

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Madison Pixler
FACULTY ADVISOR:	Dr. Ruilan Guo
PROJECT PERIOD:	Fall 2021-Spring 2021
PROJECT TITLE:	<i>Triptycene-based Polybenzimidazole (PBI) Membrane for High-Temperature H₂/CO₂ Separation</i>
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input checked="" type="checkbox"/> Sustainable and Secure Nuclear <input checked="" type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> 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
Develop synthesis process for triptycene-based dicarboxylic acid.	The synthesis procedure has been developed with good repeatability. Triptycene-based dicarboxylic acid could be produced with high yield and high purity.	100%
Develop synthesis procedure for triptycene-based polybenzimidazole (TPBI).	TPBI was synthesized via poly-condensation. Reaction time and temperature were adjusted to achieve high molecular weight. TPBI films with good mechanical properties were fabricated.	90%
Investigate separation performance of TPBI.	H ₂ permeability of TPBI was 5 times higher than the commercial PBI. TPBI also displayed promising selectivity at 35 °C.	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	
EXTERNAL AWARDS RECEIVED	
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	
INTERNAL COLLABORATIONS FOSTERED	Mengdi Liu, 4th year PhD student in the Guo Lab, Mentorship, weekly
EXTERNAL COLLABORATIONS FOSTERED	CSIRO (Australia), free volume characterization using PALS (positron annihilation lifetime spectroscopy) Prof. Michelle Galizia, University of Oklahoma, exploring these new PBIs for organic solvent nanofiltration (OSN) applications
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	Instruments: ¹ H NMR, Gas Cell

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?

I really enjoyed the opportunity to continue my research in the Guo group during the spring and fall semesters of the 2022 calendar year. I had previously completed a semester of research for class credit in the Fall of 2021. Based on my experience that semester I expected to continue to have a hands-on research experience where I was directly contributing to the overall goals of the Guo group. One of the main reasons why I decided to apply for a fellowship to cover my work with the Guo group was due to my personal relationship with lab personnel, specifically my mentor Mengdi Liu. Mengdi's teaching style was incredibly effective. She would start our meetings by explaining what experiment we would be running that day. If the experiment was new, she would demonstrate how to effectively complete the experiment. Then she would give me an opportunity to complete the experiment myself. This hands-on, three-fold mentorship strategy was very engaging and helped me to quickly master new laboratory skills. Additionally, Mengdi was very helpful and responsive when I posed questions.

One area of improvement would be developing a very clear outline of how the experiments were interrelated. I would have found it easier to understand the complicated polymer synthesis if there was a visual explanation of what the goal of each individual experiment was and how that goal related to the overarching goal. I tend to learn better when I am presented with information visually so I think developing a map or web of experimental interaction would have helped in solidifying my conceptual base earlier in my research journey.

Overall, the research experience met my expectations, and I am very grateful for the opportunity to continue to grow in my creative, analytical problem-solving skills.

FINAL WRITTEN REPORT

H₂/CO₂ separation has attracted increasing attention in the Integrated Gasification Combined Cycle (IGCC) process which is currently used to produce H₂ fuel from methane reformation and mitigate CO₂ emission to the atmosphere. In industrial processes, high operating temperatures are required for the economic feasibility of the separations as it avoids the cooling of syngas. Current technologies for H₂/CO₂ separation are highly energy intensive because they usually involve toxic solvents and require high input energy. In contrast, polymeric membranes have been widely studied and applied to gas separation processes due to the less energy intensive, operational simplicity and smaller carbon footprint. However, most existing polymer materials are not ideal for high temperature (100 to 300 °C) applications. The harsh conditions lead to thermal degradation and decline of separation performance in most commercial polymer membranes.

One possible solution is Polybenzimidazole (PBI) Membranes. PBIs have outstanding thermal and mechanical stability when exposed to high temperatures for extended periods of time. The commercial PBI, *m*-PBI has demonstrated thermal stability and promising size-sieving property. However, the strong interchain interactions through hydrogen bonding and pi-pi stacking leads to tightened chain packing, lower free volume, and in turn, extremely low permeability, which limits the industrial applications of *m*-PBI. By introducing bulky groups such as triptycene or pentiptycene units to the PBI structure, it is expected that free volume elements and permeability can be improved. The main objective of this research project was to develop a series of novel iptycene-based PBI membranes which exhibits promising gas separation performance at high temperatures. This would extend the high-temperature applications of polymer membranes and fulfill the fundamental knowledge gap.

