A Study of the Anion Conducting Ionomer Processing and Corresponding Properties for Membrane-Based Energy Storage Devices

Nickolas Murdakes, Wayz Rana Khan, Chris J. Cornelius

Department of Chemical and Biomolecular Engineering, University of Nebraska, Lincoln, NE 68504

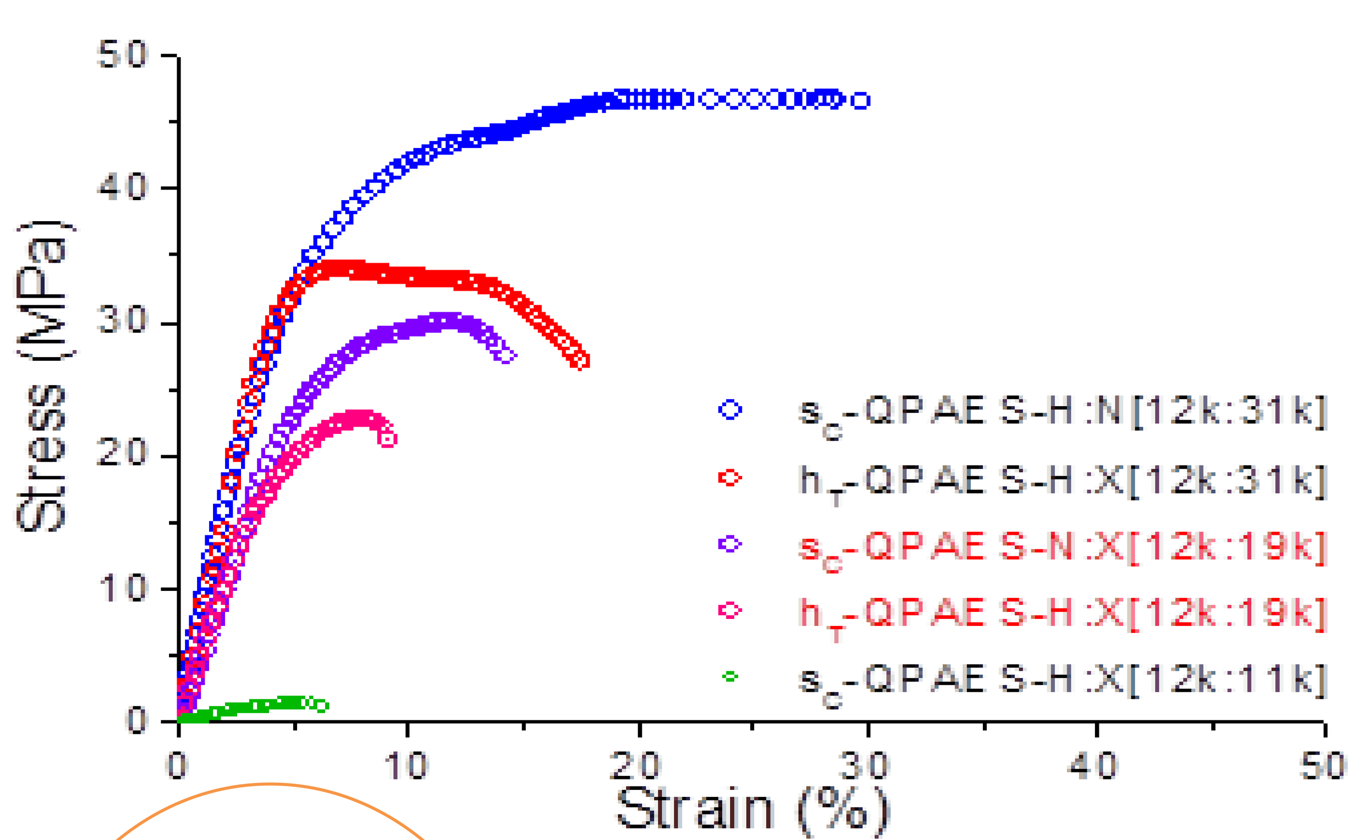
Introduction

Ionomers have been a large area of research over the last half century. These ionomers have three main features: ion conduction, hydrophilicity and the fixed charge carriers within electrically neutral repeat units. Ionomers are used as membranes for separation in a large number of fields including electrodialysis, electrolysis batteries, biomedical, proton exchange membranes (PEM) anion exchange membranes (AEM) fuel cells among others. There has been large amounts of research in ionomer processing in many of these fields however one of the areas that hasn't been widely explored are AEMs. These films can be prepared by either heterogeneous or solution casting conversion. The heterogeneous method involves converting a chloromethylated or brominated polymer into an AEM by submersing the film in trimethylamine (TMA) at room temperature (25 °C). Once submerged the bromomethylbenzyl groups are converted to benzyltrimethyl ammonium moieties. The film is then converted into its hydroxide form by being soaked in an alkaline solution. The solution casting method uses a TMA solution that is added slowly over time to a chloromethylated or brominated polymer solution. This solution is then cast to create a film.

This study takes a series of multiblock quaternary ammonium (QA) ionomers using both conversion techniques. The films properties were studied to find ion-exchange capacity (IEC), electrochemical impedance spectroscopy (EIS) and dynamical mechanical analysis (DMA). The tensile properties, swelling behavior, and stabilized ion transport properties were also compared between the two conversion methods.

