High-Temperature Polymer Electrolyte Fuel Cell Electrolytes Based on Dendronized Polymers

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Outline of presentation

- **Motivation for high temperature membranes**
- **Objectives**
- **Materials synthesis**
- **Characterization / evaluation**
- **Conclusion**
- **Acknowledgement**

Motivation for high-temperature membranes

Proton conducting membranes to operate at temperatures above 80°C to facilitate

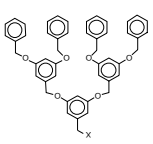
- **Easier water management: low humidity**
- **Easier heat rejection from stack**
- **Improved kinetics on cathode electrocatalyst**
- **Higher CO tolerance on anode electrocatalyst**

Objective

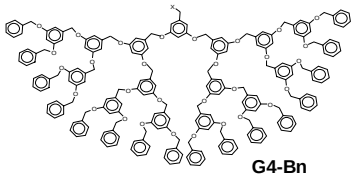
- ***Develop a proton-conducting membrane electrolyte to meet DOE's technical targets***
  - ✓ **High proton conductivity (>0.1 S/cm) at 120°C and 25% RH (automotive)**
  - ✓ **Low oxygen and hydrogen cross-over**
  - ✓ **Low cost, <$5/kW**
  - ✓ **Durability of >5,000 hours**
  - ✓ **Able to withstand temperatures as low as -40°C**

ANL's strategy for high-temperature membranes

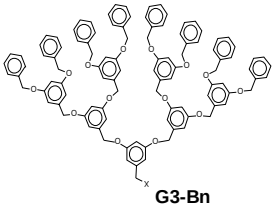
- **Dendrimers are highly branched molecules with high density of functionalizable moieties**
- **Aryl ether dendrimers for high thermal stability**
- **Dendrimers cross-linked for controlled pore size and film forming characteristics**
- **Sulfonation of dendritic blocks for proton conduction**
- **Attaching dendrimers to polymer backbone to enable film formation and impart water insolubility**



