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

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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

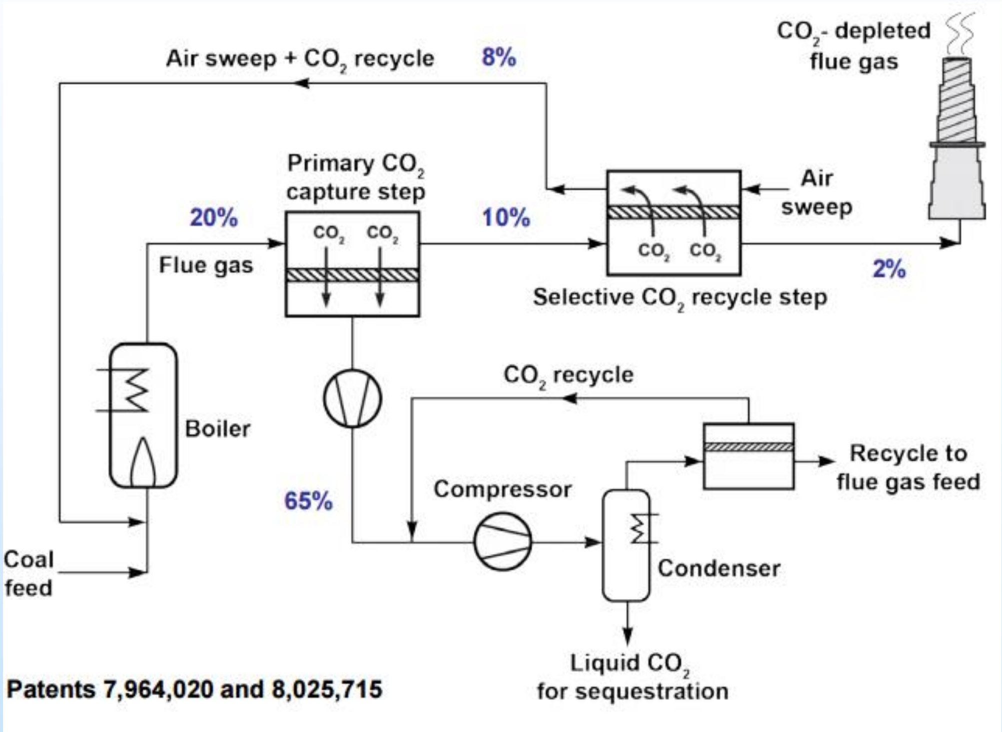
BP 1: Rationally design and prepare freestanding **mixed matrix films** with CO_2 permeability of 1000 Barrer and CO_2/N_2 selectivity of 75 and CO_2/O_2 selectivity of 25 **(7/19 - 6/21)**

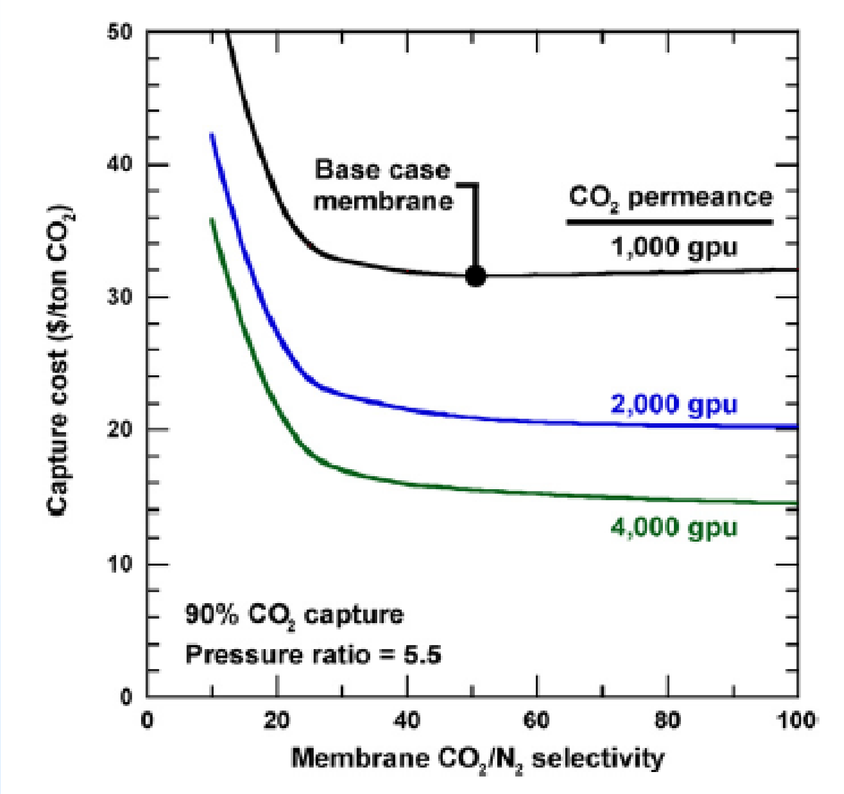
BP 2: Prepare and optimize thin film **mixed matrix composite membranes** with CO_2 permeance of 3000 GPU and CO_2/N_2 selectivity of 50 and CO_2/O_2 selectivity of 20 **(7/21 - 6/23)**

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** **(7/23 - 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

Promise of Membranes for Postcombustion Carbon Capture

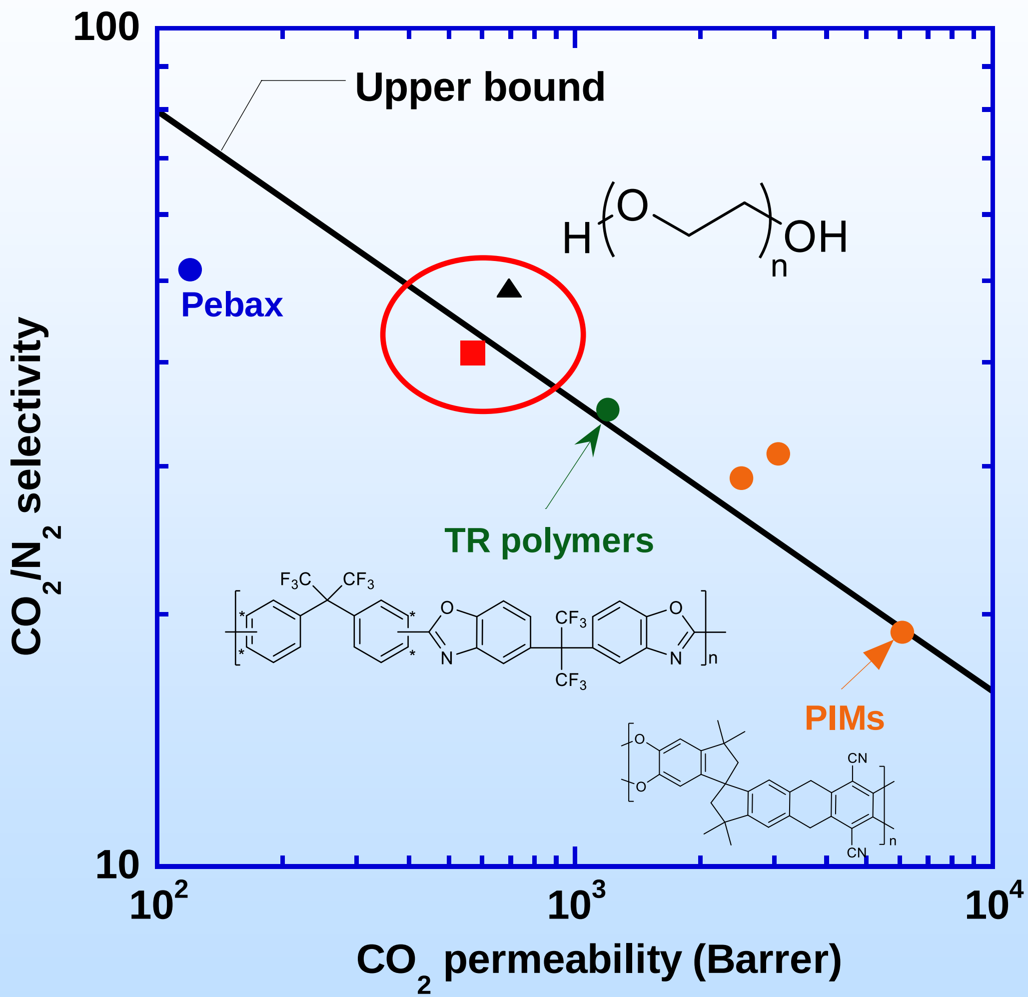




- **Low pressure and air sweep design**
- **Hybrid of membrane and cryogenic units**

