Rational Development of Novel Metal-Organic Polyhedra-based Membranes for CO_2 Capture

DE-FE0031736

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 28 - 31, 2023

Project Overview

– Funding (DOE $2,857,896 and Cost Share $975,484)

– Overall Project: 7/1/2019 – 6/30/2024

– Project manager: Krista Hill

– Overall Project Objectives

- Rationally develop solubility-selective mixed matrix **materials** comprising polar rubbery polymers and metal organic polyhedra (MOPs);
- Develop thin film composite **membranes** achieving high CO_2 permeance (3000 GPU) and high CO_2/N_2 selectivity (50);
- Demonstrate separation **performance** and stability with raw flue gas at NCCC; and
- Perform **techno-economic analysis** on the membrane processes.

BPs and Team Members

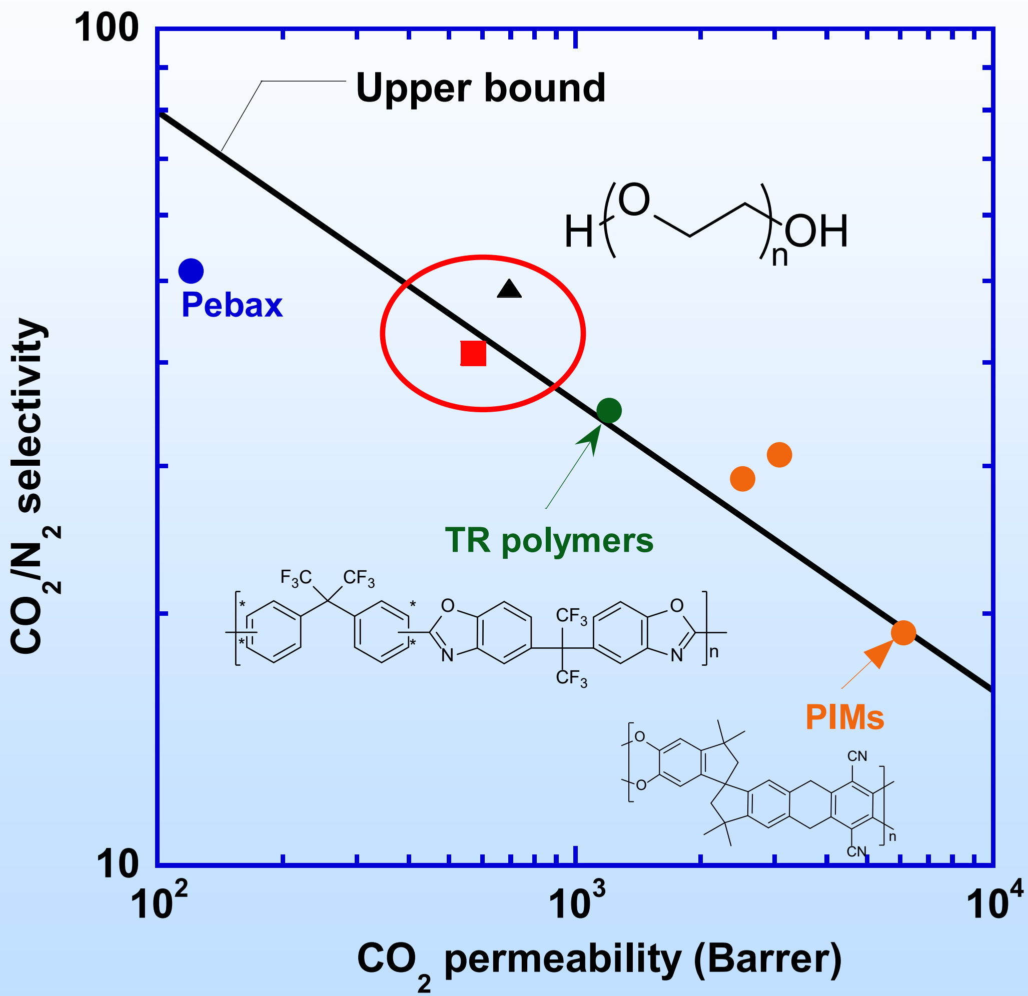
BP 1: Rationally design and prepare freestanding **mixed matrix films** with CO_2 permeability of 1000 Barrer and CO_2/N_2 selectivity of 75 and CO_2/O_2 selectivity of 25 **(7/19 - 6/21)**

BP 2: Prepare and optimize thin film **mixed matrix composite membranes** with CO_2 permeance of 3000 GPU and CO_2/N_2 selectivity of 50 and CO_2/O_2 selectivity of 20 **(7/21 - 12/23)**

BP 3: Prepare bench-scale spiral-would membrane **modules** and perform **field tests with real flue gas** at NCCC; and complete the **techno-economic analysis** **(1/24 - 6/24)**

Members	**Role**
UB	**Materials development**
Caltech	Computational simulation
RPI	Polymer synthesis scale-up
MTR	Membrane development & field test
Trimeric	TEA
NCCC	Host site

