

NDnano Summer Undergraduate Research 2018 Project Summary

1. Student name & home university:

Santiago Maria Calderon Novoa - University of Notre Dame

2. ND faculty name & department:

Dr. Ruilan Guo - Chemical and Biomolecular Engineering Department

3. Summer project title:

Synthesis and performance testing of pentiptycene-based polymeric membranes for mixed gas separation

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

- Organic chemical synthesis & characterization
 - I was involved in lots of work to synthesize and isolate monomers with high degrees of purity to produce high quality polymeric films. I learned how to use and adapt synthetic pathways appearing in the literature, how to isolate desired synthetic intermediates using purification steps, and how to use ¹HNMR to validate the purity and efficiency of the reactions.
- Lab management and safety
 - During my time in the Guo lab, I helped in updating and checking the chemical inventory, as well as organizing stored chemicals.
- Technical writing and communication
 - By participating in the Undergraduate REU Symposium, I was able to hone my technical writing skills through the drafting of an abstract and presentation of my poster.

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

Polymeric gas separation membranes are a promising field of study because they can provide an energy-efficient method to separate industrial gas mixes that currently employ costly separation processes. Currently, industrially used membranes are robust and can endure years of use, but lack the stellar performance shown by many polymers of intrinsic microporosity (PIMs). The research done by the Guo group seeks to find PIMs that not only show excellent, and tunable, separation properties, but also, can form robust films to be used industrially.

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

Microporous polymeric gas separation membranes are sought out for their ability to sieve gases based on their molecular size and interactions with the membrane itself. This project focuses on the bottom-up fabrication of polymers of intrinsic microporosity (PIMs), which contain pentiptycene-based monomeric units with rigid, highly contorted, and robust chemical structures. This allows the polymer to have a tight micropore size distribution, which can yield high permeability and selectivity for challenging gas separation applications.

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

- ¹ David F. Sanders, Zachary P. Smith, Ruilan Guo, Lloyd M. Robeson, James E. McGrath, Donald R. Paul, Benny D. Freeman. Energy-efficient polymeric gas separation membranes for a sustainable future: A review. *Polymer*. Volume 54, Issue 18, 2013, Pages 4729-4761, ISSN 0032-3861, <https://doi.org/10.1016/j.polymer.2013.05.075>.
- ² Carta, M., Malpass-Evans, R., Croad, M., Rogan, Y., Jansen, J. C., Bernardo, P., . . . Mckeown, N. B. (2013). An Efficient Polymer Molecular Sieve for Membrane Gas Separations. *Science*. 339(6117), 303-307. doi:10.1126/science.1228032
- ³ Ze-Xian Low, Peter M. Budd, Neil B. McKeown, and Darrell A. Patterson. Gas Permeation Properties, Physical Aging, and Its Mitigation in High Free Volume Glassy Polymers. *Chemical Reviews*. 2018 118 (12), 5871-5911, DOI: 10.1021/acs.chemrev.7b00629
- ⁴ Peter M. Budd, Kadhum J. Msayib, Carin E. Tattershall, Bader S. Ghanem, Kevin J. Reynolds, Neil B. McKeown, Detlev Fritsch. Gas separation membranes from polymers of intrinsic microporosity. *Journal of Membrane Science*. Volume 251, Issues 1–2, 2005, Pages 263-269, ISSN 0376-7388, <https://doi.org/10.1016/j.memsci.2005.01.009>
- ⁵ Jennifer R. Weidman, Ruilan Guo. The Use of Iptycenes in Rational Macromolecular Design for Gas Separation Membrane Applications. *Industrial & Engineering Chemistry Research*. 2017, 56 (15), 4220-4236. DOI: 10.1021/acs.iecr.7b00540
- Perez, Edson & Karunaweera, Chamaal & Musselman, Inga & Balkus, K & Ferraris, John. (2016). Origins and Evolution of Inorganic-Based and MOF-Based Mixed-Matrix Membranes for Gas Separations. *Processes*. 4. 32. 10.3390/pr4030032.
- Lloyd M. Robeson. The upper bound revisited. *Journal of Membrane Science*. Volume 320, Issues 1–2. 2008. Pages 390-400. ISSN 0376-7388. <https://doi.org/10.1016/j.memsci.2008.04.030>.

Introduction

Polymeric gas separation membranes provide an energy-efficient alternative to competing separation processes such as cryogenic distillation, pressure swing adsorption, and chemical absorption processes used to separate common industrial gas mixes. These membranes make use of micropores in their structure to sieve gases according to their size and interaction with the membrane itself. Gas-separation performance is characterized in terms of the permeability of a species, or how fast it diffuses; and the selectivity towards one component of a gas pair, how fast it permeates with respect to other gases in the mix. According to Sanders et al., using the solution-diffusion model, the gas permeability coefficient (P_A) is the product of the gas solubility coefficient, S_A , and the effective diffusion coefficient, D_A . Selectivity is the ratio between the permeability coefficients of two gases.

$$P_A = D_A S_A \quad (1)$$

$$S_{A,B} = P_A / P_B \quad (2)$$

Even though polymeric separation membranes show promise in the field, they run into the issue of the permeability-selectivity trade-off², wherein a polymer's permeability for a specific gas is inversely correlated with its selectivity for that gas in a mixed gas environment. The higher the permeability, the lower the selectivity for that gas. This is because most polymers used in the field have flexible chains that make the micropores change dimensions, thus reducing their ability to separate gas molecules according to their size. Another issue plaguing the progress of polymer membranes relates to their tendency to physically age. This can be explained as the trend glassy polymers have to reach an equilibrium conformation where the chains efficiently pack, reducing the free-volume (or the volume of the voids within the pores), thus increasing selectivity, but drastically decreasing permeability.

