Materials Research Society
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ADVANCES IN POLY(PHENYLENE)-BASED ANION-EXCHANGE MEMBRANES FOR ALKALINE ELECTROLYSIS CELLS

Michael Hibbs[1] and Cy Fujimoto[2]

[1]Sandia National Laboratories
Microsystem Packaging & Polymer Processing Department
Albuquerque, New Mexico 87185

[2]Sandia National Laboratories
Organic Materials Science Department
Albuquerque, New Mexico 87185

National Nuclear Security Administration

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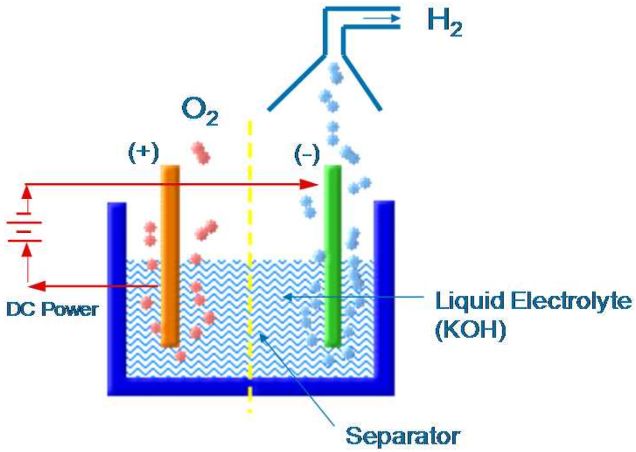
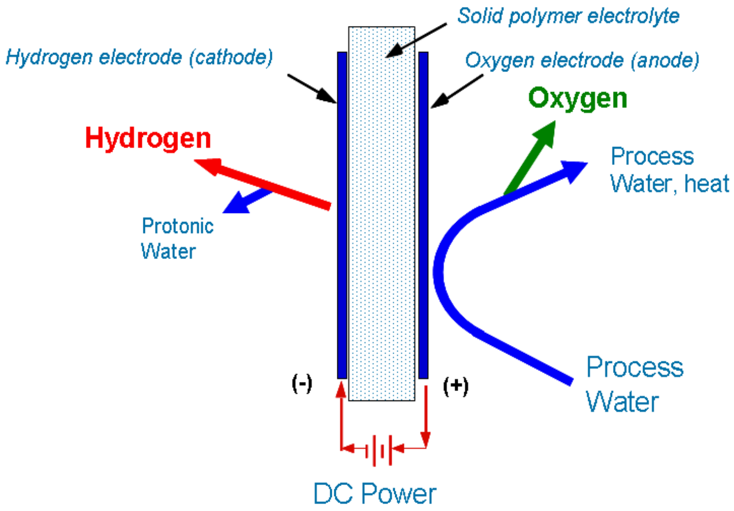
Alkaline Electrolysis Cell Configurations





Liquid electrolyte Cell **Membrane-based cell (PEM or AEM)**

- Commercialized systems are either liquid KOH or PEM-based.
- Liquid electrolyte systems contain corrosive solutions (handling and materials costs) and porous separators (gas crossover and high resistance across gap)
- PEM systems require platinum group metal catalyst such as iridium oxide, whereas alkaline systems electrolysis can be conducted with Ni or Ag.
- An anion-exchange membrane based system would provide the advantages of both alkaline liquid electrolyte and PEM systems.

Membrane Issues

There is no commercial standard AEM (such as Nafion® for PEM).

1. Backbone stability
   - Membrane must maintain mechanical integrity for up to 5000h at high pH.
   - Must be stable to MEA fabrication (hot and dry)
2. Stable cationic groups
   - Quaternary ammonium groups can be attacked by OH^-.
3. Conductivity
   - OH^- inherently 2-3x less mobile than H^+
   - Identity of anions (OH^-/CO_3^{2-}/HCO_3^-)
   - Conductivity at low RH
4. Water swelling
   - Physical stress on cell hardware due to expansion/compression.
   - Delamination of electrodes from membrane.

[1]From DOE Alkaline Membrane Fuel Cell Workshop, May 8-9 2011.

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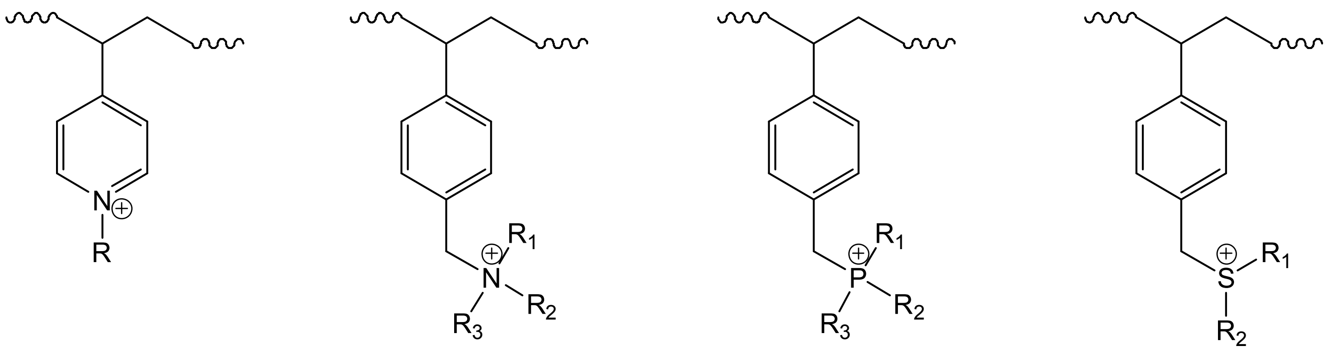
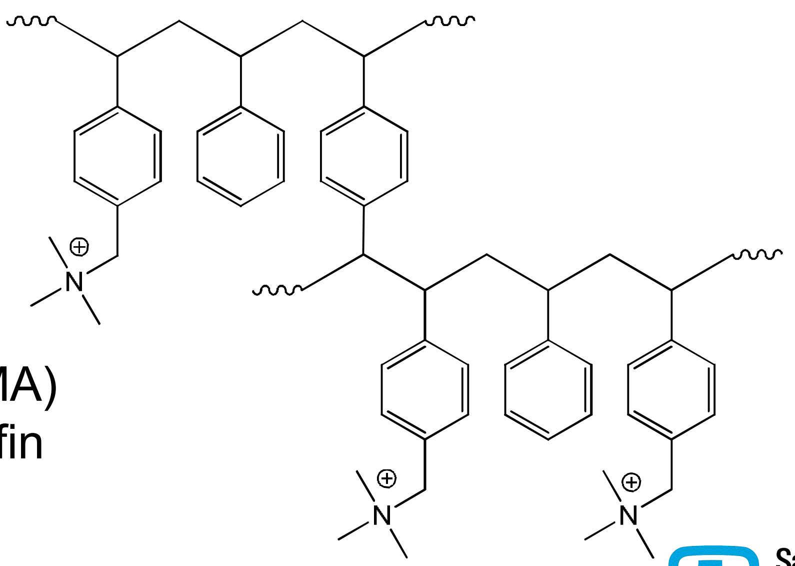
Cations on Anion Exchange Membranes (AEMs)

Typical functional groups with fixed positive charges in AEMs:



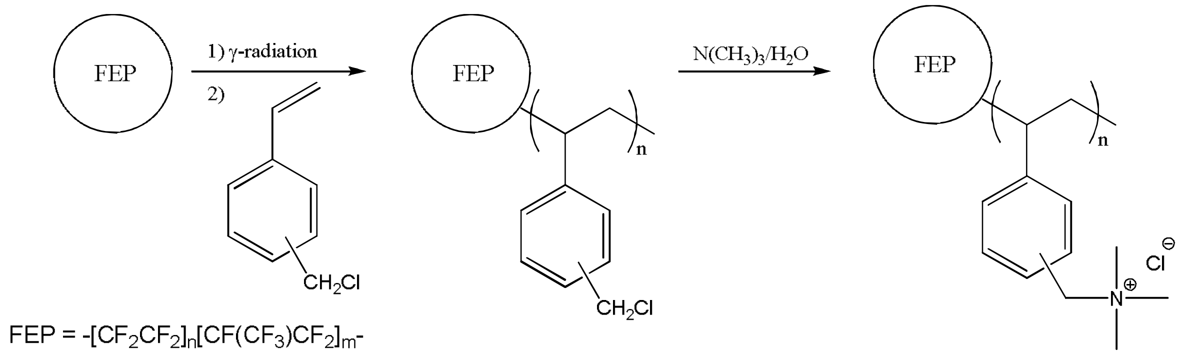
A Typical Commercially-available AEM:



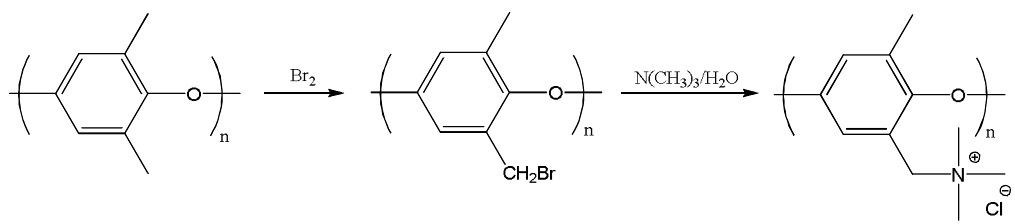
- Crosslinked polystyrene with benzyl trimethylammonium groups (BTMA)
- Typically blended with PVC or a polyolefin
- Cast on fabric support
- Used for electrodialysis

AEMs: The State of the Art

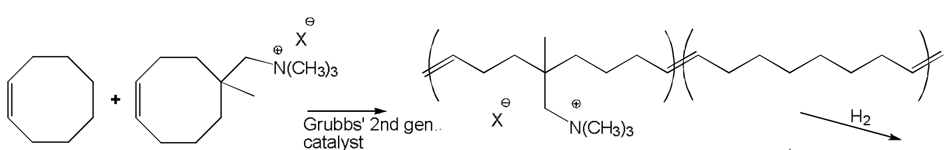
Radiation-grafting of functionalized poly(styrene) onto fluorinated polymers[1]:

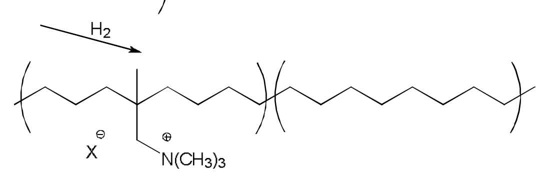


Bromination of poly(2,6-dimethyl-1,4-phenylene oxide)[2]:



Poly(ethylene)-based AEM from ROMP[3]:





[1]Danks, T. N.; Slade, R. T. C.; Varcoe, J. R. *J. Mater. Chem.*, **2003**, 13, 712.
[2]Wu, Y.; Wu, C.; Xu, T.; Lin, X.; Fu, Y. *J. Membr. Sci.*, **2009**, 338, 51.
[3]Kostalik, H. A.; Clark, T. J.; Robertson, N. J.; Mutolo, P. F.; Longo, J. M.; Abruna, H. D.; Coates, G. W. Macromol., **2010**, 43, 7147.