State-of-the-Art Polymers for CO_2/N_2 Separation

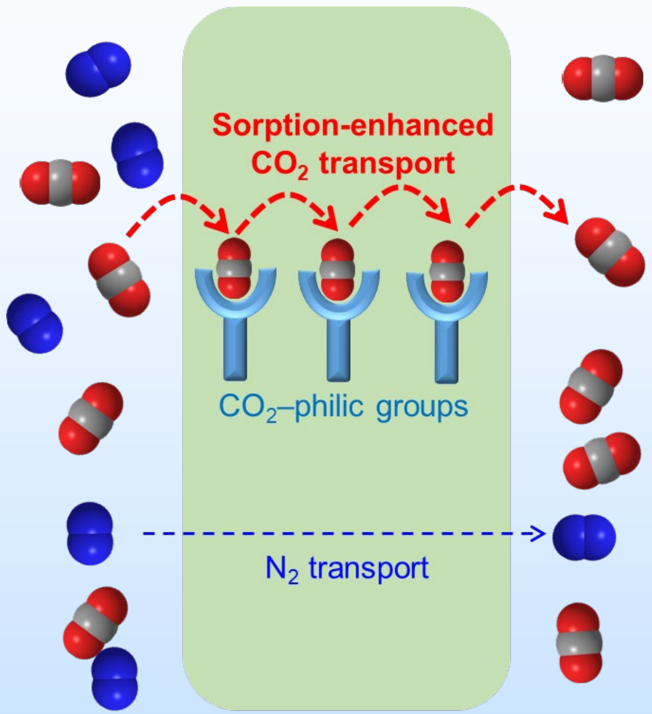


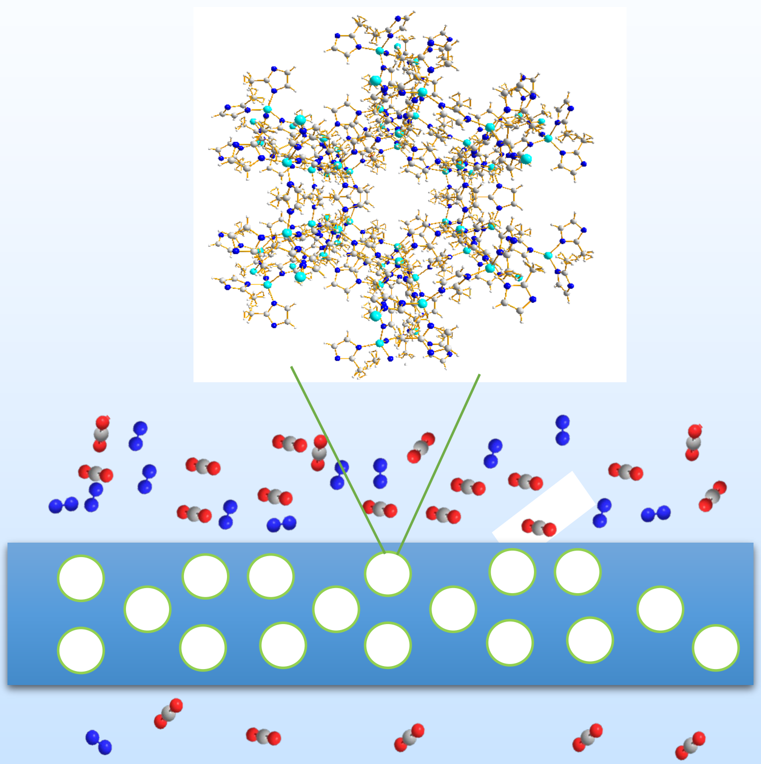
$$\alpha = \frac{P_{CO_2}}{P_{N_2}} = \frac{S_{CO_2}}{S_{N_2}} \times \frac{D_{CO_2}}{D_{N_2}}$$

	T_C (K)	D_A (Å)	V_C (cm^3/mol)
CO_2	304	3.3	93.9
N_2	126	3.64	89.8

$$\frac{S_{CO_2}}{S_{N_2}} >> 1 \qquad \frac{D_{CO_2}}{D_{N_2}} \approx 1$$

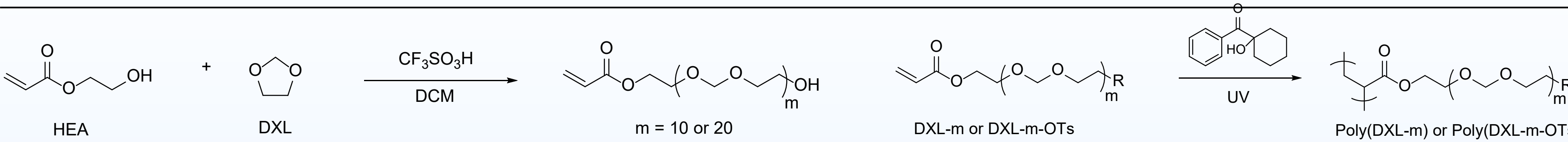
Our Approach: Sorption-Enhanced Mixed Matrix Membranes

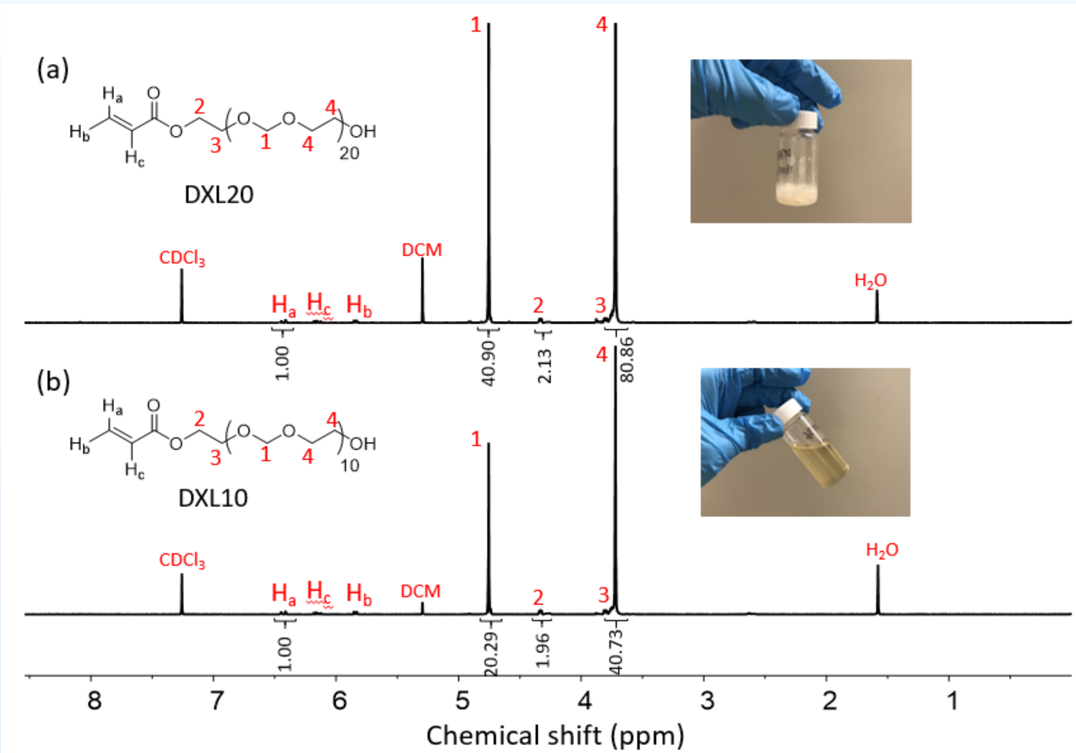




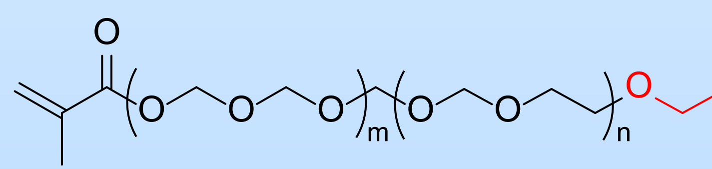
- **CO_2-philic rubbery polyethers**
- **Porous metal organic polyhedra (MOPs)**

Design and Synthesize Functional Polyethers





Varying ether oxygen content and chain end groups

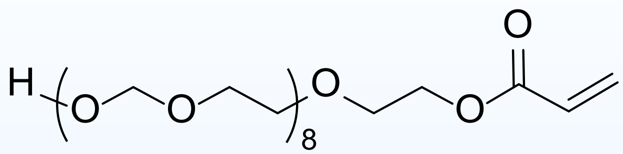


POM-*ran*-PDXLEA

50 - 100 g/batch production demonstrated

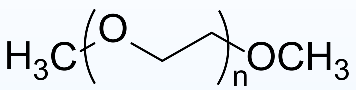
Advanced Materials for CO_2/N_2 Separation

(a)



PDXLA8

(b)



