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

Hans Wijmans, Zhen Sun, Jenny He, Steve White, Tim Merkel
Membrane Technology and Research, Inc.
Haiqing Lin
University of Buffalo
Nathaniel Lynd
University of Texas at Austin

DOE NETL CO2 Capture Technology Project Review Meeting
Pittsburgh, PA
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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 – May 31, 2021
- **Funding:** $2,905,620 DOE; $726,805 cost share (MTR and University of Buffalo)
- **DOE Project Manager:** Isaac Aurelio
- **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:** Commercial-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

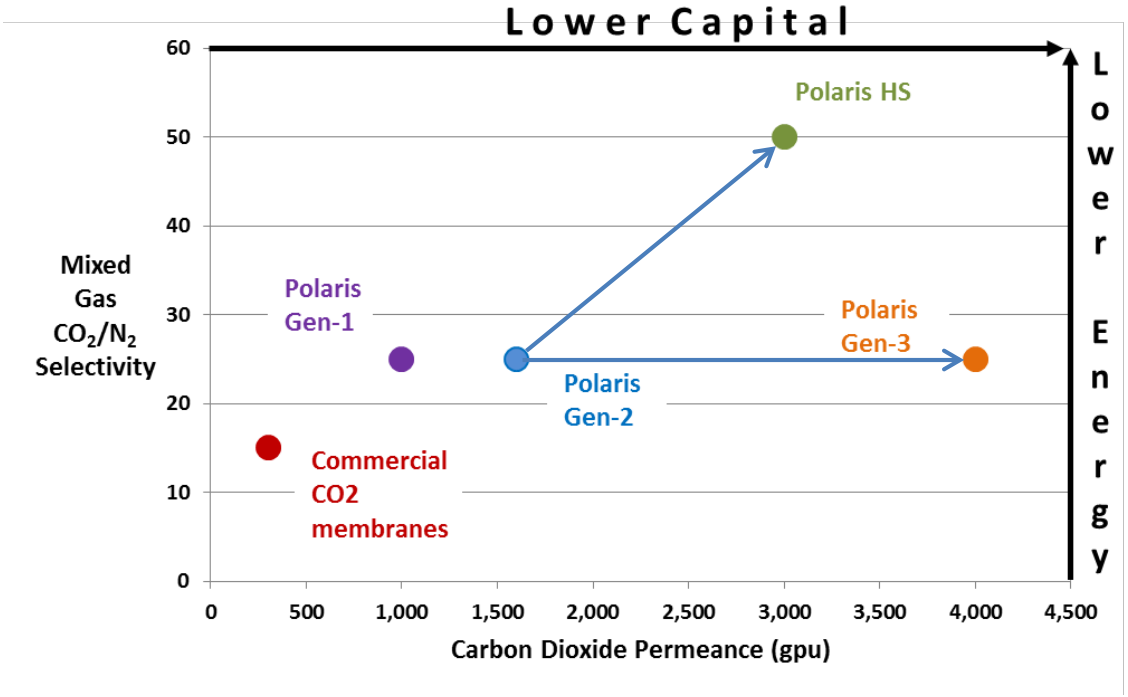
MTR

Project Objectives, Success Criteria

1. Composite membranes produced with transformational performance, based on improved supports and improved selective materials