Merkel, Lin, Wei, and Baker, *J. Membr. Sci.*, 359, 126 (2010)

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



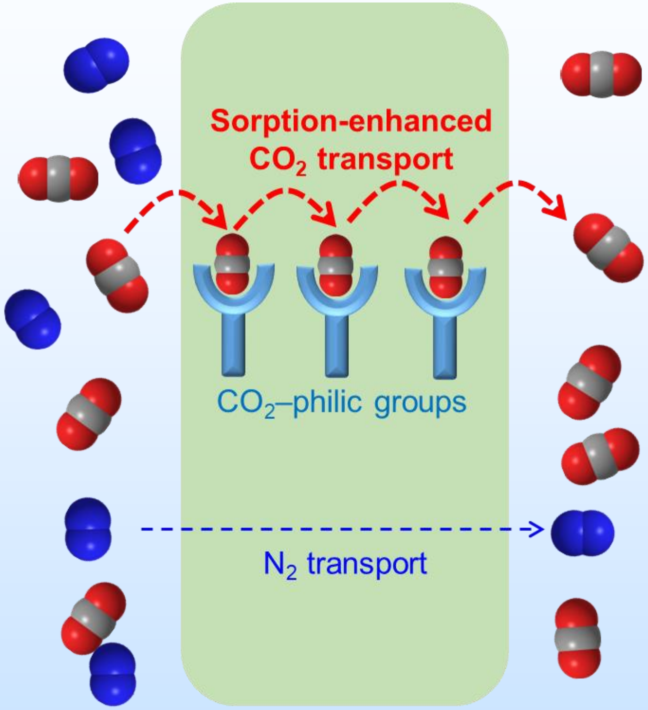
$$\alpha = \frac{P_{CO_2}}{P_{N_2}} = \frac{S_{CO_2}}{S_{N_2}} \times \frac{D_{CO_2}}{D_{N_2}}$$

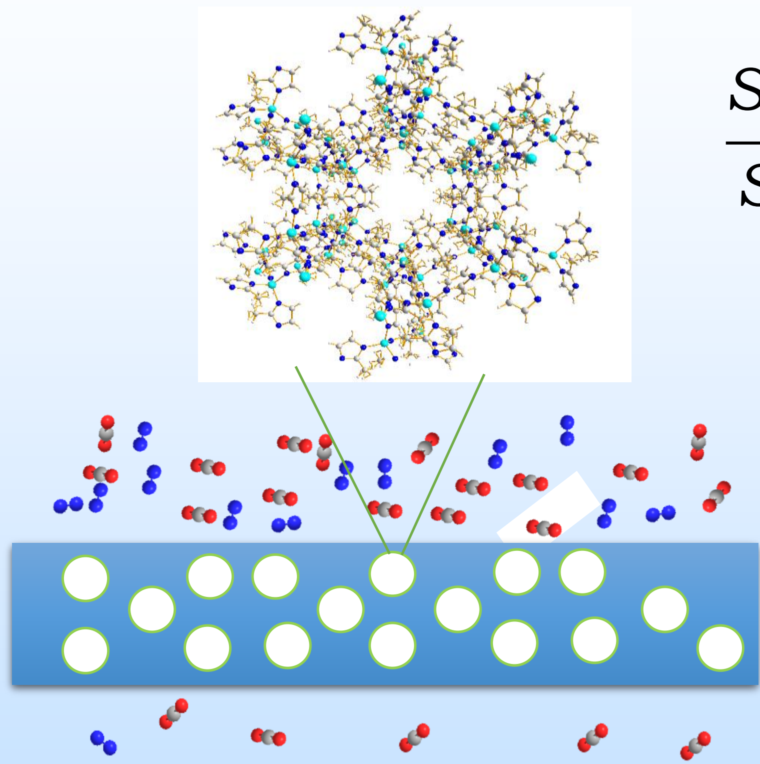
	T_C (K)	D_A (Å)	V_C (cm^3/mol)
CO_2	304	3.3	93.9
N_2	126	3.64	89.8