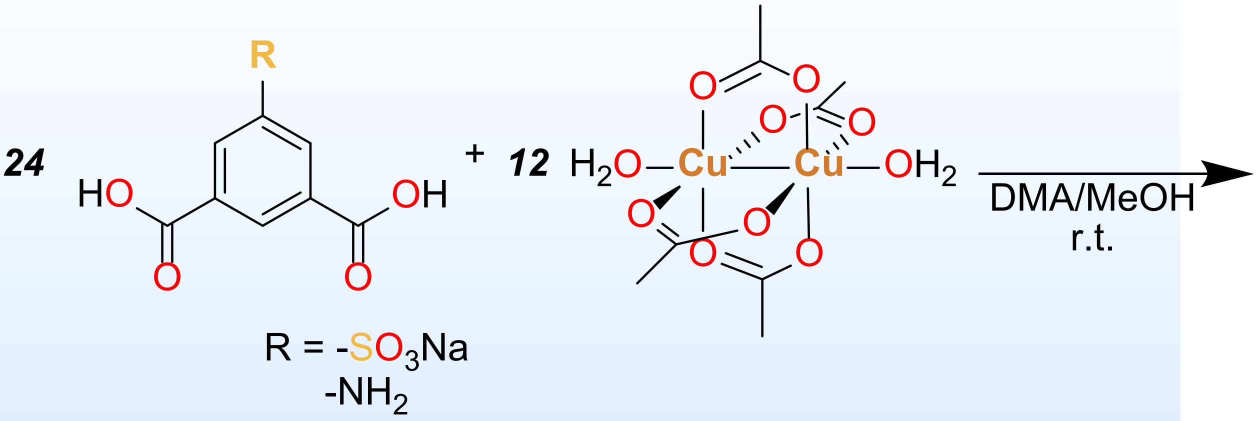
Poly(ethylene glycol) dimethyl ether (PEGDME)

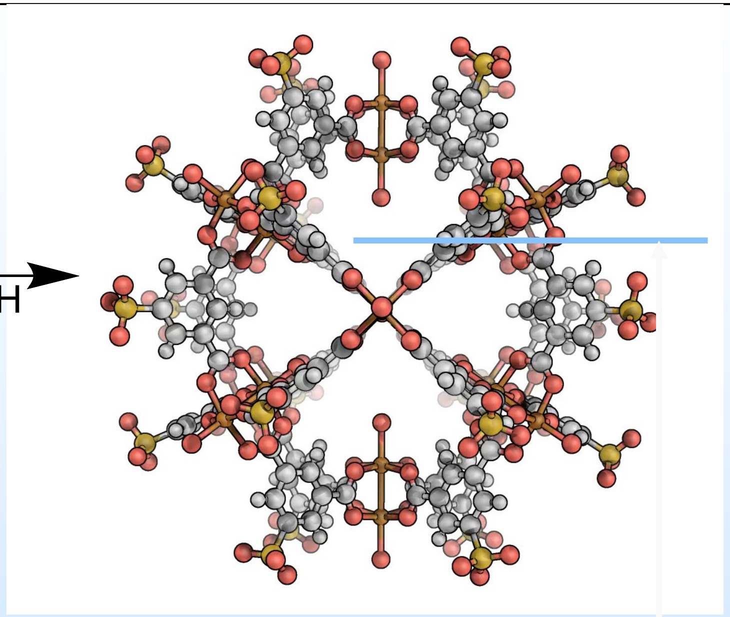
PEGDME (wt%)	T_g (°C)	CO_2 permeability (Barrer)	CO_2/N_2 selectivity
0	-59	223	56
10	-68	380	51
30	-81	830	48
45	N/A	1406	45
50	N/A	1681	42
60	N/A	1671	46

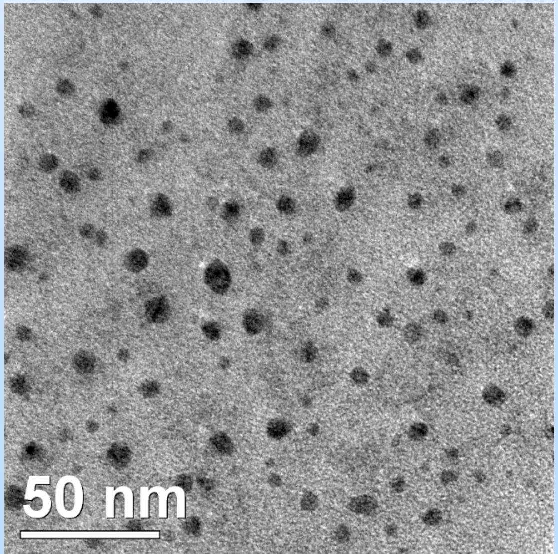
Increasing PEGDME content increases chain flexibility and gas permeability

Pure-gas at 35°C

MOP Synthesis: 10 g/batch







Unexpected Improvement by Low-loading MOP-3

PDXLA8; test at 35°C

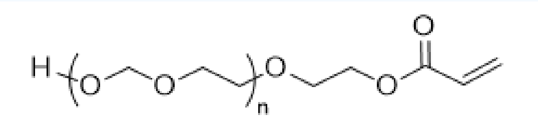
MOP-3 content (wt.%)	P_{CO2} (Barrer)	CO_2/N_2
0	**223**	**56**
1	293	56
2	**344**	**59**
3	**362**	**57**
10	263	55
20	233	57

PDXLA8/PEGDME (50/50)

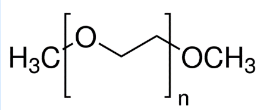
MOP-3 content (wt.%)	T (°C)	P_{CO2} (Barrer)	CO_2/N_2	CO_2/O_2
0	**25**	**1005**	**56**	**22**
1	25	662	48	25
3	**25**	**1343**	**62**	**24**
3	**21**	**1106**	**74**	**31**
5	25	703	59	-

