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Synthesis and Phase Transition Characterization of Liquid Crystal Membranes with Slit-Like Pores

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Abstract

Membranes with slit-like pores have been of interest for some time due to their ability to reject smaller particles than traditional cylindrical-pored membranes at the same fluid flux. However, using liquid crystals as a template for this sort of membrane has not been thoroughly investigated. In this study, the liquid crystal mixture of RM257 (2-Methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate)) and 5CB (4-Cyano-4'-pentylbiphenyl) for the purpose of manufacturing membranes with slit-like pores, the phase transition behavior of this LC mixture at various mole fractions of RM257, and the impact of mole fraction of RM257 in the liquid crystal (LC) mixture and membrane manufacturing conditions on pore morphology are investigated. Ultimately, the impact of mole fraction on pore morphology was found to be statistically significant, and a linear relationship between mole fraction of RM257 and phase transition temperature was determined, which will go on to aid further investigation of the impact of manufacturing conditions on membrane quality.

Introduction

Membranes with slit-like pores have a higher particle rejection rate than traditional membranes with cylindrical pores due to the ability to control more than a single length scale of the pore. Many conventional membranes have cylindrical pores, which have a circular surface area on the surface of particle interaction. With this sort of pore, the radius of the pore is the only alterable dimension, meaning that increasing the pore size both increases the fluid flow through the pore and increases the size of particles that can pass through the pore. On the other hand, elliptical, or slit-like, pores have both a major and minor axis, giving an additional degree of freedom in controlling the fluid flux and particle rejection through a membrane. Compared to cylindrical pores, slit-like pores have an increased pore aspect ratio (ratio of the major axis/minor axis of the pore), which allows them to reject smaller particles at the same given fluid flux [1], as seen qualitatively in Figure 1. While this interest in membranes with slit-like pores has been present for some time, the use of liquid crystals as a template for these membranes has not been thoroughly investigated. Di-acrylate mesogens (DAM) in the presence of thermotropic LCs (TLC) enables formation of membranes with slit-like pores in the nematic phase through UV polymerization, but the optimum manufacturing parameters, along with how these parameters impact pore morphology, has not been investigated. In this work, the liquid crystal mixture of RM257 (2-Methyl-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate)) and 5CB (4-Cyano-4'-pentylbiphenyl) is investigated for this application through phase transition experiments, membrane manufacturing, and pore analysis.

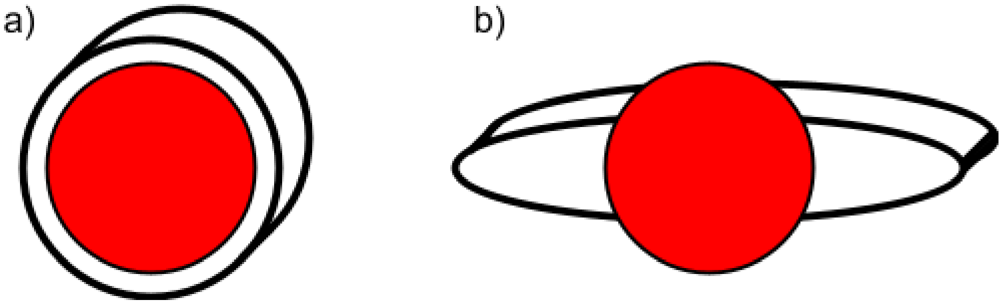

Figure 1 - an equal sized particle approaching
a) a cylindrical pore and b) an elliptical pore

Background

Liquid crystals have been a point of interest for a variety of uses due to their unique mechanical behaviors and properties. Specifically, the ability for liquid crystals to flow like a liquid while maintaining a level of molecular ordering allows for exciting and novel applications. One such application is the use of liquid crystals to manufacture membranes with slit-like pores that are highly preferential to particulate capture of varying sizes while still providing a reasonable fluid volume throughput.

