NDnano
Center for Nano Science and Technology

NDnano Summer Undergraduate Research
2019 Project Summary

1. Student name & home university:

Evan Ferguson, Bethel University

2. ND faculty name & department:

Dr. Ruilan Guo, Department of Chemical and Biomolecular Engineering

3. Summer project title:

Polymer membranes with tunable microporosity for gas separations

4. Briefly describe new skills you acquired during your summer research:

Over the course of my summer research, I had the opportunity to learn new organic synthesis, polymerization reaction, as well as how to use several new pieces of equipment, such as an NMR, a rotary-evaporator, a vacuum oven, and a gas permeation cell. I also learned how to keep track of multiple reactions at the same time, how to use reaction conditions to control desired product purity and yield, and how to present research in a scientific way.

5. Briefly share a practical application/end use of your research:

The most common alternatives for gas separation have high capital cost as well as a large carbon footprint. Research from the Guo group is focused on creating high efficiency polymer membranes for gas separations, in the hopes that they can start to replace existing energy-intensive separation processes whenever applicable.

6. 50- to 75-word abstract of your project:

The market for membrane-based technology for gas separations is expanding rapidly as membranes achieve higher levels of permeability and selectivity. This project focuses on the design and production of pentiptycene-based ladder polymers, in the hopes to push the known limit for permeability and selectivity. By increasing purity and optimizing polymerization defect free membranes are produced, while changing the functionality of substituent groups creates more selective performance.

7. References for papers, posters, or presentations of your research:

ACS Macro Lett. 2015, 4, 947−951

Macromolecules 2017, 50, 7809-7843

Chem. Rev. 2018, 118, 5871−5911

Ind. Eng. Chem. Res. 2017, 56, 4220−4236

Polymer, 2013, 54, Issue 18, Pages 4729-4761

Macromolecules 2015, 48, 6553−6561

Intro:

Gas separations are an important step in production or purification for many gasses, including natural gas purification and carbon capture to help the environment. Polymer membrane-based gas separations are becoming much more desirable due to their affordability and reduced energy-consumption relative to alternative methods like cryogenic distillation and pressure swing adsorption. However, as membranes are becoming more common in industrial settings, the challenges membranes face also become more prominent. Membranes for gas separations struggle with three main fundamental issues: the permeability vs selectivity tradeoff, physical aging, and plasticization. Permeability and selectivity are the main ways the performance of a membrane is determined, where permeability is the rate at which a gas passes through the membrane and selectivity is the preference of one gas's permeability relative to another. Currently, there seems to be a limit of combined permeability and selectivity that cannot be surpassed (2015 bound for H_2, O_2/N_2 and 2019 bound for CO_2 related separations) (Figure 1). Physical aging is an issue that results in a loss of permeability over time as the packing of polymer chains in the membrane begin to densify after long periods of use. Finally, plasticization can occur when condensable gasses under high pressure dissolve into the membrane, resulting in swelling of the polymer chains and a reduced selectivity in mixed gas environments due to competitive sorption effects. The research done by the Guo group seeks to address these issues by incorporating pentiptycene into a polymer membrane. Pentiptycene's hierarchical structure (Figure 2) provides configuration based free volume that helps improve permeability, it creates a rigid "ladder-like" structure that impedes membrane densification over time, and it allows for tunable performance through the incorporation of different functionalization of substituent groups on the center ring.

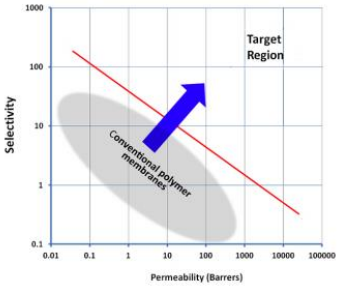

Figure 1:
Depiction of Robeson Upper Bound

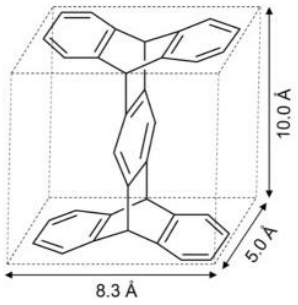

Figure 2:
Pentiptycene Molecular Structure

Current Work Summary:

The work this summer has largely been focused on the design and production of the pentiptycene monomers and the pentiptycene copolymers with PIM-1. To achieve the best performance possible, some time was spent trying to increase the purity of the pentiptycene monomers. Each reaction in the production process was methodically examined and its efficiency was evaluated. The reaction for 2,3 – dimethoxy 9,10 – anthraquinone showed a high degree of impurity, so a recrystallization in acetic acid was tried and showed to be an effective method of purification. Additionally, time this summer was spend in the systematic production of tetramethoxy pentiptycene with differing substituent groups. Specific groups attached to the center ring of the "S-shape" pentiptycene monomer from the starting carbonyl group were an isopropoxy group and a linear propoxy group, with both structures being ^{1}H NMR confirmed. This is important because it shows that different substituent groups can be successfully added to the center ring, which makes it much easier to test whether different substituent groups play a significant role in a membrane's separation performance. Finally, polymerization conditions and film casting conditions were examined and adjusted in order to produce solution processable and high molecular weight polymers that yielded defect-free films after casting. To do this, model polymerizations were done with PIM-1, as it is used in the copolymer and has a similar symmetric tetrahydroxyl functionality and polymerization mechanism to our tetrahydroxy pentiptycene. These model polymerizations allowed for experimentation with the reaction time and reagent concentrations, and after several trials, more ideal conditions were determined, although they could be further improved. The film-casting was adjusted by the addition of a controlled nitrogen flow to help steady the solvent evaporation rate, which should help reduce the number of pinholes in the membrane.

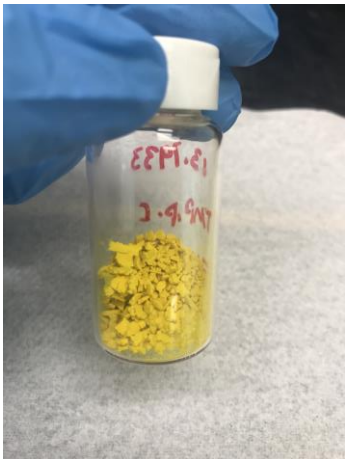

Figure 3:
TMPiP : PIM-1
Copolymer (before reprecipitation)

Results:

Overall, the work this summer contributed to produce a more efficient and physically robust film that shows better permeability, selectivity, and aging performance than its predecessors. By optimizing the reaction and post-process conditions, we inevitably helped increase the purity of the monomers, which greatly helps in the production of more accurate and consistent high molecular weight polymers. While the films for the "S-shape" pentiptycene with the differing substituent groups have yet to be created and tested, it is

promising that these structures were able to be created as it is one step closer to the goal of designing a more customizable polymer membrane for gas separations. Finally, the improvement of polymerization and film casting conditions helped to speed up the process for testing as each batch is now more likely to yield a more workable, defect-free membrane.