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

Hu, Clark, Alebrahim, and Lin, *J. Membr. Sci.* (2022) 644, 120140

Our Approach: Sorption-Enhanced MMMs

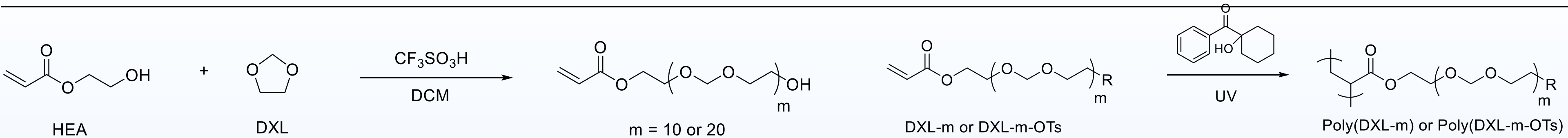


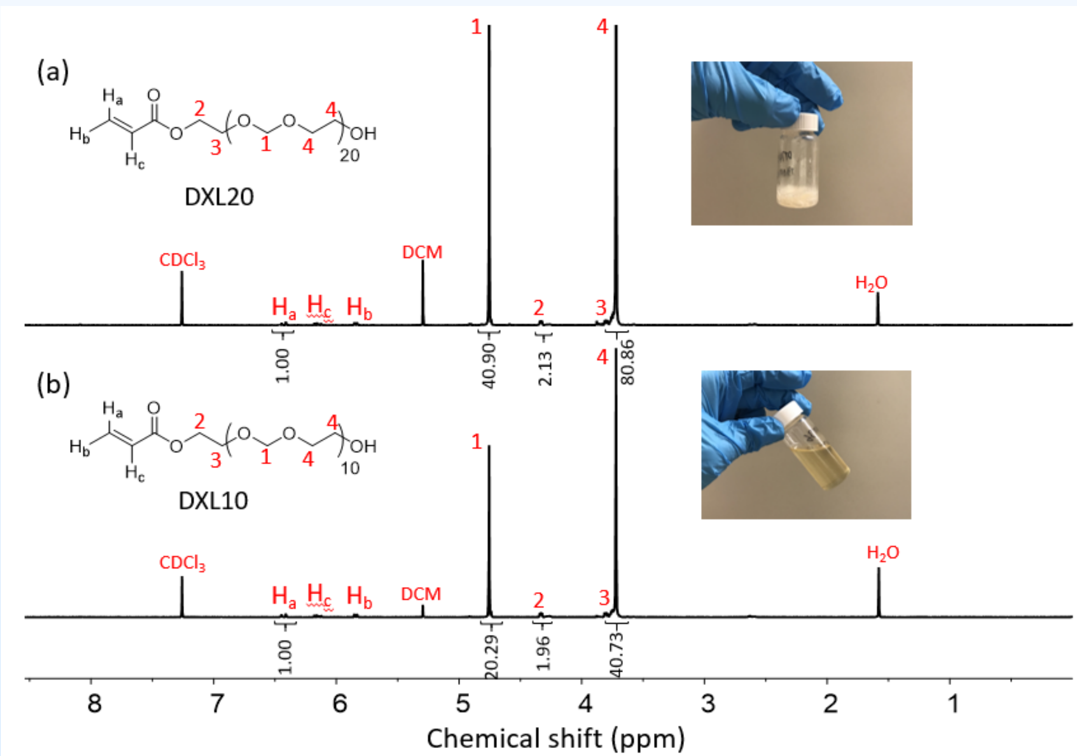


$$\frac{S_{CO_2}}{S_{N_2}} >> 1$$

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

Design and Prepare Functional Polyethers



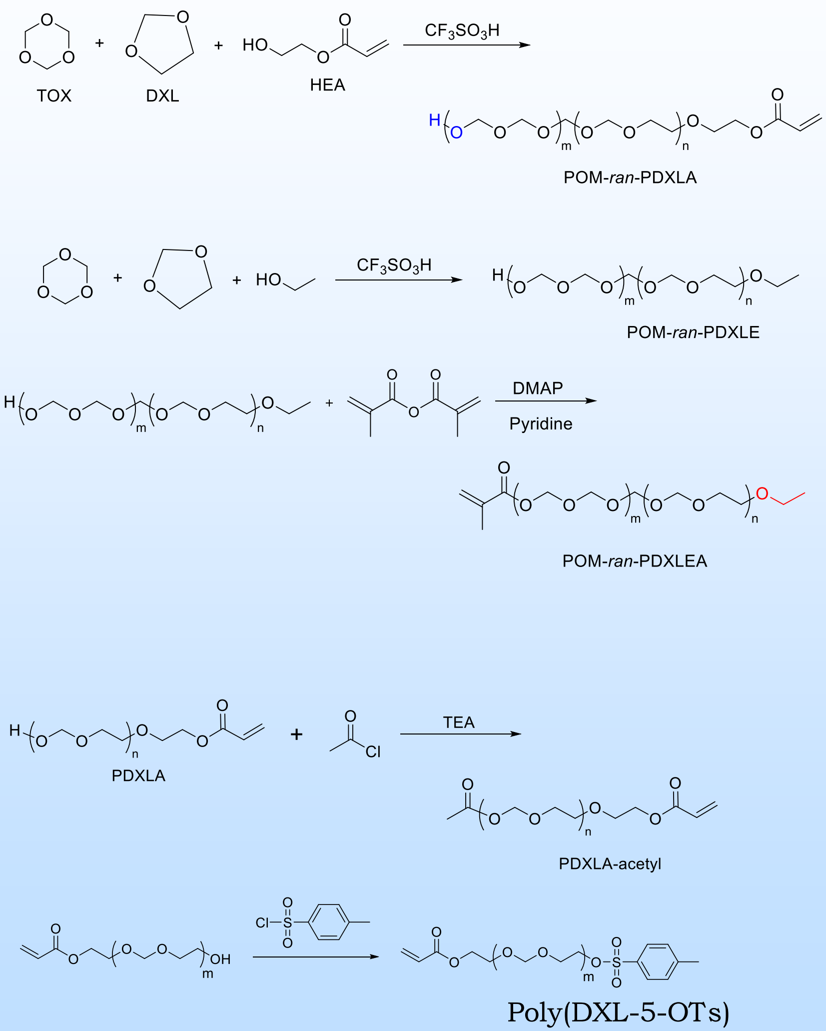


Pure-gas at 35°C

PDXLA	CO_2 perm. (Barrer)	CO_2/N_2 selectivity	T_g (°C)
m=4	96	46	-46
m=6	164	57	-58
m=8	**223**	**56**	**-60**
m=10	223	54	-60
m=12	249	59	-60

10 – 50 g/batch production had been demonstrated

Functional Polyethers with Different Oxygen Contents and Chain End Groups



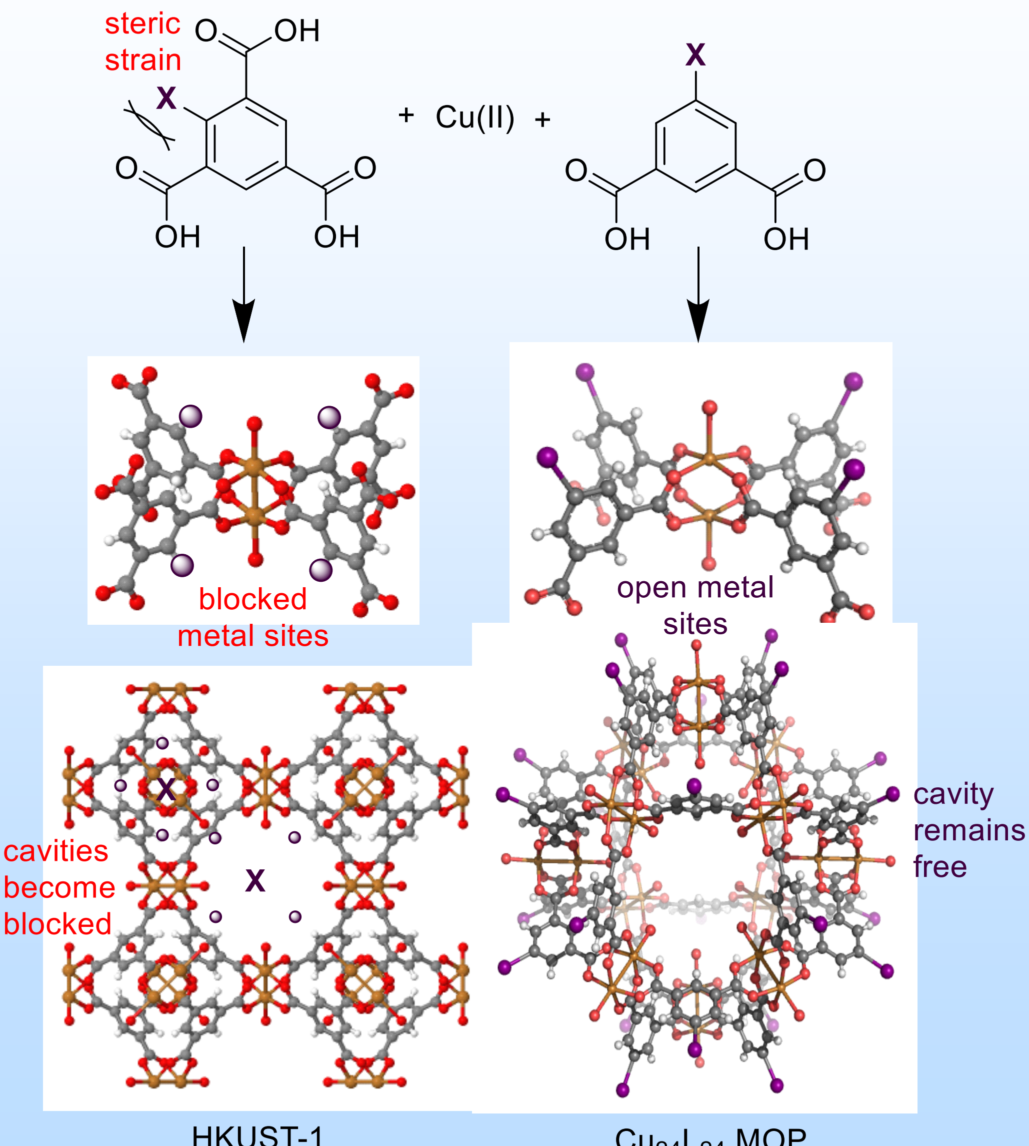
Pure-gas at 35°C

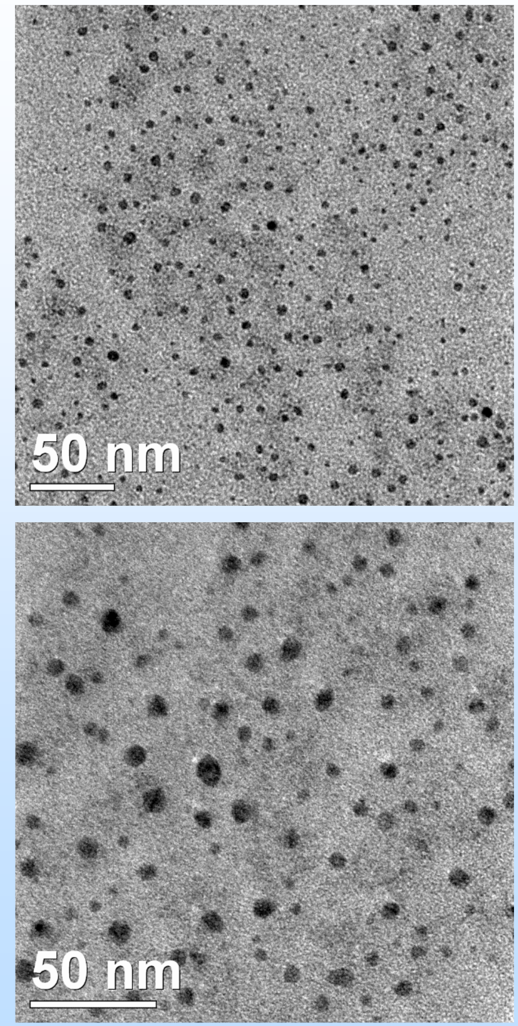
Polymers	CO_2 permeability (Barrer)	CO_2/N_2 selectivity
PDXLA8	220	56
POM4-*ran*-PDXLA8	140	61
POM12-*ran*-PDXLEA21	**422**	**58**
PDXLA8-acetyl	390	51
Poly(DXL-5-Ots)	212	53