2. Membrane and small modules fabricated at MTR, and tested at MTR and at NCCC

3. Techno-economic analysis validates that the goal of \$30/tonne CO_2 captured can be reached

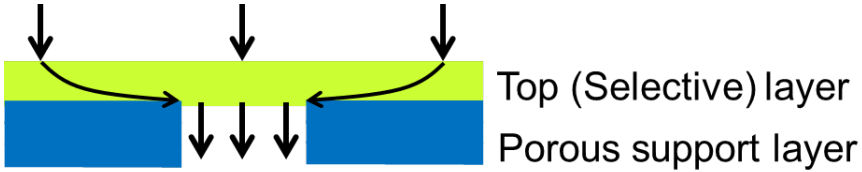


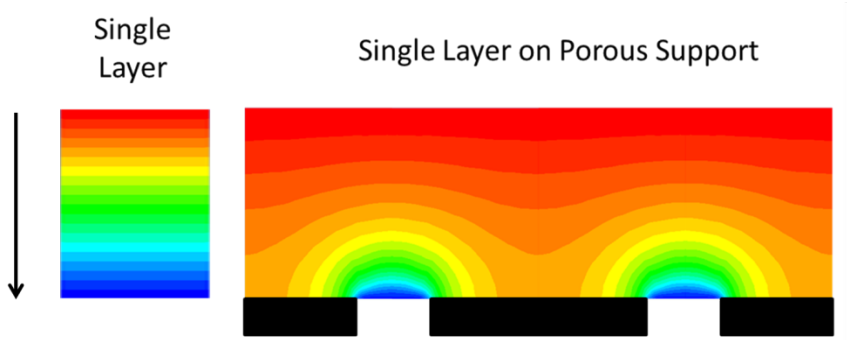
Technology Background and Rationale

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

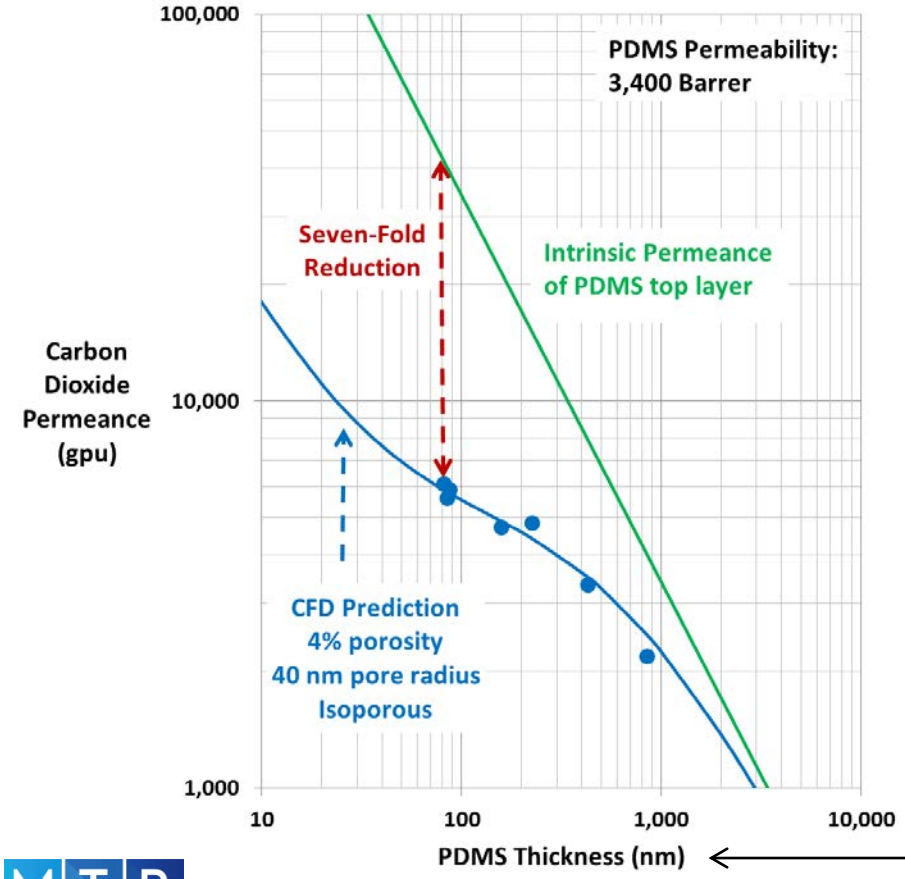
- Higher permeance membranes will benefit capture, particularly in power plants
- Higher selectivity membranes will benefit capture, particularly in industrial capture

- Higher permeances are achieved by making composite membranes with thinner selective layers.
- The surface pore structure of the support membrane has become a limiting factor:

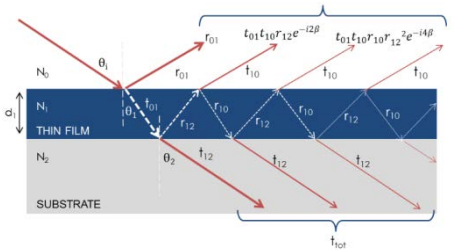




Effect of Support Membrane Surface



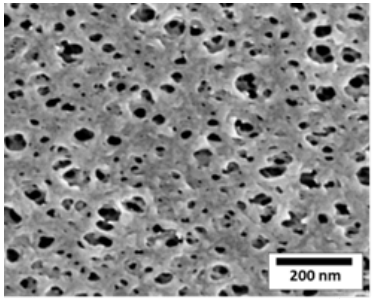
Ellipsometry



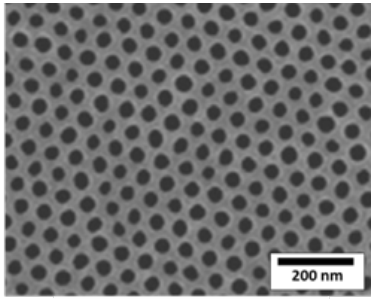
Computational Fluid Dynamics simulations show that non-uniform distribution of surface pores is a major contributor to the reduction in measured permeance.

→

Isoporous membranes are ideal supports for composite membranes.



Surface of Conventional Support

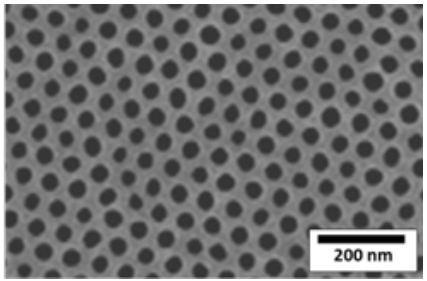


Surface of Isoporous Support

Structure of the Project

Self Assembly of Block Copolymers **MTR**

Improved Support Membranes



Dual Slot Die Casting Technique **MTR**

Synthesis Novel Block Copolymers **UT Austin**

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**

MTR

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

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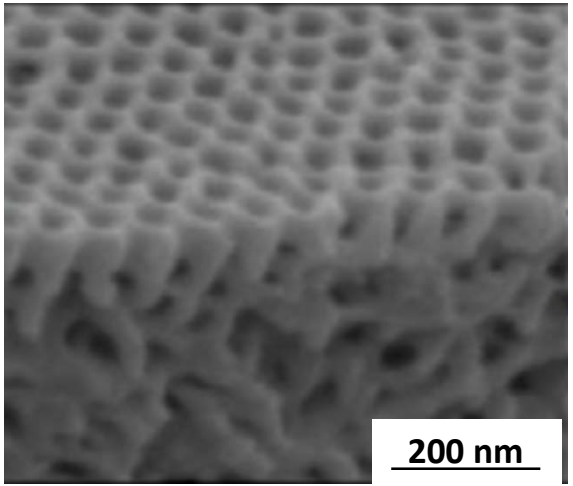


- Amphiphilic Block Copolymer in mixed solvent, evaporation step followed by immersion precipitation
- Block copolymers consist of two blocks, each block has a controlled molecular weight (mono disperse): Expensive

- Method creates top surface with highly ordered porous structure
- Structure below top layer has a “tendril” like structure, and is different from the porous structure in conventional porous supports

Self assembly, Isoporous

MTR:

- Purchased block copolymers, including custom synthesized for MTR
- Hand casting of block copolymers (5 to 10 cm^2)
- Evaluation of structure with Electron Microscope
- Samples are too small to be coated

Process is very sensitive to operating conditions:

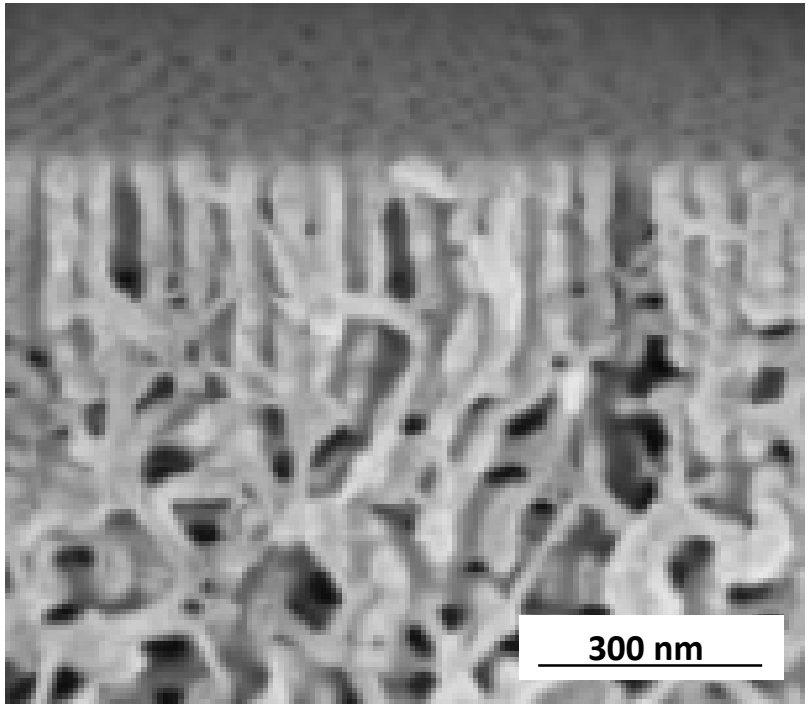
- Composition of the casting solution
  - Mixed solvent ratios
  - Additives (polar interactions, hydrogen bonding)
- Additives to water casting bath
- Evaporation time prior to immersion, air flow, presence of water vapor

Everything has to be “just right” to create perfect cylindrical pores at the top surface.

SEM Example

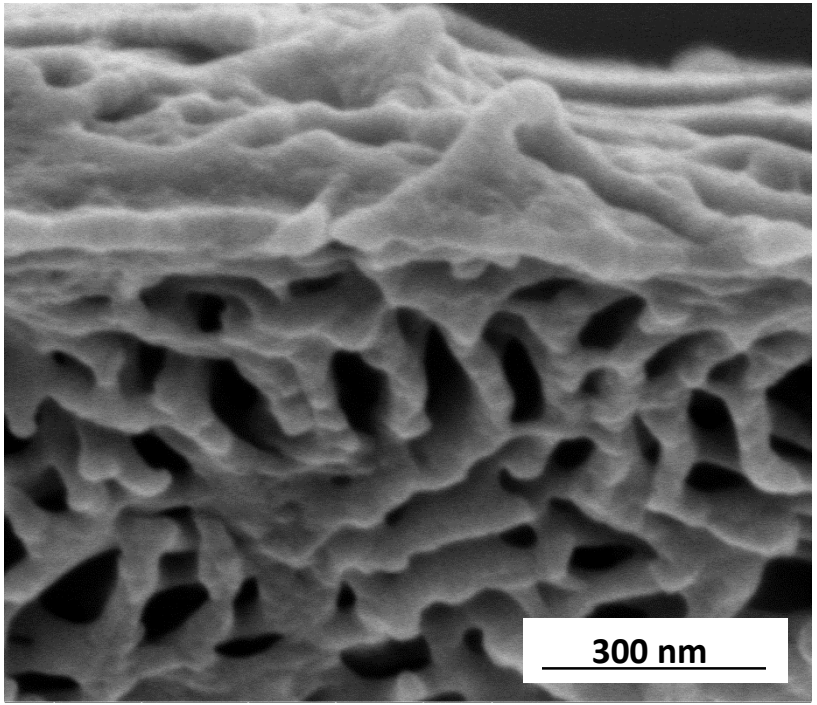
Literature

Peinemann, Abetz, Simon (2007)