Results and Discussion

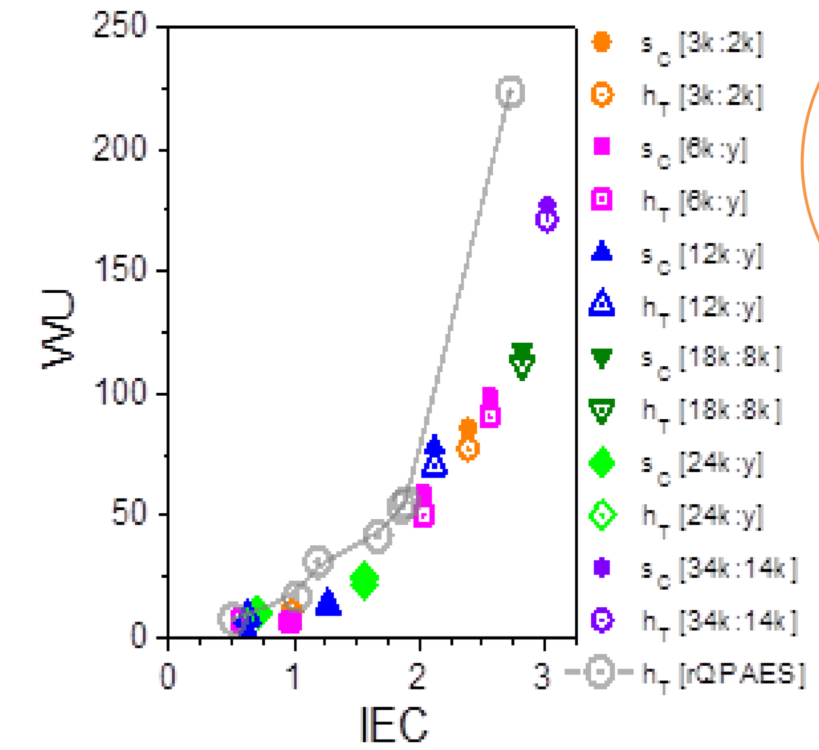
Stress-Strain



Stress-strain curves of wet homogenous and solution cast membranes

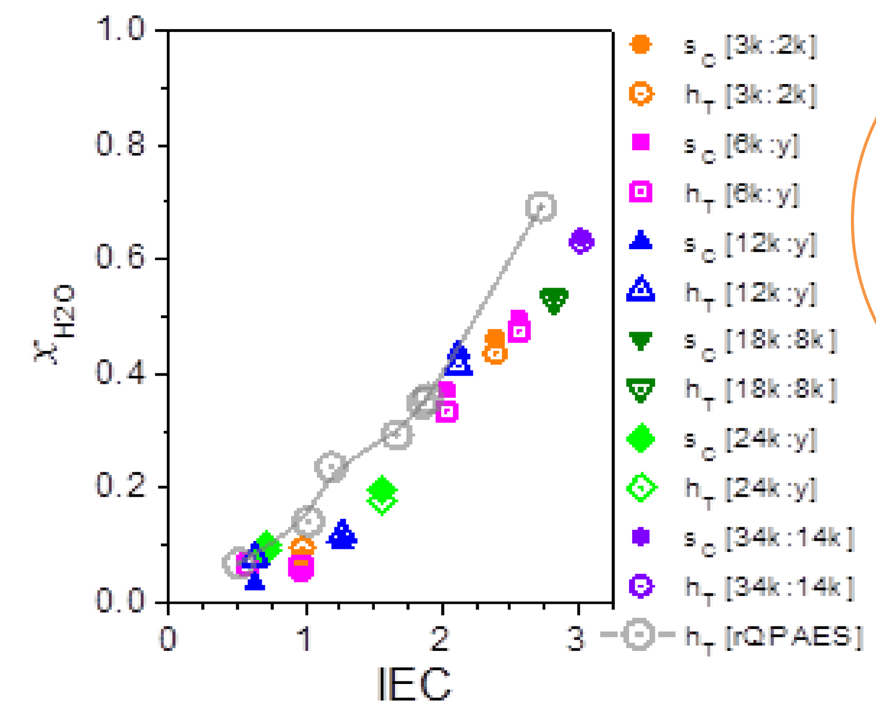
Membrane	Toughness (10^4 J/m^3)	
Samples	Solution Cast	Homogenous
12k-31k	1185 ± 157	498 ± 91.7
12k-19k	321 ± 79.1	148 ± 67.2