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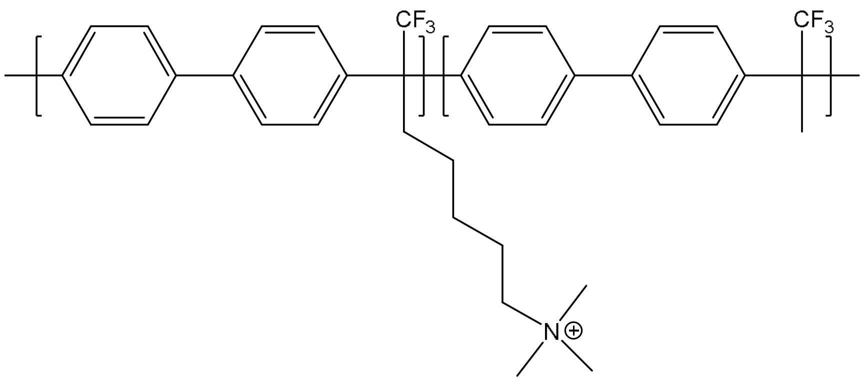
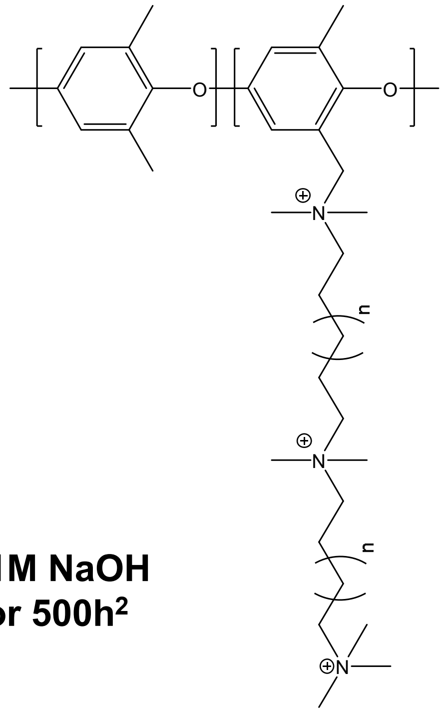
AEMs: The State of the Art

Poly(biphenylene alkylene) with tethered ammonium groups[1]



Stable in 1M NaOH at 80 °C for 700h[1]

Poly(phenylene oxide) with multication sidechains[2]

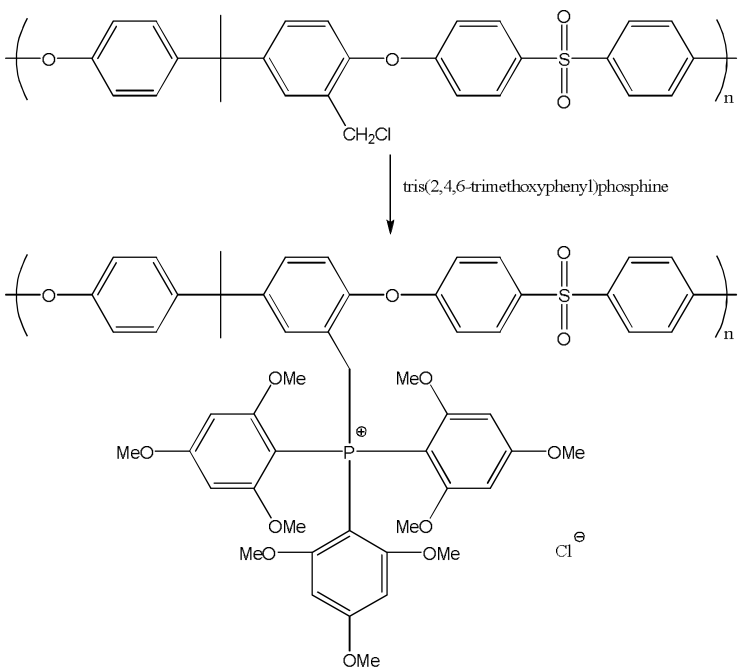


Stable in 1M NaOH at 80 °C for 500h[2]

[1]Lee, W.-H.; Kim, Y.S.; Bae, C. *ACS Macro Lett.* **2015**, 4, 814.
[2]Zhu, L.; Pan, J.; Wang, Y.; Han, J.; Zhuang, L.; Hickner, M.A. *Macromol.* **2016**, 49, 815.

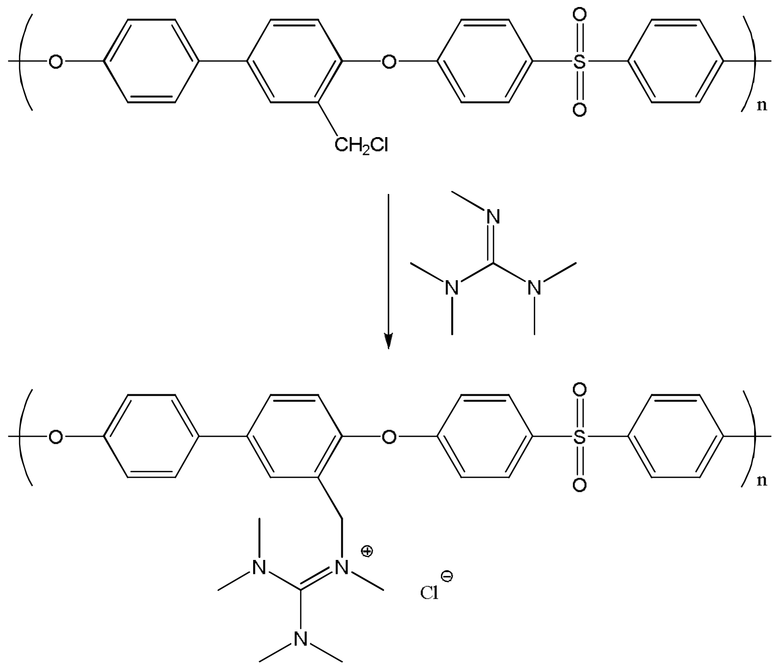
Alternative Cationic Groups

Poly(sulfone) with benzyltris(2,4,6-trimethoxyphenyl) phosphonium groups[1]



Stable in 1M KOH at 60 °C for 48h[1]

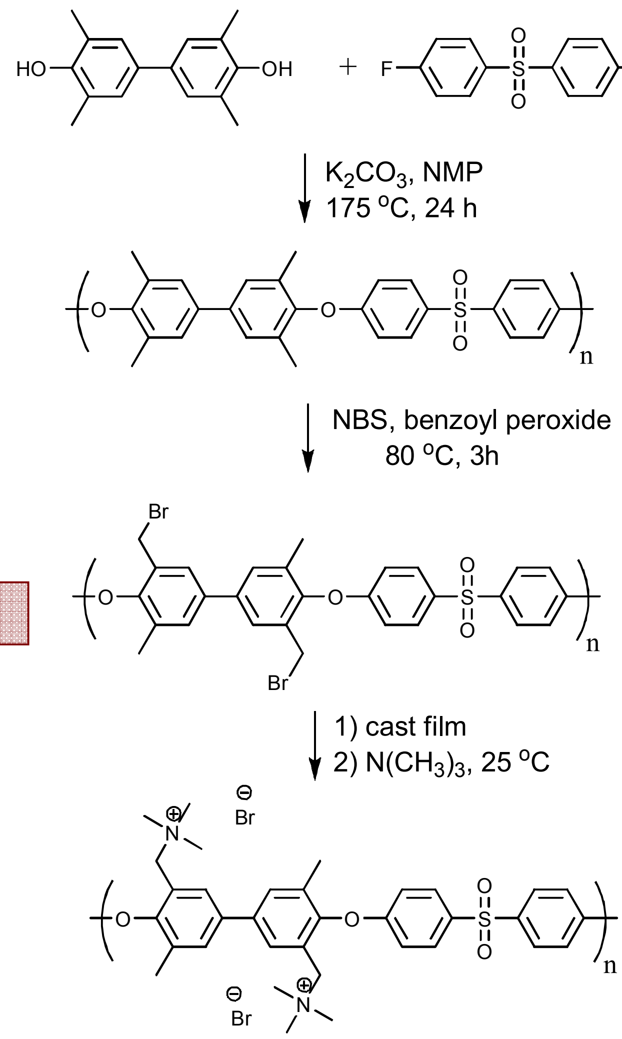
Poly(sulfone) with benzylpentamethyl guanadinium groups[2]



Stable in 1M KOH at 60 °C for 48h[2]

[1]Gu, S.; Cai, R.; Luo, T.; Chen, Z.; Sun, M.; Liu, Y.; He, G.; Yan, Y. *Angew. Chem. Int. Ed.*, **2009**, 48, 1.
[2]Wang, J.; Li, S.; Zhang, S. *Macromol*. **2010**, 43, 3890.

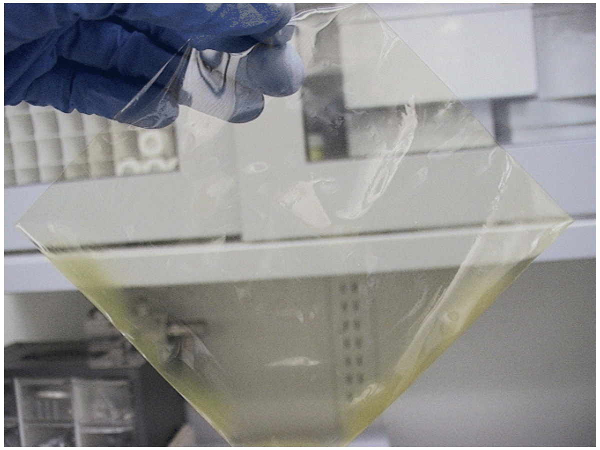
AEMs made at Sandia: Poly(sulfone)-Based Membranes