MTR

Collapse of cylindrical structure at surface

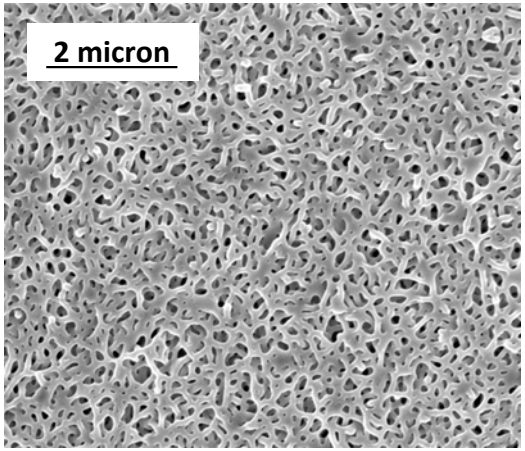


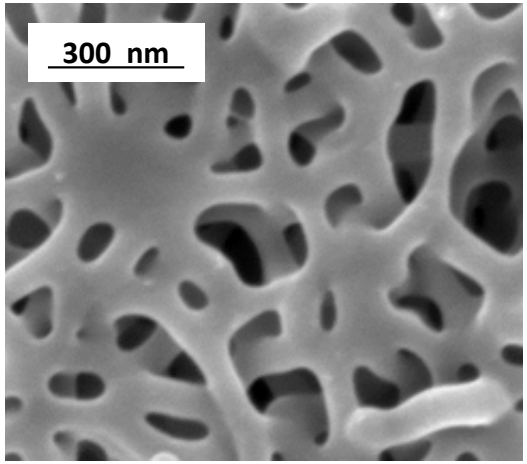
Top Surfaces

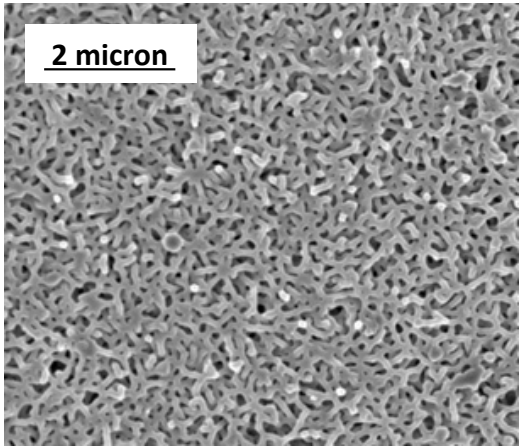
5 seconds evaporation

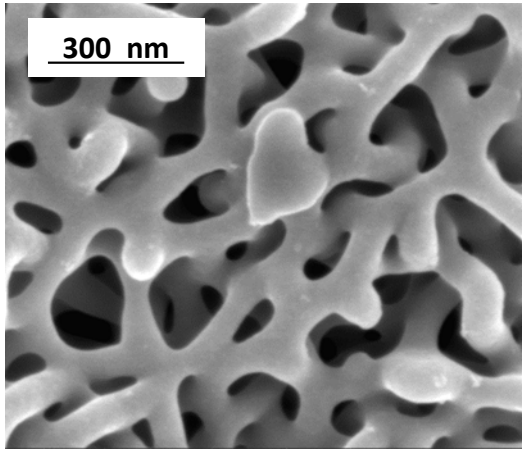
PS-b-P4VP
(Polystyrene-b-
Poly-4-vinylpyridine)