12k-11k	5.78 ± 0.99	--

Water uptake



IEC versus water uptake for homogenous and solution cast films at varying block lengths.

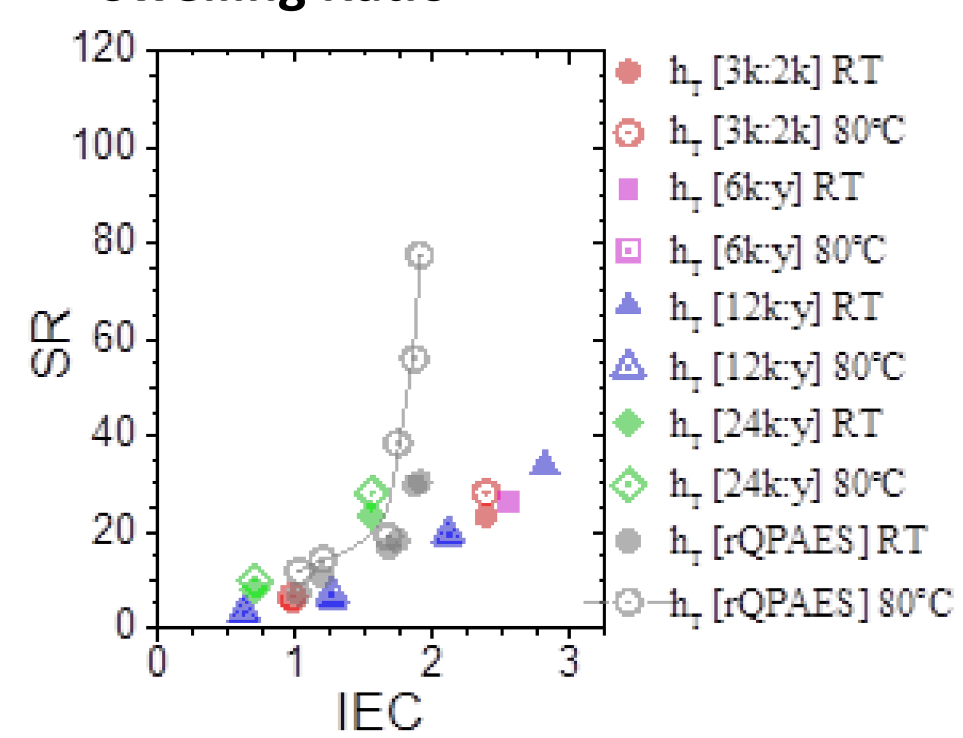
There increase in water uptake is due to IEC and block length



IEC versus water fraction for homogenous and solution cast films at varying block lengths.