Radel-type polysulfone

M_w = 80-100k

ATMPS



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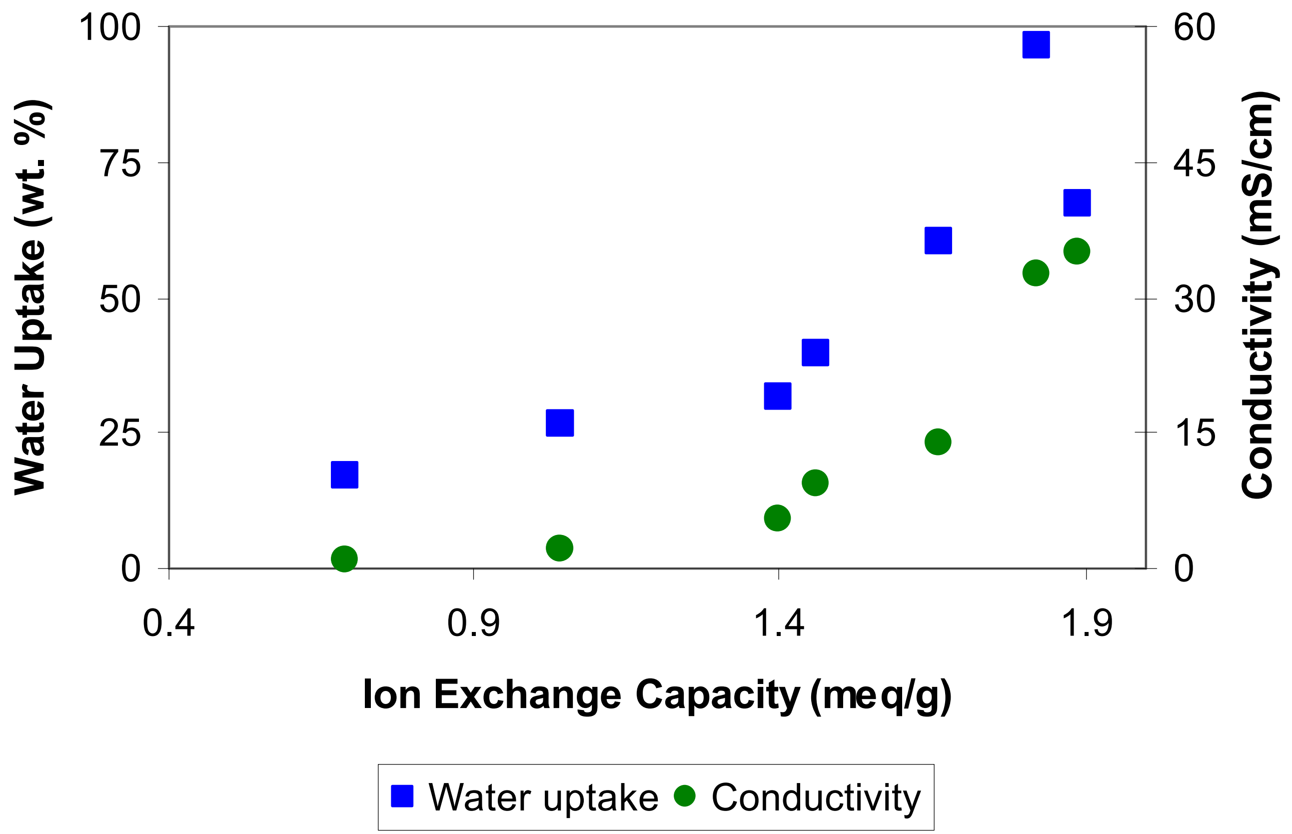
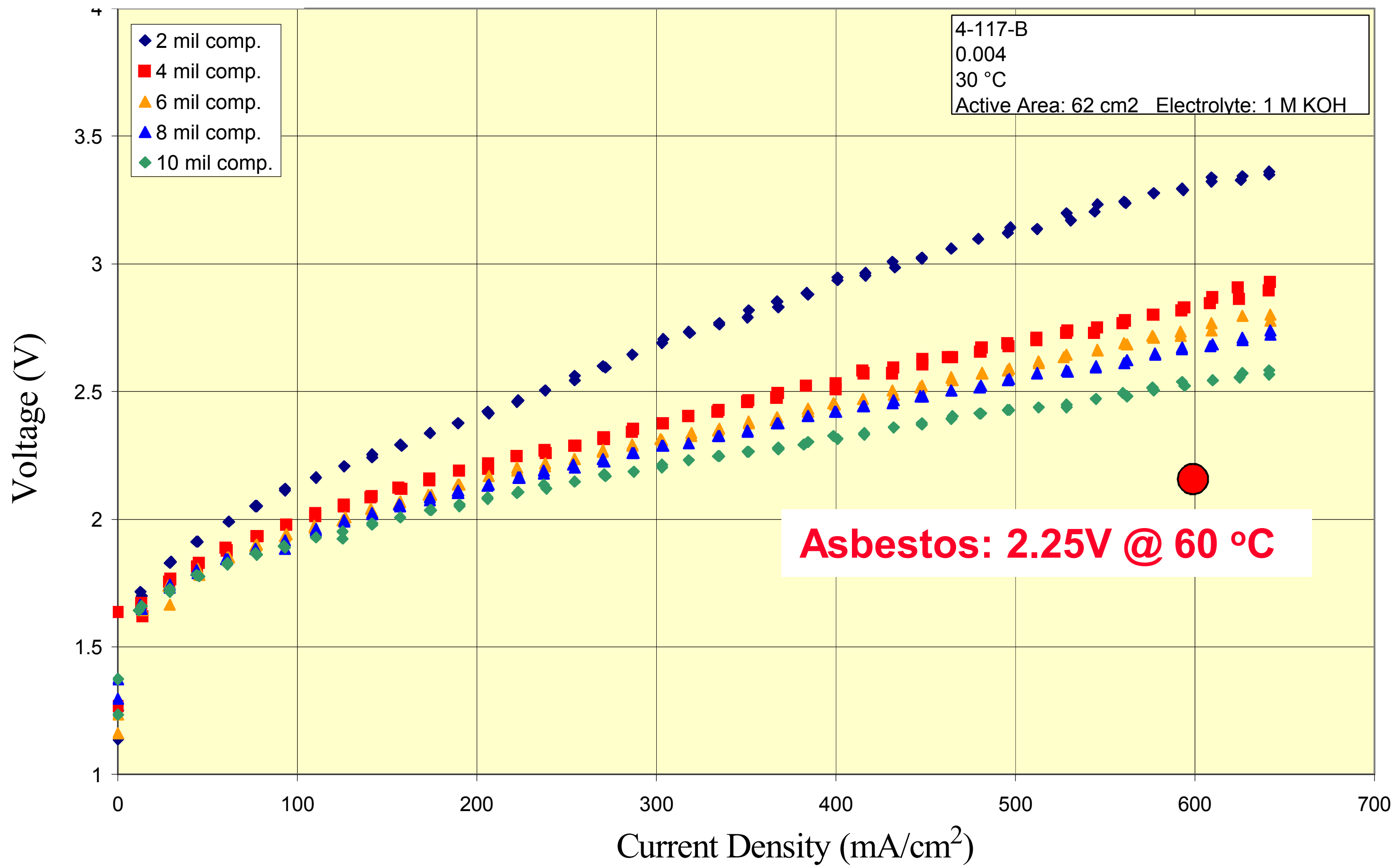
Polysulfone-based AEM Properties



Conductivities measured by impedance spectroscopy with a two-point probe immersed in water at room temperature.

Electrolysis Data: Cell Compression



Cell conditions: 30 °C, 1M KOH, foam Ni electrodes, active area = 62 cm^2 current swept from 0 – 40 Amps,

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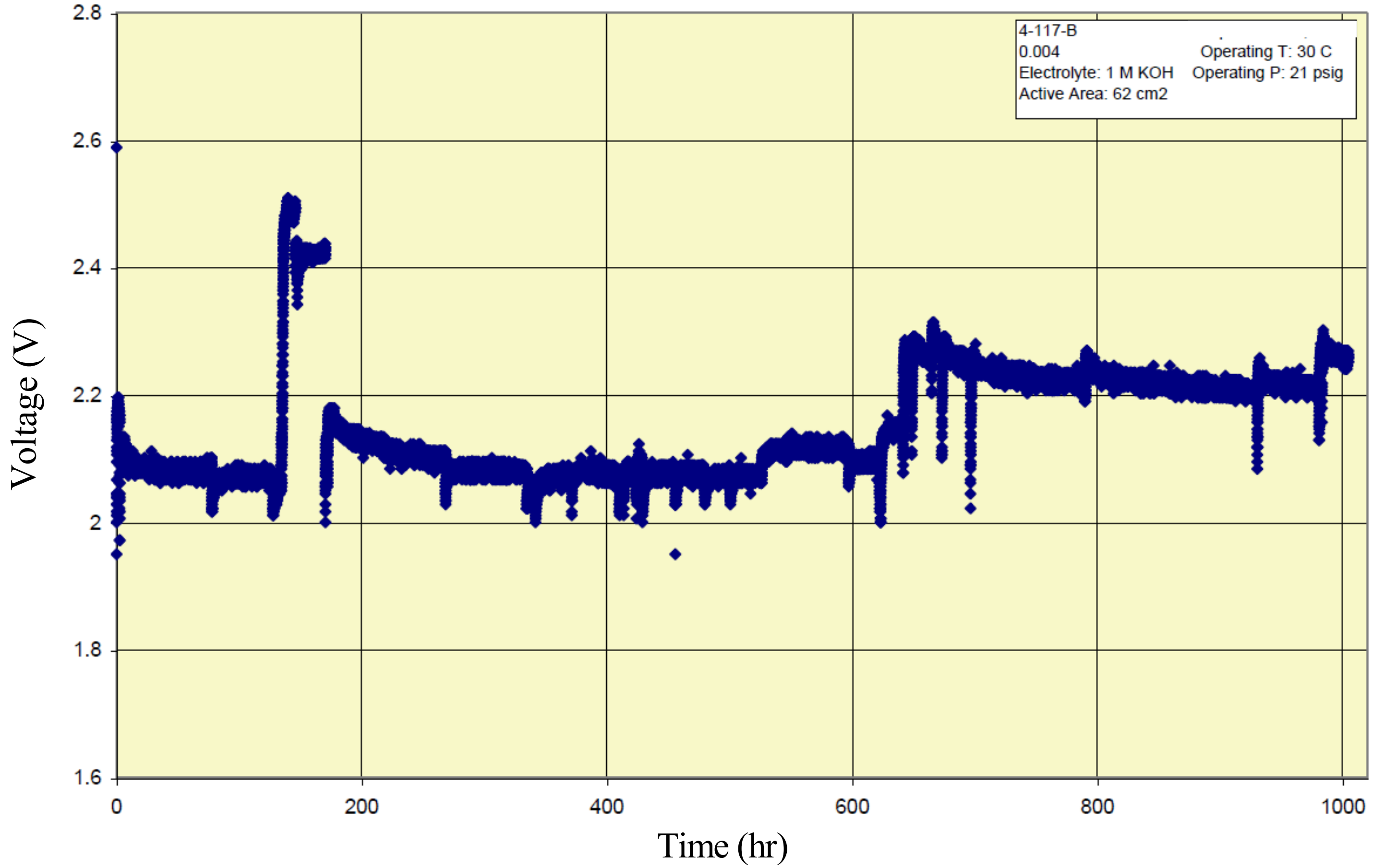
Electrolysis Data: Lifetime Test



Cell conditions: 30 °C, 1M KOH, 10 Amp. Current, active area = 62 cm^2

In a similar test in 25% KOH, membrane failed after 24 hrs.

