Novel Synthesis of PVBCl-*b*-PE-*b*-PVBCl Copolymer for Improved Stability in Water Electrolysis

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Background and Methods

- Due to an increased focus on hydrogen as a source of renewable energy storage, demand for more efficient water electrolysis has risen in recent years[1]
- Anion exchange membrane (AEM) water electrolysis has advantages in cost and scalability
- Hydrophilic/hydrophobic domain separated polymers like PVBCl-*b*-PE-*b*-PVBCl have shown strong potential in terms of cell performance and mechanical stability[2,3]

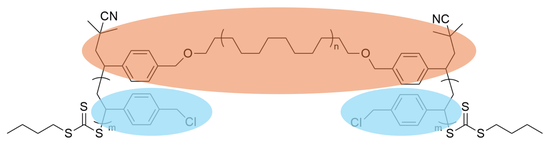

Fig 1. Previous iteration of poly(vinylbenzyl chloride)-*b*-poly(ethylene)-*b*-poly(vinylbenzyl chloride) with ether linkage. Hydrophilic and hydrophobic domains shown in blue and orange, respectively.

- Due to the alkaline environment in AEM water electrolysis devices, there are concerns the ether linkage could be susceptible to degradation
- The goal is to develop a PVBCl-*b*-PE-*b*-PVBCl which replaces the ether linkage with a methylene linkage

References and Acknowledgments

References:
1. Office of Energy Efficiency & Renewable Energy. *Hydrogen Shot*. Energy.gov. https://www.energy.gov/eere/fuelcells/hydrogen-shot.
2. Zhang, Wenxu. Synthesis and Characterization of Polymeric Anion Exchange Membranes. Ph.D. Dissertation, University of Massachusetts Amherst, Amherst, MA, 2016.
3. Wu, Ivy, et al. “Effects of the Hydrophobic Block Length Ratio of Poly(Vinylbenzyl N-Methylpiperidinium Carbonate)-b-Polyethylene-b-Poly(Vinylbenzyl N-Methylpiperidinium Carbonate) Block Copolymers for Anion Exchange Membrane Electrolysis.” *ACS Applied Polymer Materials* 5, no. 8 (August 11, 2023): 5834–45.

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Current Progress

Step 1. Difunctional Chain Transfer Agent

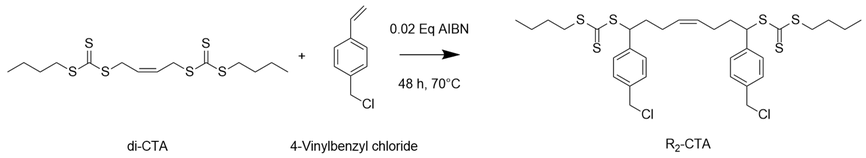

Fig 2. R2-CTA was purified using column chromatography with a mobile phase of 50:1 hexanes:ethyl acetate volume ratio and a silica gel stationary phase. Structure was confirmed with ^{1}H NMR.

Compound	Molar Ratio
di-CTA	1
4-VBCl	2
AIBN	0.02
Ethyl Acetate	4.1

- Benzylic carbon attached to the sulfur in R_2-CTA is able to stabilize RAFT polymerization better then the allylic carbon in di-CTA

Step 2. Chain Transfer Ring Opening Metathesis Polymerization

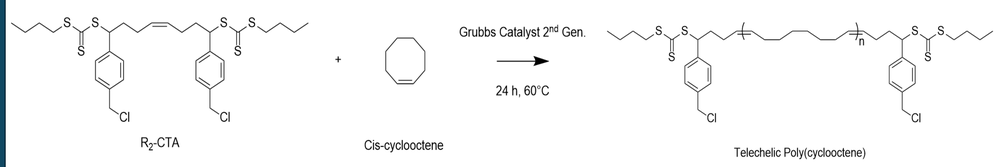

Fig 3. PCOE was purified by dissolving in chloroform and precipitating in methanol. Number average molecular weight found to be 19 kDa with a polydispersity of 1.55 using gel permeation chromatography in THF.

Compound	Molar Ratio
R_2-CTA	85
Cis-COE	10,000
G_2 Catalyst	1
Toluene	10,000

- Step 2 exhibits a conversion rate of 75-85%, showing comparable efficiency to previous PVBCl-*b*-PCOE-*b*-PVCBl synthesis

Next Steps and Goals

Step 3. Reversible Addition-Fragmentation Chain-Transfer Polymerization

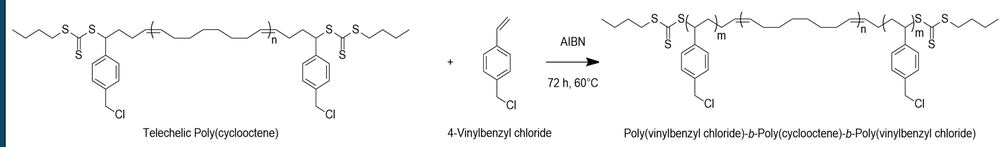

Fig 4. PVBCl-*b*-PCOE-*b*-PVBCl purified by dissolving in dichloromethane and precipitating in methanol twice then stirring in 6:5 THF;methanol volume ratio for two days. Aim for a 2.5:1 n:m/2 ratio as literature has shown it to be the optimal ratio for this polymer[3].

Compound	Molar Ratio
Telechelic PCOE	100
4-VBCl	2,500
AIBN	1
Chlorobenze	40,000

- Post hydrogenation, polymer can be functionalized with quaternary ammoniums to be used as ionomer or polymer electrolyte membrane
- Polymer will have same hydrophilic/hydrophobic domain separation quality as the ether-linked iteration
- Once synthesized, polymer to be fully characterized with IEC, SAXS, water uptake, conductivity, chemical stability, mechanical stability and cell performance and compared to ether-linked iteration
- Polymer expected to exhibit superior stability and may allow for improvements in cell efficiency by allowing for thinner membranes or higher PVBCl ratios

Step 4. Hydrogenation

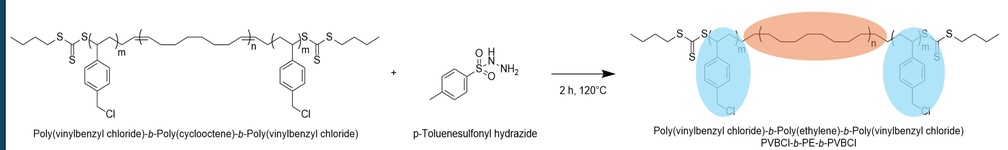

Fig 5. PVBCl-*b*-PE-*b*-PVBCl washed with 100°C DI water to remove any byproducts and excess TSH. Full hydrogenation is verified by examining melting peak with differential scanning calorimetry. Hydrophilic and hydrophobic domains shown in blue and orange, respectively.

Compound	Molar Ratio
PVBCl-*b*-PCOE-*b*-PVBCl	1
TSH	8
p-Xylene	100