POM12-*ran*-PDXLEA21

Temp. (°C)	Permeability (Barrer)		CO_2/N_2 selectivity
	CO_2	N_2	
25	154	1.9	81
35	422	7.6	58
60	1330	40	39

Metal-Organic Polyhedra (MOPs)

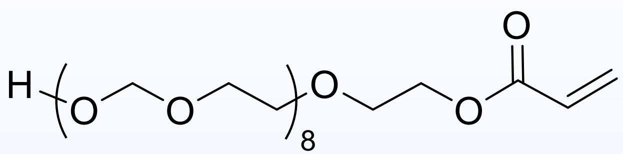




- 2 – 5 nm
- Soluble in solvents

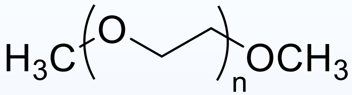
Advanced Materials for CO_2/N_2 Separation

(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

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
30	213	25

PDXLA8/PEGDME (50/50)

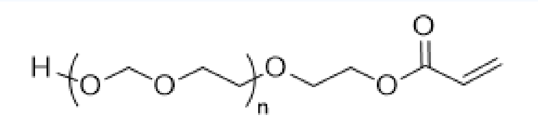
MOP-3 content (wt.%)	T (°C)	P_{CO2} (Barrer)	CO_2/N_2	CO_2/O_2
0	**25**	**1005**	**56**	**22**
1	25	662	48	25
3	**25**	**1343**	**62**	**24**
5	25	703	59	-
3	**21**	**1106**	**74**	**31**

Meet the project target

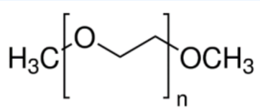
CO_2: 1000 Barrer; CO_2/N_2: 75

Pure- and Mixed-gas Tests

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



PDXLA8, n = 8



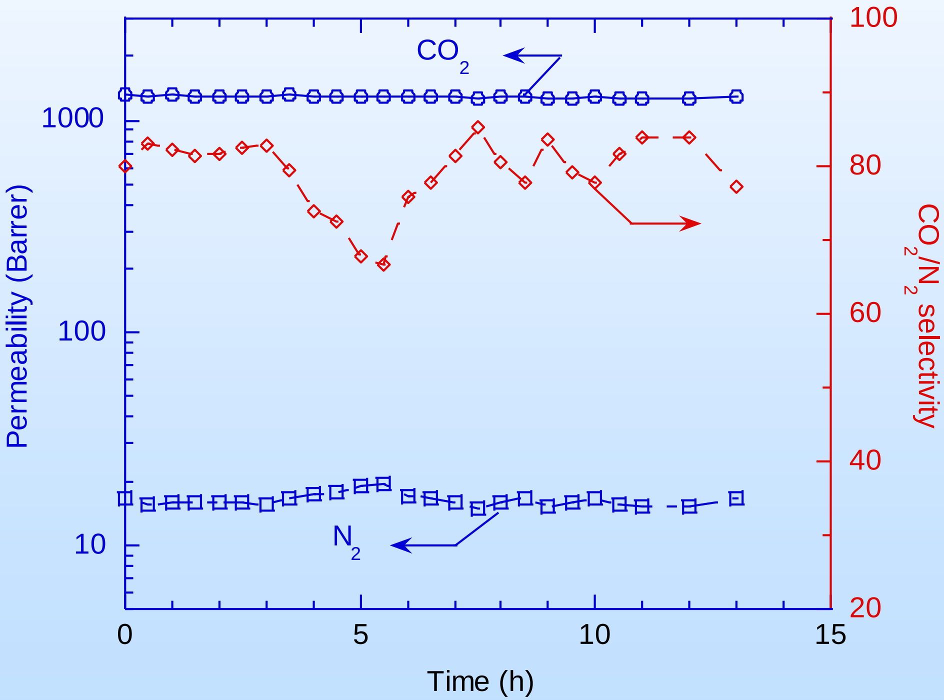
PEGDME
240 g/mol

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**

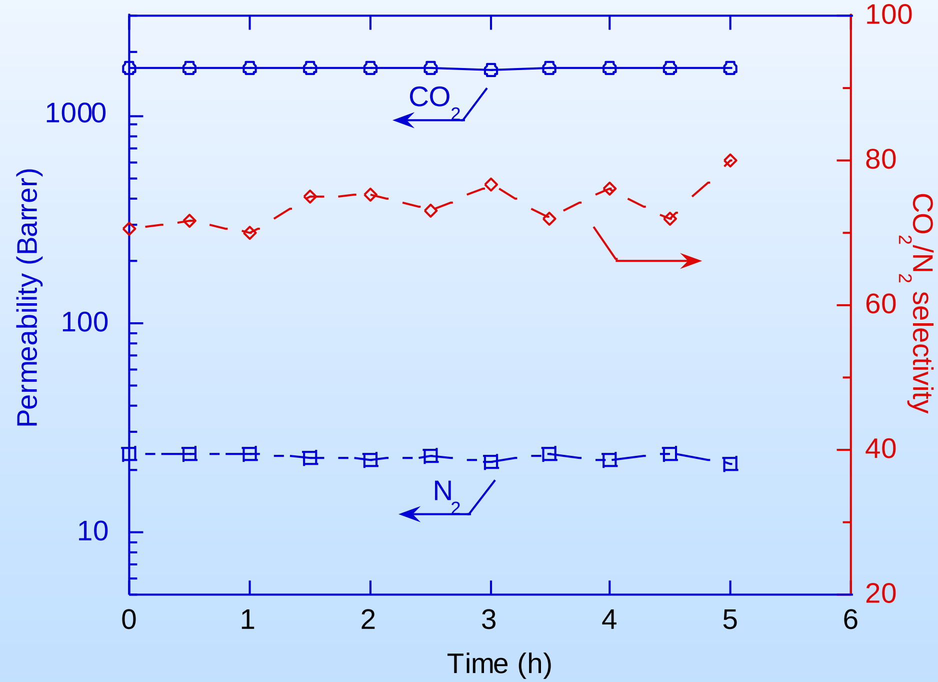
Meet the project target
CO_2: 1000 Barrer; CO_2/N_2: 75

Mixed-Gas Stability Tests

PDXLA8/PEGDME (50:50)
25°C; 160 psi



PDXLA8/PEGDME (50:50)
3% UiO66-NH_2
25°C; 160 psi



Computational Methodology

Polymer Library:

Name	PE	PTMO	PEO	PDXLA	POM
O:C Ratio	0	0.25	0.50	0.67	1.0

Gas Pairs of Interest:

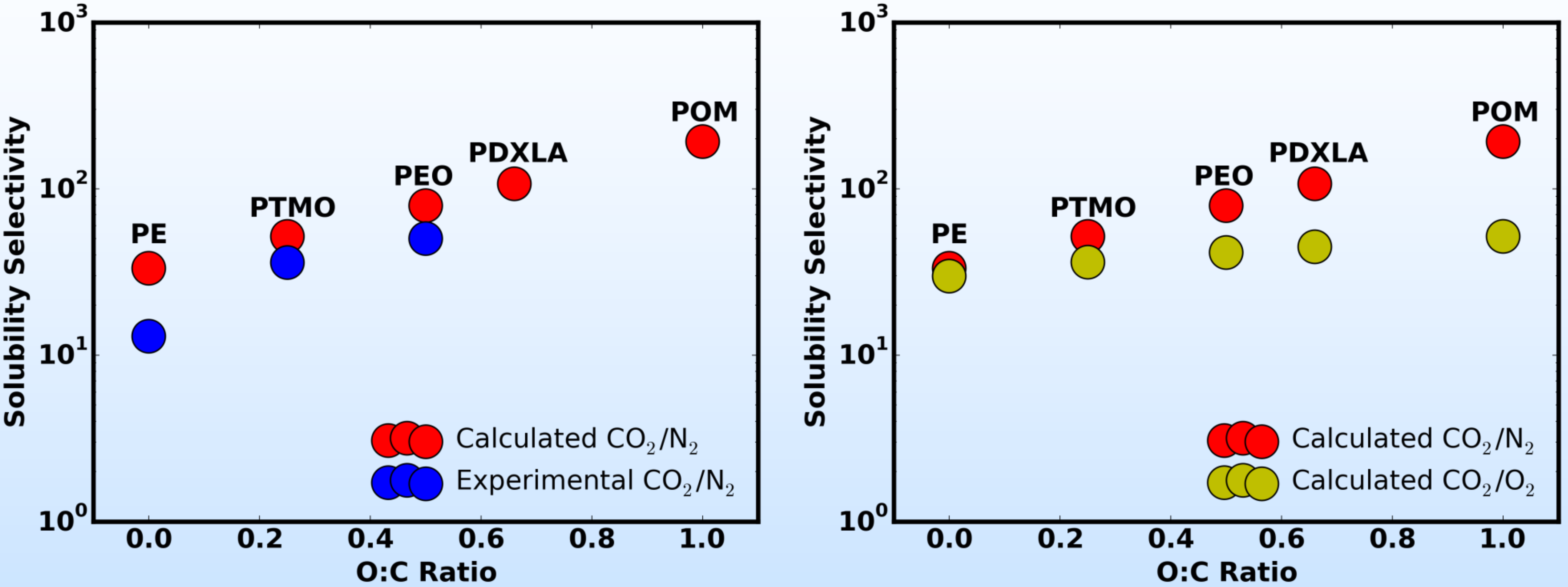
CO_2/N_2 and CO_2/O_2

Understanding CO_2-philic rubbery polymers

PC-SAFT calculations to calculate solubility selectivity

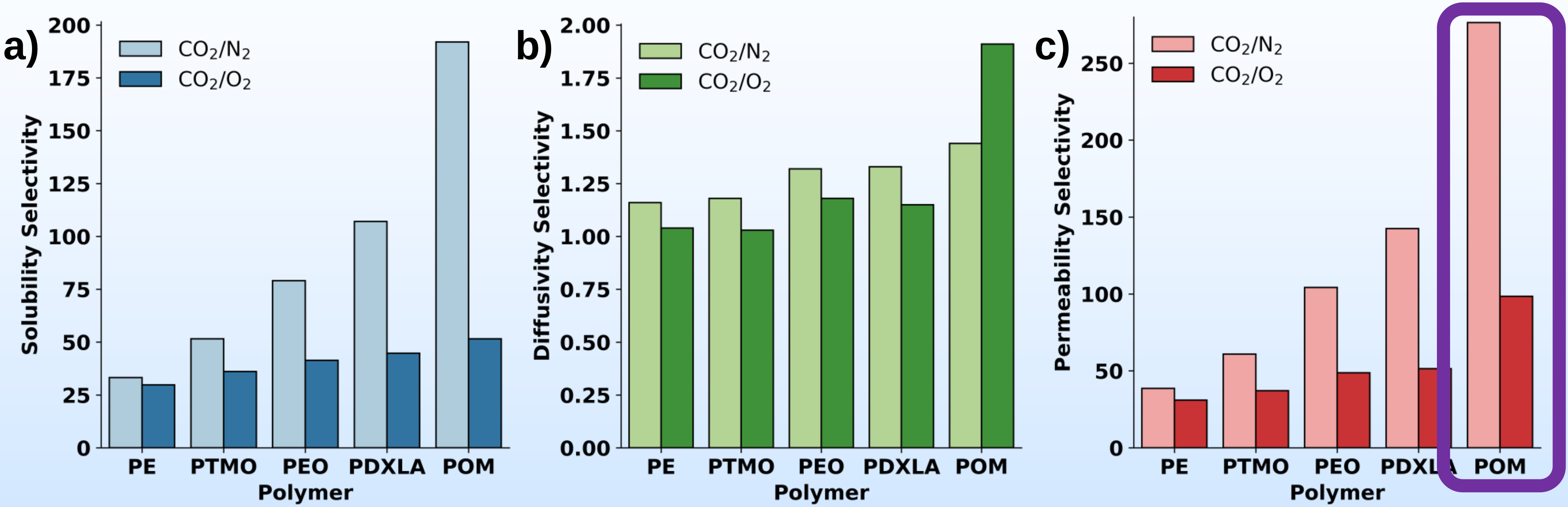
MD simulations to calculate polymer dynamics and diffusivity selectivity.

Solubility Selectivity



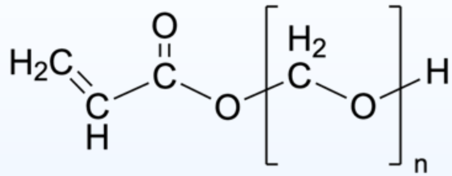
CO_2/N_2 solubility selectivity increases with increasing O content

Solubility × Diffusivity = Permeability

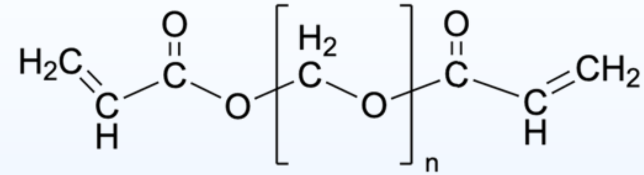


POM exhibits both high solubility selectivity and diffusivity selectivity

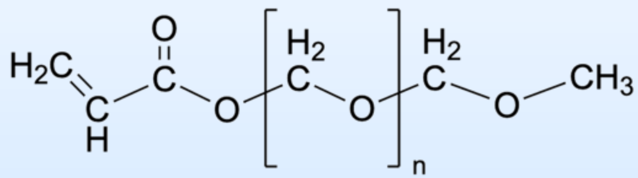
CO_2 Diffusion in POM with Increasing Oxygen Content

1) 

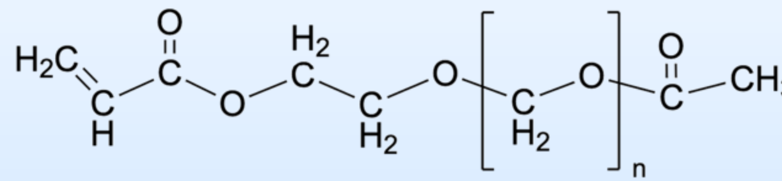
Acrylate + POM

4) 

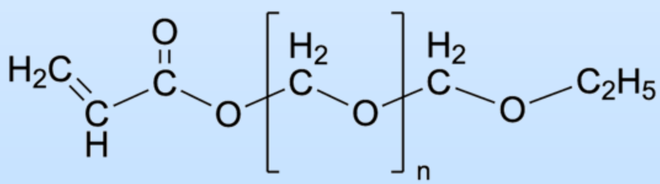
Acrylate + POM + Acrylate

2) 

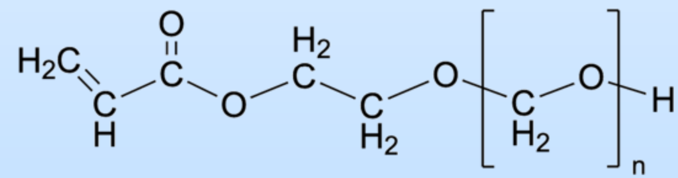
Acrylate + POM + Methoxy

5) 

Acrylate + Ethoxy + POM + Acetyl

3) 

Acrylate + POM + Ethoxy

6) 

Acrylate + Ethoxy + POM

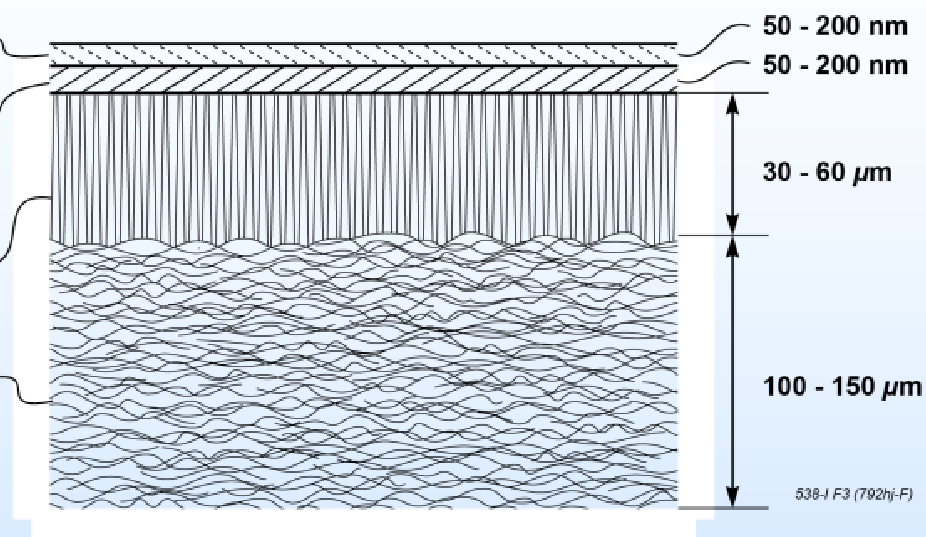
Six new polymers with different chain endings and oxygen content