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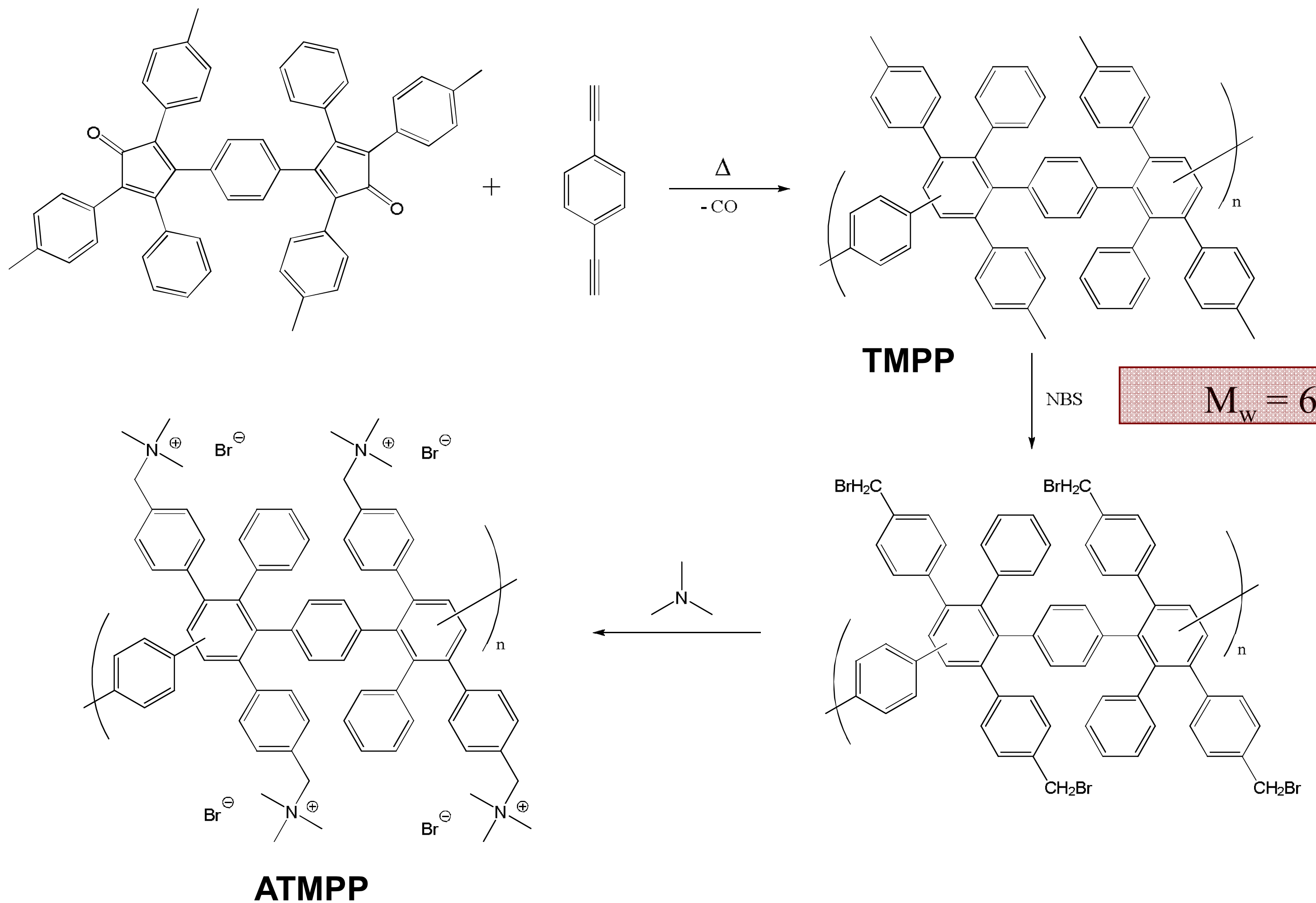
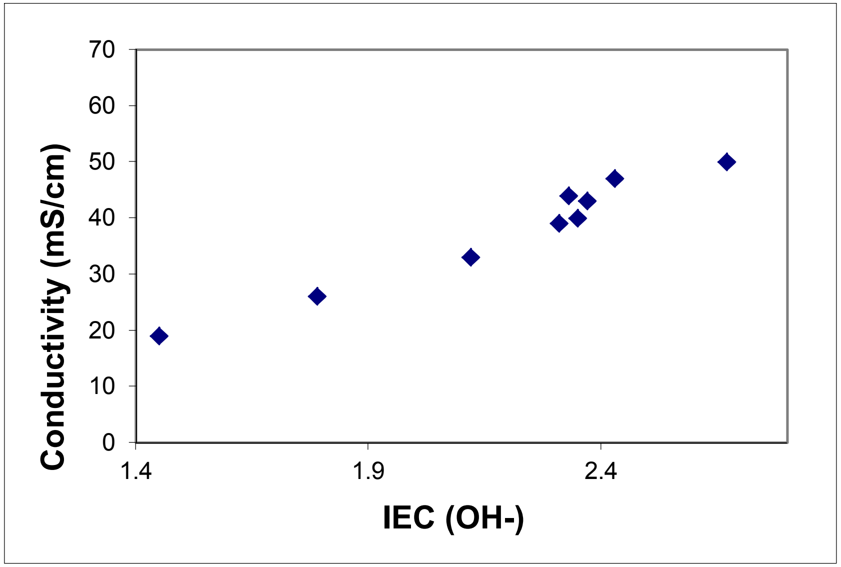
AEMs made at Sandia: Poly(phenylene)-Based Membranes

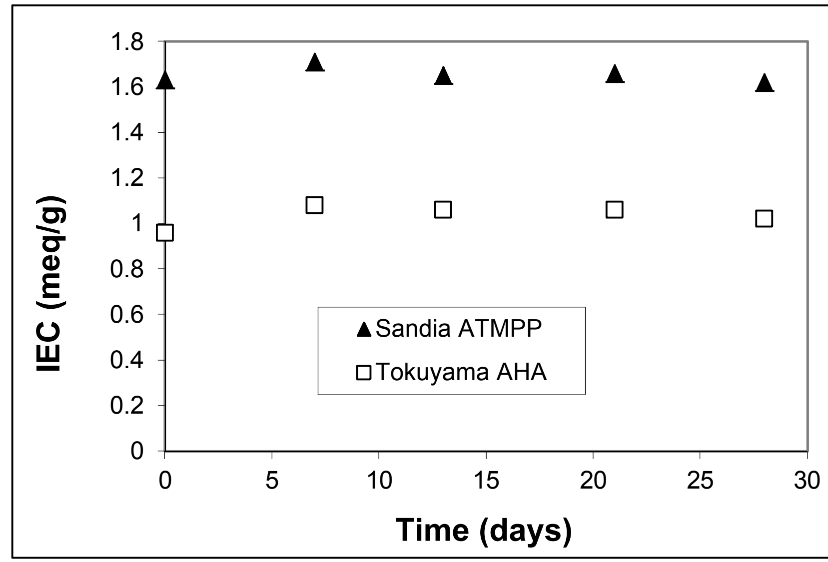


M_w = 60-80k

Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *Macromol*. **2009**, 42, 8316.

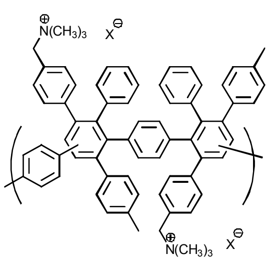
ATMPP Properties & Stability



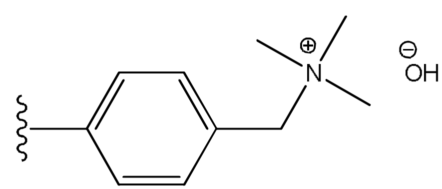


- Hydroxide conductivities were measured in liquid water at room temperature.

- Test conditions: 4M NaOH (aqueous), 60 ^{o}C, no stirring.
- AHA is “base stable” electrodialysis membrane – crosslinked polystyrene.
- Both membranes have BTMA cations.



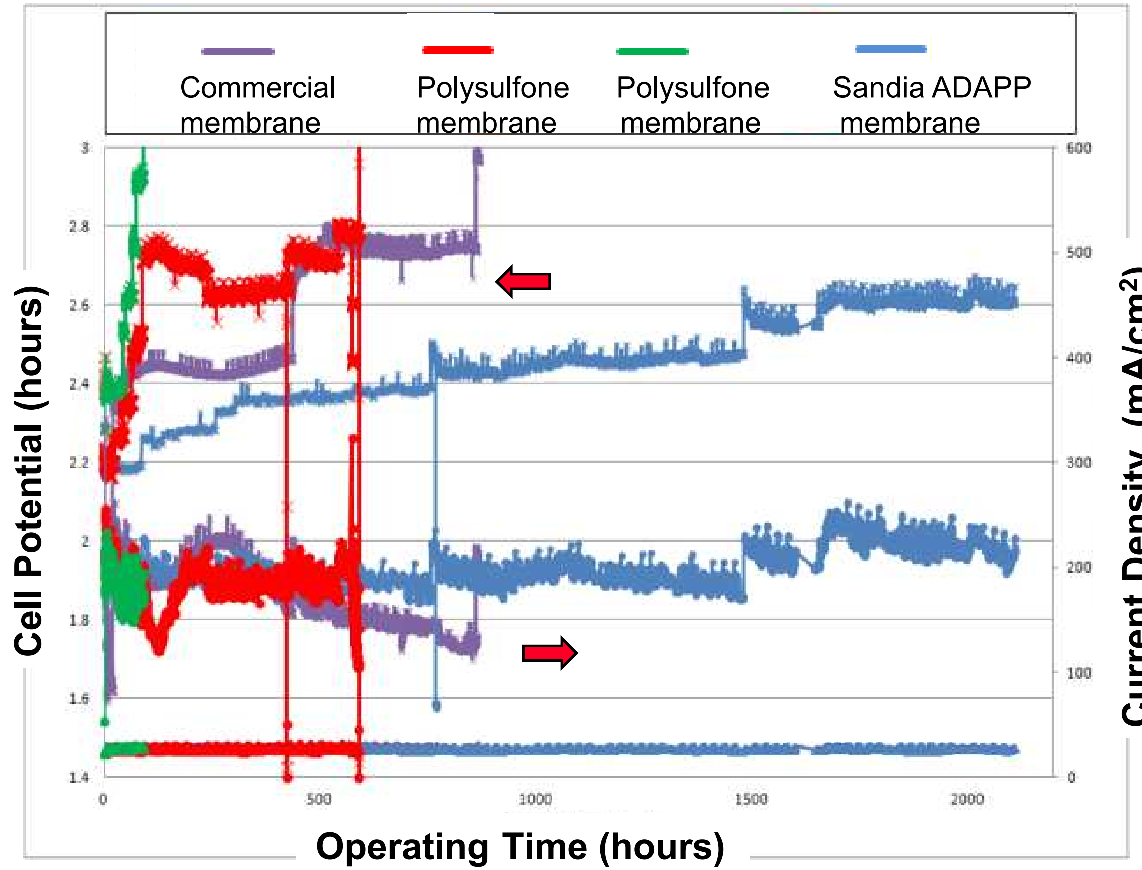
ATMPP
poly(phenylene)



Electrolysis Testing at Proton OnSite

Durability test at 27 ^{o}C with PGM catalysts and no added electrolyte

- Established test bed for multiple materials collaborators
- Failure criterion = 3.0 V.
- Achieved 2000 hrs of stable operation using ADAPP membrane + ADAPP ionomer.
- Need to improve voltage stability.



PROTON ON SITE

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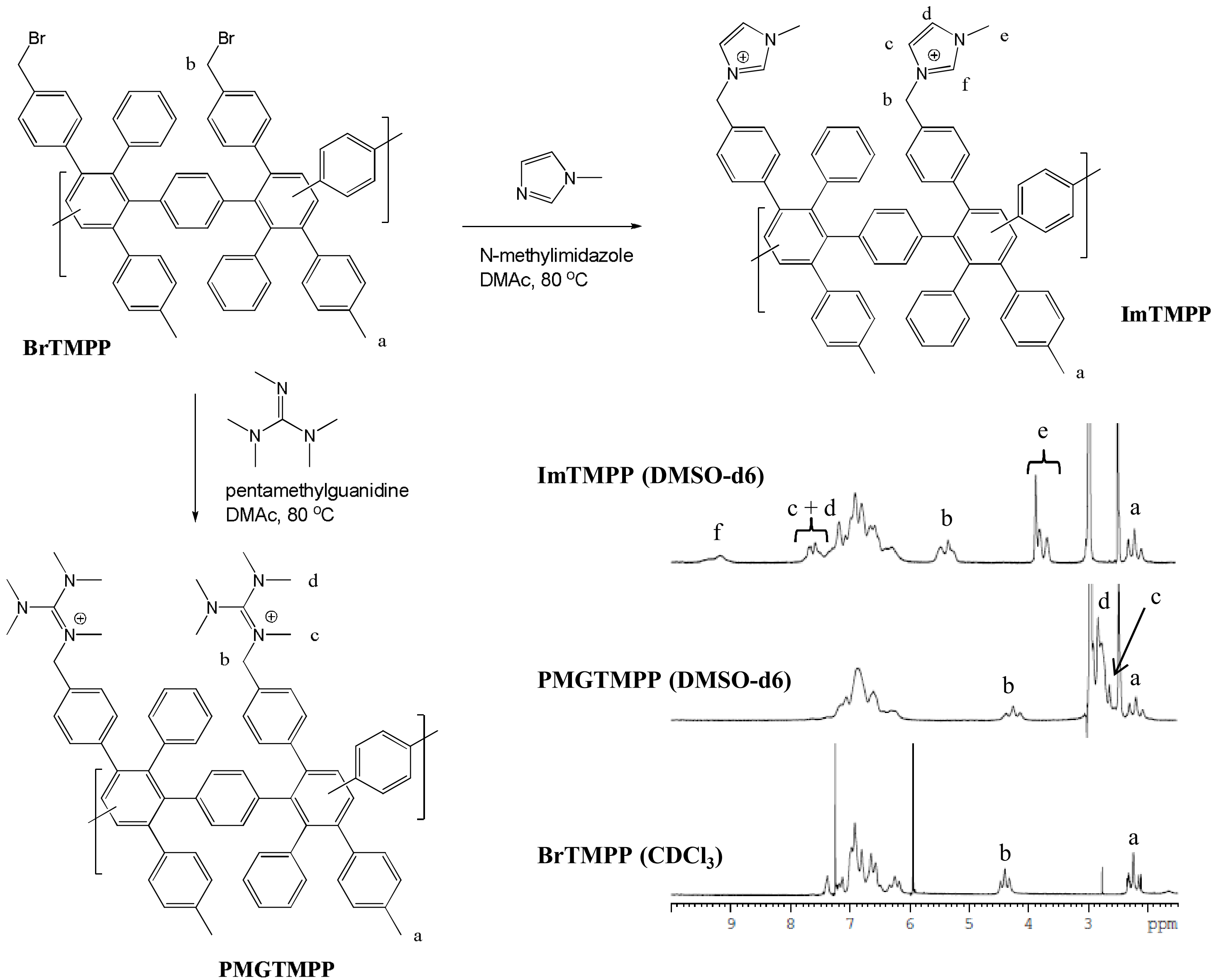
Resonance-Stabilized Cations