Meet the project target
CO_2: 1000 Barrer; CO_2/N_2: 75

Mixed-gas Tests



PDXLA8, n = 8



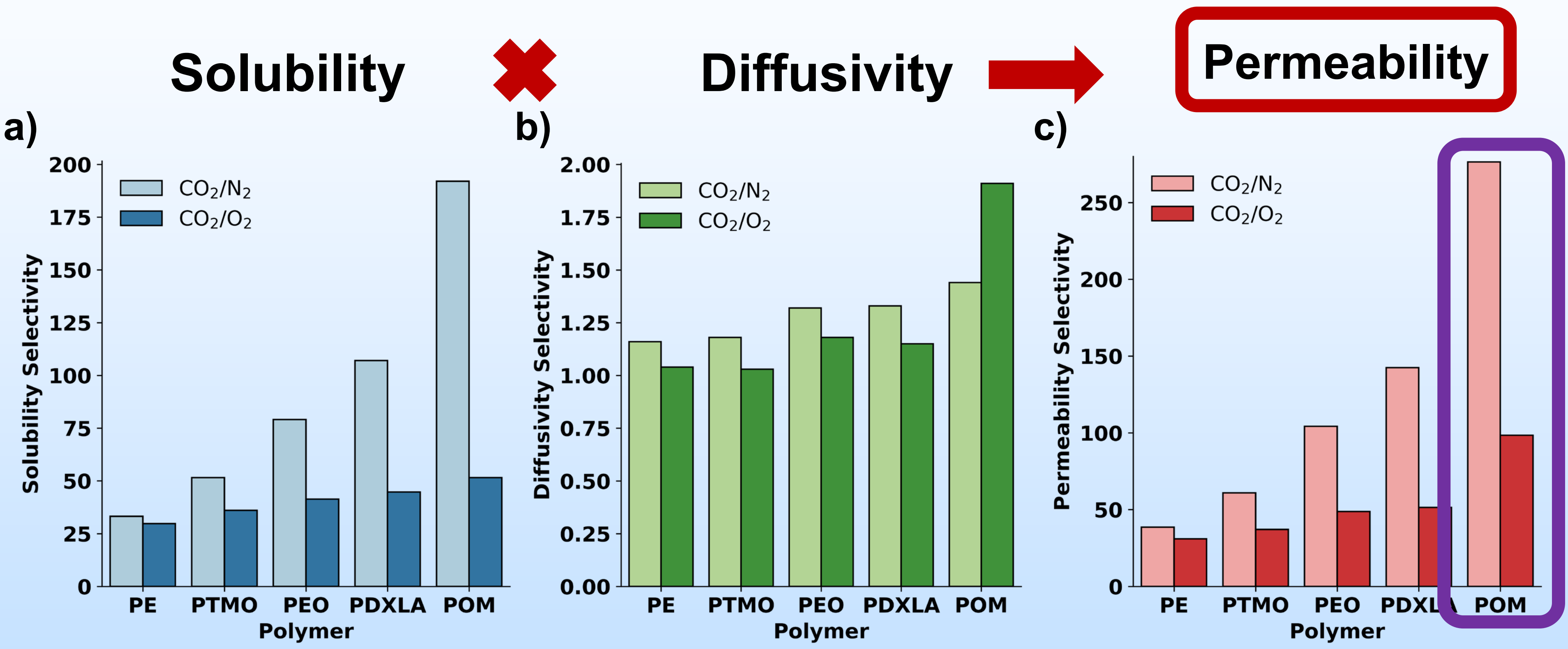
PEGDME
240 g/mol

PDXLA8/PEGDME
Mixed gas: CO_2/N_2=15/85, 100-160 psig

PEGDME (wt%)	T (°C)	Mixed-gas CO_2 (Barrer)	Mixed-gas CO_2/N_2 selectivity
45	35	1200	60
50	35	1450	62
50	**25**	**1290**	**79**

Meet the project target
CO_2: 1000 Barrer; CO_2/N_2: 75

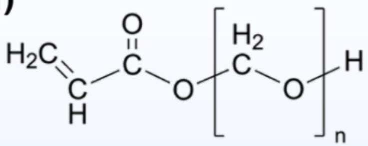
Simulate Gas Transport Properties



Increasing ether oxygen content increases separation properties

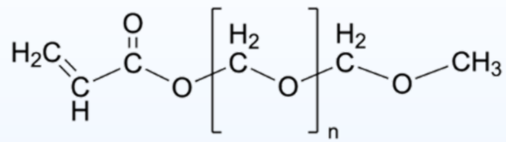
Effect of Chain End Groups and Ether Oxygen Content

1)



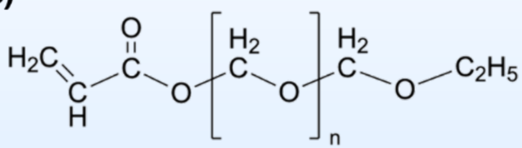
Acrylate + POM

2)



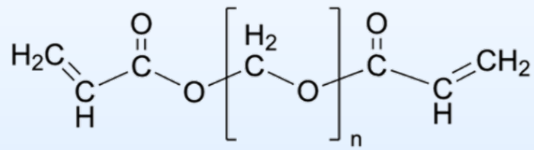
Acrylate + POM + Methoxy

3)



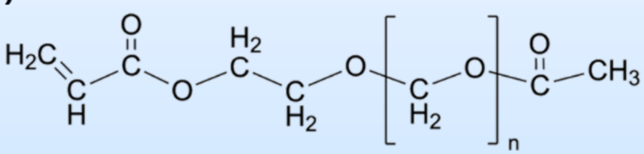
Acrylate + POM + Ethoxy

4)



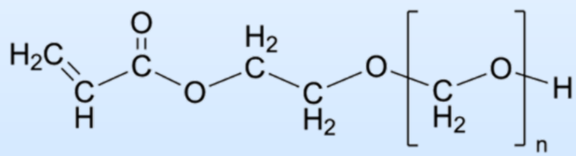
Acrylate + POM + Acrylate

5)



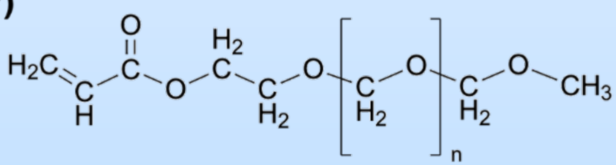
Acrylate + Ethoxy + POM + Acetyl

6)



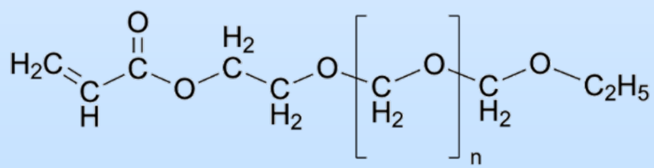
Acrylate + Ethoxy + POM

7)



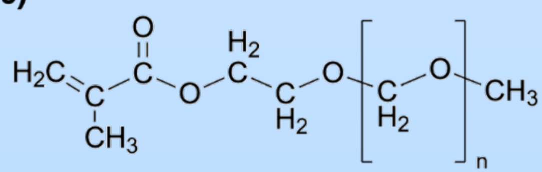
Acrylate + Ethoxy + POM + Methoxy

8)



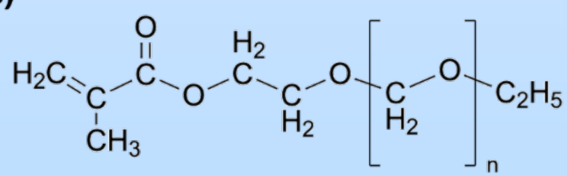
Acrylate + Ethoxy + POM + Ethoxy

9)



Acrylate + Ethoxy + POM + Methyl

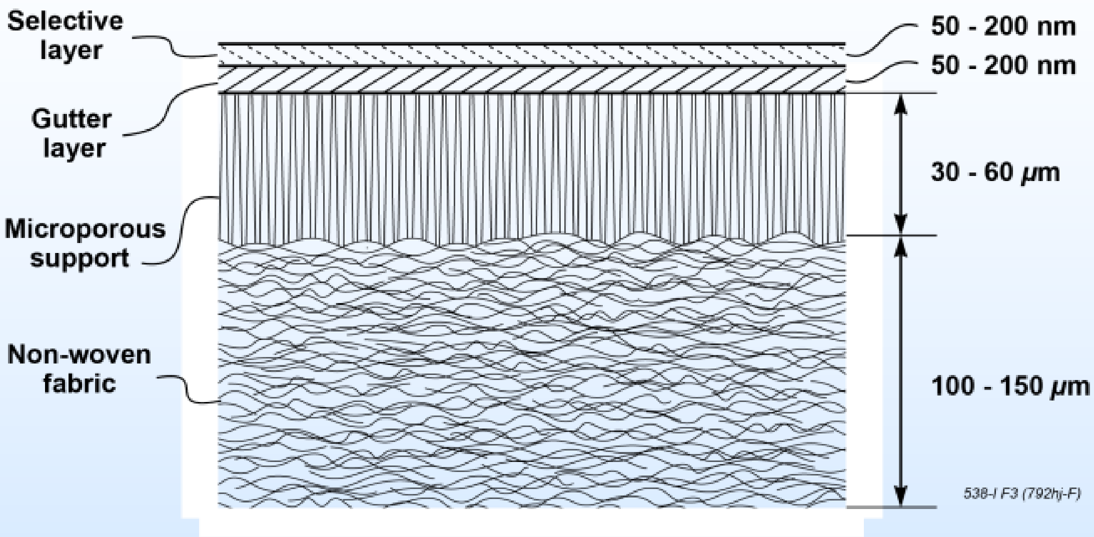
10)