G2-Bn

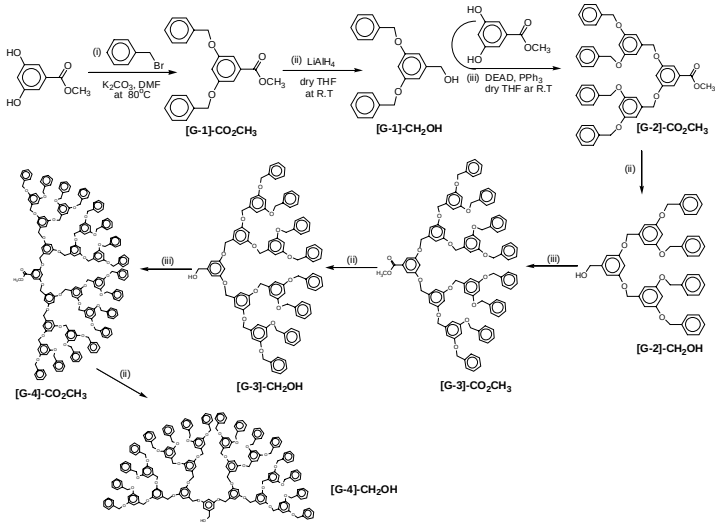


G4-Bn

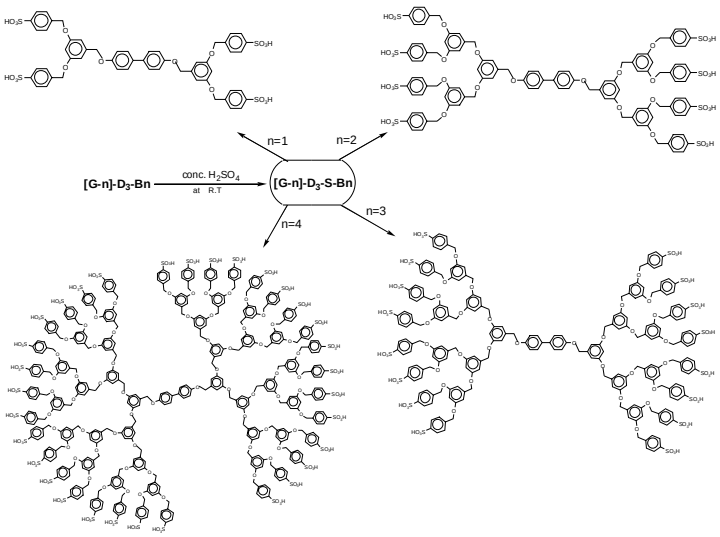


G3-Bn

Dendritic building blocks G1 through G4 were successfully prepared



Sulfonated dendrimers are water soluble



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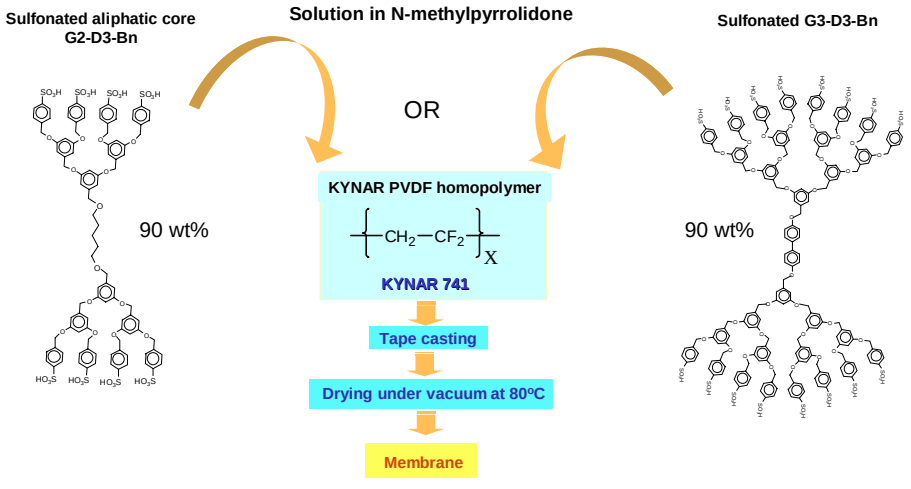
Dendrimers were blended with water insoluble polymer to prepare membranes



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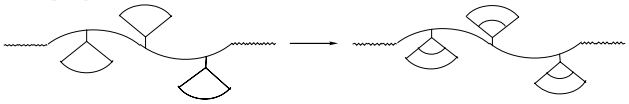
In spite of immiscibility, the blend materials are conductive without external humidification

Conductivity (S/cm) vs. Temperature

	Temperature (°C)			
	69	85	98	105
PVDF/G2-SO_3H (10/90 wt ratio)		0.050	0.001	0.002
PVDF/G3-SO_3H (10/90 wt ratio)	0.010	0.002		

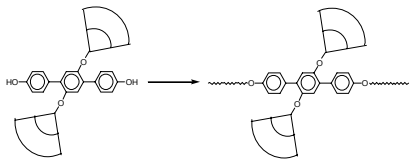
Two distinct routes to water insoluble polymer electrolytes from dendritic building blocks

- **Dendronized or side chain dendritic polymers**
  - **Bearing pendant dendritic wedges on repeating units of a polymer backbone**
    - **Construction through attachment of the dendritic side groups on preformed linear reactive polymeric chains**
    - **Divergently developing the dendritic fragments onto suitable side groups of the polymeric backbones**

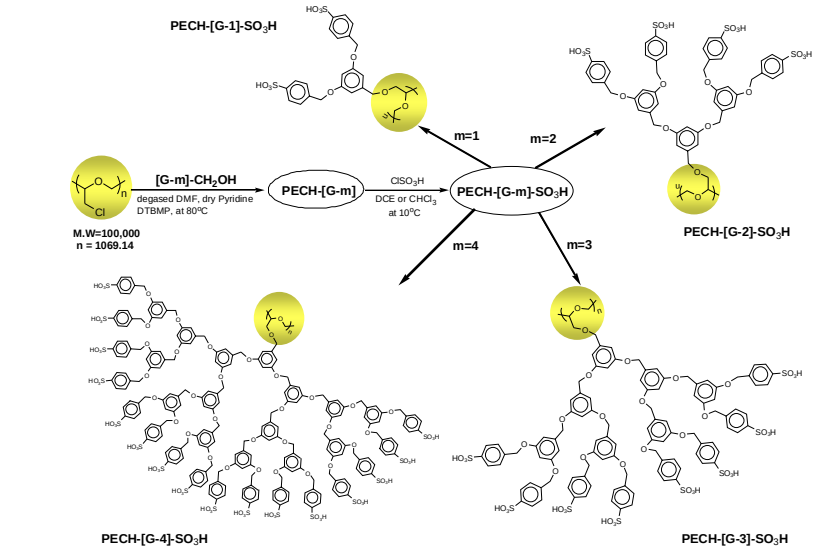


- **Polymerizing monomer units bearing the desired dendrons**

"Macromonomer"

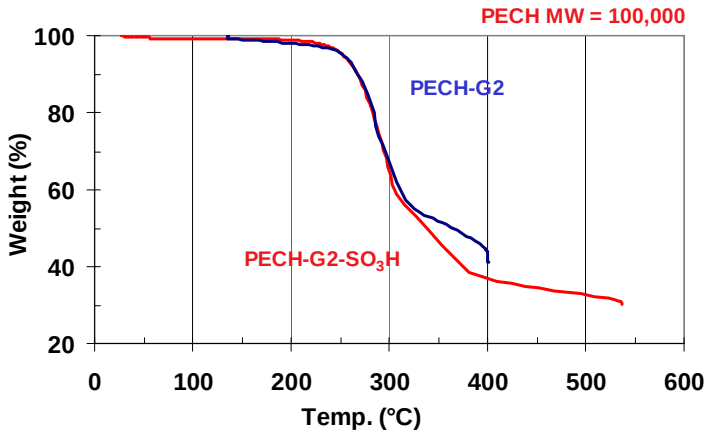


Water insoluble dendronized polymer electrolytes were prepared from polyepichlorohydrin backbone