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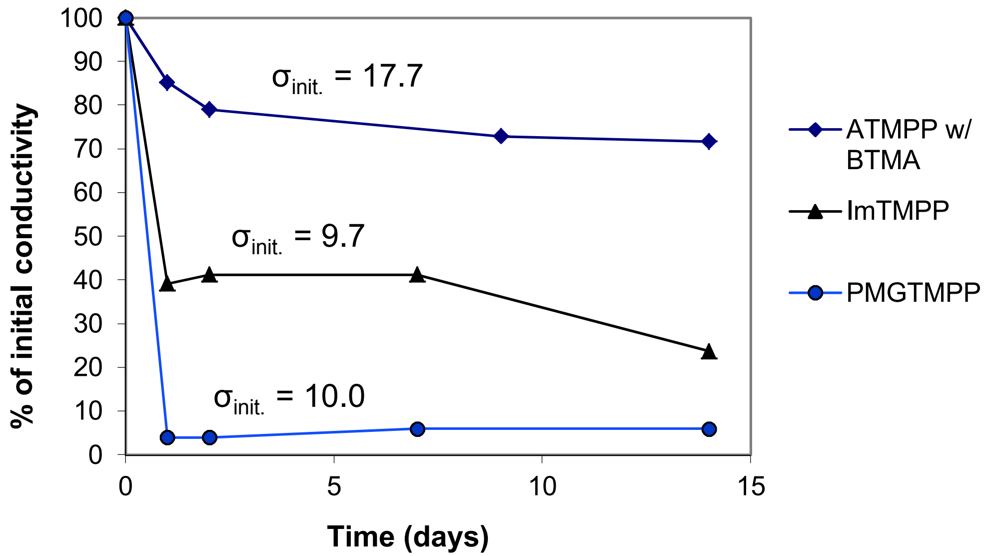
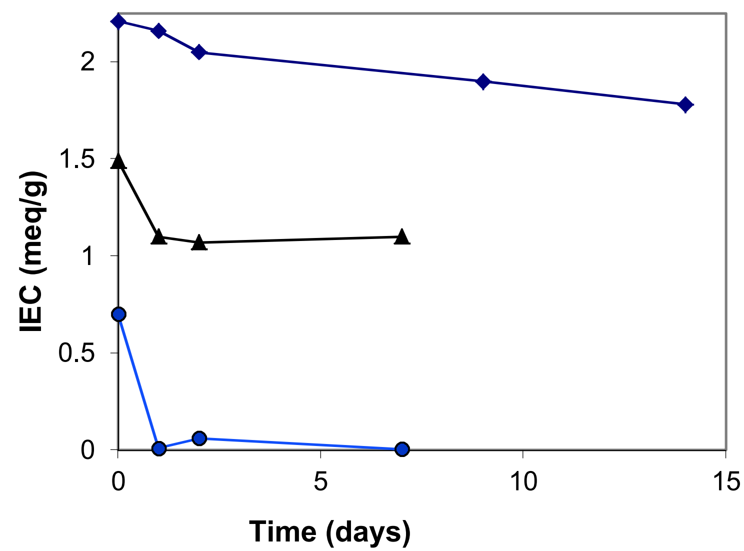
KOH Stability Test
Resonance-Stabilized Cations

Test conditions: Membranes immersed in 4M KOH at 90 °C.





- Conductivities were measured with membranes in Cl^- form in 25 °C water.
- Hydroxide conductivity is generally 2-3x higher than chloride conductivity.
- Benzyl imidazolium and benzyl guanidinium cations are much less stable than BTMA.

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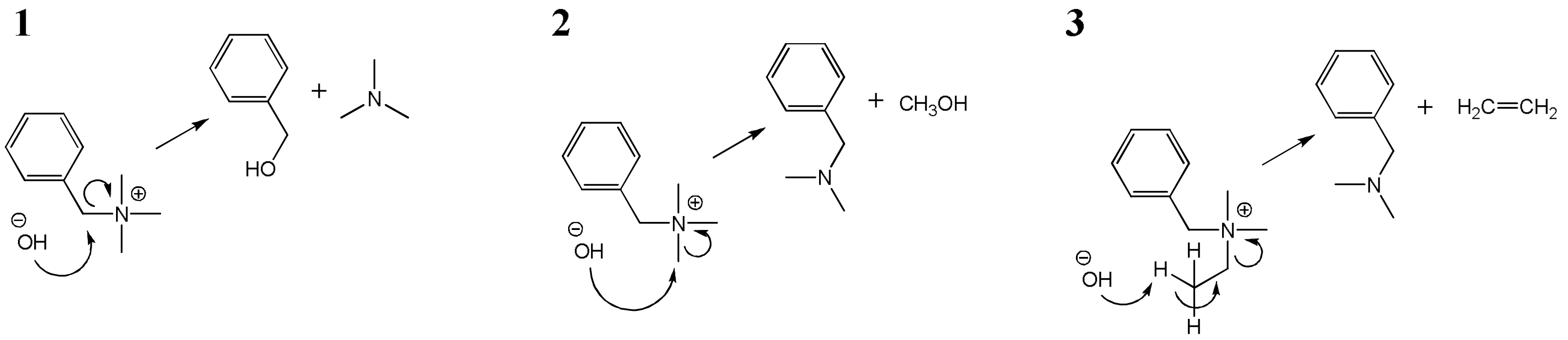
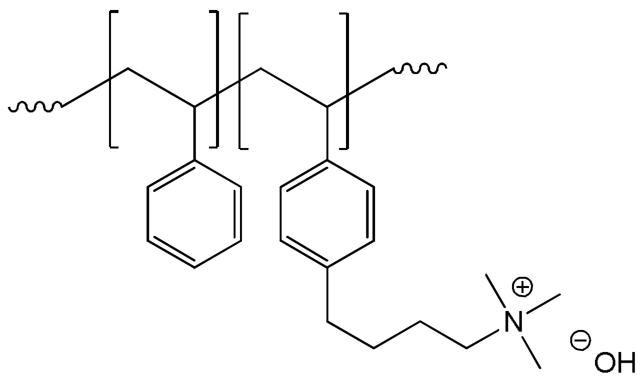
Stability of Alkyl Trimethylammonium Groups

Three Degradation Mechanisms:



Alkylene spacers can increase stability[1]

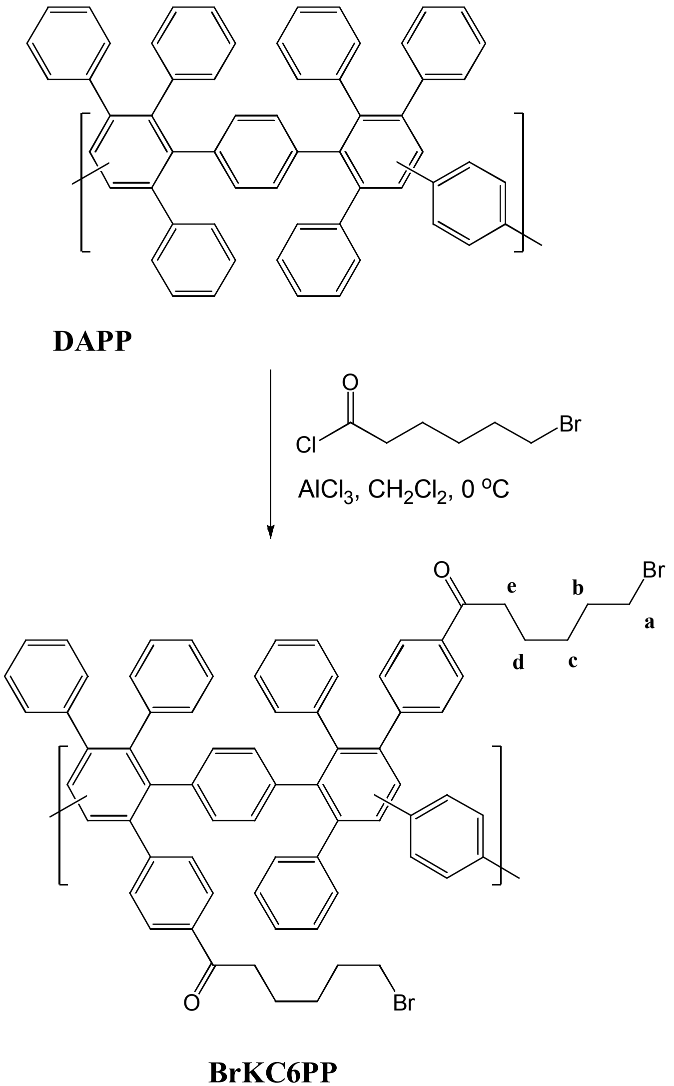


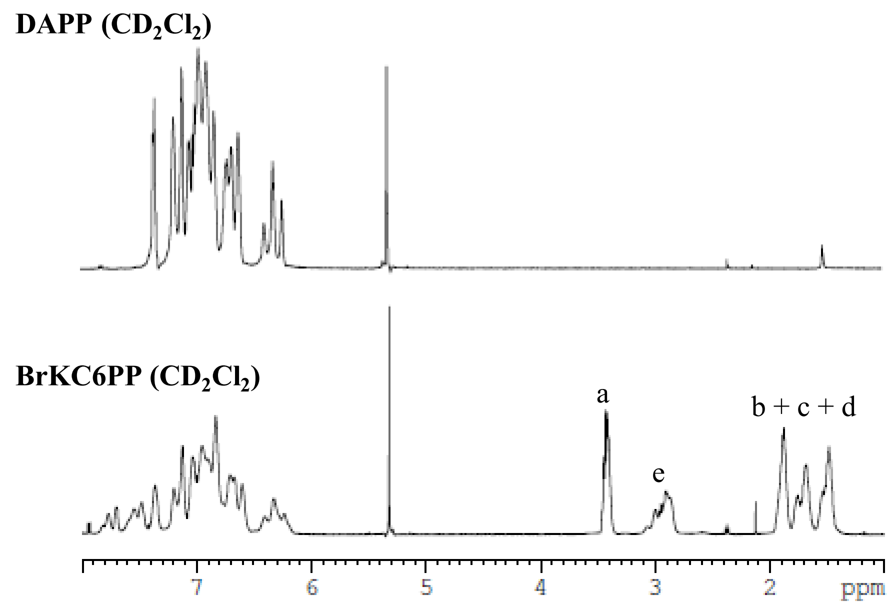
Tested for 30 days in 100 °C water (OH^- form):

	IEC (after/before)
Benzyltrimethylammonium	**79 %**
Tetramethylene spacer	**92 %**

[1] Tomoi, M.; Yamaguchi, K.; Ando, R.; Kantake, Y.; Aosaki, Y.; Kubota, H. *J. Appl. Polym. Sci*. **1997**, *64*, 1161.

Addition of Side Chains to Poly(phenylene)





Hibbs, M. R. *J. Polym. Sci. Part B, Polym. Phys*. **2013**, 51, 1736.