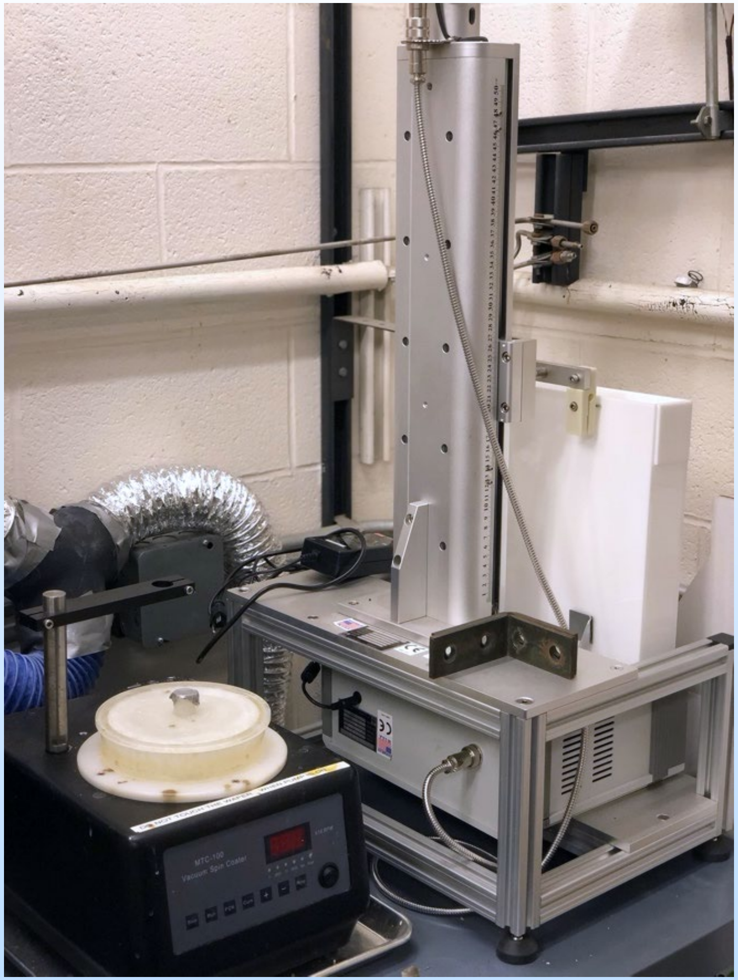


Acrylate + Ethoxy + POM + Ethyl

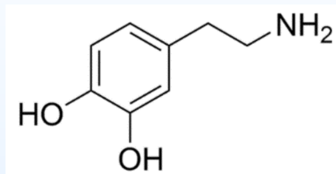
Polymer 9 shows the most promise with better CO_2/N_2 and CO_2/O_2 separation performance.

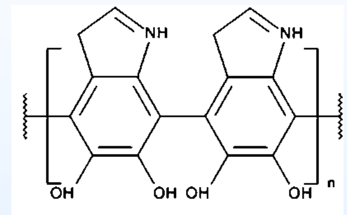
Thin Film Composite (TFC) Membranes





Improve PDMS Surface Compatibility via Dopamine Modification

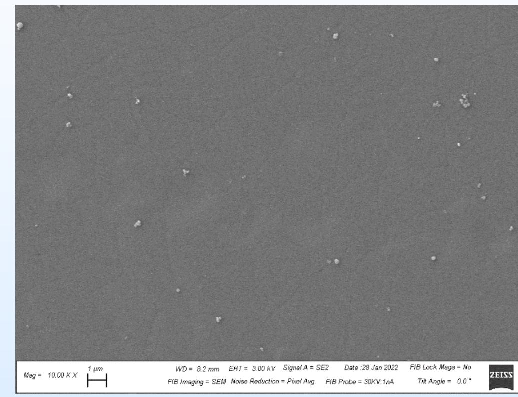


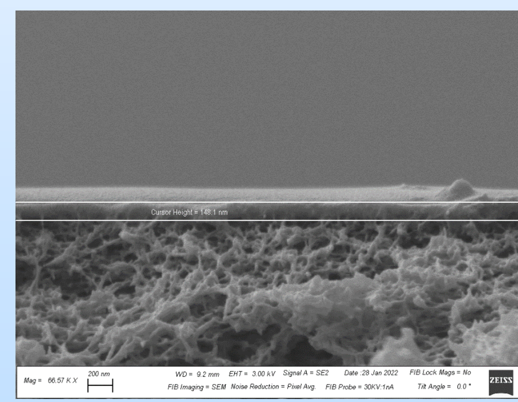


PDMS

Dopamine
2g/L; 20 min

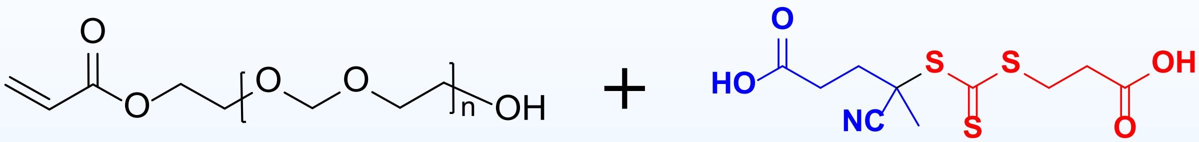
***d*PDMS**





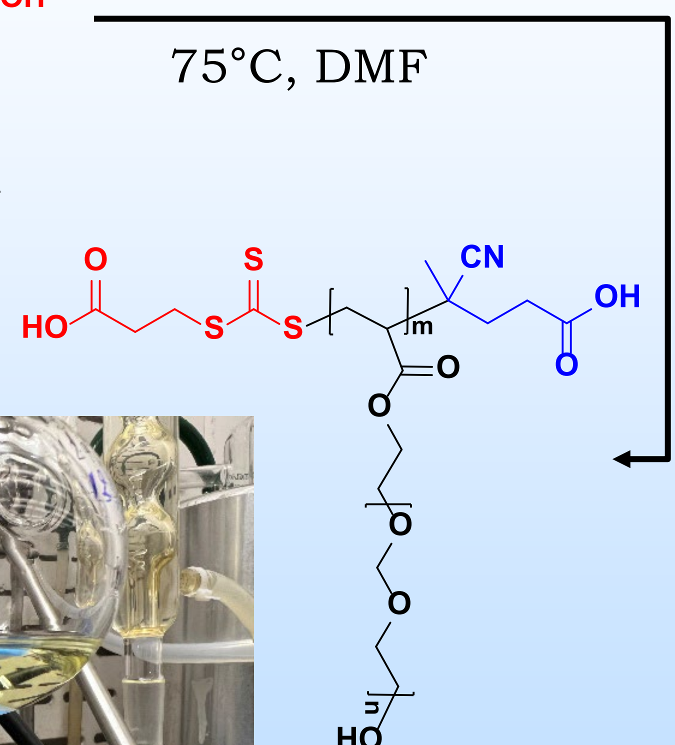
Gutter layer	Water contact angle (º)	CO_2 permeance (GPU)	CO_2/N_2 selectivity
PDMS/PSF	110	9,000	8.0
***d*PDMS/PSF**	**95**	**6,800**	**8.7**

