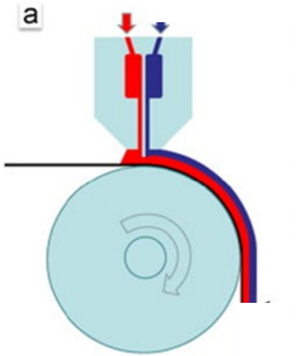
- Two separate layers created in a single step
- Top layer can be very thin (10 micron or less)

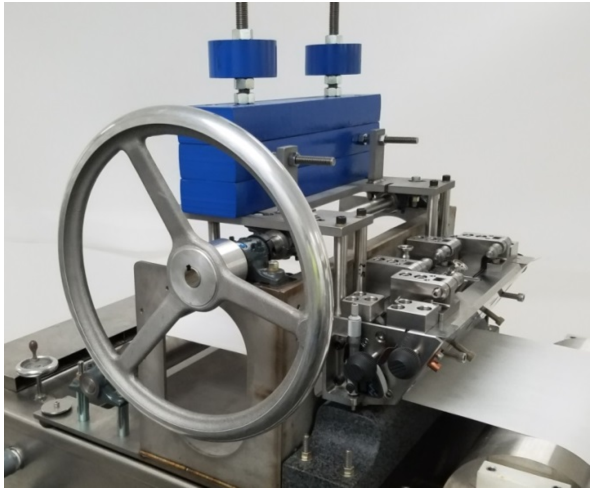
- Makes it possible to reduce block copolymer usage
- Independent optimization of two layers

- Dual slot die installed on MTR R&D caster
- Installation, pump system, completed in Sep 2019

- Each run requires at least 20 gram of polymer (top layer)

- Initial work on dual layer supports was carried out with conventional polymers





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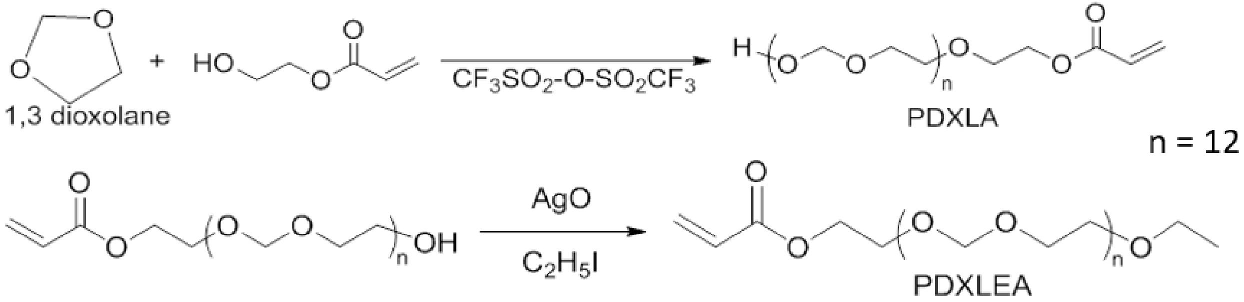
Materials with High Oxygen/Carbon Ratio