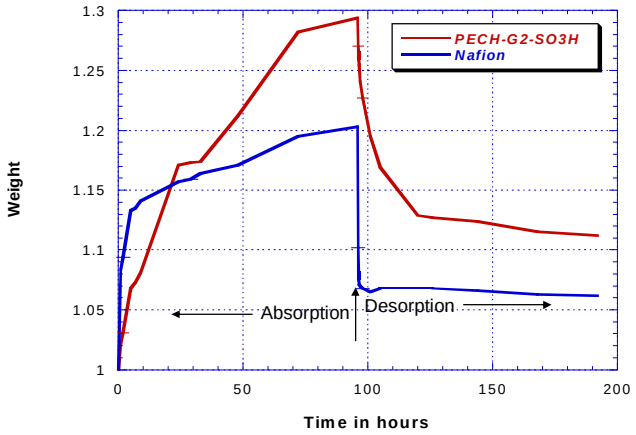
TGA shows PECH-G2-S0$_3$H to be stable up to 180°C

- **Solvent removal up to 150°C**
- **Sulfonate group is decomposed at temps. >180°C**
- **Material decomposes at temps. >230°C**



Sulfonated dendronized PECH retained 30% more moisture than Nafion

- **Moisture absorption at 25°C and 97% RH followed by desorption at 25°C and 40% RH**
- **Polymers of comparable equivalent weights**



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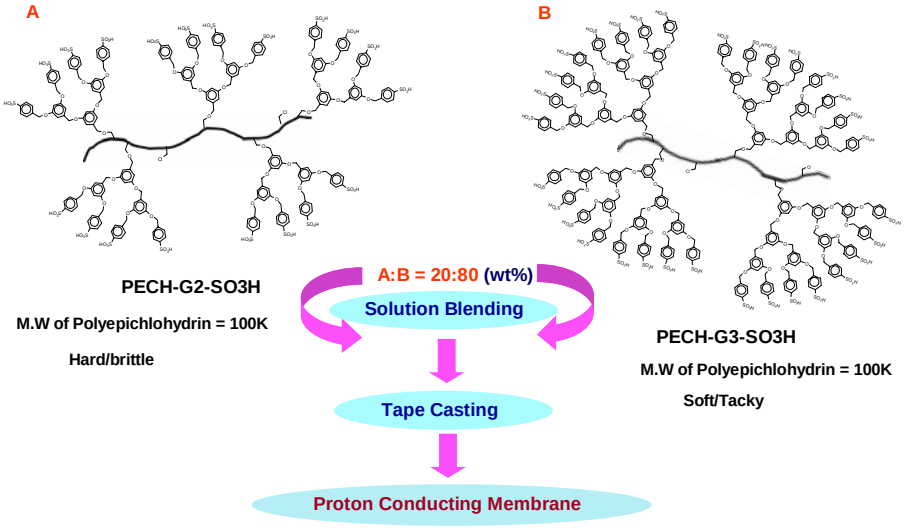
G2 & G3 dendronized PECHs were blended to allow film formation



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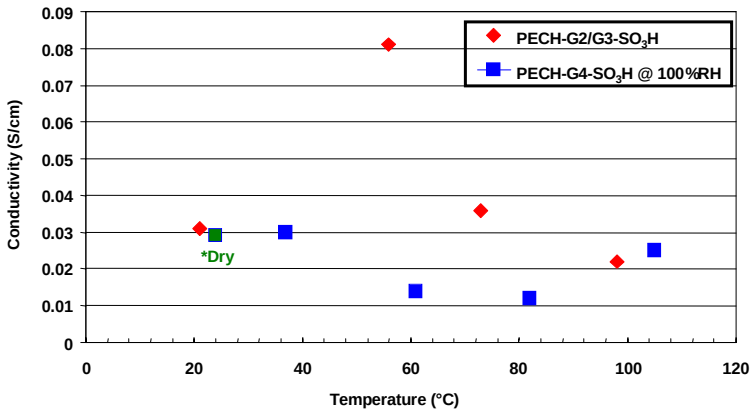
Conductivity (S/cm) of Sulfonated Dendronized PECHs

PECH-G2/G3-SO_3H (20/80)
PECH-G2-SO_3H: 215 G2 units/backbone
PECH-G3-SO_3H: 130 G3 units/backbone
Gas humidifier temperature = 61°C

PECH-G4-SO_3H
Acid functionality not yet determined



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Conclusions

- Sulfonated dendritic blocks conduct protons without external humidification
- Sulfonated dendritic blocks were attached to polyepichlorohydrin to obtain water insoluble proton-conducting membranes
- Dendronized polymers are thermally and oxidatively stable up to 150°C and retain nearly 30% more moisture than Nafion under low RH
- Encouraging conductivity data have been obtained for dendronized polymers at low humidity levels during initial phase of evaluation

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Acknowledgments

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