The first step in this set of experiments was to synthesize the monomer and polymers. Figure 1, below, shows the reaction scheme used to develop the triptycene-diacid monomer from the anthracene, 1,4-benzoquinone, xylene reactants.

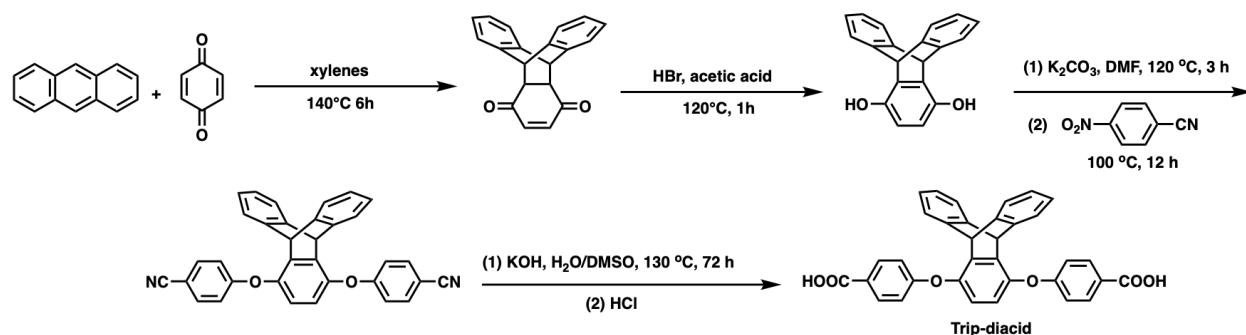


Figure 1. Reaction scheme for triptycene-based dicarboxylic acid monomer synthesis

The first step is to clean and dry the necessary glassware. This was done to ensure that there is no residual water left that would contaminate the reaction. A round bottom flask, condenser, and nitrogen converter connection combination was assembled. Additionally, 15 grams of anthracene, 10.9 grams of 1,4 Benzoqizone, and 97 mL of xylenes were measured out and added to the flask. The spin bar was set to 300 rpm and the temperature of the surrounding oil bath was set at 140 degrees Celsius. The reaction mixture was refluxed for 6 hours and then allowed to cool. Then, the Benzoqizone product was added to a two-neck flask along with acetic acid and hydrogen bromide in order to reduce the carbon oxygen double bond to the hydroxyl group.

The triptycene dinitrile intermediate was synthesized by reacting a mixture of 4.30 grams triptycene 1,4-hydroquinone, 4.25 grams of anhydrous potassium carbonate, 45 mL of dime- thylformamide (DMF), and 9 mL of toluene in a two-neck flask that was capped with a Dean–Stark trap and a nitrogen inlet. This mixture was stirred and refluxed under nitrogen at 120 °C for three hours. It was then cooled to room temperature at which point 4.7 grams of 4-nitrobenzonitrile were added. After reacting at 100 °C overnight, the mixture was precipitated in a, 1:4 volume ratio, water/methanol mixture. The solid was filtered and washed repeatedly with water and methanol, and then dried at 120 °C under vacuum to produce the purified triptycene dinitrile intermediate.

The final triptycene diacid was prepared through a hydrolysis of the preceding triptycene dinitrile compound. 5 grams of the triptycene dinitrile intermediate, 50 mL of DMSO, 50 mL of water, and 20 grams of potassium hydroxide were added to a two-neck flask. This mixture was refluxed for 48 hours. It was then cooled to room temperature and acidized with HCl solution which helped to form precipitation of the triptycene dicarboxylic acid. This desired final product was collected through filtration and repeated steps of washing with deionized water.

Following the successful completion of the monomer synthesis, the triptycene-containing polybenzimidazole (PBI)-based polymers were synthesized as shown in Figure 2 below.