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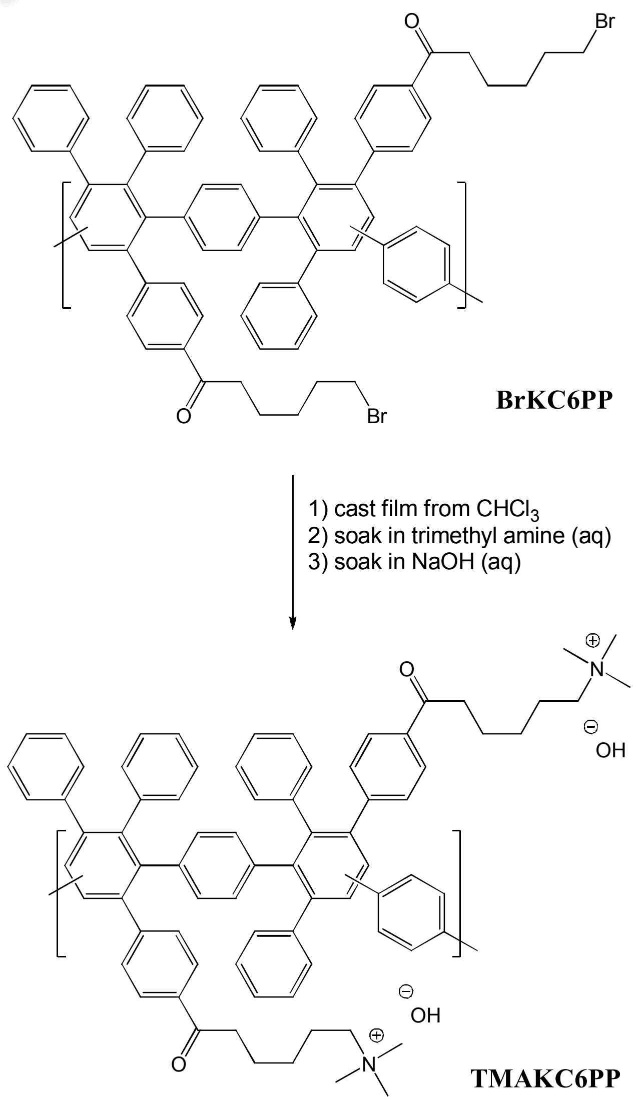
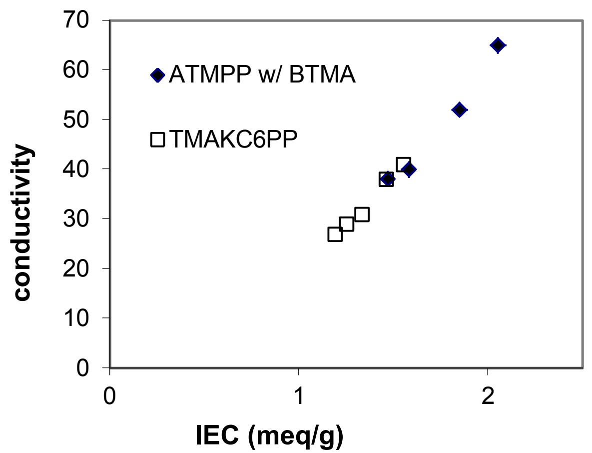
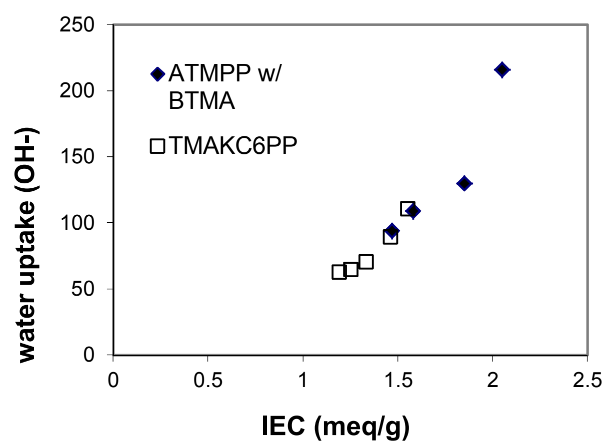
Poly(phenylene) with Alkyltrimethylammonium Groups







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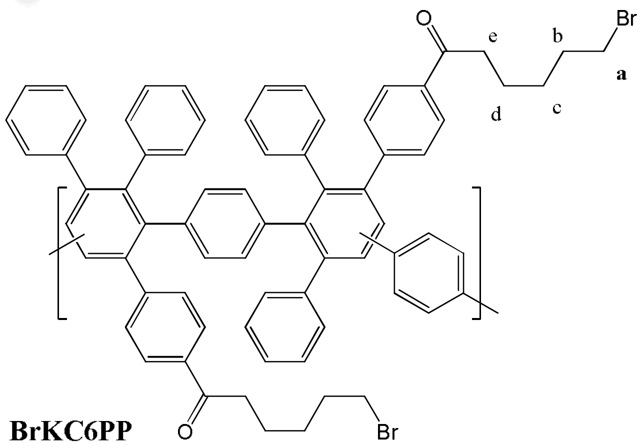
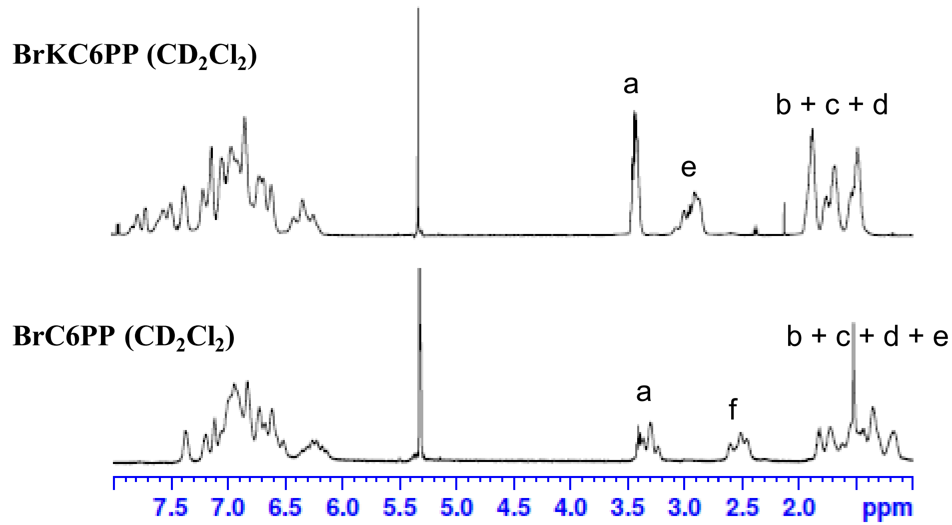
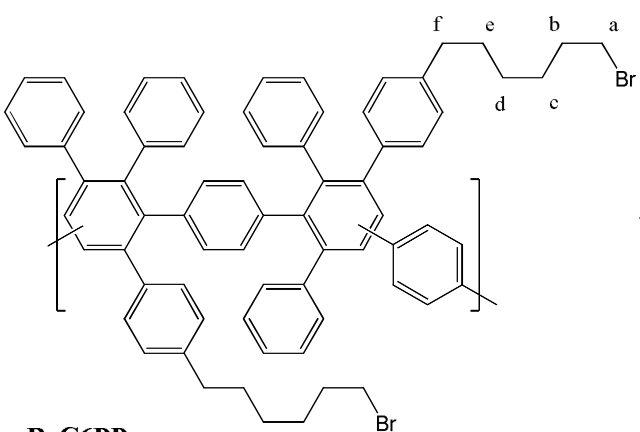
Poly(phenylene) with Alkyl Side Chains without Ketone



BrKC6PP

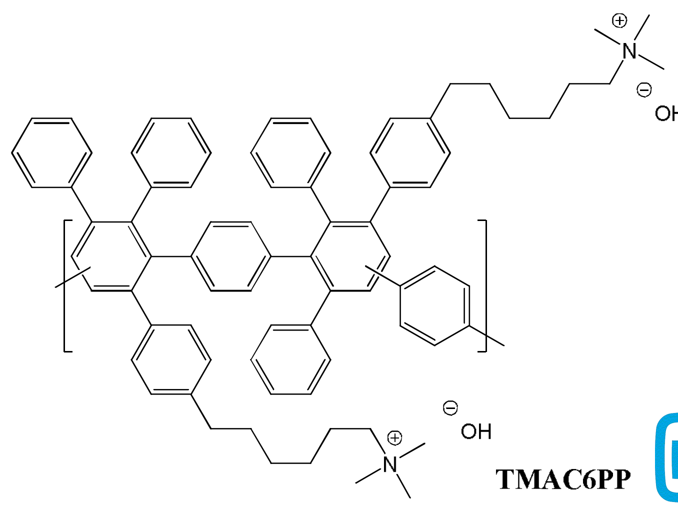


Et_3SiH, TFA, $CHCl_3$
reflux



BrC6PP

1) cast film from CHCl3
2) soak in trimethylamine (aq)
3) soak in NaOH (aq)



TMAC6PP

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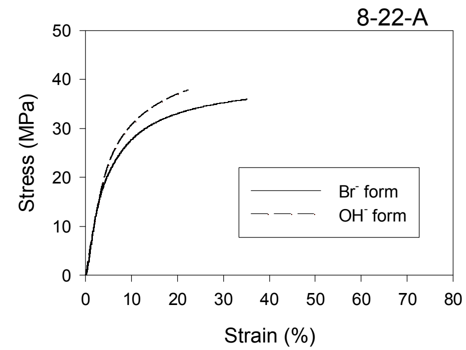
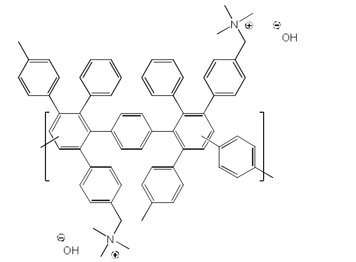
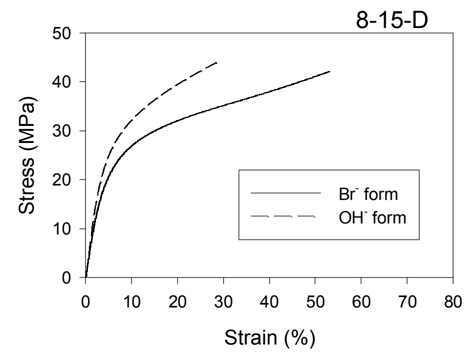
TMAC6PP Stress/Strain Testing

- AEMs with sidechains show better mechanical properties.
- With samples of similar molecular weights, TMAC6PP has over twice the elongation at break as ATMPP.
- Elasticity (lack of brittleness), especially when dry, is an important property for membrane-electrode assembly fabrication.
- This testing was performed at 50% relative humidity and 50 ^{o}C.