Liquid crystals have several phases as they transition from a pure liquid to a pure solid and vice versa. As a solid, the materials are crystalline, behaving as a rigid solid. As temperature increases, the crystalline form gives way to a viscous, flowing liquid. This is called the nematic phase; in this phase, the liquid crystal can flow like a liquid, but still maintains an internal molecular structure like a solid. This phase is where the term "liquid crystal" originates from. As the temperature continues to rise, the nematic phase transitions to the isotropic phase. This phase is most like a pure liquid phase, in which the molecular structure found in the nematic phase is replaced with random molecular orientation and a fully free-flowing liquid.

Karausta and Bukusoglu [2] outlined a method for manufacturing liquid crystal membranes using a mixture of RM257 and 5CB. RM257 acts as the reactive mesogen, which interacts with the photoinitiator to be crosslinked under UV light. 5CB acts as a non-reactive mesogen which will ultimately be extracted from the membrane. The voids that 5CB leaves behind act as the pores of the membrane. The liquid crystals would be mixed in the desired mole fractions (converted more easily from mass fraction using a calculator developed in this study) plus an additional 2wt% of photoinitiator (1-hydroxylcyclohexyl phenyl ketone) with respect to the mass of RM257 in the mixture. So, as the mole fraction of RM257 increases in the LC mixture, the density of the final membrane will also increase, as there are less proportional amounts of 5CB being removed from the membrane to create the pores.

This LC mixture would then be deposited into a polyimide-coated slide cell. Lee et al. [3] discuss how surfactant stabilizers can anchor liquid crystals into preferred molecular orientations, and Berreman [4] discusses the entropical preference of molecules to align when placed along sinusoidal groves. For this experiment, polyimide (PI) is used as the stabilizer and, once coated on a microscope slide, is rubbed with sandpaper to create parallel grooves in a single direction along the slide to encourage LC flow and molecular alignment through the cell.

One of the main ways the manufacturing in this report differs from previous RM257/5CB membrane manufacturing is that in this report the liquid crystal membranes were strategically heated during crosslinking based on phase transition experiments performed. The optimum mechanical properties to be achieved during crosslinking to yield the membranes of proper flexibility and pore distribution is still unknown, but there is ample information to make a hypothesis: the crosslinking temperature should be close to, but not beyond, the nematic-to-isotropic transition temperature (T_{NI}). Within the nematic phase, the liquid crystal mixture maintains an orderly structure, which is necessary for evenly distributed pores, and keeping the temperature on the higher end of the nematic phase will ensure that the LC mixture can flow as easily as possible through the cell.

RM257 is crystalline at room temperature, with a crystalline-to-nematic transition temperature (T_{CN}) of 70°C and a T_{NI} of 126°C [5], while 5CB has T_{CN} of 22°C and a T_{NI} of 35.5°C [6]; however, the phase transition characteristics of RM257/5CB mixtures are unknown. The purpose of this report is to investigate the phase transition characteristics of RM257/5CB liquid crystal mixtures and investigate how varying the ratio of RM257 and 5CB impacts the pore morphology of the resulting membranes.

Methods

Making polyimide-coated slides

The membranes were manufactured using polyimide-coated microscope slides; the polyimide (PI) operated as a stabilizer that encouraged structured flow of the liquid crystal along the slide. The PI-coated slides would be manufactured using the following procedure:

1. Remove the pre-prepared 1:10 PI:Thinner solution from the refrigerator and let sit at room temperature for 1 hour
2. Set oven to 250°C
3. Using a glass cutter, cut 76x52mm microscope slides to 48x48mm
4. Place slides in a glass jar such that no glass surface is complete flush with another and fill with alconox-mQ water solution
5. Place in sonicator for 10 minutes
6. Rinse detergent solution off of slides with mQ water and dry with compressed air
7. Coat slides with PI solution using the spin coater
    a. Place the slide in the spin coater and add 6-7 drops of PI solution to the middle of the slide
    b. Run spin coater profile for 1000rpm for 10 seconds, then 3000rpm for 30 seconds

8. Place slides in oven for 2 hours
9. Remove slides from oven, let cool to room temperature, then label the back of the slides as shown in Figure 2 with a permanent marker