Atom Transfer Radical Polymerization (ATRP)

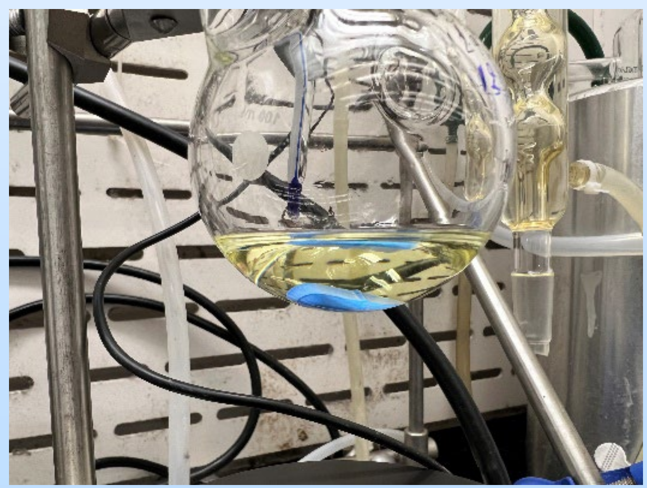


DXLA8 (J16)

BM1433
Chain transfer agent (CTA)



- [DXLA]:[BM1433]:[AIBN] = 100:1:0.1
- **[DXLA] = 0.5 M (25 wt.% DXLA in DMF)**



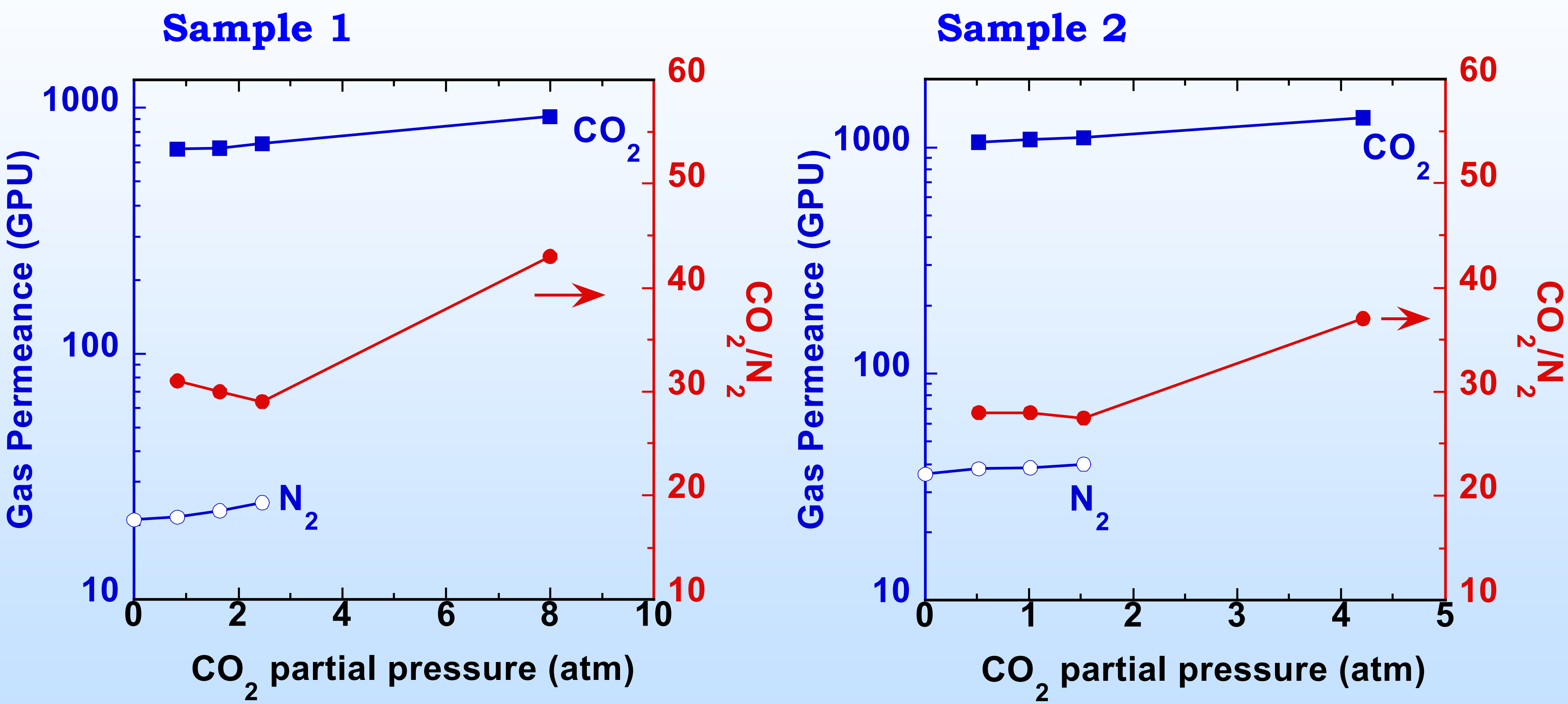
Reaction time:
3 h, 75°C

$M_{n,theo.} = 71.1\ kDa$

Representative TFC Membranes

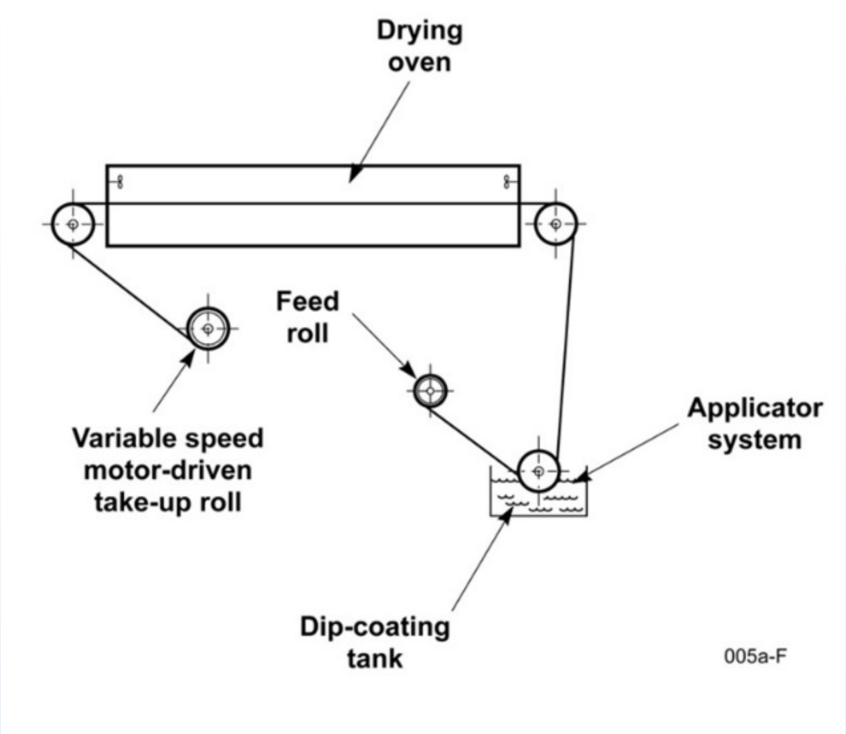
Membranes	Polymer content (wt.%)	Temp. (ºC)	CO_2 (GPU)	CO_2/N_2 selectivity
pDXLAc8	2	22	1563	47
pDXLAc12 (B2) (#1)	2	22	3690	42
pDXLAc12 (B2) (#2)	2	22	2684	57
		35	3722	38
pDXLAc12 (B2) (#3)	**1.5**	**22**	**3040**	**48**
		35	**4270**	**39**
pDXLAc12 (B2) (#3)	1.5	35	922	51
pDXLAc12 (B3) (#5)	1.5	35	1344	37