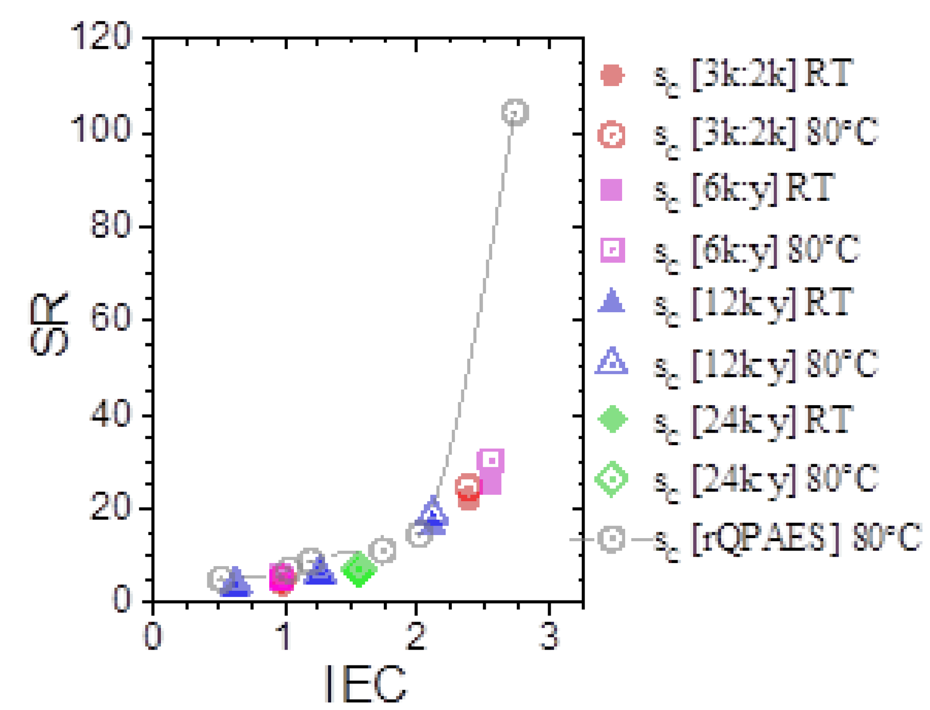
The increase in water fraction is due to IEC

Swelling Ratio



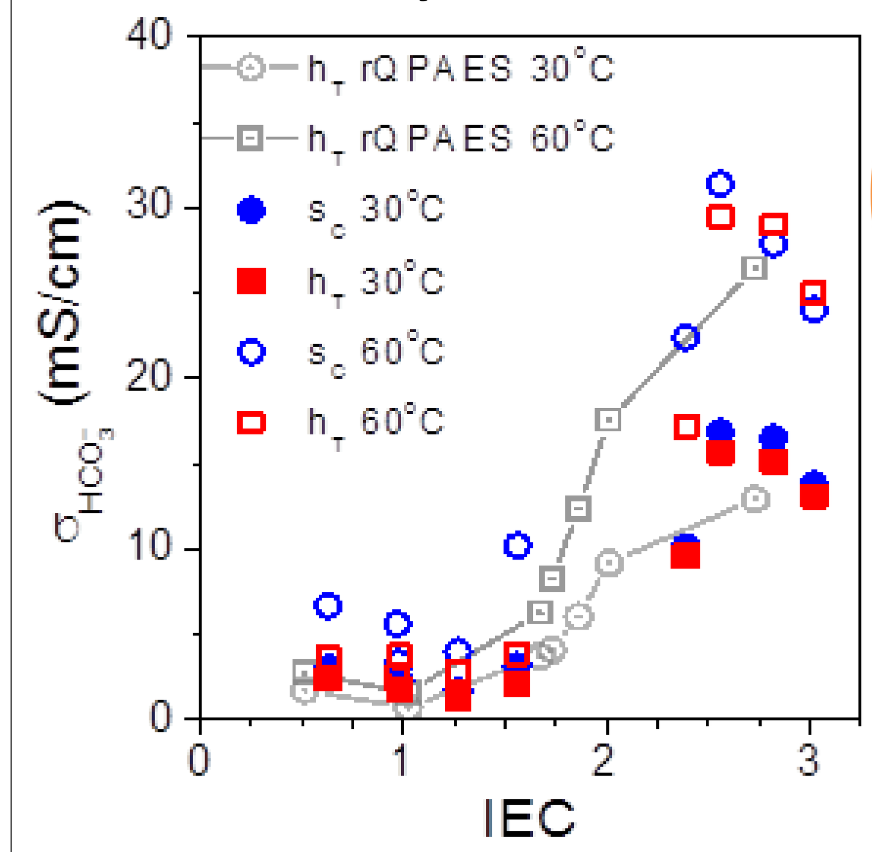
IEC versus swelling ratio for homogenous films at 25 and 80 °C.

