EILERS GRADUATE STUDENT FELLOWSHIP
FINAL REPORT

EILERS FELLOW:	Lingyu Yang
FACULTY ADVISOR:	Jennifer L. Schaefer
REPORT PERIOD:	2022/01 – 2023/01
PROJECT TITLE:	Developing a new polymer platform for alkaline fuel cell membranes
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**(✓) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear** **(✓) Smart Storage and Distribution ( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels ( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Synthesis of low-cost, highly conductive stable membranes for alkaline fuel cells	Synthesized a series of anion exchange membranes with high ionic conductivity via a one-pot inexpensive Friedel-Crafts polymerization method successfully.	100%
Control of each alkaline stability, ionic conductivity, and mechanical properties	Tuned the hydroxide ionic conductivity, chemical stability, and mechanical properties via changing the microstructural sequence of the polymer.	100%
Understanding of relationships between polymer chemical structure and bulk materials properties	Correlated polymer compositions, structures/morphologies, and performances, and found some basic structure-property relationships.	80%

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount) Sponsor: Argonne National Laboratory Project Title: Structure of anion exchange membranes based on Friedel-Crafts polymerization PIs: Jennifer L. Schaefer Submission Date: 09/29/2022 Proposal Amount: External experiment proposal without proposal amount
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount) N/A
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) Under preparation
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s) N/A
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location) 1) American Chemical Society National Meeting, 'Low-cost, highly-performing anion exchange membranes via an inexpensive one-pot polymerization', Aug. 2022, Chicago, IL 2) ND Energy PD/GS Seminar, 'Developing a new polymer platform for alkaline fuel cell membranes', Jan. 2023, Notre Dame, IN 3) American Chemical Society National Meeting, 'Low cost, highly performance anion exchange membranes via one-pot polymerization', Mar. 2023, Indianapolis, IN
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received) N/A

INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) Collaborator Name: Haifeng Gao Organization: Department of Chemistry and Biochemistry Purpose of Affiliation: The Gao group are responsible for polymer synthesis in this project
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL) N/A
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail) N/A

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

Fuel cells are electrochemical energy generation devices that can convert chemical fuels to electricity at higher efficiency than combustion power plants; reversible fuel cells operate as energy storage devices by converting electricity to chemical fuel. Therefore, fuel cells are alternative energy devices that can help us to reduce greenhouse gas emissions in the energy sector. There is renewed interest in anion exchange membrane (AEM) fuel cells due to their lower potential cost as compared with proton exchange membrane (PEM) fuel cells that depend on precious metal catalysts.[1,2] AEM fuel cells can operate without using platinum group catalysts and at reduced temperatures, however the high pH that alkaline fuel cells operate at is often damaging to membrane materials.[3-5] In addition, the ionic conductivity of AEMs is typically lower than that of PEMs. Identification of a low cost, hydroxide conducting membrane that meets the requirements for fuel cell operation is the biggest standing challenge in this field.[2, 6-8]

The Gao group (Schaefer group collaborators) developed a facile Friedel-Crafts (F-C) hydroxyalkylation polymerization method that synthesizes high-molecular-weight polymer (Figure 1) with rigid backbone in one pot using inexpensive commercial monomers.[9]

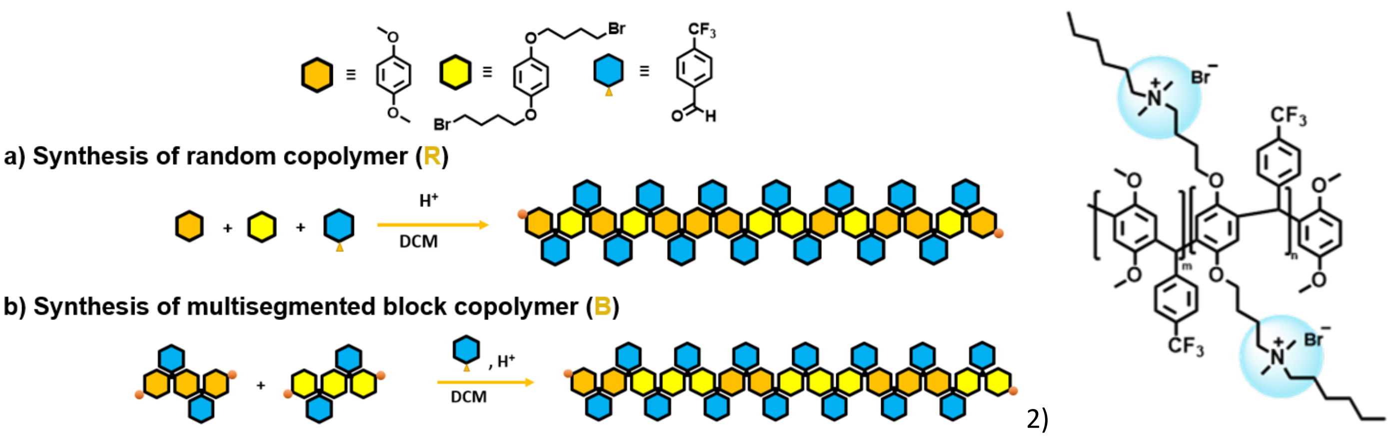
1)