10 seconds evaporation

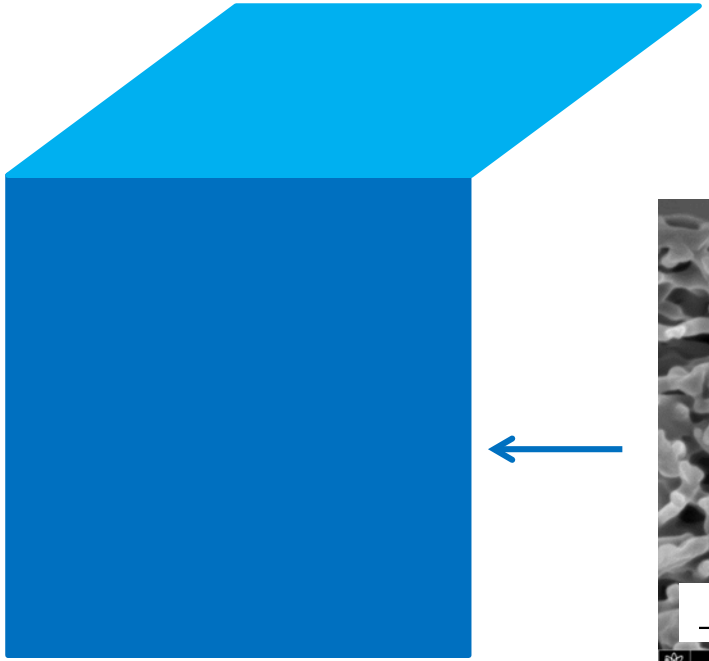


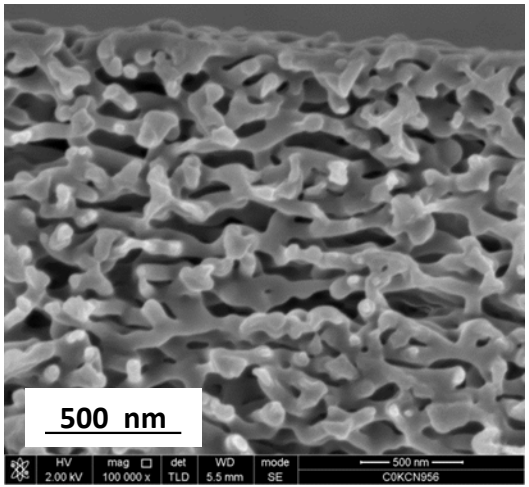


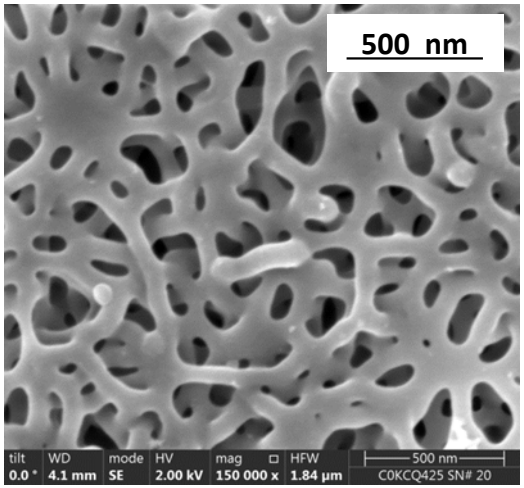




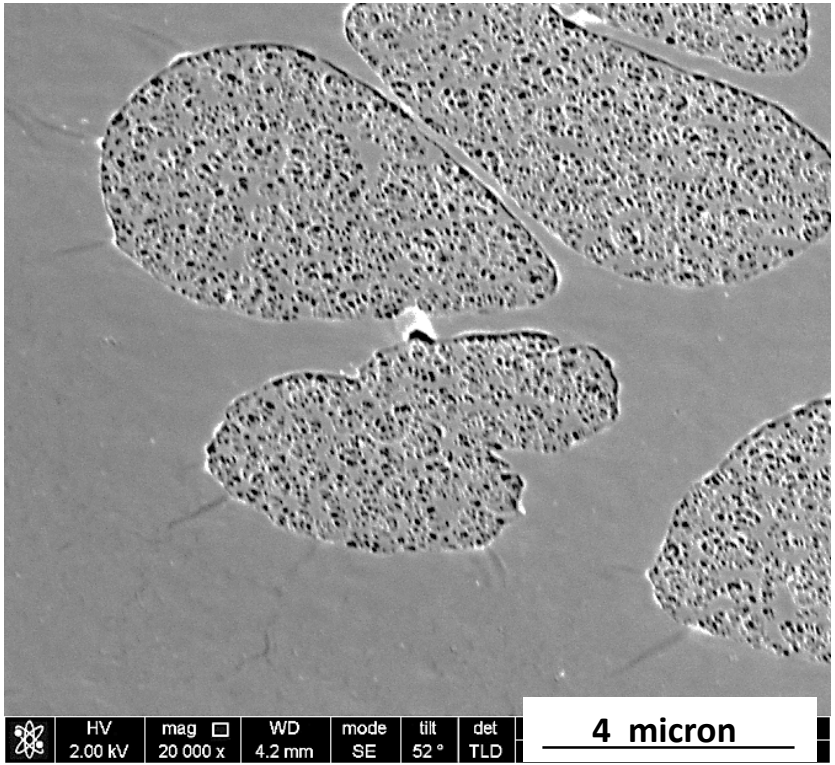
Top Surface and Cross Section

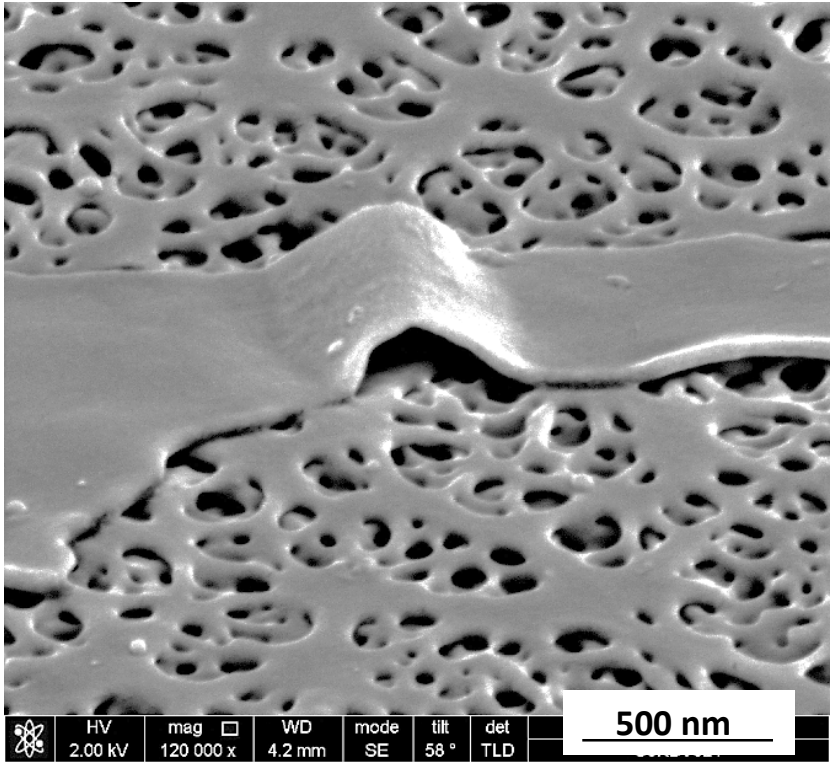






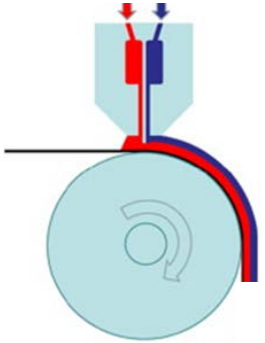
Intriguing Surface Morphology





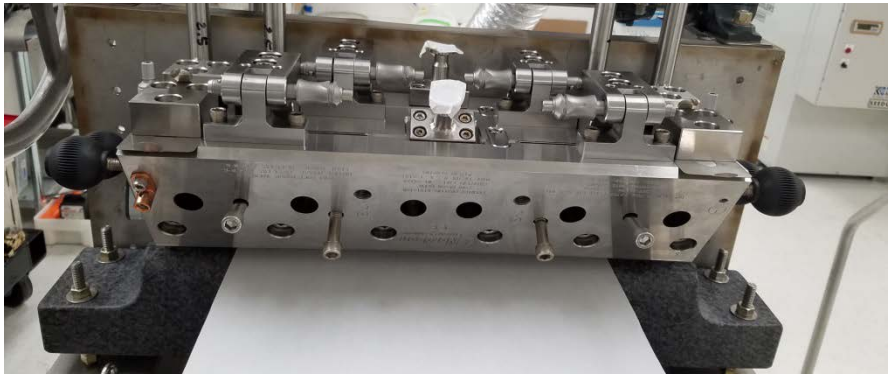
Two Layer Approach: Dual Slot Die

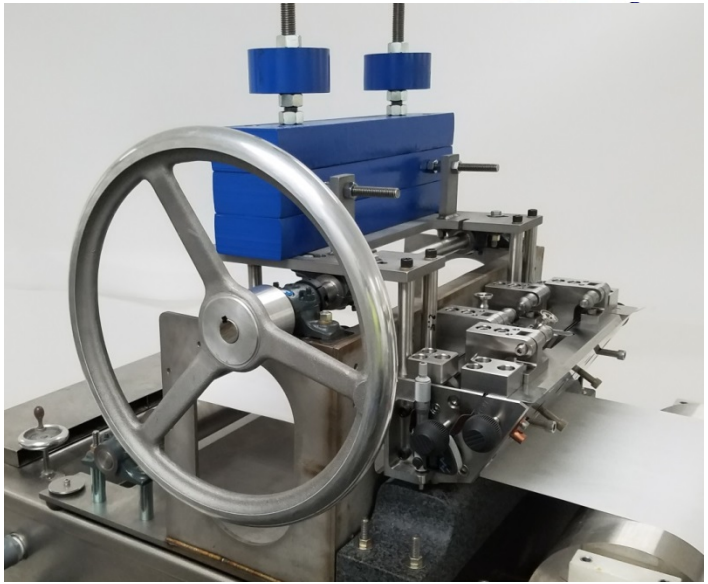