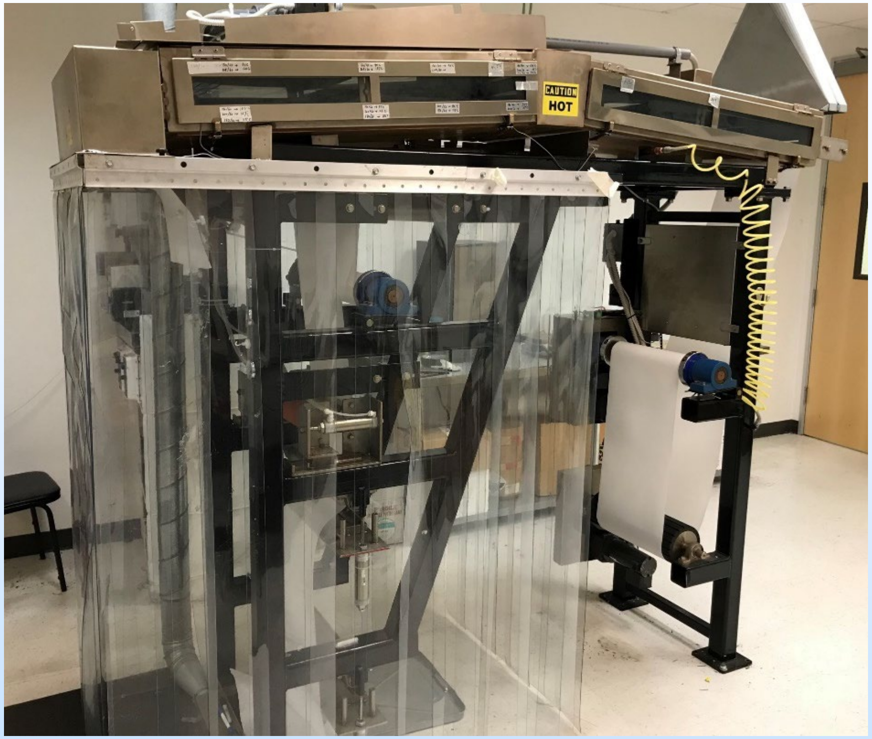
Mixed-gas performance of pDXLAc12 at 35°C



