

THE IMPACT OF DIFFERENT FORMS OF CROSSLINKING ON SULFONATED POLYSTYRENE

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INTRODUCTION

Background

Ion exchange membranes (IEMs) can be used for water filtration. Extensive research has been done to evaluate the characteristics of IEMs.

In a previous study, we showed that ionic interaction between charged groups and multivalent cations form ionic crosslinking. Due to the ionic crosslinking, membrane swelling was reduced.

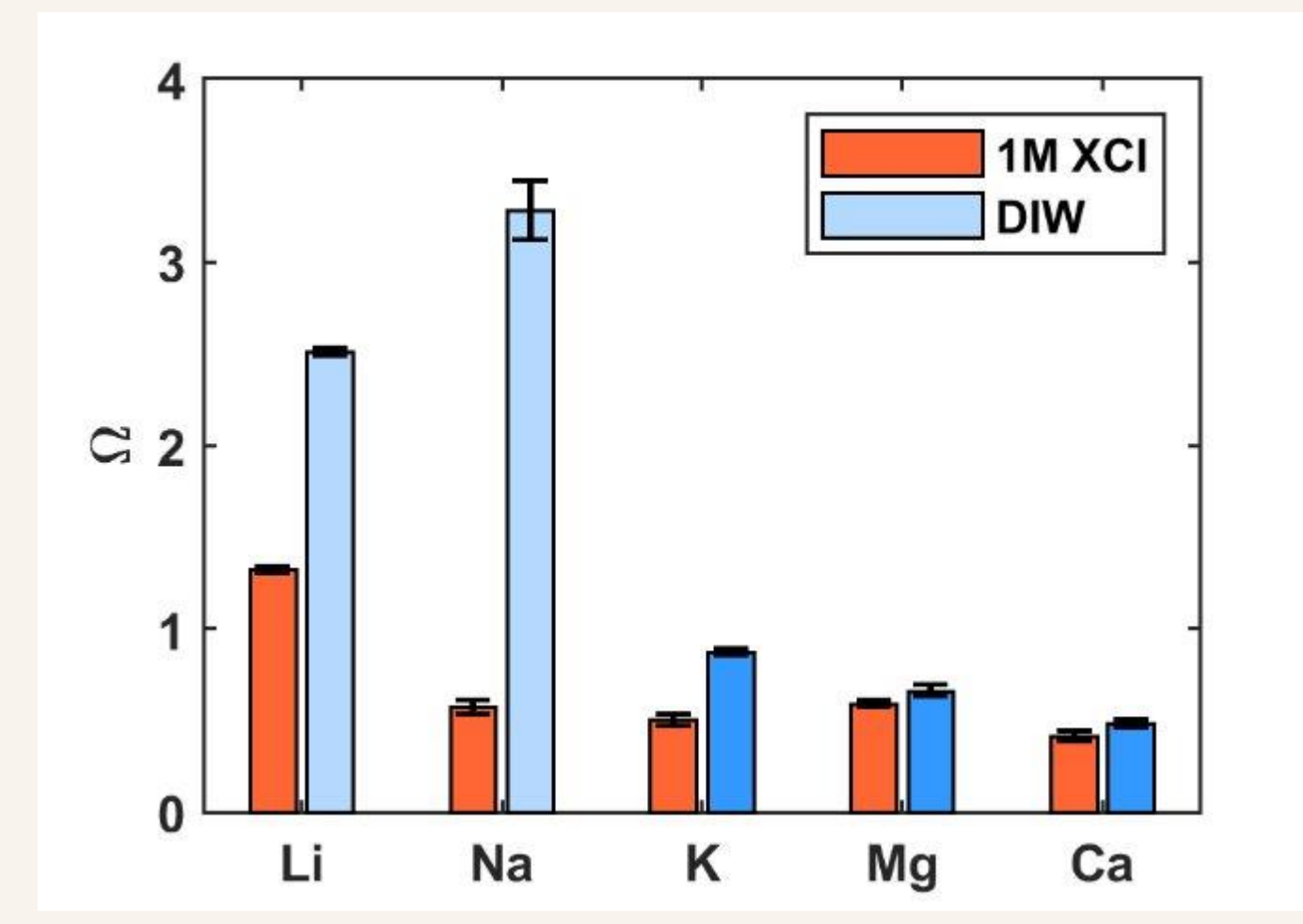


Figure 1: Water Uptake of different forms of sulfonated polystyrene

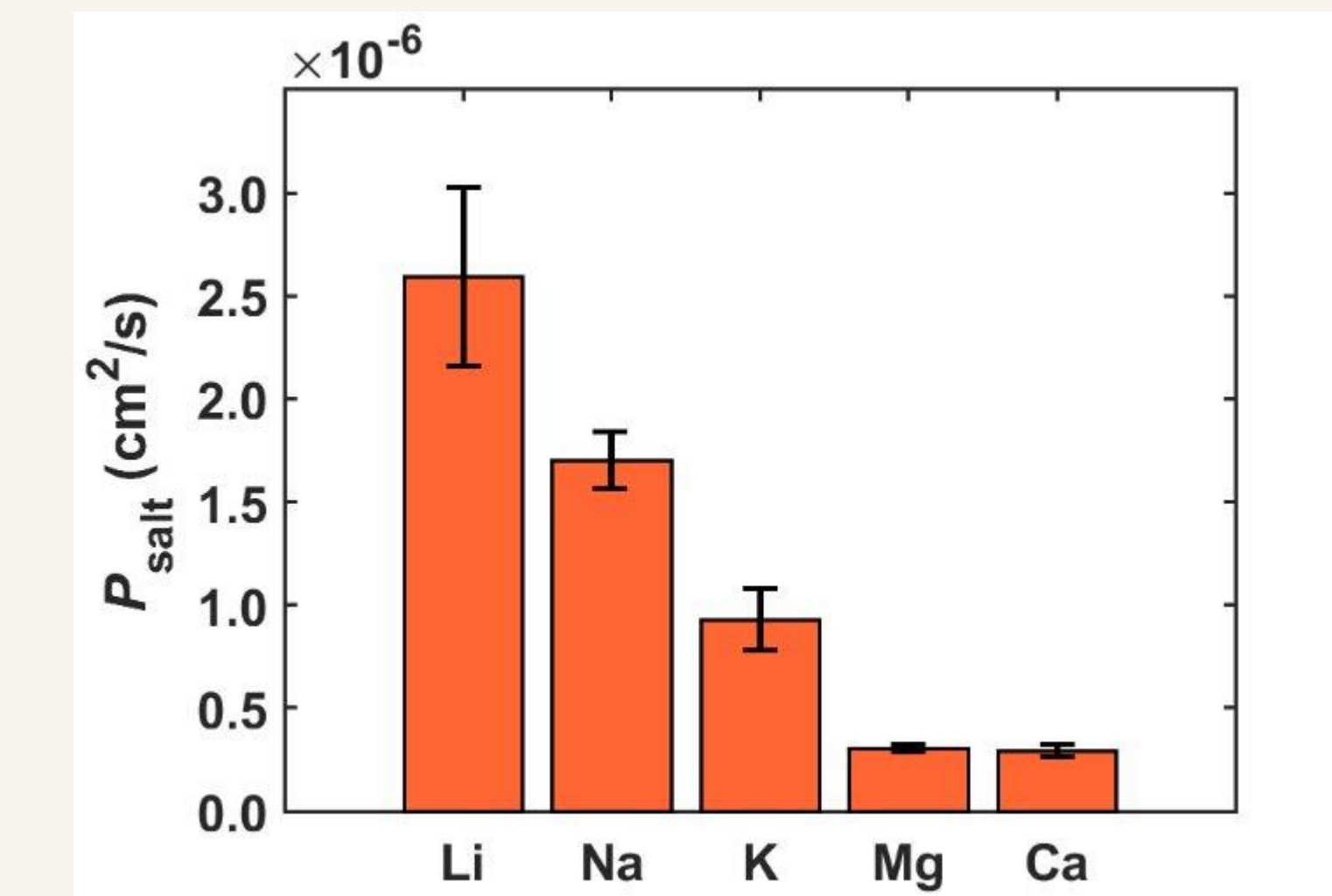


Figure 2: Permeability of different sulfonated polystyrene membranes

Ion Exchange Membrane

- Perfluorosulfonic acids: expensive and environmental impact
- Hydrocarbon-based materials: dissolve in water. Block copolymer or crosslinking poses inert volume fraction that can reduce transport performances.

