

## **NDnano Summer Undergraduate Research 2016 Project Summary**

1. **Student name:** Jin U Kim

2. **Faculty mentor name:** William A. Phillip

3. **Project title:** Implementing selective swelling agents to tailor the nanostructure and transport properties of self-assembled copolymer membranes

4. **Briefly describe any new skills you acquired during your summer research:** There were several skills I acquired during my summer research. The first set of skills were learned in order to prepare my samples to gather my data. For example, in terms of polymer synthesis, I learned the basic procedure outlining the manufacturing of basic polymers like the one I would eventually use P(AN-r-OEGMA). Along the way, I learned how to appropriately deal with liquid nitrogen, and use equipment and chemical tools that utilized liquid nitrogen to function efficiently, such as the vacuum dryer. I then learned how to actually cast the membranes from the polymer solutions that I formulated, such as by learning how to set up and use the Doctor Blade, a tool that is used to precisely form membranes that are possibly nanometers in width. This was eventually a part of the larger SNIPS (non-solvent induced phase separation) method, a simple procedure to physically cast membranes, which proved to be crucial for me to cast my various membranes of various swelling agent concentrations. To actually gather data from my casted membranes, I had to learn how to set up and gather data from stir cells, which are devices used to accurately determine the permeability of membranes under various possible pressures, and possibly collect any permeate along the way. And I learned how to collect the data provided by these stir cells, and ultimately interpret the data in a way that was reasonable for me to apply to the chemistry behind them. And perhaps most importantly, I learned basic polymer chemistry that served as an underlying base upon which my entire research project rested on.

5. **Briefly share a practical application/end use of your research:** The final data I collected from my research revealed that certain concentrations of swelling agents as part of the original polymer casting solution can have significant impact on the size of the pores of nanoporous copolymer membranes, and thereby help to increase the permeability of these membranes. The information I acquired from my research can help in the field of nanoporous copolymer membranes as it may allow other researchers to increase the permeability of their membranes without having to significantly alter the chemistry of their membranes and risk damaging the research effort altogether.

**6. Begin two-paragraph project summary here (~ one type-written page) to describe problem and project goal and your activities / results:**

The problem, or more specifically the research interest of my project for this summer, was that the nanoporous copolymer membranes used in various filtration settings are easily synthesized via what is known as the SNIPS method (non-solvent induced phase separation method) but their permeability is noticeably low due to their known pore size of ~2nm. The guiding hypothesis upon which this research was based upon is that certain chemical molecules, known as swelling agents, have the potential to alter the nanostructure of these easily manufactured membranes without destroying the delicate balance of polymers as to induce a moderately larger pore size with a noticeably higher permeability.

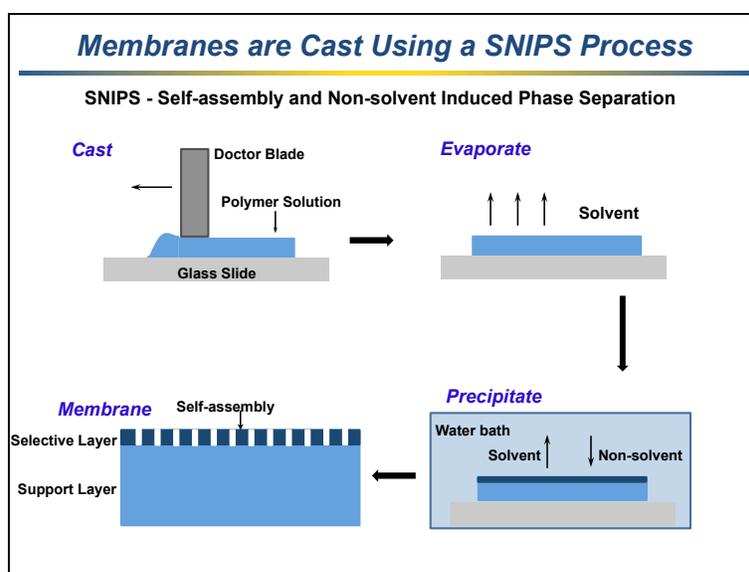
To enact upon this guiding hypothesis, firstly a strong understanding of the nanostructure of the basic polymer at hand, P(AN-r-OEGMA) was required, as was a significant amount of research done regarding potential swelling agents. Thus, the first part of the research project largely entailed this investigative process where time was spent learning about the polymer I would work with and where I also read through various publications regarding swelling agents accessing the compatibility of the swelling agents written of to the setting of mine. Towards the end of this process, I came to the conclusion that a vast majority of the swelling agents written of were incompatible with both the polymer that I was using as well as the laboratory equipment I had available, but there were still a few – namely polyacrylic acid (PAA), poly(ethylene glycol) (PEO), and propylene carbonate – that were available in the lab that I could use. From here, I moved on to the next stage of my research process, where I learned the basic procedure of synthesizing the polymer solution and how to cast membranes from them. Synthesizing the polymer solution involved just a lot of stoichiometry as I made several polymer solutions with varying percentages of swelling agents as part of the polymer mass of the polymer solutions. Casting the membrane involved the SNIPS (non-solvent induced phase separation) method, as outlined in the **Figure 1**.