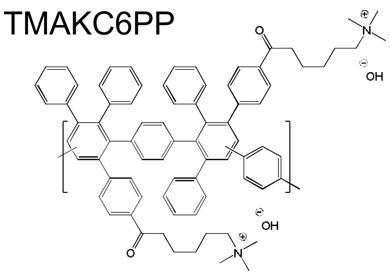


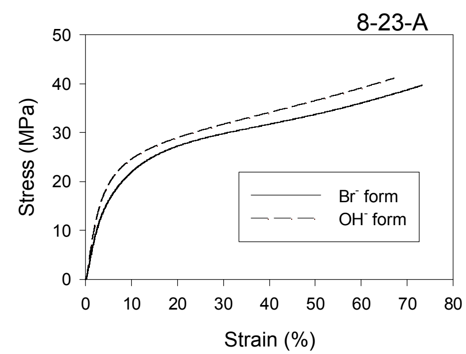
ATMPP



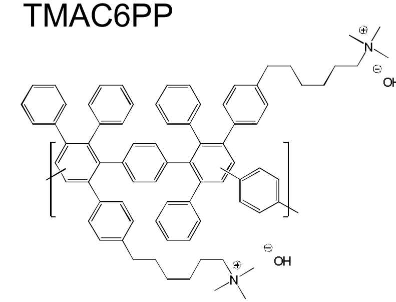


TMAKC6PP





TMAC6PP



Los Alamos NATIONAL LABORATORY

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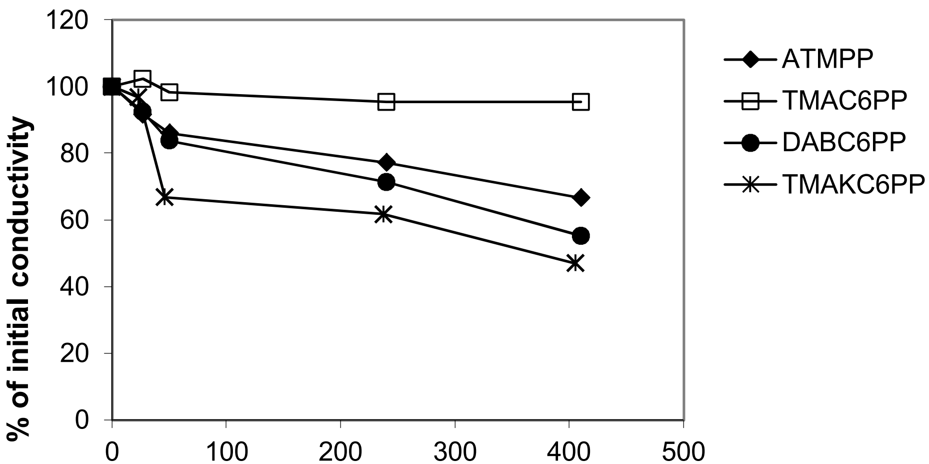
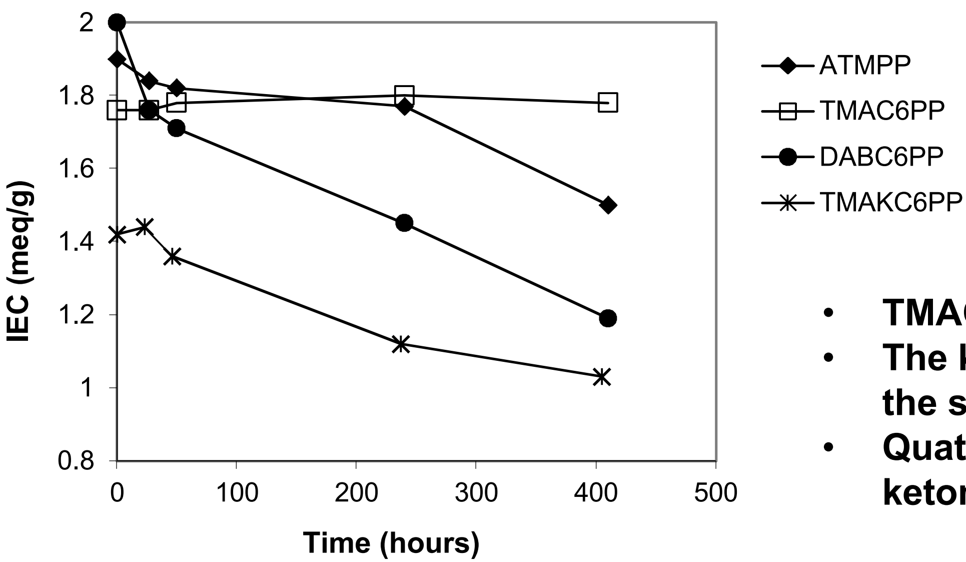
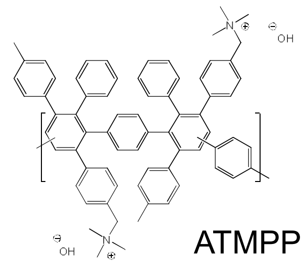
TMAC6PP Alkaline Stability

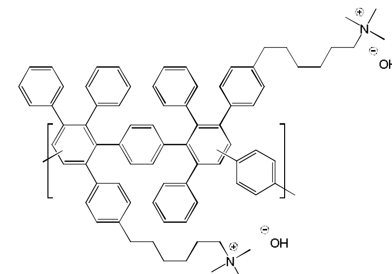
Test conditions: Membranes immersed in 4M KOH at 90 °C.



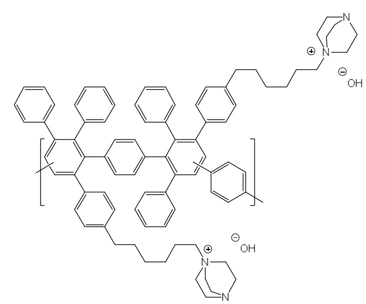




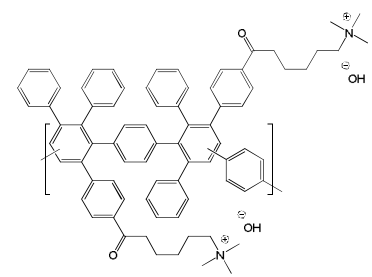
ATMPP



TMAC6PP



DABC6PP



TMAKC6PP

- **TMAC6PP shows the greatest stability in high pH test.**
- **The ketone adjacent to the phenyl ring destabilizes the side chains.**
- **Quaternized DABCO on hexyl sidechains with no ketone are less stable than BTMA.**

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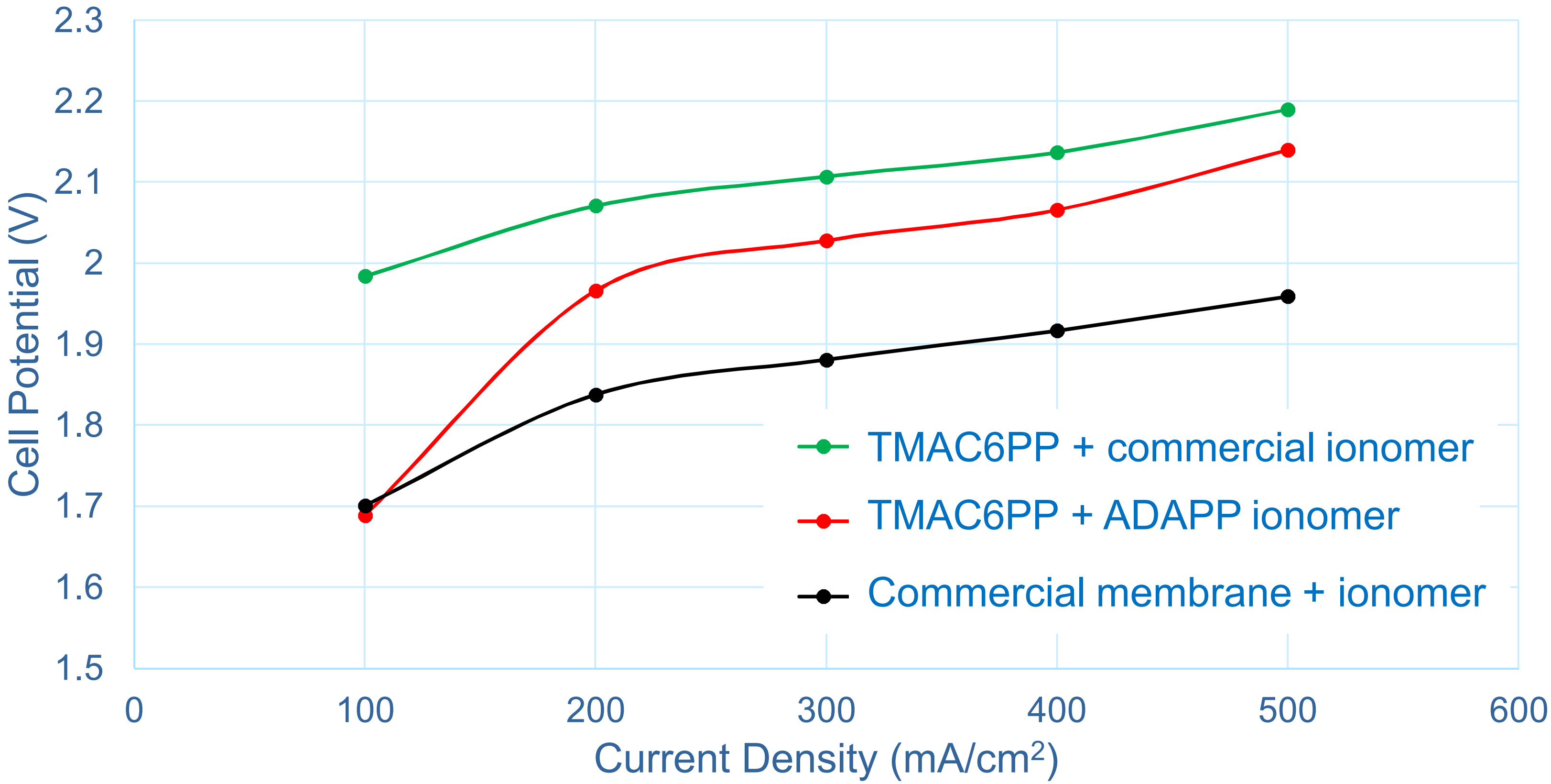
Electrolysis Testing at Proton OnSite

Initial polarization curves at 50 °C with PGM catalysts and no added electrolyte



Polarization curve ~200 mV above commercially available membrane baseline for both ionomer tests

PROTON ON SITE

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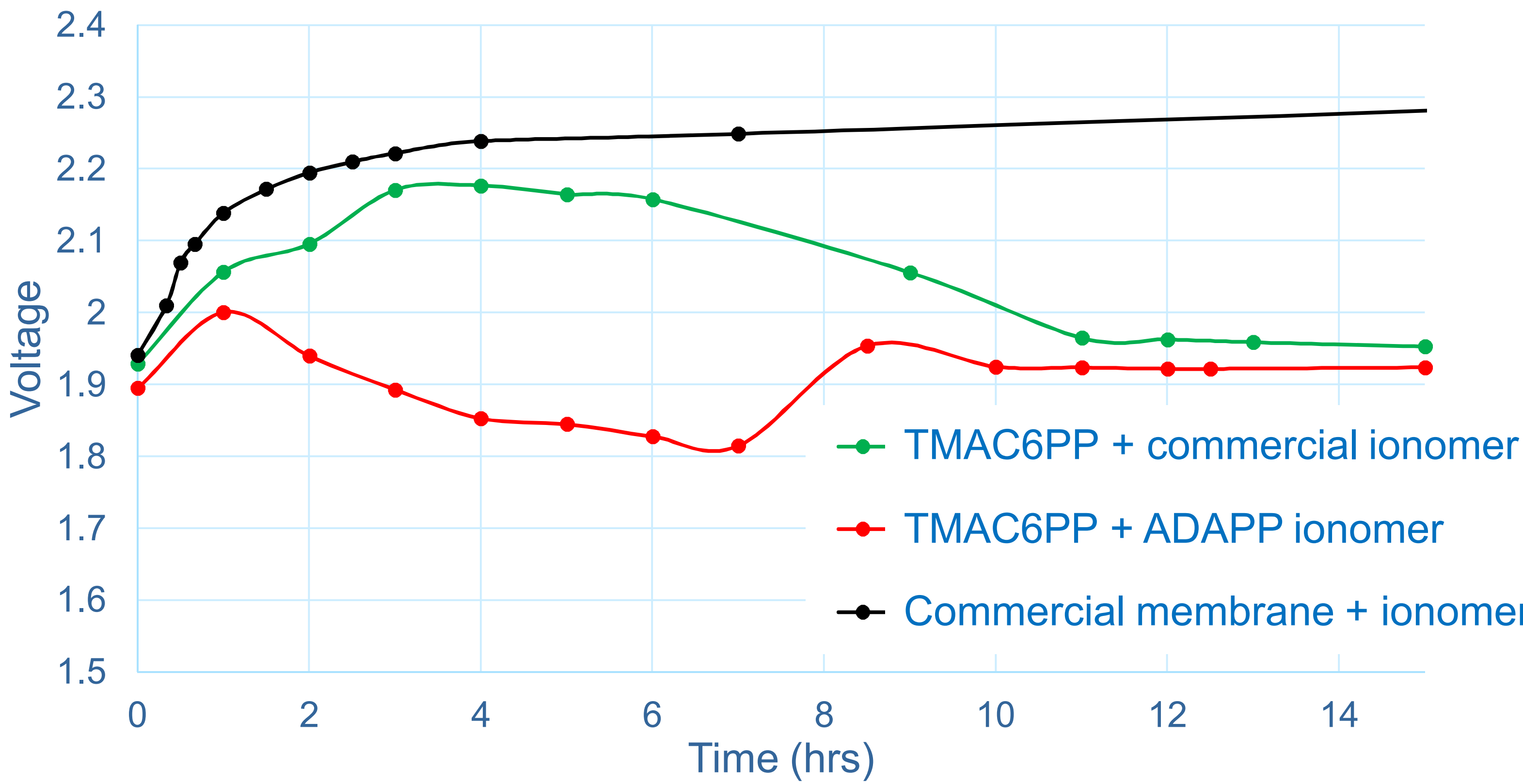
Electrolysis Testing at Proton OnSite