- Two separate layers created in a single step
- Top layer can be very thin (micron or less)



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

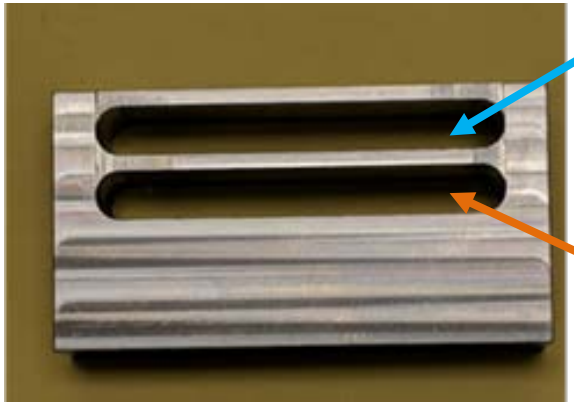
- Dual slot die installed on MTR R&D caster
- Operational in September





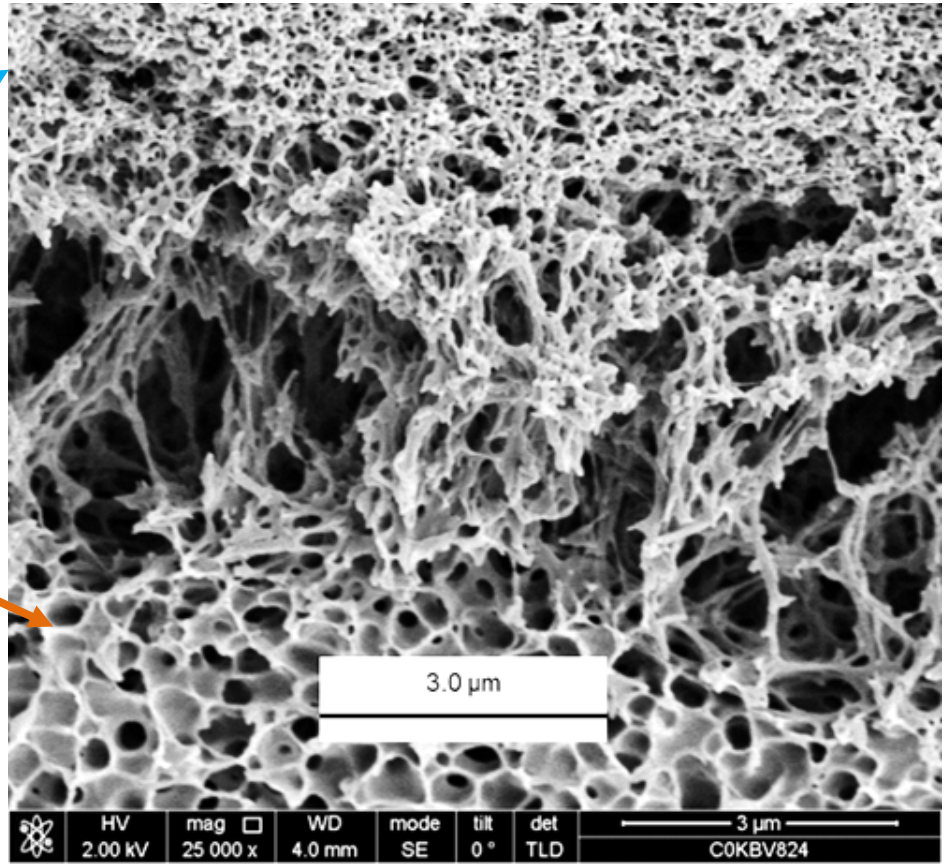
Manual Dual Casting

Block
Copolymer

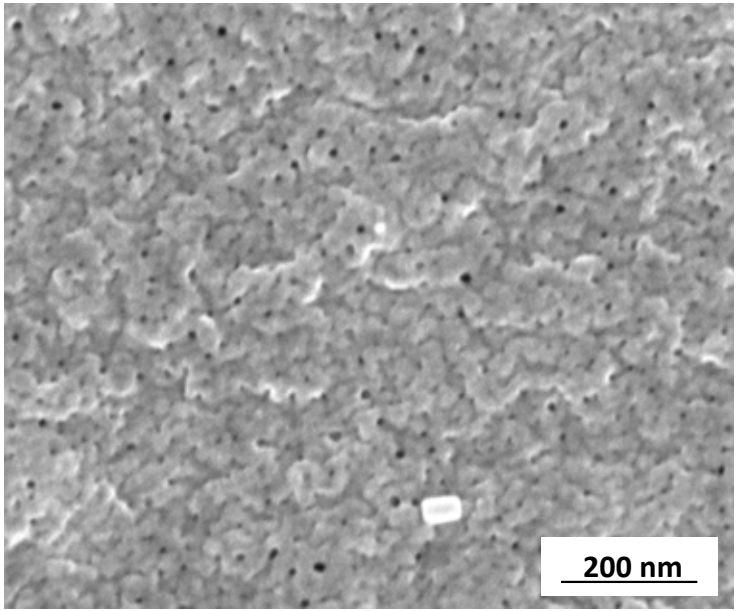


Casting Block
(on glass plate,
or on support paper)