There is variance based on production method and IEC



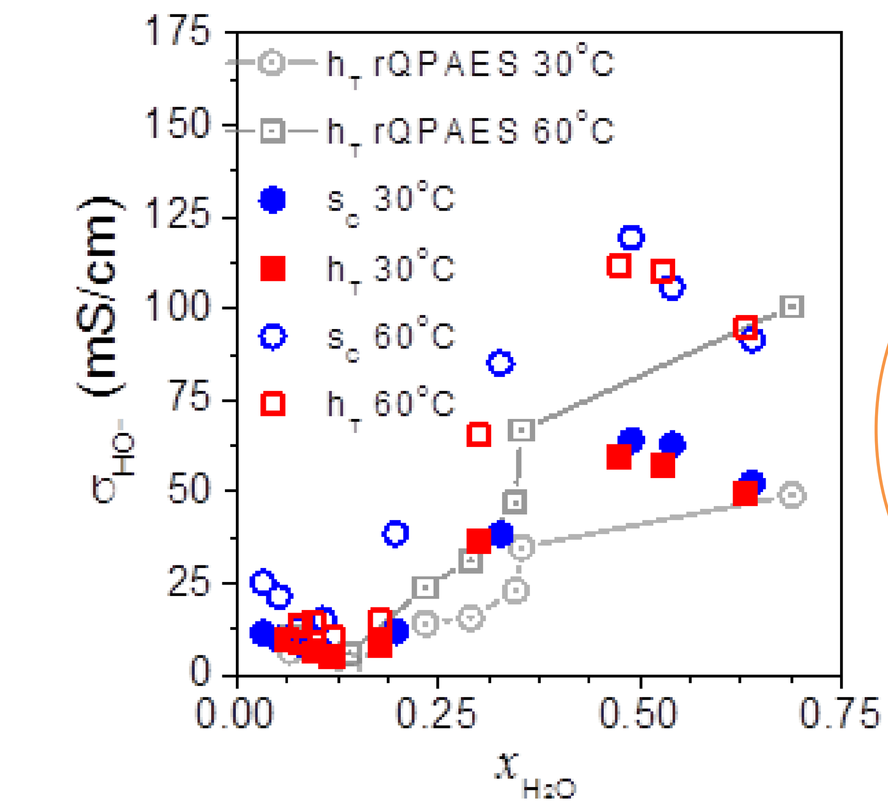
IEC versus swelling ratio for homogenous films at 25 and 80 °C

Conductivity



IEC versus conductivity for both solution cast and homogenous membranes at 30 and 60 °C

Trends based on production method as well as IEC and water fraction



Water fraction versus conductivity for both solution cast and homogenous membranes at both 30 and 60 °C.

CONCLUSION

- Overall the membranes performed as expected as the IEC increased water uptake swelling ratio and film conductivity increased.
- As for structural integrity, the solution cast membranes were much tougher especially at the higher IEC levels this can be seen in the stress over strain ratio.
- The reason for the increase in properties was due to the increase in the length of the hydrophilic blocks which allows for increased hydroxyl conductivity which is ideal for these types of ionomers.

REFERENCES

Khan, Wayz R., et al. "Tuning Quaternary Ammonium Ionomer Composition and Processing to Produce Tough Films." *Polymer*, vol. 142, 2018, pp. 99–108., doi:10.1016/j.polymer.2018.03.028