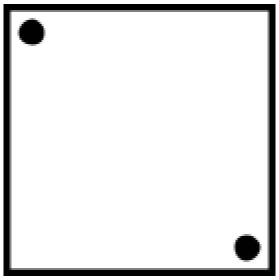

Figure 2 - Labeling method on the non-coated side of a PI-coated slide

Phase transition experiments

Various ratios of RM257 and 5CB were analyzed ranging from approximately 10-30 mol% RM257. For each ratio, the following procedure would be performed:

1. Mix the intended molar ratio of RM257/5CB in a 4ml glass vial
2. Place the glass vial in the oven at 100°C until the containing material is fully melted
3. Make a sandwich cell of rubbed polyimide-coated glasses
    a. Use sandpaper to lightly rub a 48mm x 48mm polyimide-coated microscope slide; be sure to rub in a single direction, making parallel grooves along the slide
    b. Using a glass cutter, cut the PI-coated microscope slide into two pieces, each approximately ⅖ and ⅗ of the original slide; the cut should be perpendicular to the direction of the rubbing in step 3a
    c. Place a piece of double-sided tape on either side of the larger slide piece parallel to the groves and cut off any excess tape
    d. Place the smaller slide piece on top of the tape; be sure to align the slide pieces so that the groves from step 3a are still parallel
4. Remove the LC solution from the oven and momentarily mix with a vortex mixer to fully incorporate liquid crystals
5. Set the hotplate to 50°C
6. Place the sandwich cell on the hotplate and inject approximately 50µl of the liquid crystal mixture into the cell (more or less may be required based on the size of the cell)
7. Once the LC mixture has reached the end of the cell, seal both non-taped sides of the cell with Dow Corning® High Vacuum Grease
8. Set a ramp profile of 1.25°C/min on the hotplate and observe visible changes under a microscope

Membrane Manufacturing

While crosslinking the membranes, the liquid crystal mixture is heated to a desired relative temperature (T/T_{NB}, where T is the crosslinking temperature in Kelvin and T_{NB} is the nematic-biphasic transition temperature in Kelvin). The impact of varying this relative temperature on the final membrane is beyond the scope of this project.

Membrane manufacturing procedure:

1. Mix the intended molar ratio of RM257/5CB+ 2 wt% (with respect to RM257) photo initiator in a glass vial
2. Place the glass vial in the oven at 100°C for an hour or so, until the containing is fully melted
3. Momentarily mix with the vortex mixer
4. Set oven to 80°C
5. Make a sandwich cell of rubbed polyimide-coated glasses (as described in Step 3 of Phase transition experiments procedure)
6. Set the hot plate at the intended relative temperature
7. Inject about 200-400uL (depending on the size of the membrane) into the sandwich cell while the sandwich cell is placed on the hot plate
8. Put the UV-stand box on top of the hot plate and place the UV light in the hole
9. Turn the UV on at 365 nm and let it sit for 30 minutes
10. After crosslinking, immediately transfer the cell to the oven at 80°C for 15 minutes
11. Let the cell cool to room temperature, then place sandwiched membrane in an ethanol bath for one hour
12. Remove membrane from sandwich cell using a razor blade
13. Store the membrane/film in the water

These membranes were then cut and imaged using a Nova SEM for pore-size analysis.

Results

Phase Transition Experiments

For the membrane manufacturing procedure, it is necessary to know the T_{NB} for each mixture of RM257 and 5CB in order to determine the relative temperature for crosslinking. Given the phase transition information known, as described earlier (RM257: C 70 N 126 I; 5CB: C 22 N 35.5 I), it is expected that as the mole fraction of RM257 increases in the liquid crystal mixture, the transition temperatures will increase linearly, but this exact relationship was unknown. So, phase transition experiments were an important step in understanding how manufacturing conditions affect pore morphology of the final membranes.

Beginning at 50°C, all mixtures tested in this study are in the nematic phase, which is a liquid crystal phase that flows like a liquid but still maintains some molecular structure like a crystalline solid. However, once the temperature increases and the nematic phase gives way to the isotropic phase, that crystalline structure is lost. This means that when the material is viewed with a microscope, the structured molecules of a liquid crystal in the nematic phase reflect light in such a way that one in the isotropic phase does not. This change of molecular structure is visible optically, as seen in Figure 3.