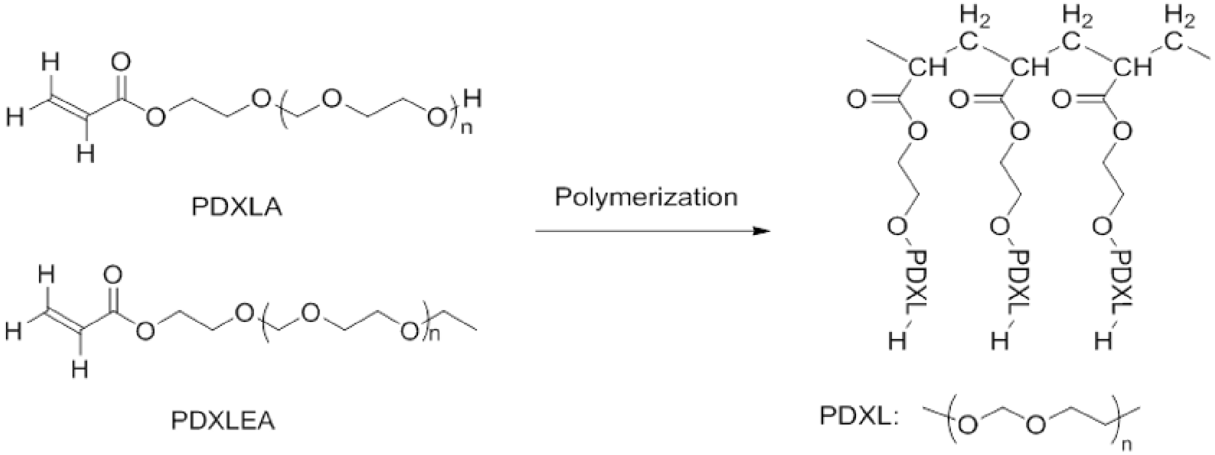
(University of Buffalo)

i. Synthesis of PDXL Macromonomers (CROP)



Successful preparation of high permeance composite membranes requires an intermediate step.

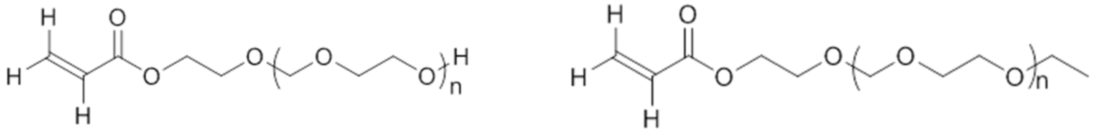
ii. Preparation of Polymers (Photo-Polymerization)