Although there are several types of polymers used industrially, there is promise in the "polymers of intrinsic microporosity" (PIMs) because they make use of their highly contorted and rigid polymer backbones to intrinsically introduce voids in the polymer³. Since PIMs are generally composed of monomers with fused ring structures, they tend to be chemically stable and mechanically robust as a membrane polymer, which is also appealing. The first PIM that was synthesized and studied was PIM-1, which its repeating unit is shown in *Figure 1*. As evidenced by its structure, it has a lack of rotatable single bonds and a "spiro-center", or the tetrahedrally bonded carbon between the two rings, which introduces kinks into the polymer chain⁴.

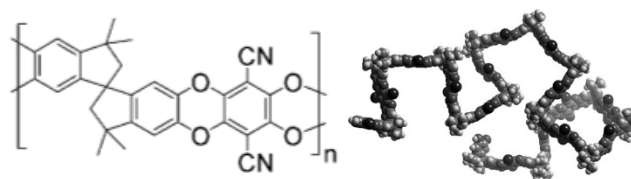


Figure 1: Monomer structure of PIM-1 and a molecular model of a segment of the polymer chain

Summary

Although there has been a considerable amount of work on PIM-1 and several other derivative polymers, the novelty of this project is the bottom-up design of a ladder polymer containing the pentiptycene unit, which has a contorted structure that can theoretically give this polymer superb gas-separation performance. To do so, a series of substituted pentiptycene monomers were successfully synthesized from cheap and widely available precursors, copolymerized with PIM-1 and cast into films, and then tested in a gas-cell.

The pentiptycene unit has an H-shaped 5-ring aromatic framework that is bulky, inflexible, and when polymerized, highly contorted, which can be seen in *Figure 2*. The tetra-hydroxy substituted monomer uses a linking monomer with tetra-fluoro substitution to form the dioxane bonds common in many ladder polymers such as PIM-1. Although the dioxane bonds are single bonds, the ring that forms cannot rotate, and thus gives super rigid backbone once it polymerizes. The structure of the pentiptycene monomer is valuable because the H-shape introduces free-volume elements (FVEs) intrinsic to the monomer, as highlighted in *Figure 2*. Therefore, the pentiptycene unit is desirable because the polymer formed with it yields a narrow, controlled, pore size distribution, which allows for improved selectivity. Additionally, it is theorized that changing the center-ring substituents can allow for the fine-tuning of gas-separation properties and provide resistance to physical aging.

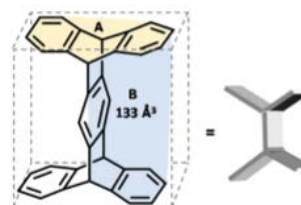


Figure 2: Pentiptycene and its FVEs A and B with 31 Å³, and 133 Å³ respectively⁵.

Experimental

My main task was to synthesize and purify the products required to obtain the pentiptycene monomers. All the intermediate products were checked for purity using ^1H NMR. Note that there are two main precursors obtained in the synthetic steps before the functionalization of the pentiptycene unit: “S-shaped” and “C-shaped” tetra-functional pentiptycene moieties. Both are useful precursors after running a separation column. Once the isomers are separated, both follow practically the same functionalization to be made into polymerizable monomers.

After synthesis of the monomers was successfully achieved, each one of these were co-polymerized with the two PIM-1 monomers, tetrafluoroterephthalonitrile and 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol, in a predetermined ratio. The polymers were then cast using CHCl_3 to obtain films.

Results

Both the “S-shaped” and “C-shaped” monomers were capable of being synthesized with high purity. Furthermore, both monomers were capable of copolymerizing with PIM-1 monomers to produce pentiptycene-based PIMs. The “C-shaped” PIM copolymer was capable of being cast into a robust film (*Figure 3*), while the “S-shaped” PIM-1 copolymer still needs to be worked on to obtain the appropriate conditions for film-casting. To be able to film-cast “S-shaped”, the copolymer could be cast into thicker films, the ratio of “S-shaped” to PIM-1 monomer changed, or even, changing the center-ring substituent might be the way to increase its mechanical strength as a film.

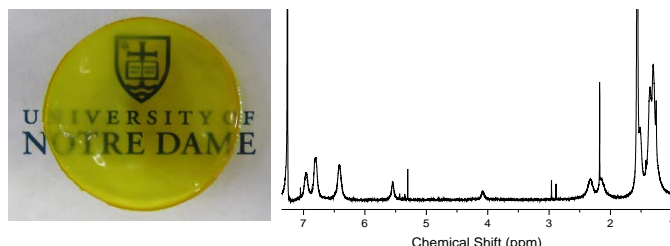


Figure 3: “C-shaped” PIM copolymer film cast on chloroform with its ^1H NMR spectrum

Another approach we have taken to making a film-castable polymer with the S-shaped monomer is to make a tetrafluoro end capped monomer, instead of a tetrahydroxy monomer. This has yet to be tested but has shown it can be synthesized with high purity.