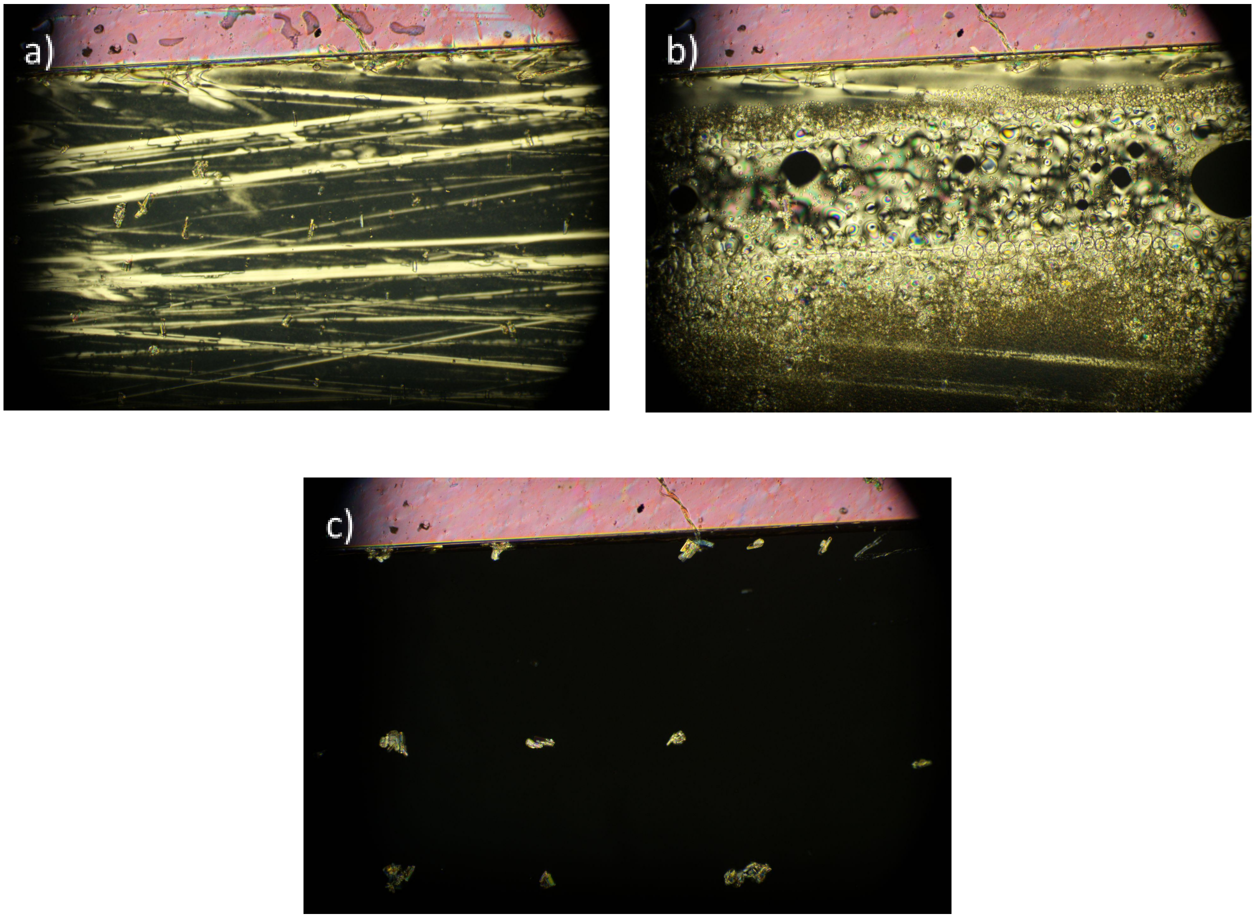

Figure 3 - 9.0 mol% RM257 a) in the nematic phase,
b) in the biphasic transition phase, and c) in the isotropic phase

The transition temperature from nematic to biphasic is recorded at the moment the "bubbles" (as seen in Figure 3b) appear under the microscope, and the transition temperature from biphasic to isotropic is recorded at the moment when nearly all of the liquid crystal under the microscope has transitioned to the isotropic phase (as seen in Figure 3c).