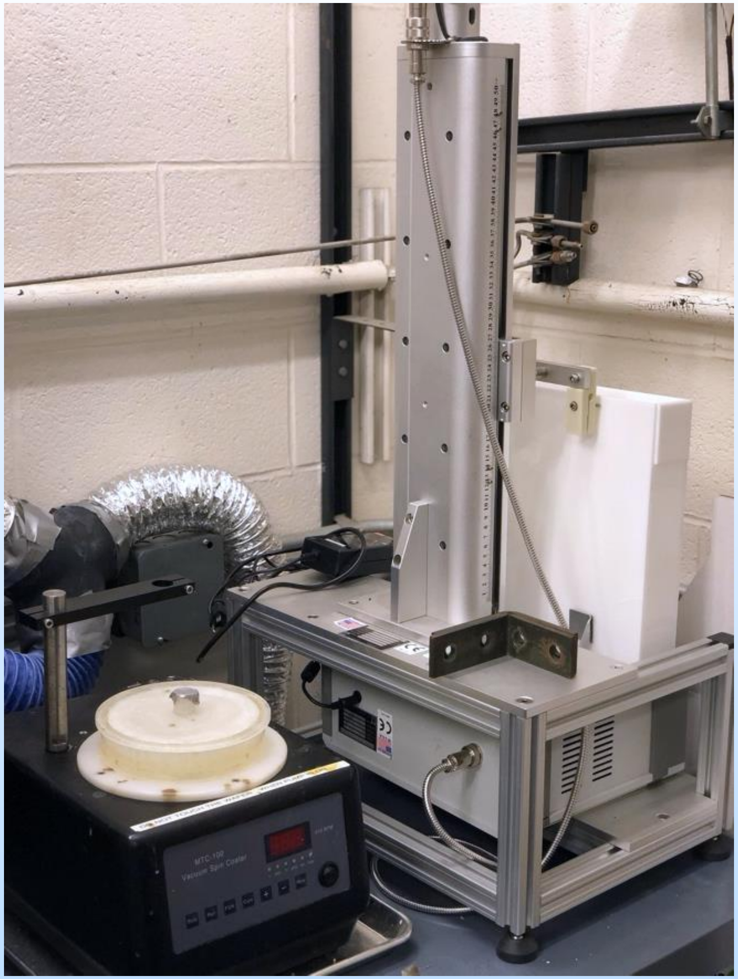
Summary of the Chain End Decorated POM Polymers

	CO_2 Diffusion	N_2 Diffusion	O_2 Diffusion	CO_2 / N_2	CO_2 / O_2
POM	0.47	0.23	0.27	2.04	1.74
1	0.41	1.86	1.09	0.22	0.38
2	0.58	1.17	0.36	0.50	1.61
3	1.26	1.53	1.15	0.82	1.09
4	0.94	0.25	1.47	3.76	0.64
5	1.20	0.34	1.22	3.53	0.98
6	**1.42**	**0.26**	**1.89**	**5.46**	**0.75**
Azo	0.54	0.27	0.32	2.00	1.69
Triazine	0.13	0.05	0.06	2.60	2.17
Triazole	0.25	0.12	0.14	2.08	1.79

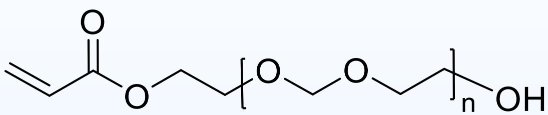
Polymer 6 performs by far the best for CO_2/N_2 separation

Thin Film Composite (TFC) Membranes



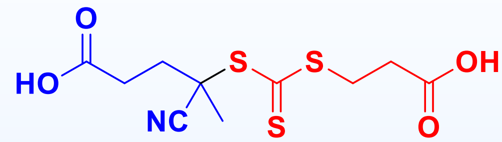


Atom Transfer Radical Polymerization (ATRP)



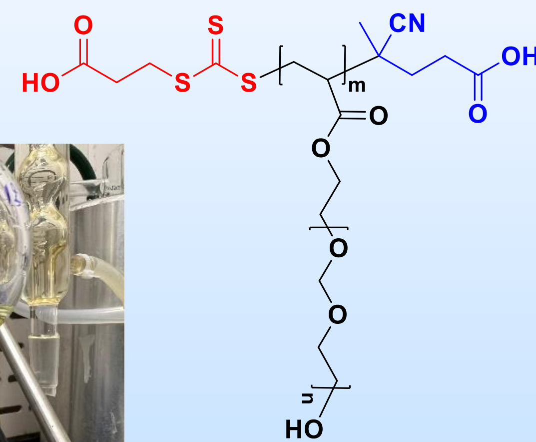
DXLA8 (J16)

+



BM1433
Chain transfer agent (CTA)

AIBN
75°C, DMF



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

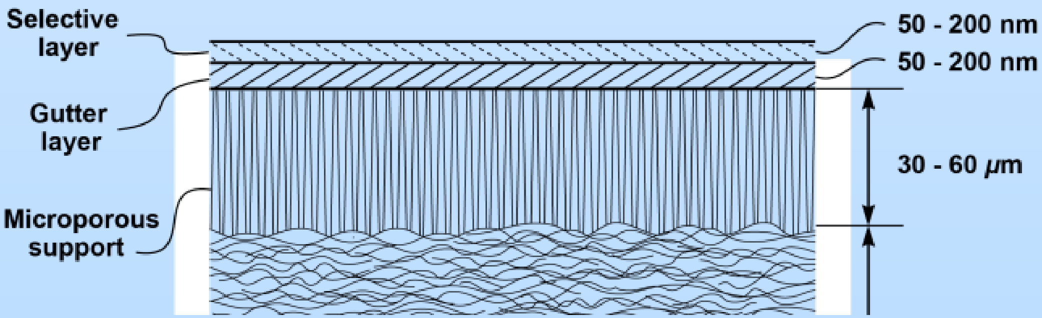
Reaction time: 3 h, 75°C
Stopping reaction:
- Inject DMF
- Quench in liquid N_2