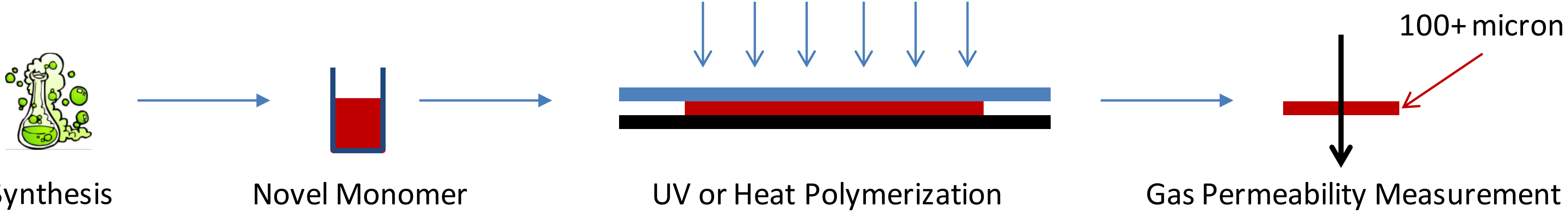


Novel Selective Materials

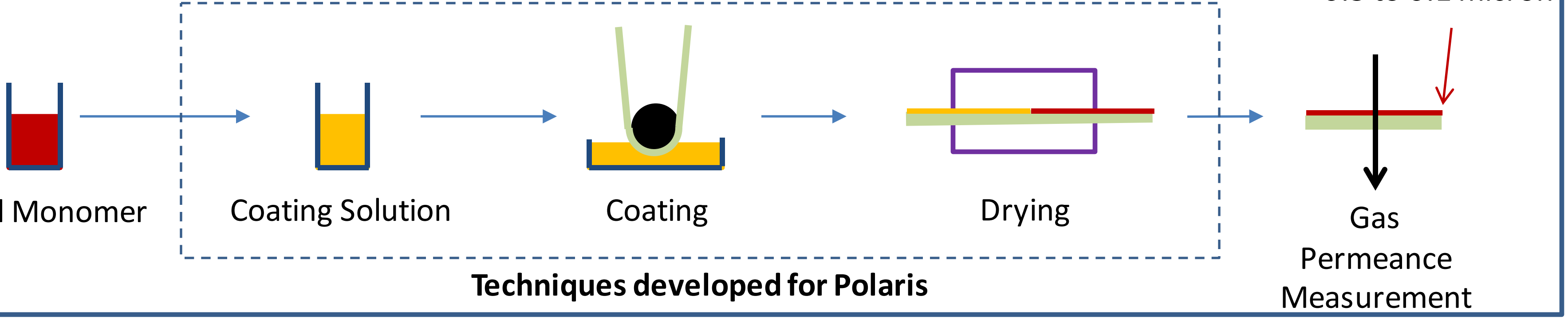
NYU Buffalo

Two high O content monomers:





MTR



Block Copolymer, Dual Slot Die

Dual Slot Die Casting Block, Bottom Layer is PEI Homopolymer, 11” wide, Top layer is PEI-b-PEO block copolymer, 4” wide

11”

4”