With these transition temperatures documented at a variety of mole fractions of RM257, a RM257/5CB phase transition diagram can be produced. The resulting phase transition diagram can be seen in Figure 4.

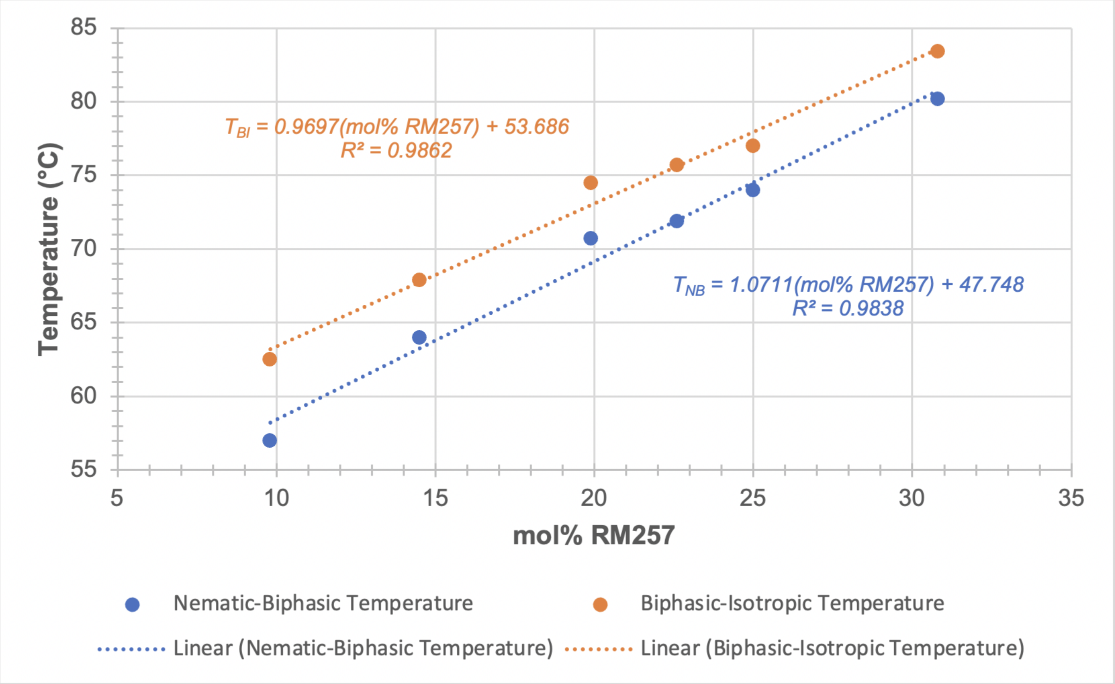

Figure 4 - RM257/5CB phase transition diagram

In Figure 4, at temperatures below the lower, blue line, the mixture is in the nematic phase; at temperatures above the upper, orange line, the mixture is in the isotropic phase; and at temperatures in between the two lines, the mixture is in a biphasic transitional phase. As hypothesized, there appears to be a linear relationship between the mole fraction of RM257 in the LC mixture and the transition temperatures: as the mole fraction of RM257 increases in the mixture, as does the transition temperatures. The following equations were found to describe the relationships:

$$T_{NB} = 1.0711(mol\%\ RM257)\ +\ 47.748 \tag{1}$$

$$T_{BI} = 0.9697(mol\%\ RM257)\ +\ 53.686 \tag{2}$$

Equation 1 describes the relationship between the mol% of RM257 in the mixture and the nematic-biphasic transition temperature (in Celcius), and Equation 2 describes the relationship between the mol% of RM257 in the mixture and the biphasic-isotropic transition temperature (in Celcius). Equation 1 can be used to find the crosslinking temperature for a given desired relative temperature, based on the following equation:

$$T_{crosslink} = [(T_{NB} + 273.15) * T_{rel}] - 273.15 \tag{3}$$

Where $T_{crosslink}$ is the crosslinking temperature in Celcius and T_{rel} is the desired relative temperature. It is worth noting that in some of the literature, the transition between the nematic and isotropic phases occur at a single temperature: T_{NI}. However, the experiments done in this work seem to indicate that a more complex phase transition occurs, which is why this transition has been split into nematic-biphasic and biphasic-isotropic.