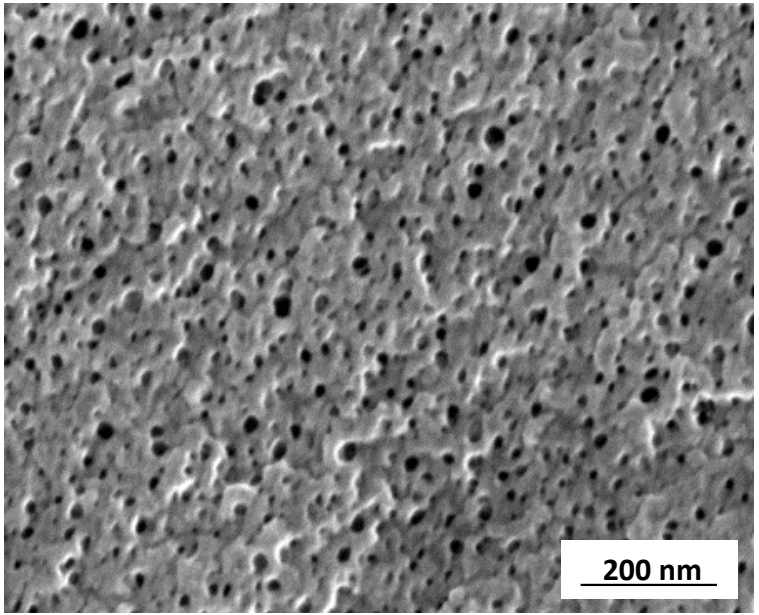
Homo
Polymer



Manual Dual Casting Homopolymer



Standard Single Cast Support Membrane
Uncoated Permeance = 140,000 gpu



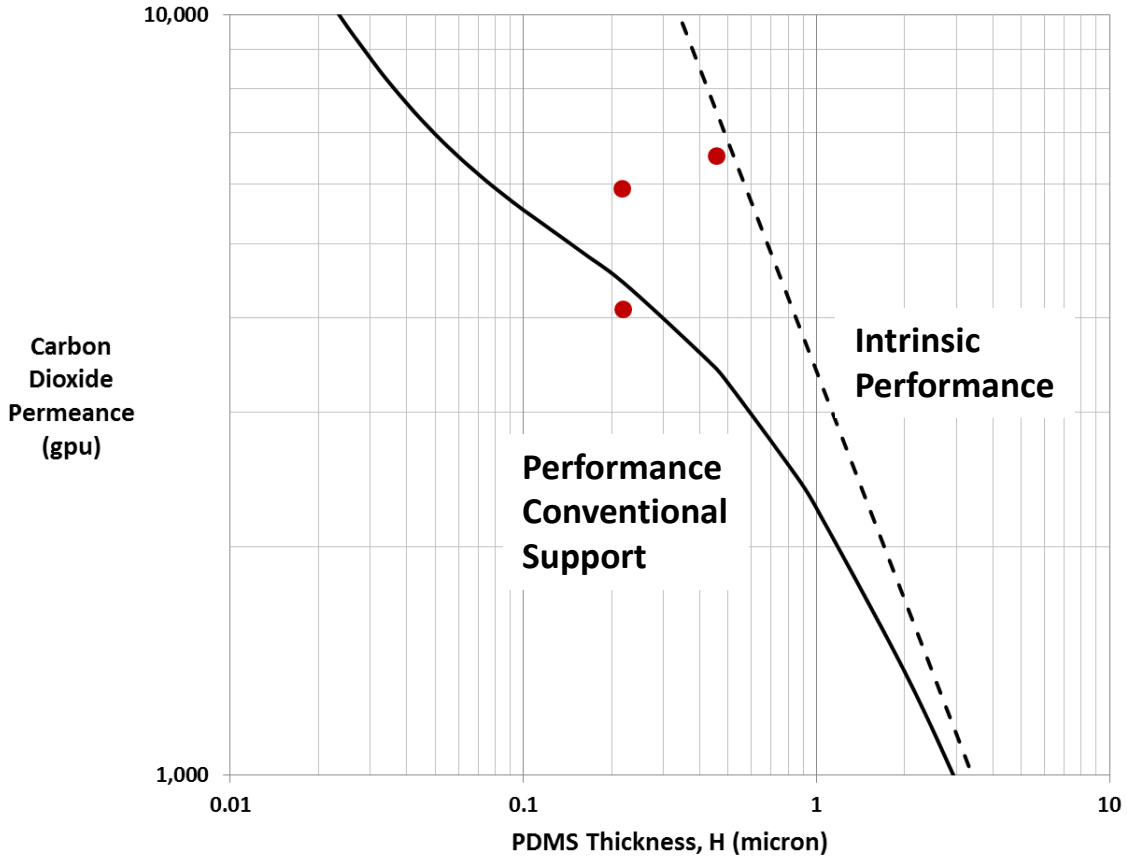
Dual Cast Support Membrane
Same polymer, but different casting solvent systems, used for top and bottom layer
Uncoated Permeance = 220,000 gpu

Manual Dual Casting Homopolymer

Polydimethylsiloxane composite membrane.