Problems

- Although studies have focused on polymer crosslinking, limited research has evaluated ionically crosslinked polymers.
- Studying the impact of covalent and ionic crosslinking on the functionality of ion exchange membranes can help us get closer to having an ideal polymer that is not only sturdy but can effectively clean water.

Approach

- Sulfonated polystyrene (PSS) will be ionically and covalently crosslinked with different agents: calcium (ionic) and divinylbenzene (DVB) (covalent).

Hypothesis

- Ionic crosslinking is not permanent that a Ca²⁺ form sulfonated polystyrene has lower structural stability in comparison to crosslinked sulfonated polystyrene.
- Water uptake in the covalently crosslinked polymer would be lower than that of the ionically crosslinked polymer because of the restricted dynamics of the polymers.
- The covalently crosslinked polymer will have higher selectivity but lower permeability in comparison to ionically crosslinked polymer.

LITERATURE BASED DATA

- Sodium Alginate was crosslinked with calcium and another polymer with adipic acid dihydrazide, ion and covalent, respectively.
- Under stress the covalent polymer holds value longer than the ionic polymer.

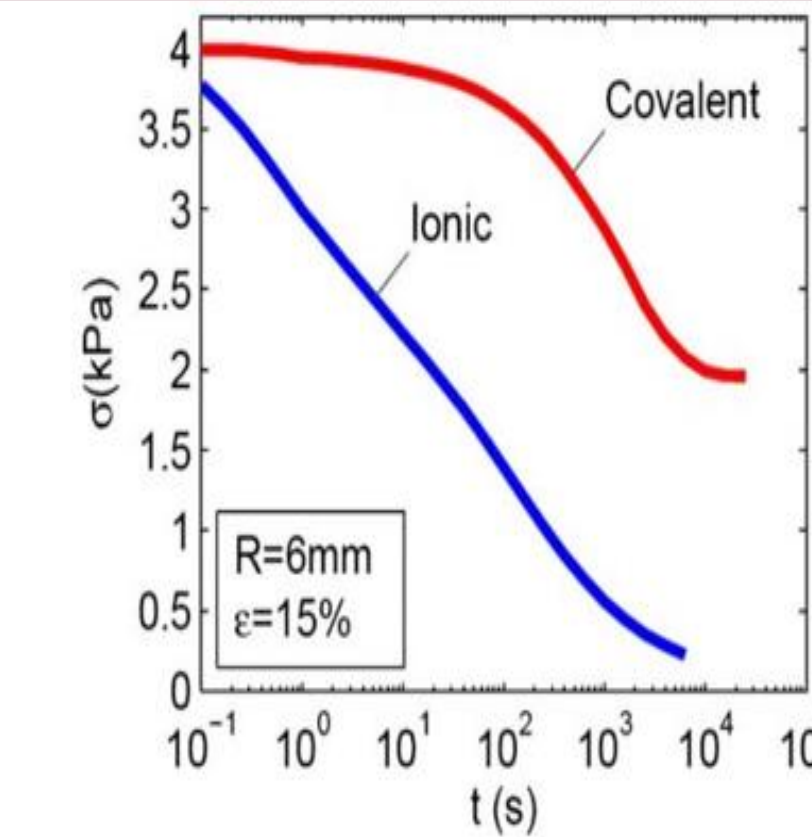


Figure 3: Covalently vs Ionically Crosslinked Polymers Under Stress

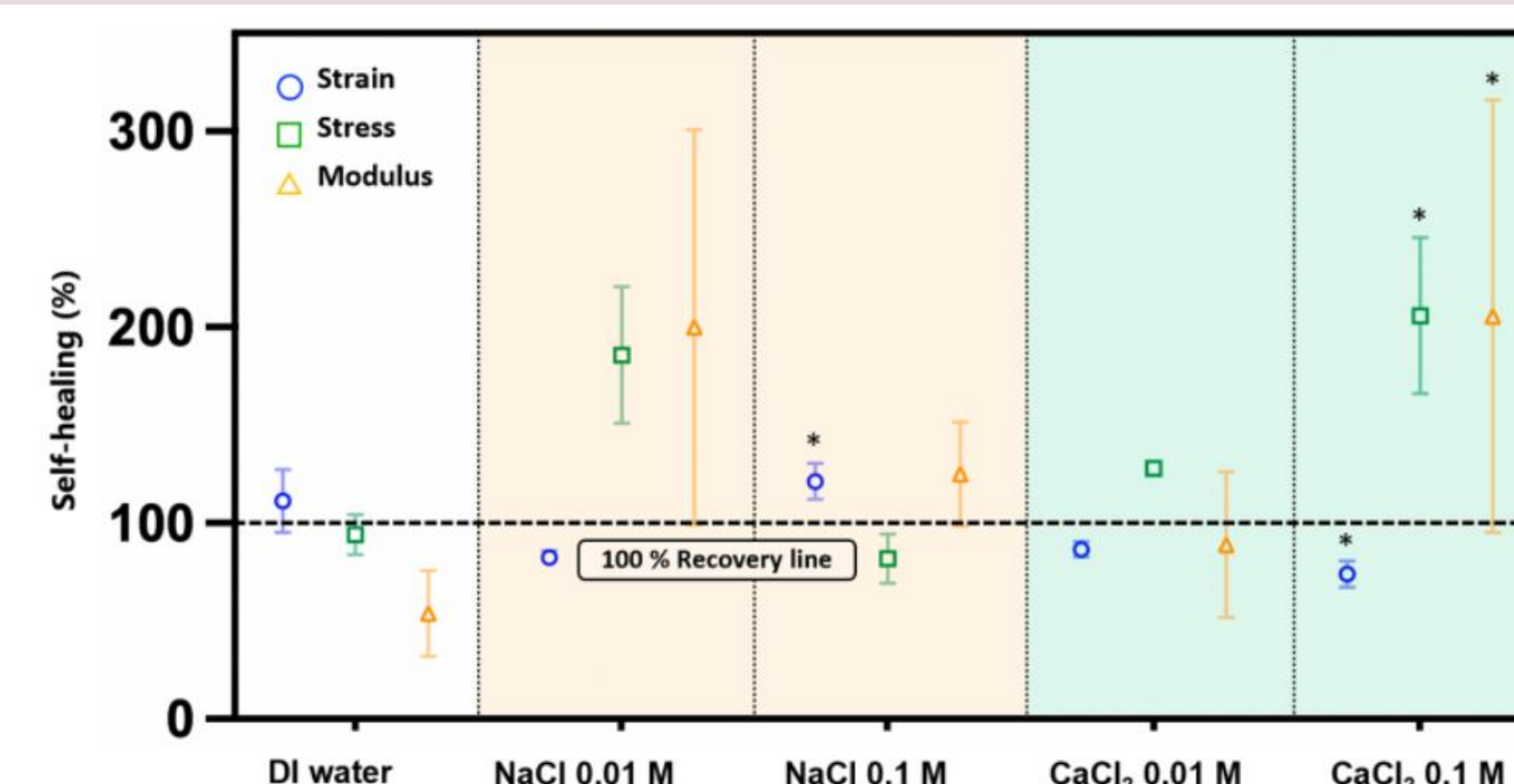


Figure 4: Properties of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) hydrogels

- Covalent crosslinking with calcium improves strength.
- CaCl₂ 0.1M has better recovery in comparison to NaCl 0.1M
- Cross bridges formed by CaCl₂ create a more complex and interconnected network.