CO_2 permeance and selectivity increase with increasing CO_2 partial pressure

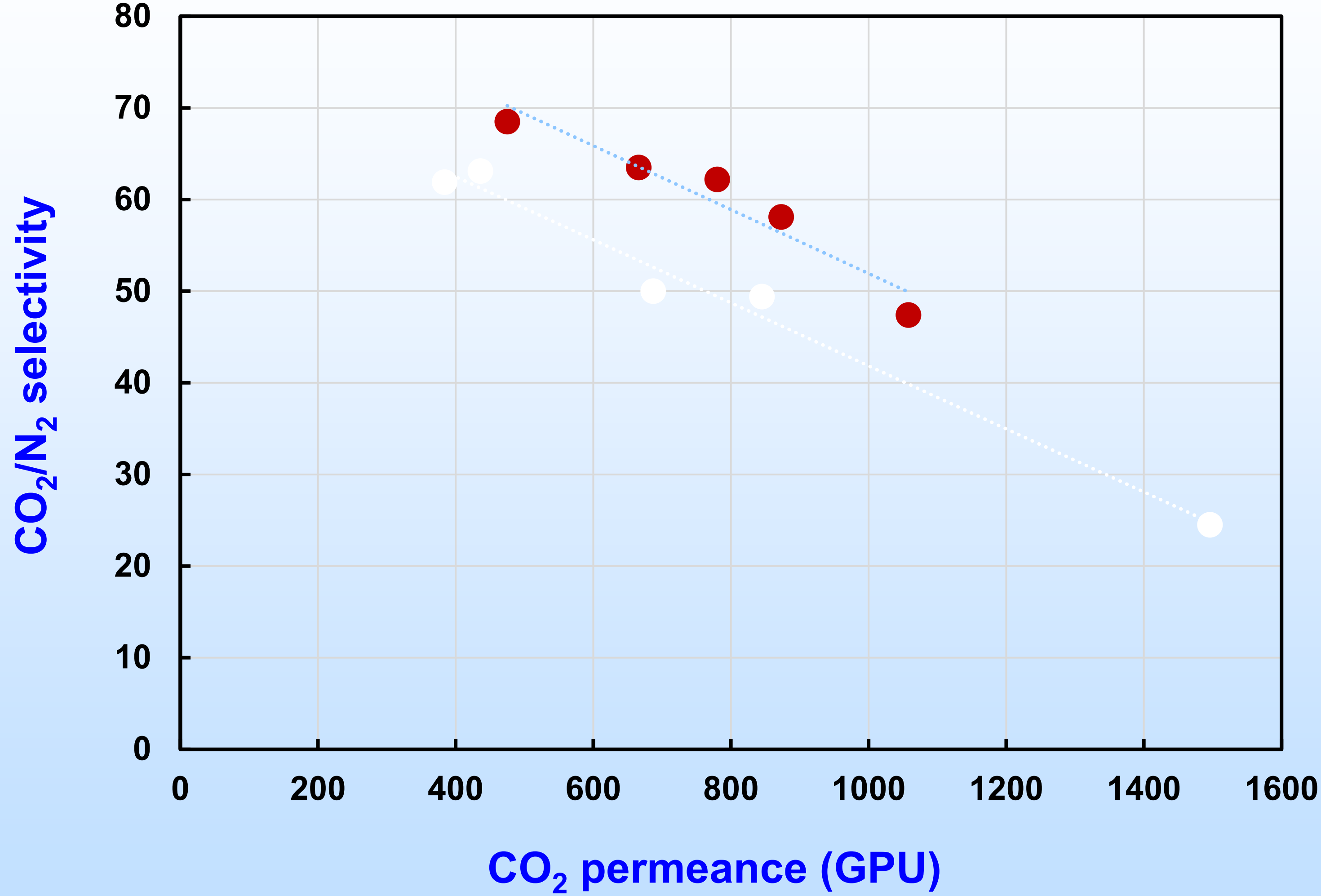
Development of Industrial Membranes





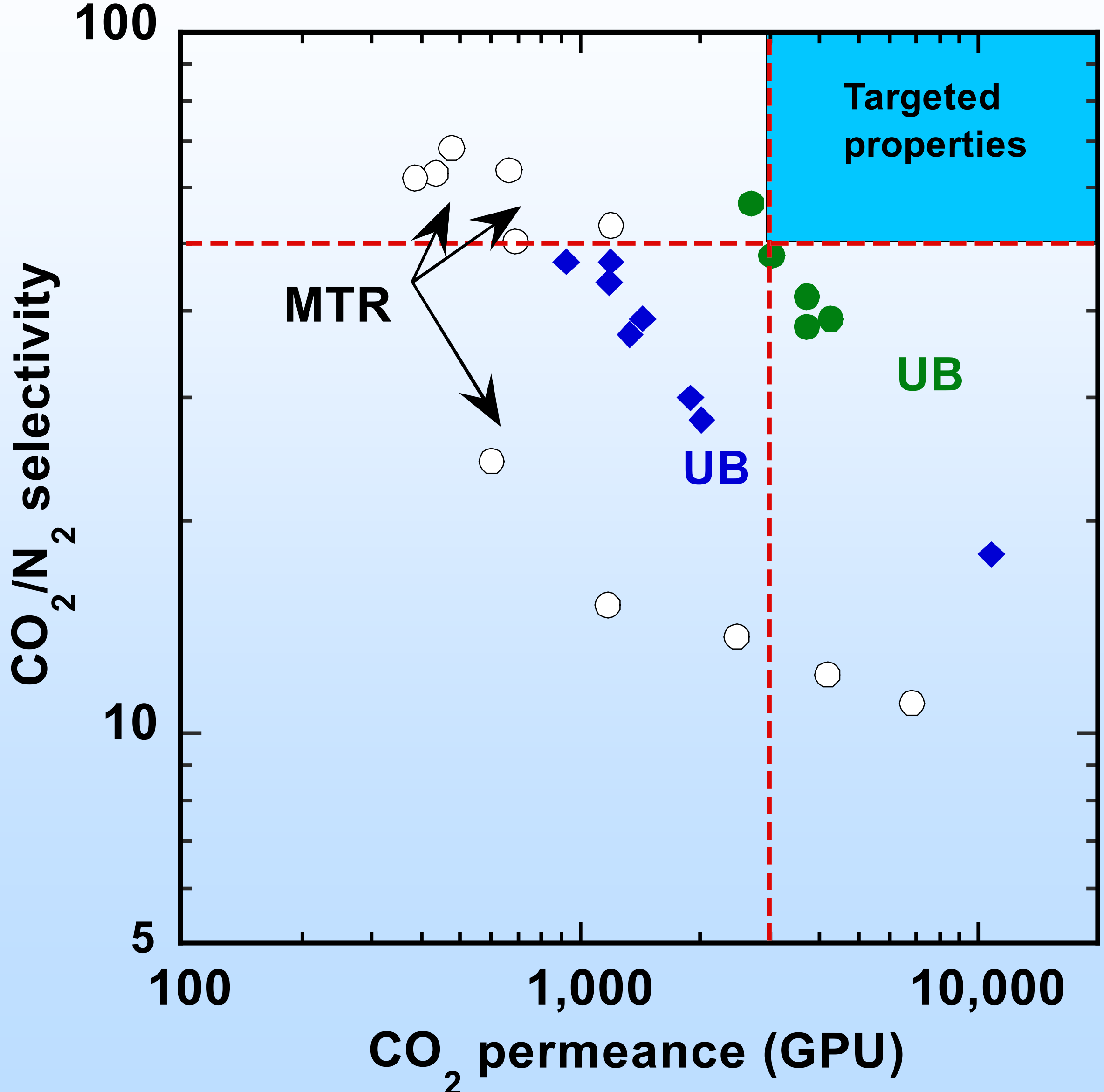
- MTR leads TFC membrane scale up activities
- Research-scale (12-inch width) roll-to-roll coating equipment has been used

Pure-gas Results of TFC Membranes



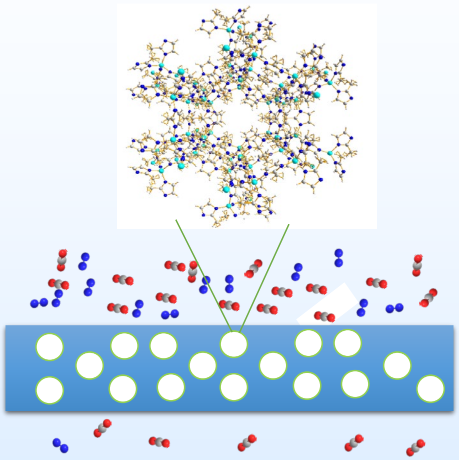
Selectivity higher than the project target of 50

Summary and Challenge of the Membrane Development

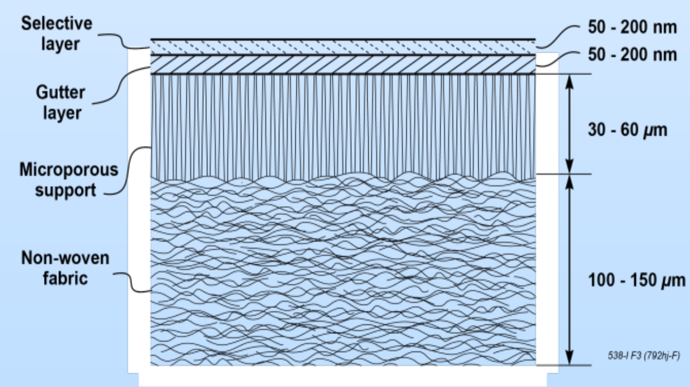


Summary

- We developed novel polyethers and MOP-3 achieving CO_2 permeability of 1000 Barrer and CO_2/N_2 selectivity of 75

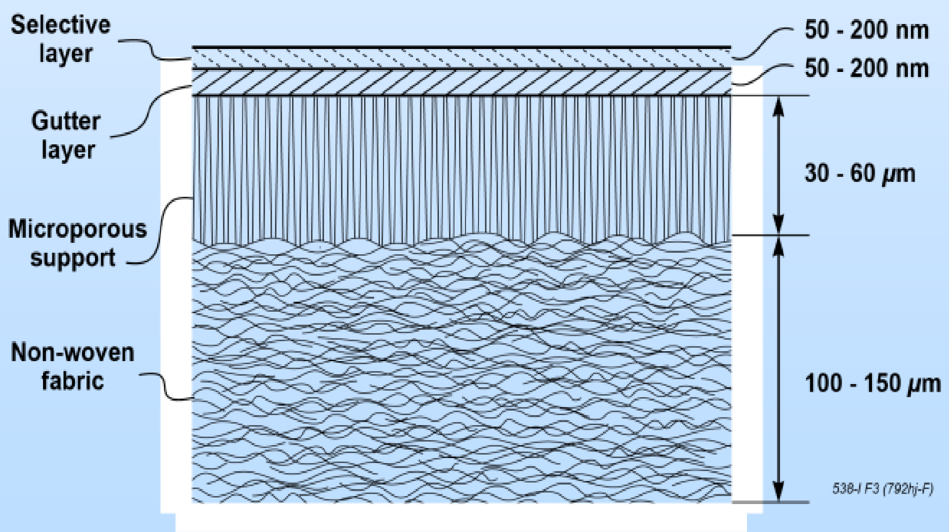


- We demonstrated the feasibility of fabricating TFC membranes using a roll-to-roll process.
- Future work will focus on the optimization of polymer synthesis and membrane fabrication to improve reproducibility



Summary: Lessons Learned

- It is not trivial to convert freestanding films to industrial thin film composite membranes, particularly for mixed matrix materials
- Reproducibility is critical to developing new polymers and membranes with various nanostructures



Acknowledgement

- Project manager: Krista Hill
- Funding from the NETL
- Costshare from NYSTAR, Caltech, RPI, and MTR