$$M_{n,theo.} = \left(X \frac{[DXLA]}{[CTA]} M_{W,DXLA} \right) + M_{W,RAFT}$$

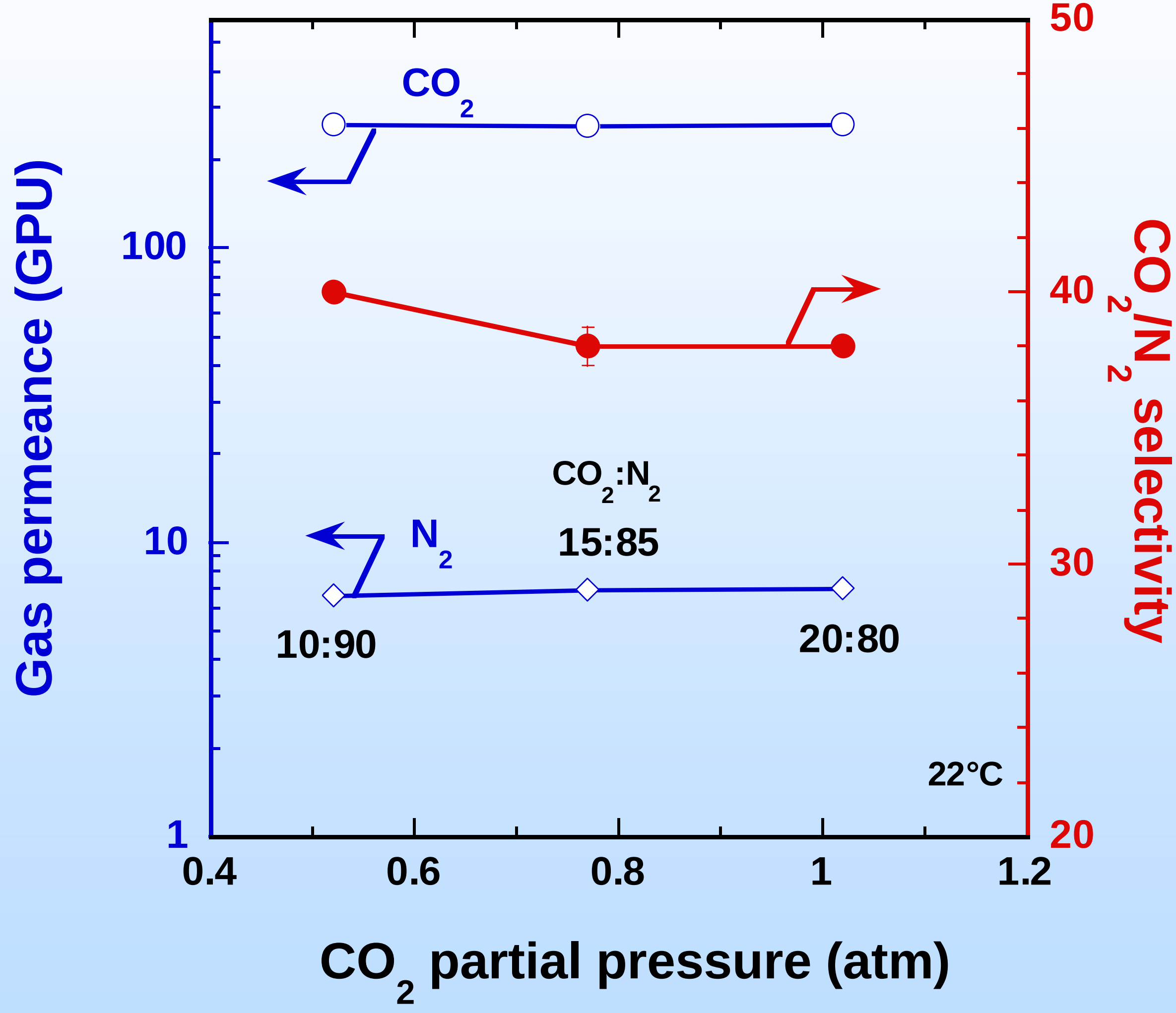
$$\mathbf{M_{n,theo.} = 71.1\ kDa}$$
(100% conversion)

Pure-gas CO_2/N_2 Separation Properties

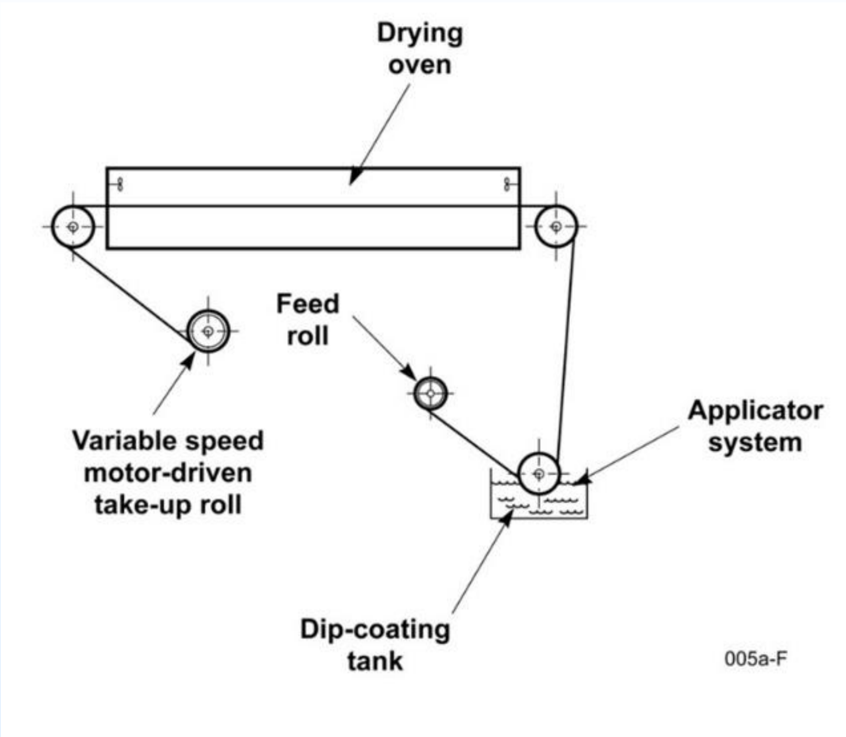
Sample	Solvent (conc.)	HPDXLA conc. (wt.%)	CO_2 Permeance (GPU)	CO_2/N_2
PDMS	-	-	9000	8
PDA-PDMS	-	-	7000	8.5
HPDXLA1/ PDA-PDMS	IPA/H_2O (70/30)	2	521	61
HPDXLA2/ PDA-PDMS	IPA/H_2O (90/10)	2	974	49

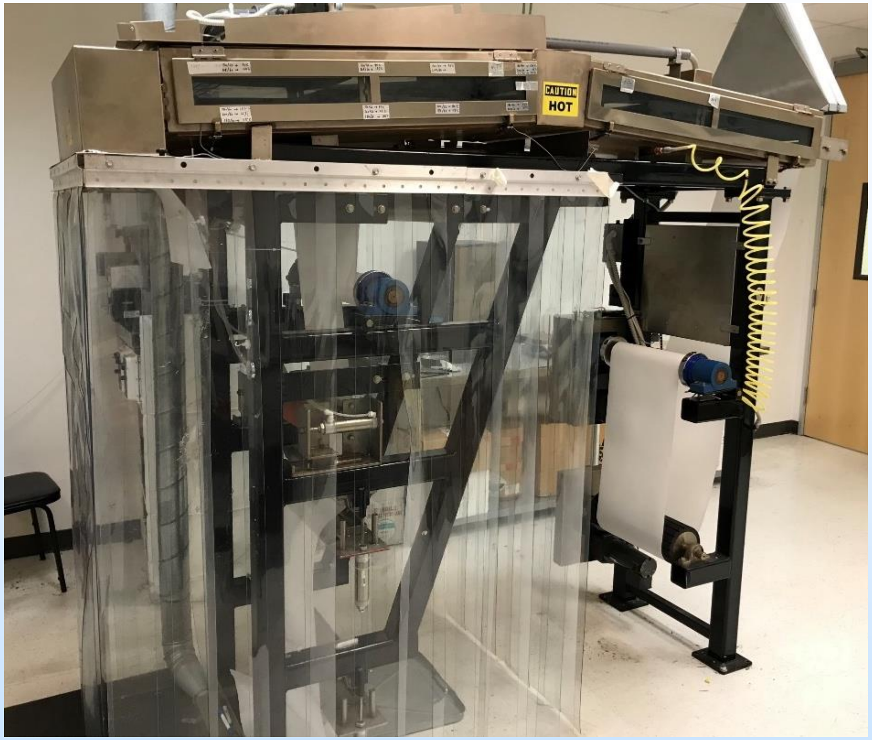


CO_2/N_2 Separation Properties



Development of Industrial Membranes





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

Moving Forward: Membrane Development

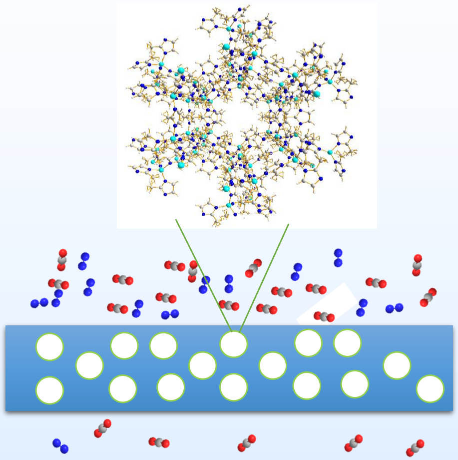
BP2 Tasks	**Start date**	**End date**
Task 7. Scale-Up Polymer Synthesis	7/1/21	6/30/23
Task 8 Scale-up Synthesis of MOP-based Nanomaterials	7/1/21	12/31/22
Task 9. Simulate Gas Transport Properties in Polymers Containing Various Functional Groups	7/1/21	6/30/23
Task 10. Scale-up of Optimized Membrane for Roll-to-Roll Production at Bench-Scale	10/1/21	3/31/23
Task 11. Conduct Parametric Laboratory Tests on Membranes	10/1/21	6/30/23