Dual Cast Support:
- **Top layer optimized for pore structure**
- **Bottom layer for mechanical properties**

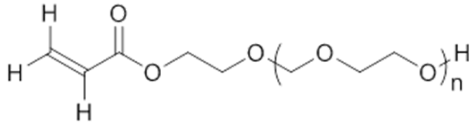
Selective Layer:
- **Hand coated**

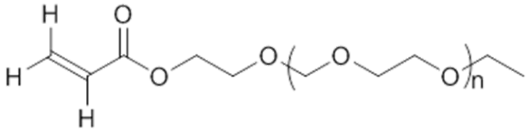


Novel Selective Materials

NYU Buffalo

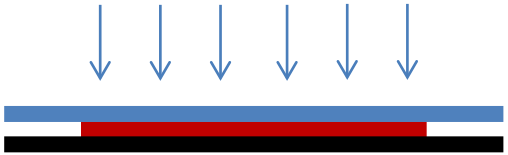
Two high O content monomers:



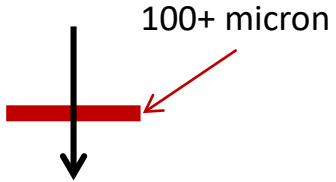


Synthesis

Novel Monomer



UV or Heat Polymerization

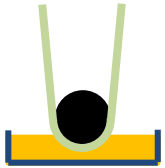


Gas Permeability Measurement

MTR

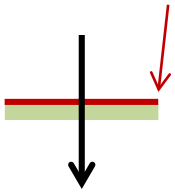
Novel Monomer

Coating Solution



Coating

Drying

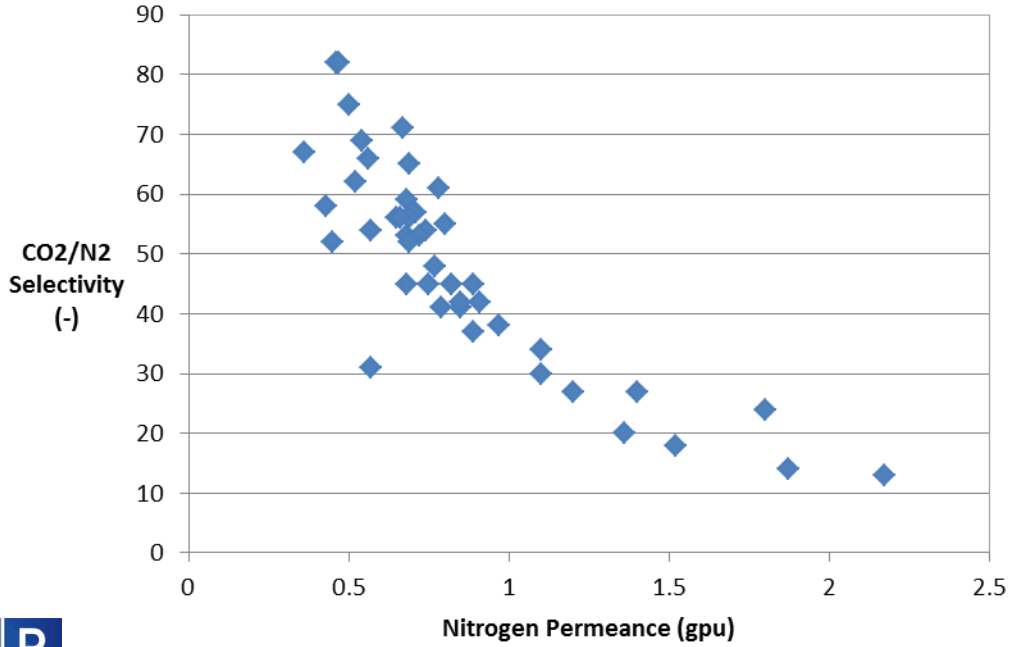


Gas Permeance Measurement

Techniques developed for Polaris

Novel Selective Materials

- Work at Buffalo has confirmed high selectivity in films.
- Not yet able to make high performance composite membranes at MTR



34 membranes
4 monomer batches

Difficulty in producing defect-free top layers. Multiple coatings are required.

→ Top layers: 3 to 4 micron

Next Steps

- Start working with dual slot die system
  - Reproduce standard, single layer, MTR supports
  - Produce dual layer supports with homopolymers
  - Produce dual layer supports with block copolymer top layers
- Evaluate supports with electron microscope
- **Machine coat** supports with polydimethylsiloxane selective layers
- **Machine coat** supports with Polaris selective layers
- Measure gas permeances

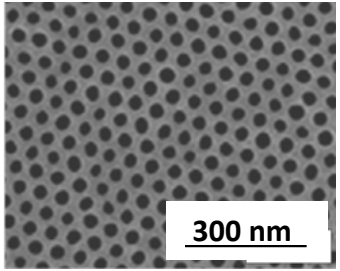
- Continue work with novel selective materials
- Make adjustments to the “current Polaris methods”

- Pursue an alternative to the “perfect” block copolymer

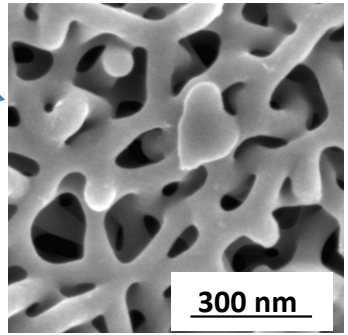
Alternative to “Perfect” Block Copolymers

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

Perfect Conditions



Less Perfect Conditions



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

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%	
25%	
25%	

Thank You

We thank the Department of Energy, National Energy Technology Laboratory, for their support for this project.

Questions?