Figure 1. 1) Structure schematic of copolymer AEM with both random and block microstructures. 2) The chemical structure of the synthesized polymer, where blue bubbles are functionalized dicationic side-chains.

The polymerization method enables the synthesis of an entire platform of membrane materials towards meeting the specifications for a high performance membrane as identified by prior literature. An intriguing feature of this polymerization method is the option to freely incorporate both charged groups and hydrophobic groups as substituents along the polymer backbone, which is expected to be critical to achieve optimized balance between ion conductivity, water swellability, and mechanical integrity when applying the polymers as AEM materials for alkaline fuel cells. High molecular weight of the polymer is easily achieved, which leads to high mechanical durability and excellent hydroxide conductivity (Figure 2), where the ionic conductivity of block copolymers outperform polymers with random microstructures.

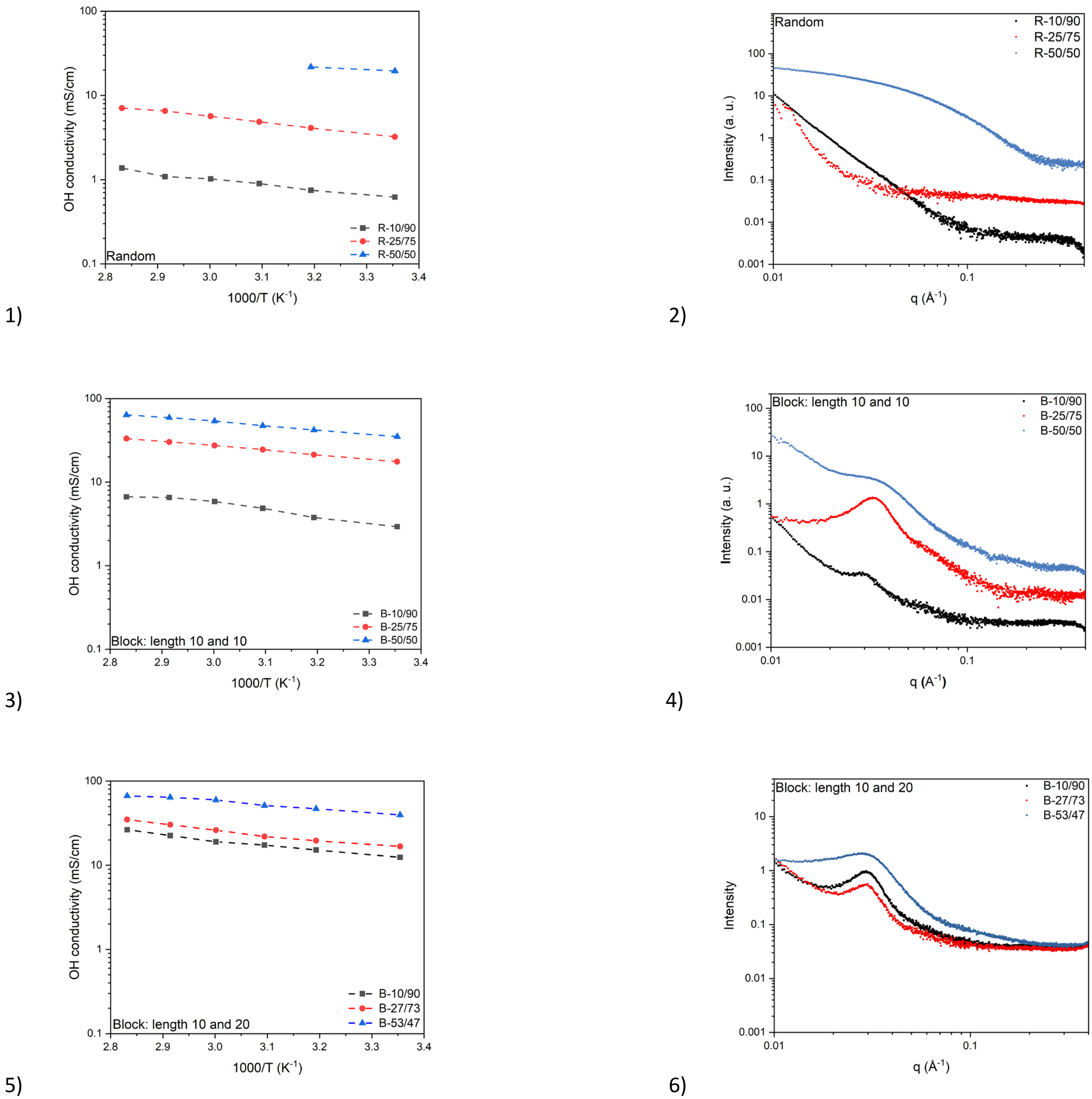


Figure 2. Ionic conductivity (1,3, and 5) and SAXS profiles (2,4, and 6) of polymer membranes with different microstructures (random and block) and varied block lengths.

The polymer backbone is composed completely from aromatic rings and C-C bonds, which leads to high mechanical strength, chemical stability in basic media, and thermal stability. Meanwhile, the versatility of the platform allows for the investigation of a multitude of macromolecular architectures, including side-chain substituents, traditional “blocks” (diblock, triblock, pentablock polymers), and multiple linear segments with varying chain sequence distribution. The AEMs that we are studying are nanostructured. The hydrophobic (polymer backbone, alkyl chains) and hydrophilic (ionic groups, water) segregate. The morphology of the ion-containing domains and the water channels – their size, shape, and connectivity – is very important in regulating the hydroxide conductivity. It is