Key Milestones

BP	Milestone Description	Planned Completion
2	**High quality polymers produced in 10–20 g/batch**	**6/30/2023**
2	**High quality MOPs produced in 10- 20 g/batch**	**12/31/2022**
2	**TFC membranes with CO_2 permeance of 3000 GPU and CO_2/N_2 selectivity of 50 and CO_2/O_2 selectivity of 20**	**6/30/2023**
3	Modeling of gas transport in MMMs and guidance to design MMMs	6/30/2024
3	Bench-scale **modules** with CO_2 permeance of 3000 GPU, CO_2/N_2 selectivity of 50 and CO_2/O_2 selectivity of 20 tested with simulated flue gas	3/31/2024
3	Testing apparatus of bench-scale modules modified and installed at NCCC	12/31/2023
3	**Field test** of bench-scale modules completed	6/30/2024
3	**Techno-Economic Analysis**	6/30/2024

Summary

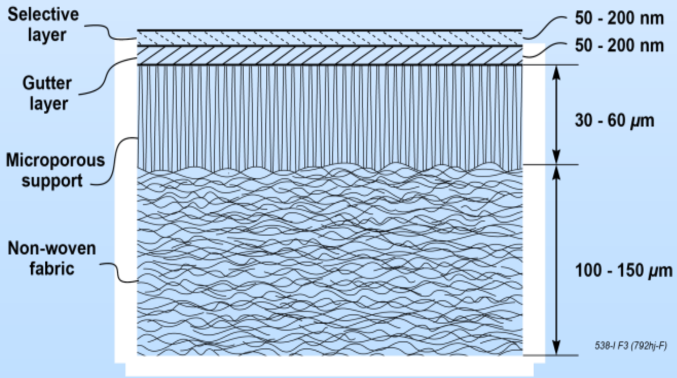
- We developed novel polyethers achieving CO_2 permeability of 1000 Barrer and CO_2/N_2 selectivity of 75



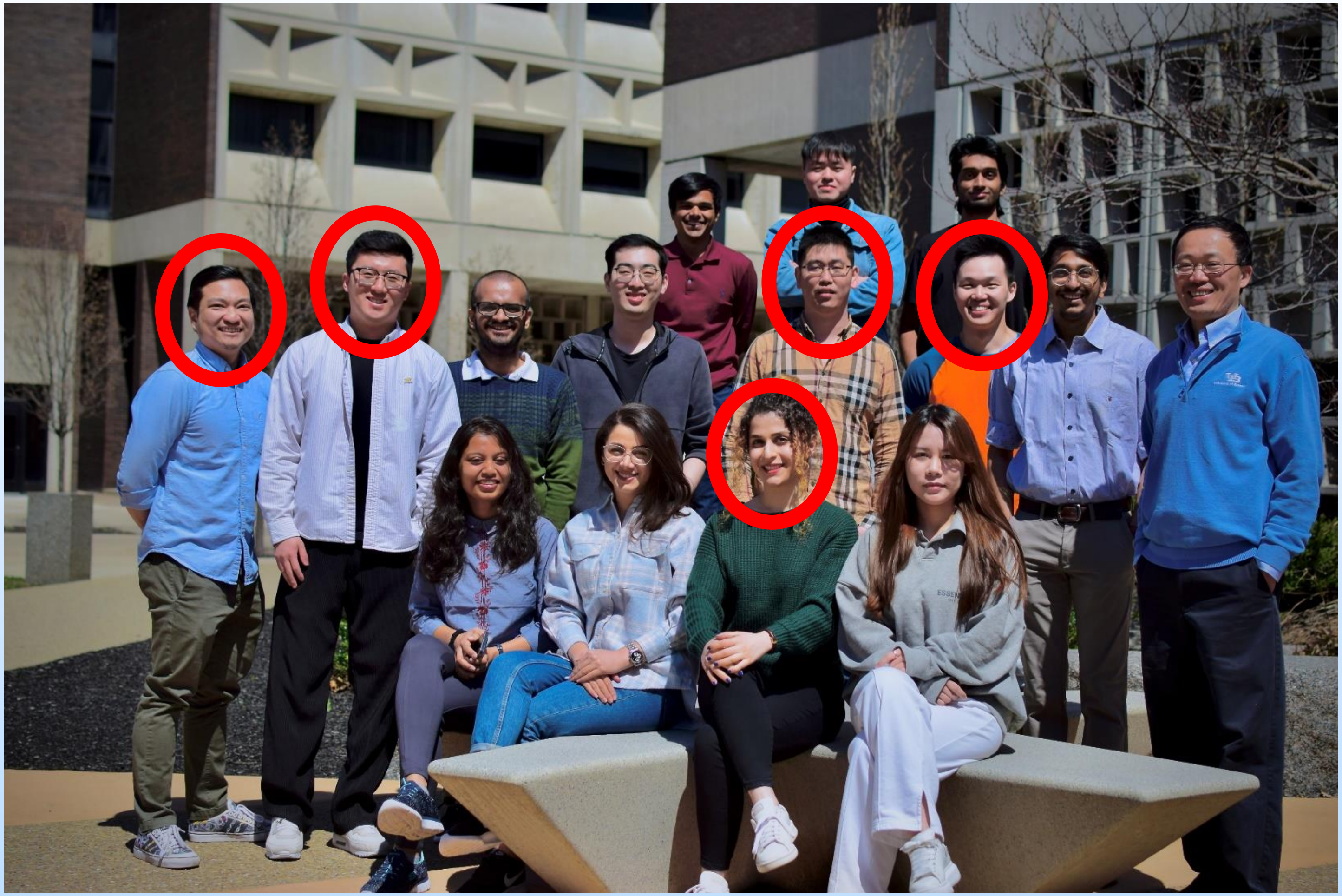
- We synthesized bottlebrush polyethers with high molecular weight

- We demonstrated the feasibility of fabricating TFC membranes

- Future work will focus on the development of high-flux TFC membranes



Acknowledgement



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BP3 Tasks	Start date	End date
Task 12. Optimize Polymer and MOP Structures and Synthesis Methods	7/1/21	6/30/22
Task 13. Simulate Gas Transport Properties in MMMs	7/1/21	6/30/22
Task 14. Scale-up of Optimized Membrane for Roll-to-Roll Production at Commercial Scale	7/1/21	9/30/21
Task 15. Fabricate Prototype Modules and Conduct Parametric Lab Testing	10/1/21	3/31/22
Task 16. Modify a Module Testing System for Operation at NCCC	7/1/21	12/31/21
Task 17. Perform Field Test of Bench-Scale Modules at NCCC	1/1/22	6/30/22
Task 18. Membrane System Simulation and Estimate Costs	7/1/21	6/30/22
Task 12. Optimize Polymer and MOP Structures and Synthesis Methods	7/1/21	6/30/22
Milestones i-p: Modeling of gas transport in MMMs and guidance to design MMMs; Bench-scale modules with CO_2 permeance of 3000 GPU, CO_2/N_2 selectivity of 75 and CO_2/O_2 selectivity of 30 at 60°C tested with simulated flue gas; Testing apparatus of bench-scale modules modified and installed at NCCC; Field test of bench-scale modules completed; State Point Data Table; Technology economic Analysis; Environmental Health and Safety Risk Assessment		

Project Milestones

BP	Milestone Description	Planned Completion
1	**Updated Project Management Plan**	**7/30/2019**
1	**Kickoff Meeting**	**8/31/2019**
1	**Updated Technology Maturation Plan**	**9/30/2019**
3	Final report	6/30/2022
1	MMMs with CO_2 permeability of 1000 Barrers and CO_2/N_2 selectivity of 75 and CO_2/O_2 selectivity of 30 at 60°C	6/30/2020
2	High quality polymers produced in 10–20 g/batch	6/30/2021
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3	Testing apparatus of bench-scale modules modified and installed at NCCC	12/31/2021
3	Field test of bench-scale modules completed	6/30/2022
3	State Point Data Table	6/30/2022
3	Techno-Economic Analysis	6/30/2022
3	Technology Gap Analysis	6/30/2022
3	Environmental Health and Safety Risk Assessment	6/30/2022