After the polymer solutions were created, and their respective membranes were casted, I immersed them in solution of pH 9 as I wanted to make sure that the pores of these membranes were completely empty and that none of the swelling agent was clogging up these. Once they were immersed in these solutions for at least several hours, I began to actively conduct permeability tests, using a combination of the stirring cells and the balance. The data from these permeability tests were recorded and eventually collected into a single excel file whereupon I was able to analyze the trend in the membrane samples as the percentage of the swelling agent used of the overall polymer mass increased. This I repeated for all three of the swelling agents polyacrylic acid, polyethylene glycol, and propylene carbonate until all of the data from them were collected.

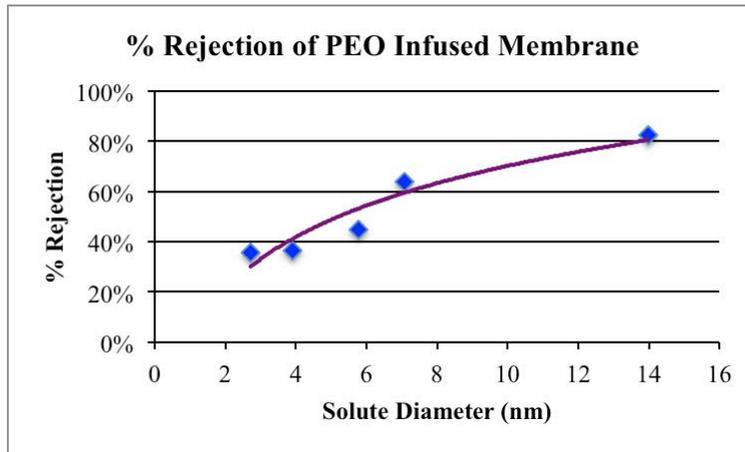
After my data collection regarding the permeability of the membranes was complete, I noticed that all three of these swelling agents exhibited a property such that there was a certain percentage of swelling agent of the total polymer mass, ranging anywhere from 10~15%, where the permeability of the membrane seemed to increase the most. This took my attention, and for the remaining part of the summer I focused on trying to determine why that was. Most notably, I conducted a total organic carbon analyzer (T.O.C.) test, aided by other graduate students in the lab, to determine a reasonable estimate for the pore size of my version of the polymer membranes that had exhibited the most increase in permeability (a 9% and a 10% for my PEO

and propylene carbonate swelling agents, respectively). An example is shown in **Figure 2**. Although I was not able to determine why the spike in permeability seemed to occur at certain percentages, the T.O.C. test revealed that, in fact, the size of the pores had moderately increased to an extent where the permeability was noticeably higher.