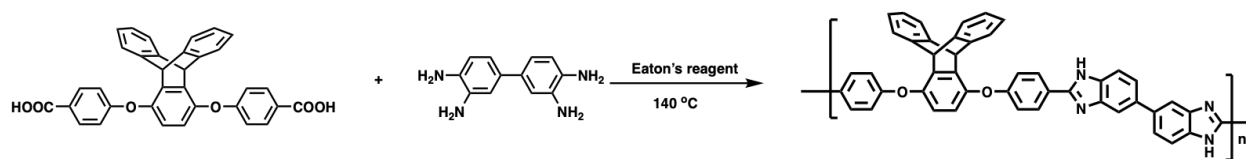


Figure 2. Reaction scheme for synthesis of triptycene-containing polybenzimidazole-based polymers.

The previously synthesized monomer, triptycene-diacid, was then converted to the triptycene-containing polybenzimidazole (PBI)-based polymer. This was done by adding tetraamine and Eaton's reagent and then stirring at 80 degrees Celsius in a three-neck flask for 30 minutes. After the solution had been fully dissolved, the temperature was lowered back to room temperature. Dicarboxylic acid and more of Eaton's reagent were then used to adjust the concentration to the desired concentration of 8% weight by volume. Finally, the temperature was raised to 140 degrees Celsius while the solution was stirred.

It was found that the viscosity quickly increased after approximately 10 minutes. This viscosity change was a source of a series of trial-and-error reactions. It was important to correct the procedure in order to successfully end the reaction when the molecular weight of the polymer was optimal. The reaction frequently ended too early or too late which resulted in suboptimal molecular weights. This either led to the polymer not successfully forming long enough chains or the polymer forming too long of chains which prevented the later filtering of the product. After the reaction was terminated at the correct viscosity, the polymer was poured into a water and ammonia hydroxide solution in which it was stirred overnight. This solution was later filtered to separate the powder.

Figure 3 shows the proton NMR results for both the final monomer and polymer products. This was important in determining the purity of the synthesized monomer. Additionally, the comparison of figure 3a and 3b helped to determine the purity and successful conversion of the monomer to the polymer.

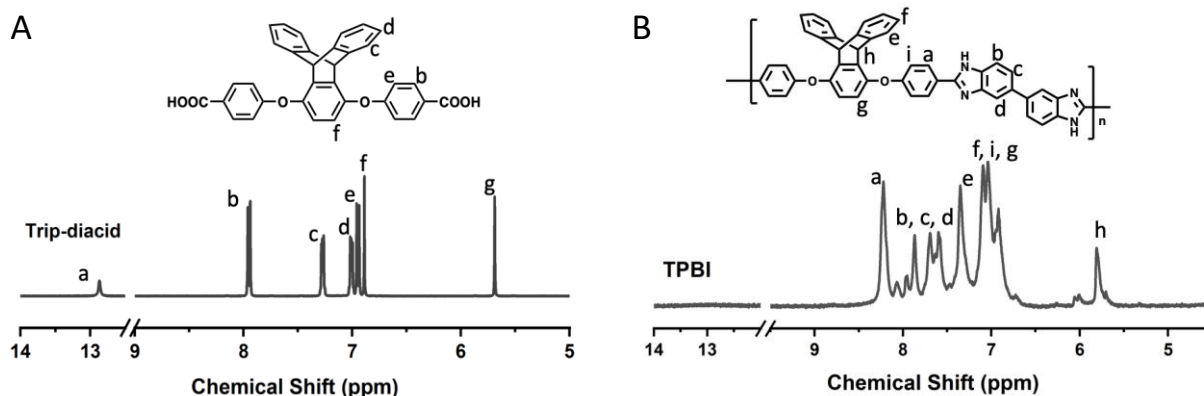


Figure 3. ^1H NMR of the final monomer (a) and polymer (b) products.

The next important step in the experimental analysis of the TPBI polymer was the preparation of a polymer film as shown below in Figure 4. Approximately 0.2 grams of polymer powder was dissolved in 4 mL of DMAc solvent to obtain the desired 6% concentration necessary for film preparation. This was then filtered in order to remove the dusts and insoluble particles. A very thin layer of the filtered polymer solution was poured onto a level glass plate. The solvent was then evaporated off using one of two methods. The IR heat lamp was found to have a lower temperature and an uneven distribution of heat, while the vacuum oven was able to reach higher temperatures and have a more even temperature distribution.