PEI Homopolymer

Thickness = 50 micron

N2 = 38,000 gpu

PEI-b-PEO block copolymer on PEI Homopolymer

Thickness = 70 micron

N2 = 140,000 gpu

More translucent

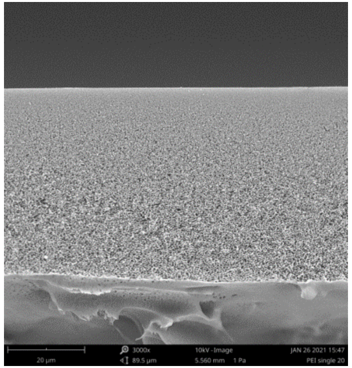
PEI Homopolymer

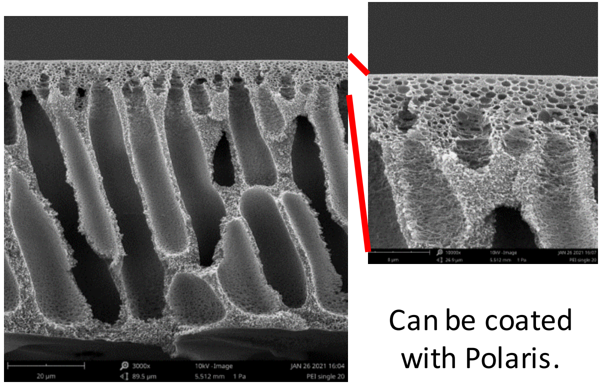
Thickness = 50 micron

N2 = 38,000 gpu

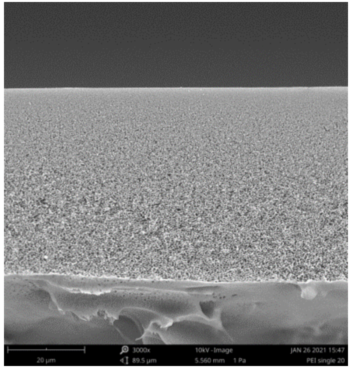
Paper

Paper



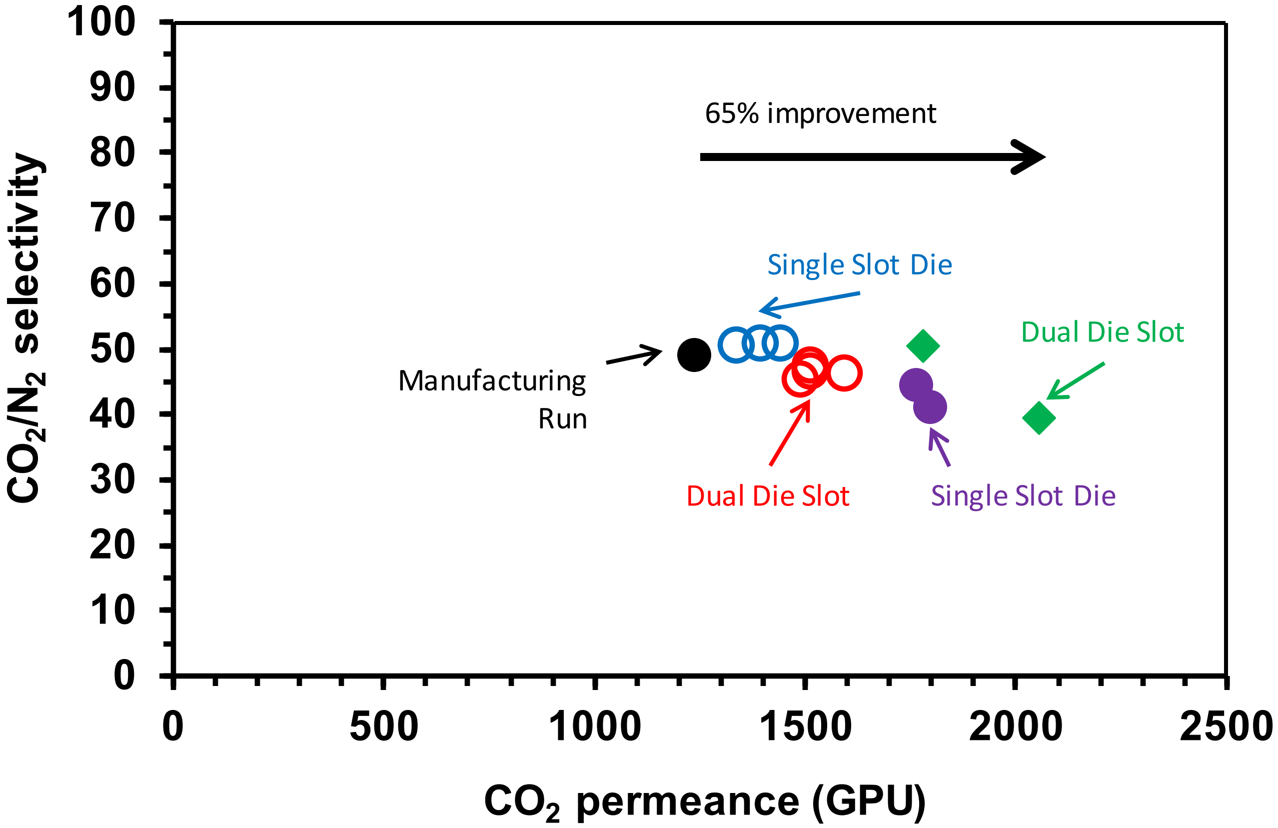


Can be coated with Polaris.