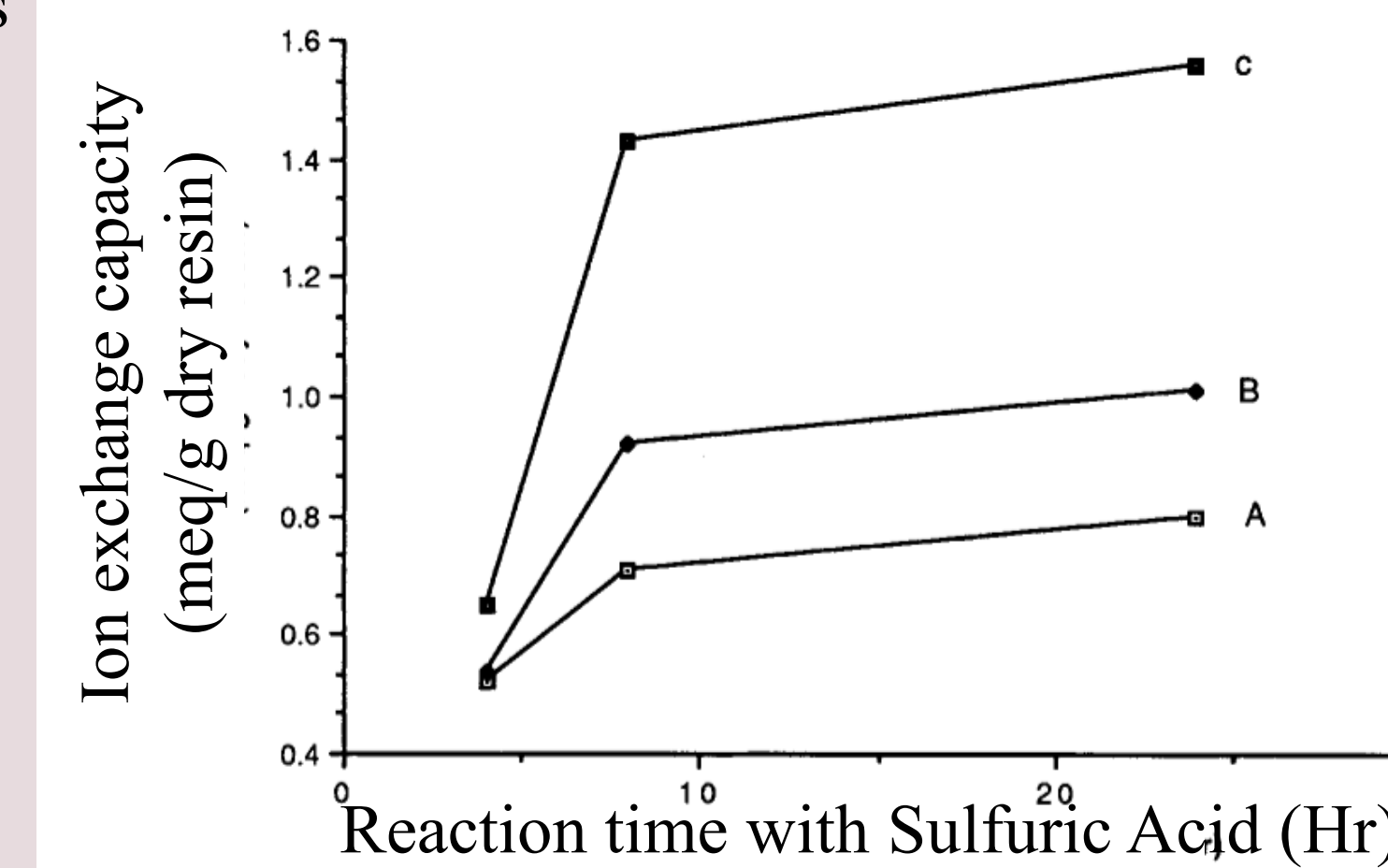


Figure 5: Impact of crosslinking and sulfonation on ion exchange capacity

- A, B, and C represent 2, 5 and 10% DVB crosslinking.
- As crosslinking increased the polymer experienced a higher IEC
- With the addition of sulfonation the IEC continued to increase.

RESULTS

- Ionic crosslinking is plastic while covalent crosslinking is elastic.
- PSS-Ca has a lower absorption than PS-DVB, because PS-DVB has a more rigid structure do to permanent cross-linkages.
- When PS-DVB is sulfonated, the polymer becomes notably more stable and able to perform greater exchanges over ranges of pH and solvents in comparison to its non-sulfonated state.