200 mA/cm^2 steady state performance at 50 ^oC with PGM catalysts and no added electrolyte



Steady state performance indicated better stability versus commercial material

Conclusions

- Sandia's polysulfone-based AEMs have shown stable 1000-hour performance in electrolysis cell with 1 M KOH.
- Polysulfone-based AEMs lack chemical stability above room temperature or at higher KOH concentrations.
- Operational stability (>2000 hours) can be achieved in electrolysis cells using polyphenylene-based membranes without added electrolyte.
- Resonance-stabilized cations (imidazolium and pentamethyl guanidinium) are less stable to alkaline degradation than BTMA cations.
- Trimethylammonium cations on alkyl sidechains have better stability than BTMA despite the possibility of Hoffmann elimination reactions.
- Further work is needed to develop ionomers to integrate non-PGM catalysts with polyphenyene-based electrolysis systems.

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Kathy Ayers
Chris Capuano
Morgan George

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Kwan-Soo Lee

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US DOE EERE Fuel Cell Technologies Office
Sandia National Laboratories Laboratory Directed Research and Development (LDRD) program

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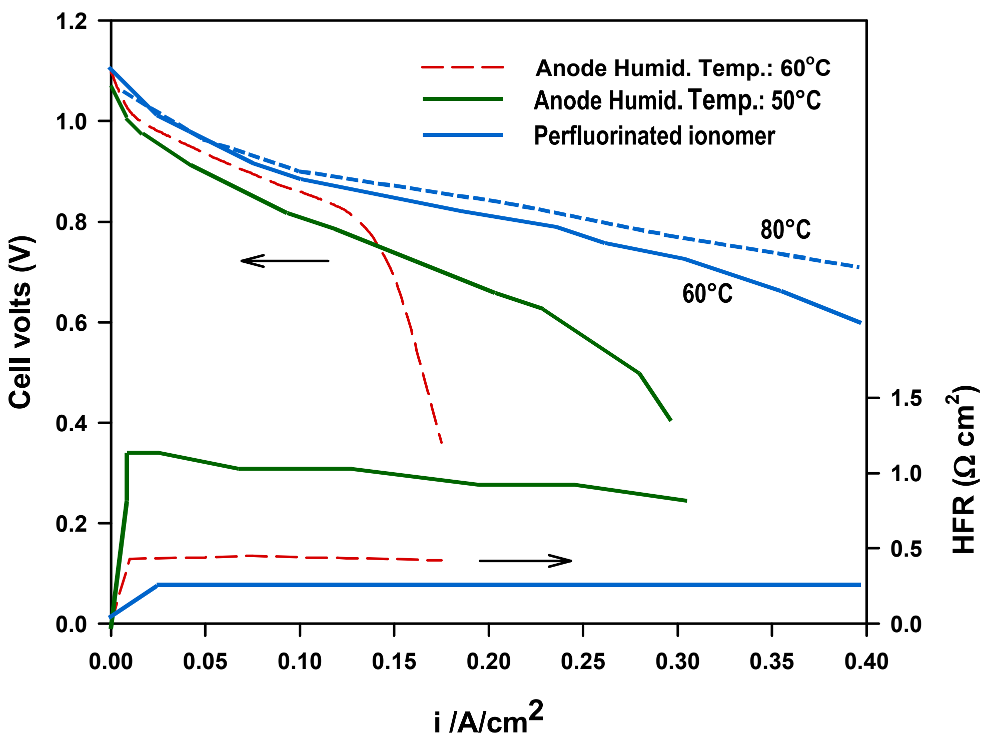
H_2/O_2 Performance of Alkaline Membrane Fuel Cells



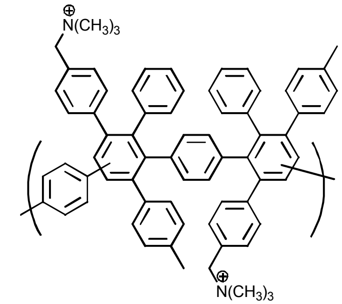
Catalyst: Pt black (3 mg/cm²), Cell temp. 60° C, Cathode humidification: 60° C, back pressure: 30 psig, high stoic. Catalyst: ionomer weight composition (9:1, not optimized); MEAs were prepared from direct painting.

Membrane/ionomer

IEC = 1.8 meq./g

σ= 55 mS/cm

Thickness: 50 μm



aminated **TMPP**

Fully hydrated conditions (anode humid. temp.: 60°C)

→ Mass transport issue due to flooding

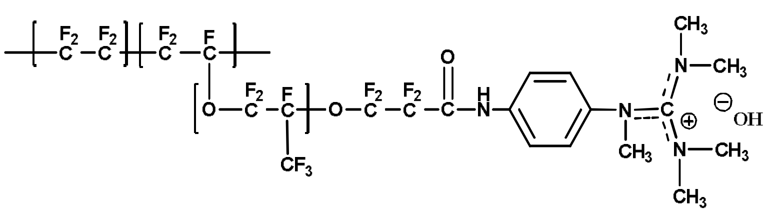
→ Possibly poor cation – catalyst structure

Partial hydrated conditions (anode humid. temp.: 50°C)

→ Improved performance with removing mass transport issue

→ Poor membrane hydration/remaining issue with cation

Ionomer (IEC = 0.74 meq./g, σ = 20 mS/cm)



Perfluorinated ionomer (anode humid. temp.: 60°C)

→ Improved performance with removing mass transport issue

→ No membrane hydration problem

→ Maximum power density:

236 (at 60°C) and 278 mW/cm² (at 80°C)

Data from Yu Seung Kim, LANL

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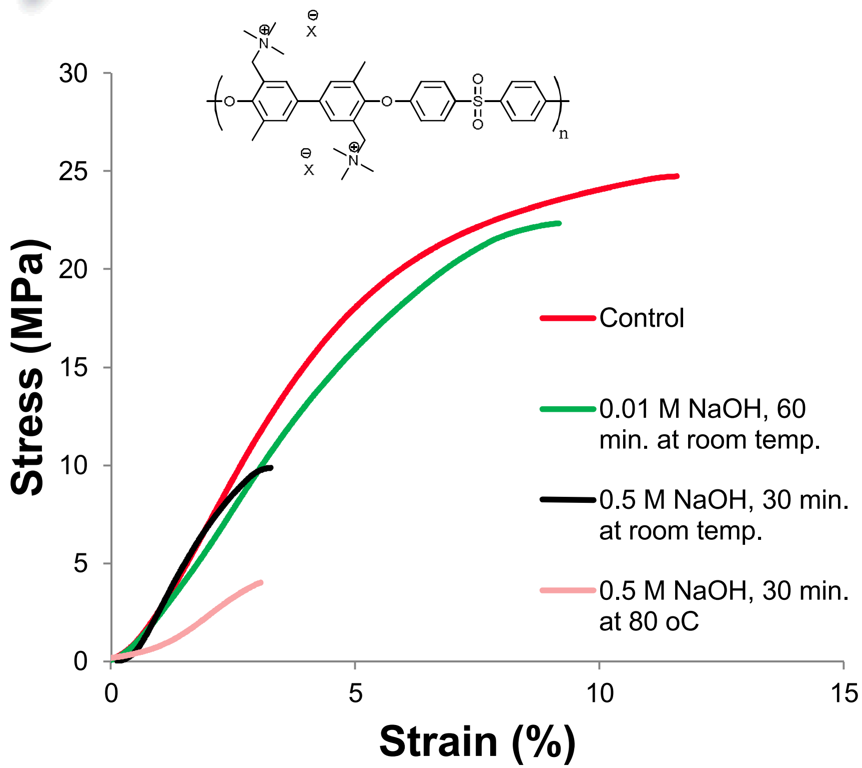
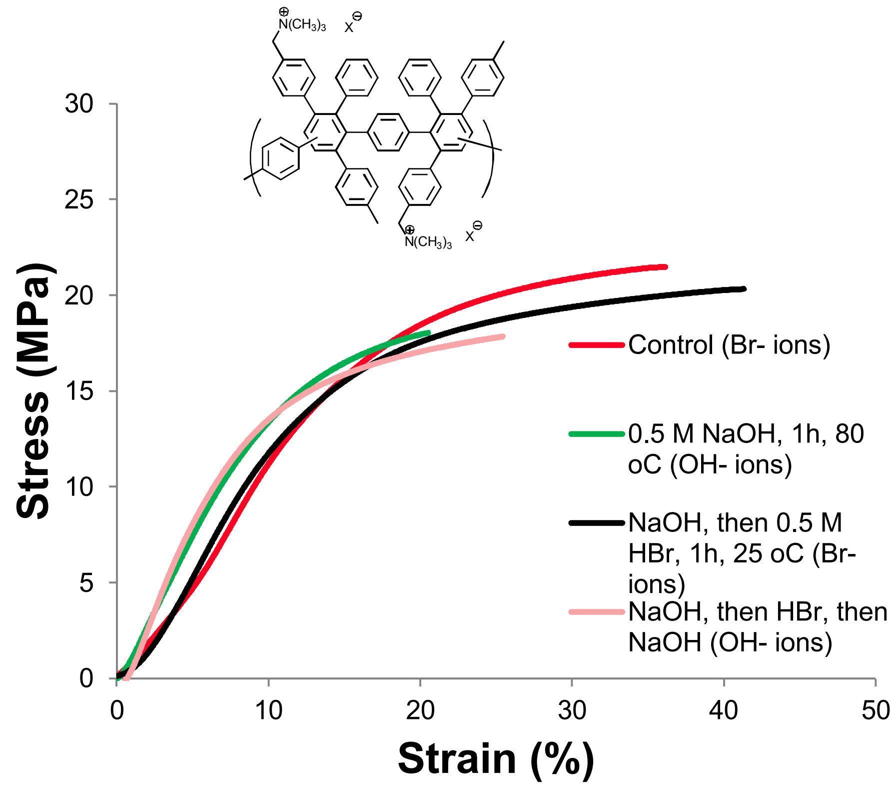
Mechanical Stability





- Test conditions: 50 °C, 50% RH.
- Poly(arylene ether sulfone) shows significant degradation.
- Poly(phenylene) is weaker in OH^- form, but there is no sign of backbone degradation.

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