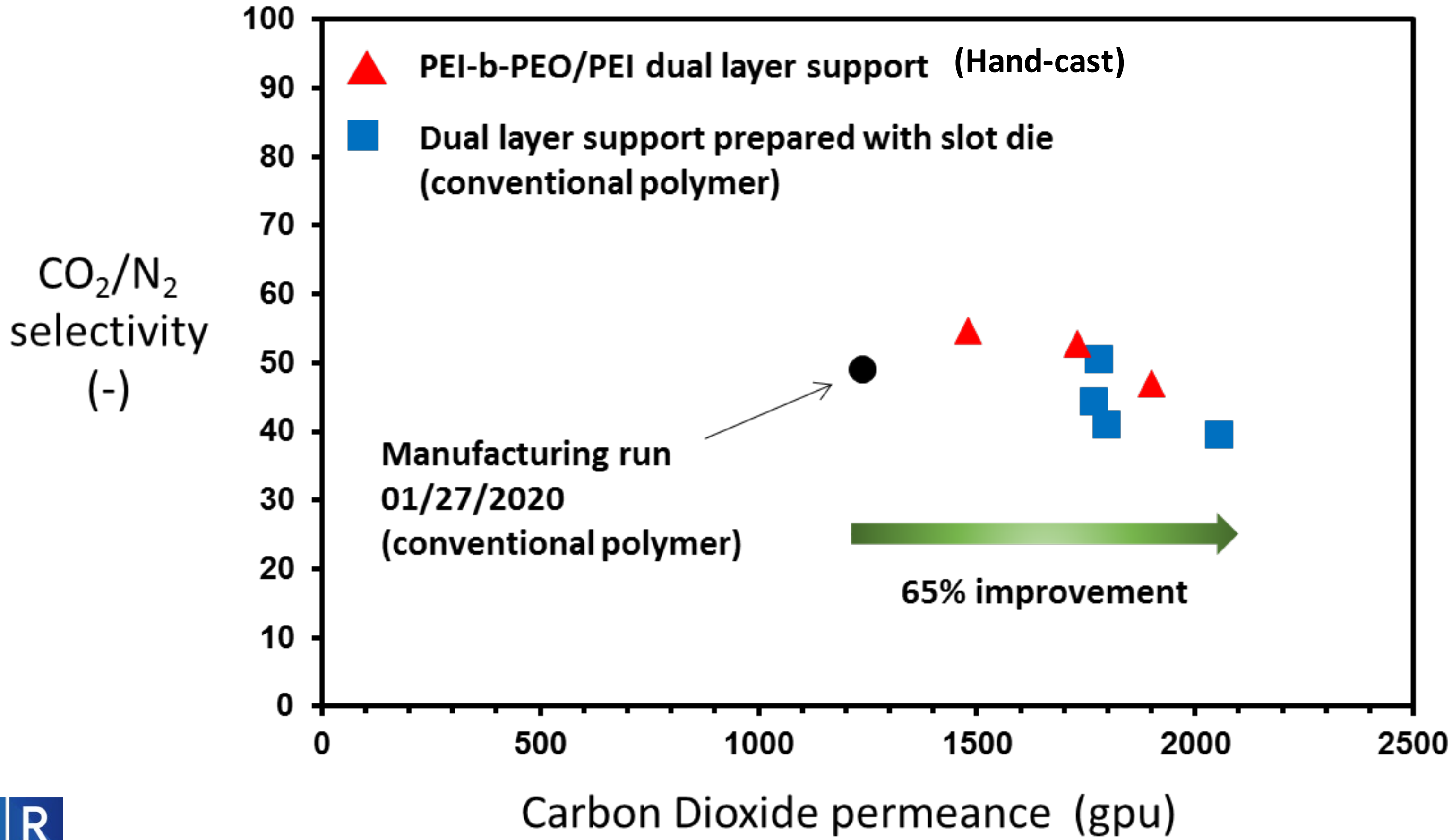


Polaris Composite Membranes

- **Conventional Polymer**
- **Dual Slot Die**
- **Dual Slot Die produces better supports**