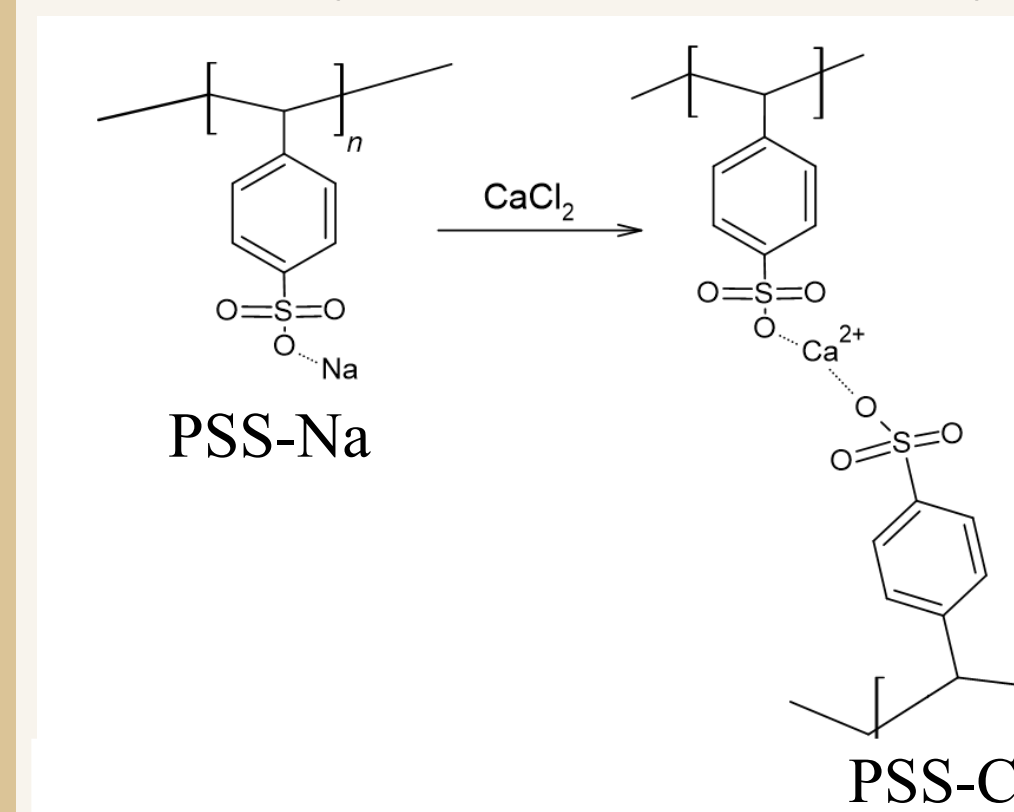
CONCLUSIONS

- There was no study that specifically compared the structure-property-performance relationship of ionic and covalent crosslinking of IEMs. This study works towards filling that knowledge gap by doing a direct comparison.
- Sulfonated polystyrene was found to be a good candidate material for this study due to the feasibility of chemical modification including sulfonation, ion-exchange and crosslinking.
- PSS-DVB is expected to have higher absorption, IEC, and structural integrity.

CURRENT EXPERIMENTAL APPROACH

Materials Preparation

Ionically Crosslinked Polymer



- Calcium chloride was added to PSS-Na to create PSS-Ca through ion exchange.
- In making PSS-Ca excess amount of CaCl₂ was used to ensure crosslinking.

Covalently Crosslinked Polymer

Polystyrene was sulfonated before it was crosslinked to protect the polymerization process and the sulfonic acid groups.

