SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Elliot Como
FACULTY ADVISOR:	Rulian Guo
PROJECT PERIOD:	CY 2023
PROJECT TITLE:	Crosslinking of PIM-1 with Macrocyclic Crosslinker for Physical Aging Resistance
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**(X) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Synthesis of linear PIM-1	Successfully synthesized many batches of the PIM-1 polymer	100%
Synthesis of PIM-1 oligomers	Successfully synthesized many types of oligomers with different end groups	100%
Casting of membranes	Successfully cast membranes both under the IR lamp and oven	100%
TGA testing of membranes	Successfully characterized membranes through TGA testing	100%
PIM-1 Hydrolysis membranes	Still exploring the aging profile of PIM-COOH membranes both with and without macrocyclic crosslinkers	50%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount) N/A
EXTERNAL AWARDS RECEIVED	(Sponsor, Project Title, PIs, Award Date, Award Amount) N/A
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) N/A
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s) N/A
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	(Event, Presentation Title, Presentation Date, Location) N/A
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	(Purpose, Title, Date Received) N/A
INTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions) N/A
EXTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions) N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL) N/A
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail) N/A

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

Overall, my research experience was great. I gain a ton of valuable laboratory experience and problem-solving experience that will be extremely beneficial to me as I begin my career. Everyone in the lab was a pleasure to work with and were great mentors to me.

FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

Polymer-based membranes for gas separations represent a great opportunity for reducing cost, energy usage, and CO2 emissions in chemical separation processes. One of the primary concerns with using polymers for gas separation is physical aging. Aging occurs due to polymer chain relaxation to approach thermodynamic equilibrium of chain packing. Aged polymers have lower free volume and are more densely packed which corresponds to a permeability drop. The PIM-1 polymer is a representative high-free-volume glassy polymer membrane material, showing ultrahigh permeability and good selectivity. However, PIM-1 is viewed as imperfect for industry applications due to its rapid physical aging. This research attempts to address this issue by exploring a macromolecule design of self-semi-interpenetrating networks (ss-IPN) where linear PIM-1 chains penetrate through cross linked unimodal networks of PIM-1 to mitigate crosslinking-induced permeability loss and prevent the free volume collapse via the rigid network 'scaffold'.

As my research period progressed another preventative method for physical aging, random crosslinking, was explored. The main drawback to crosslinking is it also causes large permeability losses. The goal of this new scope of research is to utilize bulky crosslinkers to minimize these permeability losses due to crosslinking. This is done by introducing macrocyclic crosslinkers with hollow interiors such as beta-cyclodextrin to incorporate permeant free volume elements within the structure. The base polymer for the random crosslinking trials is created through the hydrolysis of PIM-1 to PIM-COOH.

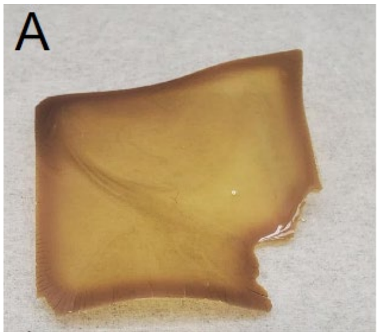
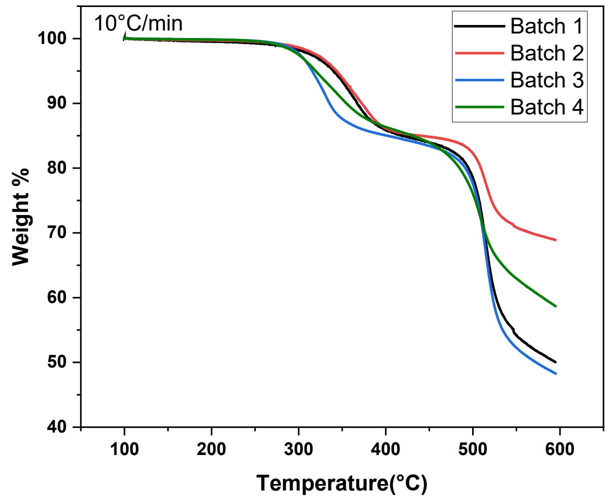


Image of PIM-COOH film casting

As seen in the above image, we have been able to successfully cast a flexible, homogeneous film of PIM-COOH. This film could be cut up and tested in the gas cell for permeability testing.

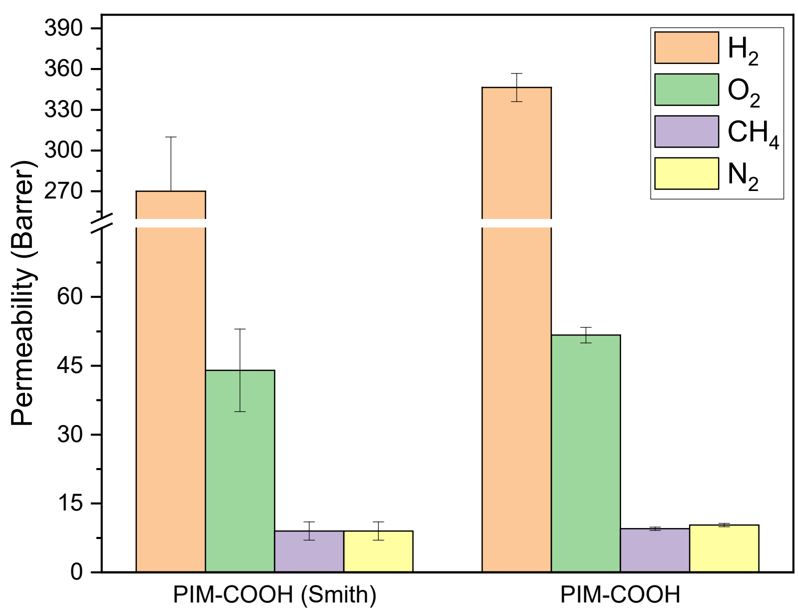
TGA Testing for PIM-COOH



TGA shows weight loss of Carboxylic acid from the PIM-1 chain

The TGA data showed that a consistent conversion of around ~70% for the PIM-COOH. This gave us confidence that the reaction mechanism used provides a consistent resullt.

PIM-COOH Membranes in the Gas Cell



Fresh data comparison between our film and a literature example (Source 1. Katherine Mizrahi Rodriguez et al. *Macromolecules* 2020 *53* (15), 6220-6234)

The gas cell results show that our PIM-COOH membranes replicate previous literature data from Smith, giving us confidence in our pure PIM-COOH membrane data going forward as we compare it to the crosslinked PIM-COOH. The next step in the research is to produce crosslinked PIM-COOH and test the physical aging compared to pure PIM-COOH over a 1-week, 2-week, 1-month, and 3-month time span.