Polaris Composite Membrane on BCP



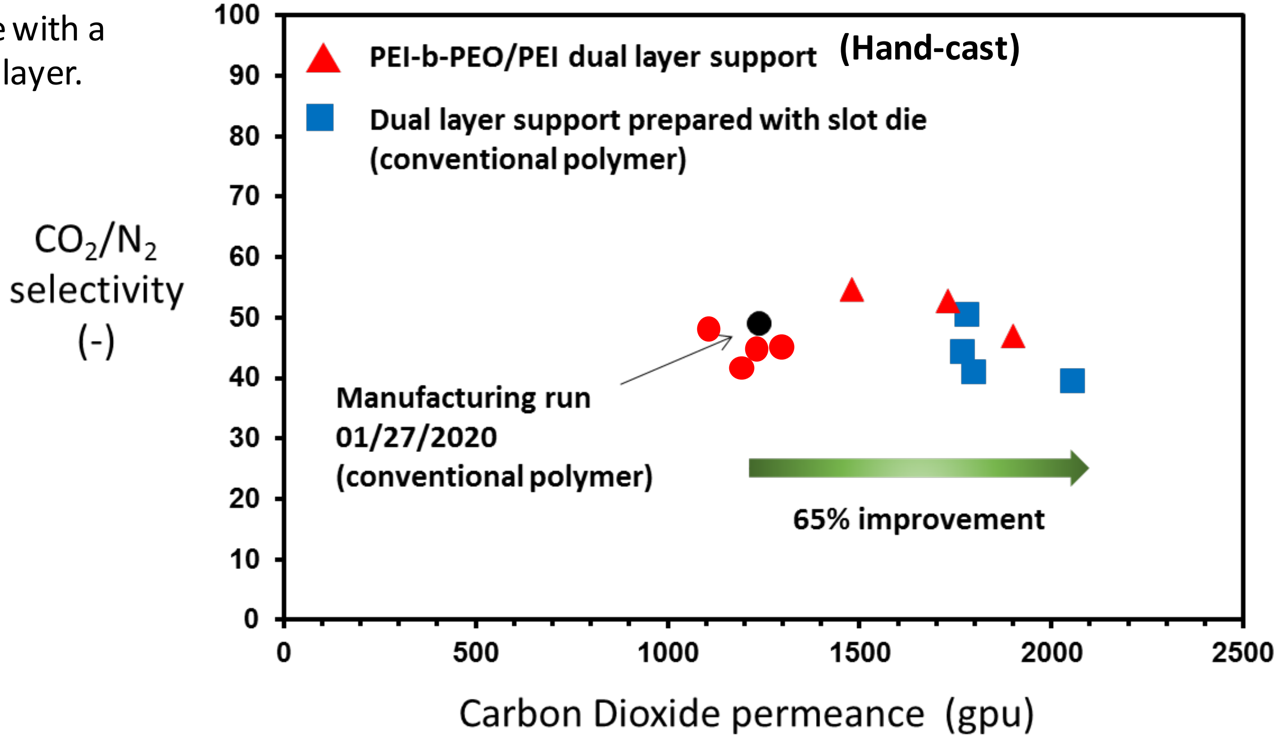
MTR

Polaris Composite Membrane on BCP

January 20, 2021:

First machine dual slot casting run producing a support membrane with a PEI-b-PEO block copolymer top layer.

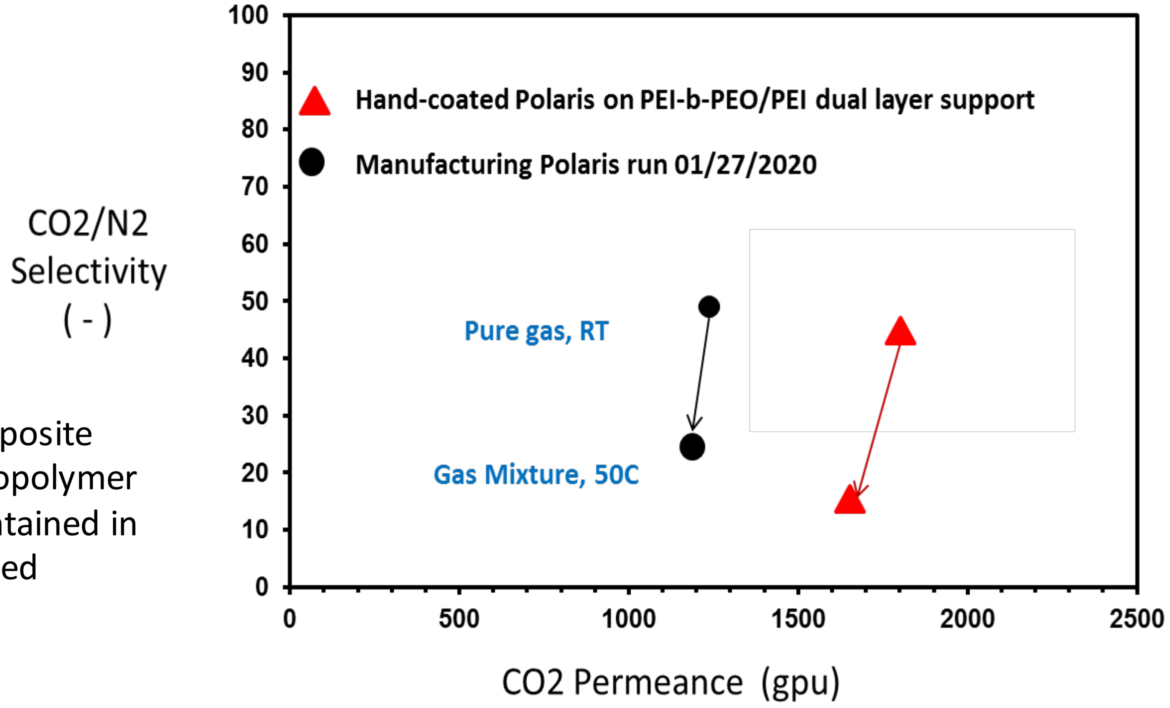
Coated on the R&D coater with Polaris: ●