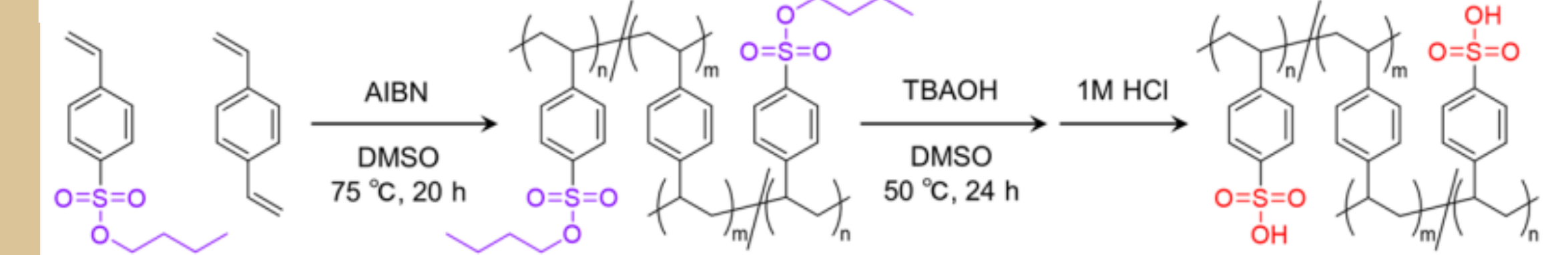


Figure 6: Chemical Structure of PSS-Na and PSS-Ca following Ion Exchange Conversion

Characterization

Fourier-Transform Infrared Spectroscopy (FTIR)

- Allows to observe ionic interaction by observing shift of frequencies and intensity.

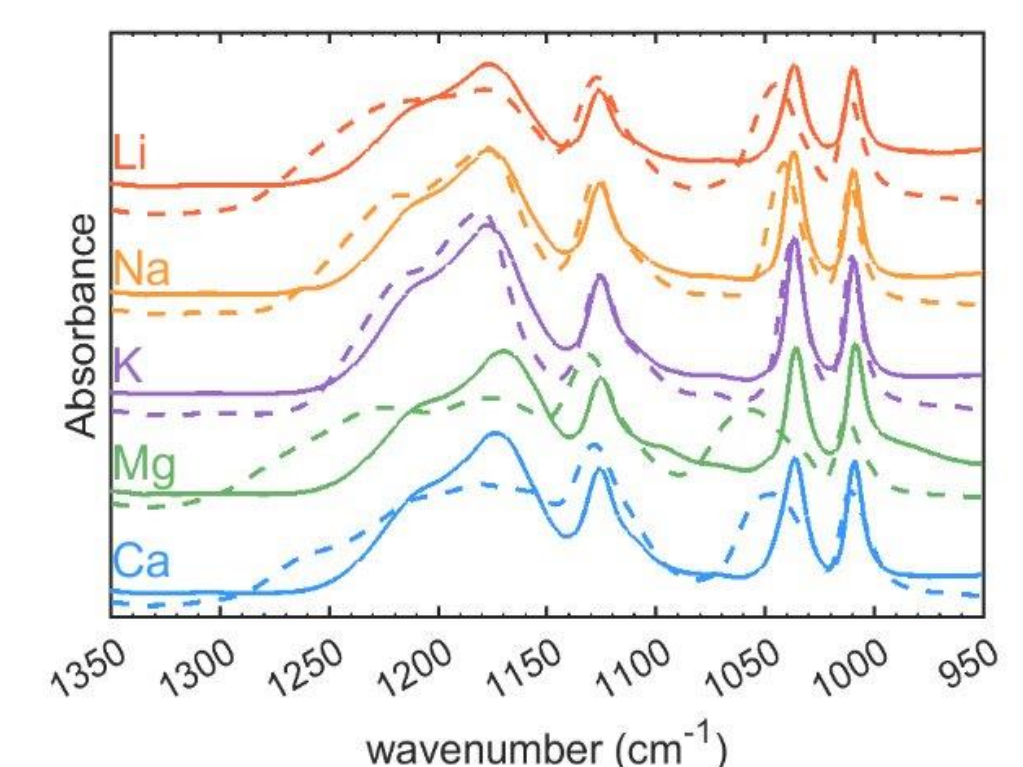


Figure 8: Sample FTIR depicting ionic relationships with sulfonated polystyrene

Water Uptake

- Water the membranes absorb.
- This can allow information on swelling.

$$WU = \frac{M_{wet} - M_{dry}}{M_{dry}}$$

M_{wet}: Wet mass
M_{dry}: Dry mass

Acid-Base Titration

- An acid base titration allows us to measure the ionic exchange capacity of the membranes.
- Resins are titrated with NaOH

$$IEC = \frac{CV}{M}$$

C: NaOH Concentration
V: NaOH Volume
M: mass of material

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