Ultimately, my results reveal that with the additions of swelling agents such as PAA, PEO, and propylene carbonate, among other potential candidates, it is possible to moderately increase the pore size of the membranes and induce a noticeable increase in the permeability of nanoporous copolymer membranes. The interesting observation I made to which I have no explanation as of yet is that there appears to be a certain percentage of swelling agent of the total polymer mass around which the permeability increases at a degree larger than the other percentages, and that this percentage hovered around the 10~15% mark. Therefore, in the near future I would like to determine other potential swelling agents, conduct further permeability tests regarding these swelling agents, and further substantiate my hypothesis regarding the effectiveness of adding swelling agents to polymer casting solutions. Furthermore, I would also like to further investigate the properties of swelling agents and polymer solutions in general that led to my interesting observation of there existing a certain percentage whereupon the permeability seems to have increased the most.



**Figure 1:** A detailed diagram depicting the step-by-step procedure of the SNIPS (non-solvent induced phase separation) method, which is used to easily cast membranes from polymer solutions using a doctor blade, a chemical fume hood, and a solvent solution such as isopropyl alcohol (IPA)



**Figure 2:** One of the charts that is the result of the T.O.C. tests conducted where percent rejection is shown for the various solute diameters for the PEO infused membrane, where the PEO was 9% of the overall polymer mass

Publications (papers/posters/presentations):



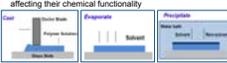
**Tailoring the Nanostructure of Copolymer Membranes Through the Use of Selective Swelling Agents**

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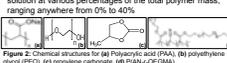
**Introduction - Background**

- Nanoporous copolymer membranes are an emerging set of filtration and purification mechanisms harnessing the potential to filter out unwanted toxins or other organic substances from a fluid system.
- As such, these devices are finding meaningful application in water purification settings and biotech processing plants.
- One particular trait of nanoporous copolymer membranes that make them so attractive to the scientific community is the ease involved with their manufacture.
- The SNIPS (non-solvent induced phase separation) procedure allows for facile manufacturing membranes with room for changes that can affect their nanostructure, thereby affecting their chemical functionality.

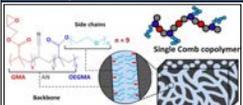


**Purpose of Research**

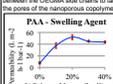
- One characteristic of copolymer membranes that can be modified during SNIPS is pore size; a guiding hypothesis suggests pore size can be modified by varying the identity and usage amount of substances known as swelling agents.
- This study discusses the impact of swelling agents, which are incorporated into the casting solution of poly(acrylonitrile-rigidolefinene glycol) methyl ether methacrylate) or P(AN-r-OEGMA) copolymer membranes, when they partition selectively into the pore-forming OEGMA segments of the copolymer material.
- Three swelling agents - polyacrylic acid, polyethylene glycol, and propylene carbonate were added to the casting polymer solution at various percentages of the total polymer mass, ranging anywhere from 0% to 40%.



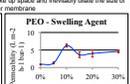
**Permeability Data Collection with Additives**



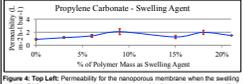
**PAA - Swelling Agent**



**PEO - Swelling Agent**

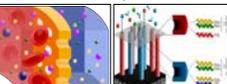
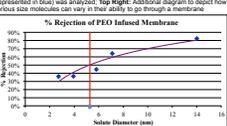


**Propylene Carbonate - Swelling Agent**



**Total Organic Carbon Analyzer Tests**

- T.O.C. (Total Organic Carbon Analyzer) tests were used after collecting permeate through the membranes with the additions of the PEO and Propylene Carbonate swelling agents to determine the estimated range of pore sizes.
- The original copolymer casting solution P(AN-r-OEGMA) had mostly pore sizes of 2nm-3nm, which was the standard to which data from the PEO and Propylene Carbonate membrane test results were compared with.

**Conclusions - Future Work**

- Further tests with other potential swelling agents such as propylene glycol or glycine could strengthen case behind the effectiveness of swelling agents and lead to a more accurate understanding of how they influence the chemical structure of chemical polymer.

**Acknowledgements**

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