Membrane Manufacturing and Pore Analysis

As discussed previously, as the mole fraction of RM257 increases in the LC mixture, the final membrane should grow more dense, as less and less material (5CB) is being removed from the membrane. The expectation is that as this density increases, the slit-like morphology of the pores will remain, but the spaces in between the pores would fill in with membrane material (RM257), thus increasing the average pore aspect ratio (major axis diameter/minor axis diameter). SEM photos provided by Savage [7] in Figure A1 show pores on the surface of a 9.6mol% and 15mol% RM257 membrane, and the bar charts in Figure A2, also provided by Savage, display the resulting pore size and morphology analysis from these membranes. This analysis indicates that there is a clear relationship between pore morphology and mole fraction of RM257 in the LC mixture; as the mole fraction of RM257 increased from 0.096 to 0.150, the frequency of higher pore aspect ratio and longer length of major axis increased, an increase which was found to be statistically significant, as seen in Table A1 provided by Savage.

Conclusion and Future Work

In conclusion, liquid crystals' unique physical properties make them an interesting candidate for templating membranes with slit-like pores for particle rejection. In this study, the LC mixture of RM257 and 5CB were analyzed for this purpose. The relationship between mole fraction of RM257 in the mixture and nematic-biphasic and biphasic-isotropic transition temperatures were found to be linear, as hypothesized, and the investigation performed in this report will aid in consistent membrane manufacturing going forward. It was also found that as the mole fraction of RM257 in the LC mixture increased, the pore aspect ratio and length of the major axis increased with statistical significance.

Moving forward, there is still much work to be done regarding the impact of manufacturing conditions on pore morphology. Now that the mole fraction/transition temperature relationship has been determined, the impact of relative temperature ($T_{crosslink}/T_{NB}$) on pore morphology and membrane quality can be determined. This relationship can also be confirmed via other mechanical testing methods, such as Differential Scanning Calorimetry (DSC). There is only so much information one can gain from pore analysis, and eventually fluid throughput and particle rejection tests will be performed on these membranes, and the impact of pore morphology, manufacturing conditions, and LC mixture makeup on membrane quality can be more thoroughly investigated.

Acknowledgements

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Appendix

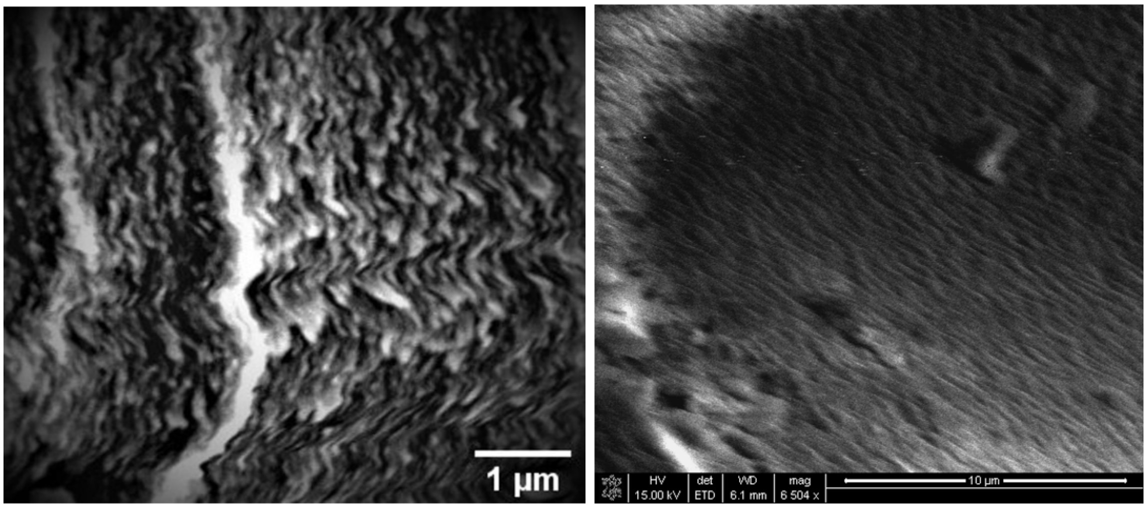


Figure A1 - SEM images of membranes a) 9.6mol% RM257 and b) 15.0mol% RM257
Source: Savage, 2022