Gas Mixture Data, hand cast support

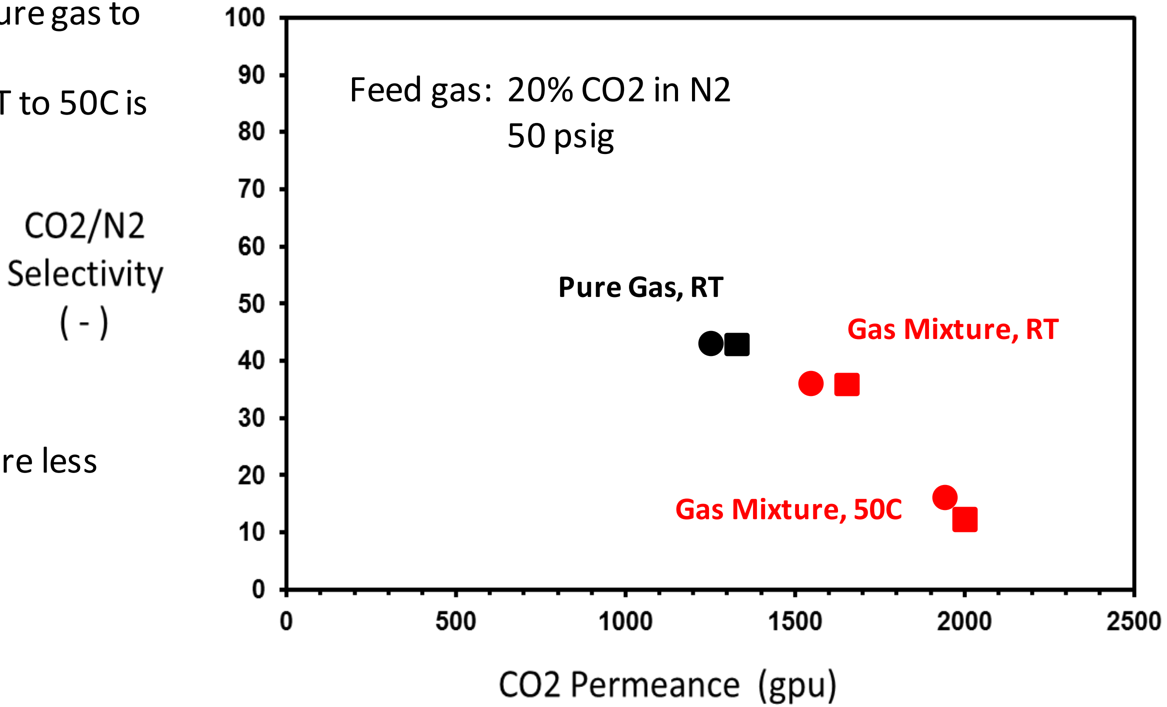
Feed gas: 20% CO_2 in N_2
50 psig

Permeance advantage of the composite membrane prepared on a block copolymer based support membrane is maintained in gas mixture experiments at elevated temperature.



Gas Mixture Data, machine cast support

- Decrease in selectivity from pure gas to mixed gas at RT is as expected
- Decrease in selectivity from RT to 50C is also as expected



- Increases in CO2 permeance are less expected.
- To be investigated further

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