Figure 4. Prepared polymer film.

This prepared polymer film was then analyzed in the gas cell by running a series of permeability tests. The results of these tests are summarized in Table 1 and Figure 5 below.

Table 1. Results of Permeation Tests

Sample	<i>m</i> -PBI	TPBI
H ₂ Permeability (Barrer)	2.4±0.1	10.0±0.2
CO ₂ Permeability (Barrer)	0.1±0.003	1.24±0.026
H ₂ /CO ₂ Selectivity	24	8.03±0.2

These permeation results compared previous PBI materials to the TPBI that was synthesized throughout the series of experimental iterations. Permeation tests were run on both the *m*-PBI and the TPBI for H₂ and CO₂. The selectivity was then found by taking the ratio of the single-gas tests. The permeability of H₂ was much higher than that of CO₂ for both polymer membranes. This was expected because hydrogen has high permeability through the membranes while carbon dioxide exhibits

strong interactions with the polymer.

It was found that the TPBI had a greater permeability to both H₂ and CO₂ as compared to the *m*-PBI. This matches what was previously known through literature. Commercial PBIs exhibit promising H₂/CO₂ separation performance but have extremely low permeability due to hydrogen bonding and pi-pi stacking. One of the goals of using TPBIs was to increase the permeability of the polymer membranes. Synthesis of the TPBI was successful in that regard. Additionally, it was found that the selectivity of the TPBI to hydrogen gas was lower as compared to the *m*-PBI. This was also expected because by introducing the bulky functional groups like iptycene, membrane permeability will increase while decreasing membrane selectivity. These bulky units disrupt chain packing and install configurational free volume elements. The results were further confirmed in the upper bound plot depicted in Figure 5.

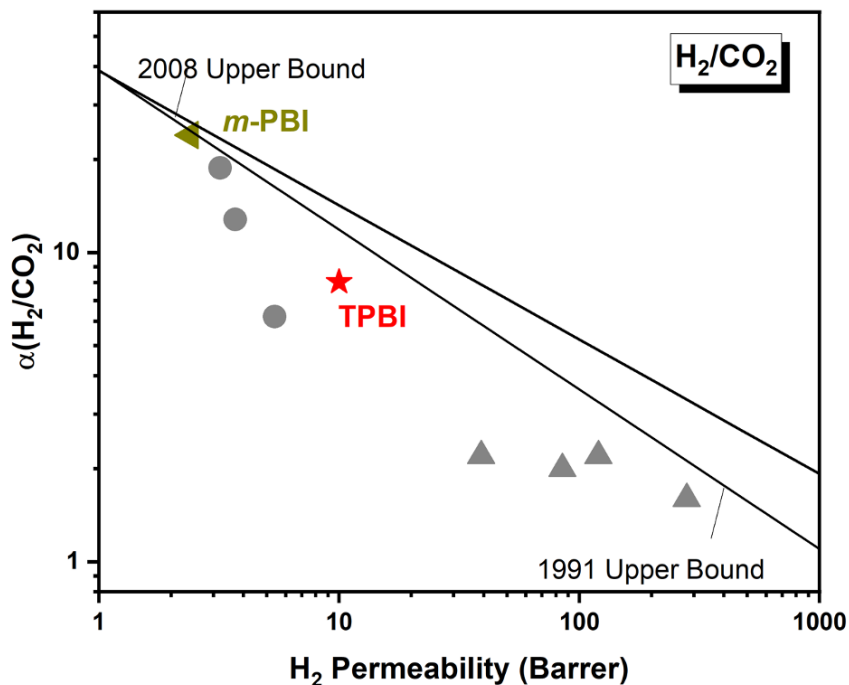


Figure 5. Upper Bound plot comparison of previous TPBI materials to the TPBI synthesized in this experiment.

The gray data points on the upper bound plot are previous TPBI materials. This plot shows how the *m*-PBI exceeds previous PBI material by comparing the distance between the data point and the upper bound. However, when analyzing the tradeoff between wanting high selectivity and high permeability, the TPBI synthesized is shown to have the highest ratio of the two desirable properties. This is extremely promising and provides rationale for the continued study and perfection of these polymer membranes.