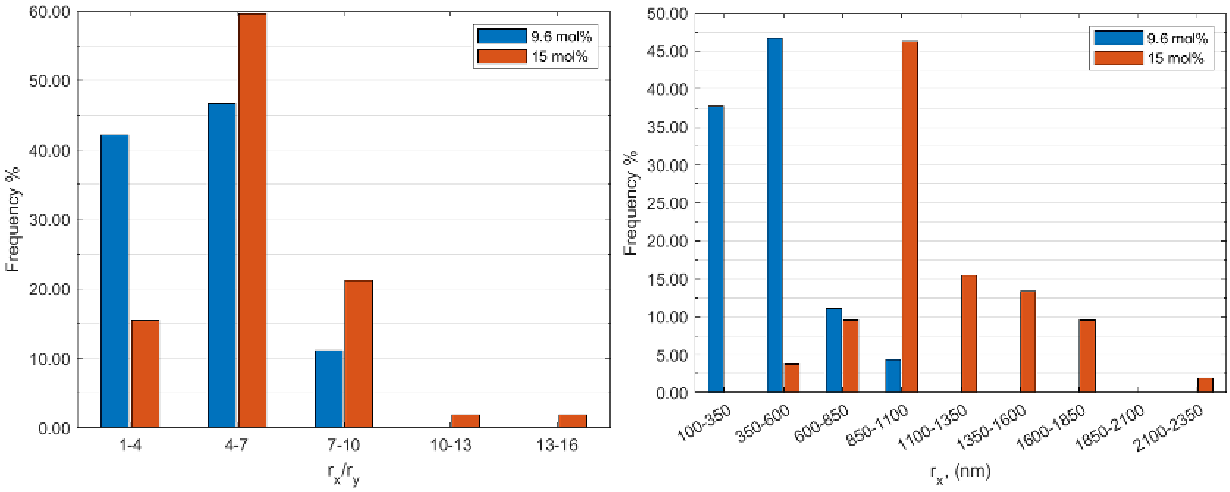
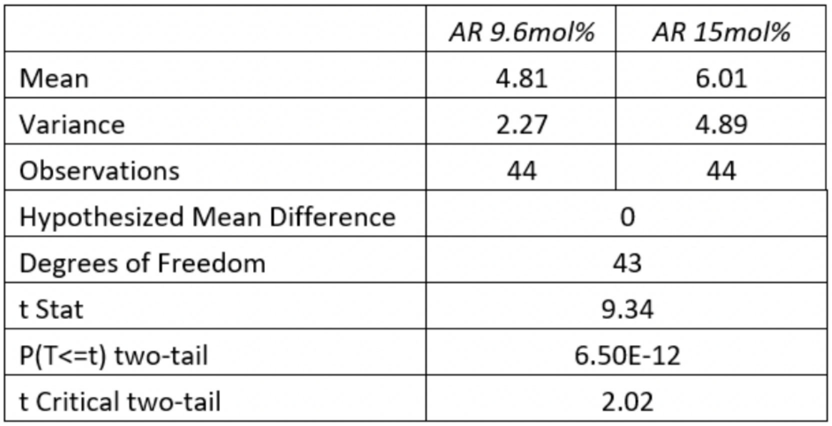


Figure A2 - For varying mol% RM257, a) aspect ratio vs. frequency and b) major axis length vs. frequency
Source: Savage, 2022

Table A1 - Statistical Significance between pore analysis of 9.6mol% and 15mol% membranes
Source: Savage, 2022



	AR 9.6mol%	*AR 15mol%*
Mean	4.81	6.01
Variance	2.27	4.89
Observations	44	44
Hypothesized Mean Difference	0	
Degrees of Freedom	43	
t Stat	9.34	
P(T<=t) two-tail	6.50E-12	
t Critical two-tail	2.02	