not possible to predict the exact morphology of the membranes based solely on chemical intuition and knowledge of the macromolecular chain sequence. Therefore, small-angle X-ray scattering (SAXS) (Figure 2)was utilized to characterize the micro morphology of the membranes. And it was consistent that copolymers with longer hydrophobic block lengths showed higher ionic conductivities and more obvious phase segregation in SAXS.

References:

(1) Gottesfeld, S.; Dekel, D. R.; Page, M.; Bae, C.; Yan, Y.; Zelenay, P.; Kim, Y. S. Anion Exchange Membrane Fuel Cells: Current Status and Remaining Challenges. J. Power Sources 2018, 375, 170–184.

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(3) Lu, S.; Pan, J.; Huang, A.; Zhuang, L.; Lu, J. Alkaline Polymer Electrolyte Fuel Cells Completely Free from Noble Metal Catalysts. Proc. Natl. Acad. Sci. 2008, 105 (52), 20611–20614.

(4) Lee, K. H.; Cho, D. H.; Kim, Y. M.; Moon, S. J.; Seong, J. G.; Shin, D. W.; Sohn, J. Y.; Kim, J. F.; Lee, Y. M. Highly Conductive and Durable Poly(Arylene Ether Sulfone) Anion Exchange Membrane with End-Group Cross-Linking. Energy Environ. Sci. 2017, 10 (1), 275–285.

(5) Hugar, K. M.; Kostalik, H. A.; Coates, G. W. Imidazolium Cations with Exceptional Alkaline Stability: A Systematic Study of Structure-Stability Relationships. J. Am. Chem. Soc. 2015, 137 (27), 8730–8737.

(6) Pan, J.; Chen, C.; Li, Y.; Wang, L.; Tan, L.; Li, G.; Tang, X.; Xiao, L.; Lu, J.; Zhuang, L. Constructing Ionic Highway in Alkaline Polymer Electrolytes. Energy Environ. Sci. 2014, 7 (1), 354–360.

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(8) Zhu, L.; Pan, J.; Wang, Y.; Han, J.; Zhuang, L.; Hickner, M. A. Multication Side Chain Anion Exchange Membranes. Macromolecules 2016, 49 (3), 815–824.

(9) Zou, L.; Cao, X.; Zhang, Q.; Dodds, M.; Guo, R.; Gao, H., Friedel-Crafts A(2)+ B-4 Polycondensation toward Regioselective Linear Polymer with Rigid Triphenylmethane Backbone and Its Property as Gas Separation Membrane. Macromolecules 2018, 51, 6580-6586.