NOVEL HYDROCARBON IONOMERS FOR DURABLE PROTON EXCHANGE MEMBRANES

CONTRACT #DE-SC0015215

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NanoSonic

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Project ID #FC152

OBJECTIVE

Develop cost effective, durable hydrocarbon ionomers for proton exchange membrane (PEM) fuel cells to achieve the DOE's global goals for energy efficient transportation applications.

APPROACH

Synthesize high molecular weight aromatic hydrocarbon membranes that will possess polar moieties along the polymer backbone and pendant quaternary ammonium groups. This innovative chemistry will facilitate the fabrication of stable phosphoric acid-doped membrane composites capable of 120 ^{o}C operation.

PHASE I TECHNICAL OBJECTIVES

TECHNICAL OBJECTIVE 1	Synthesize and characterize aromatic poly(arylene benzonitriles) precursor membranes and composites containing highly basic functionality as high temperature polymer electrolyte membranes for fuel cells.
TECHNICAL OBJECTIVE 2	Empirically establish structure – property relationships of synthesized materials that will afford optimal membrane properties through monomer selection and compositional manipulation
TECHNICAL OBJECTIVE 3	Measure fuel cell performance of down-selected proton exchange membrane composites

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Desirable Properties of Proton Exchange Membranes

- High ionic (protonic) conductivity but low electronic conductivity
- Low fuel and oxidant permeability
- Good thermal and oxidative stability
- Low cost
- Good mechanical properties
- Easy fabrication into membrane electrode assembly

Current Proton Exchange Membranes

Perfluorosulfonic Acid: Nafion®

- Industry benchmark
- High proton conductivity of up to 0.1 $S \cdot cm^{-1}$ under fully hydrated conditions
- Limited to <100°C
- Expensive

Fuel Cell performance is dependent upon hydration/humidification of membrane

Sulfonic Acid-containing Hydrocarbon Polymers

- Aliphatic ionomers
  - Inexpensive synthetic route
  - Lack thermal durability and chemical (oxidative) stability Limited to <80°C operation
- Aromatic ionomers
  - Variety synthetic route
  - Lower cost than Nafion
  - Limited to <100°C operation

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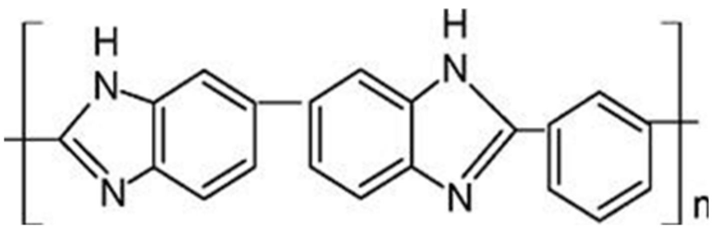
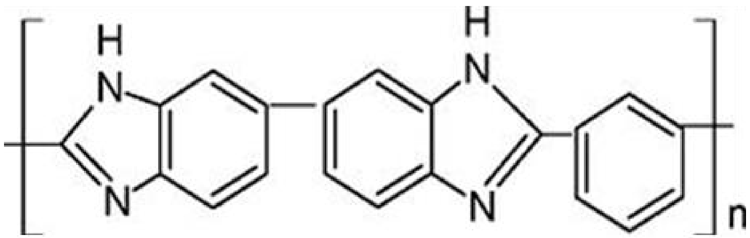
Phosphoric Acid-doped Polybenzimidazoles (PA-PBIs)



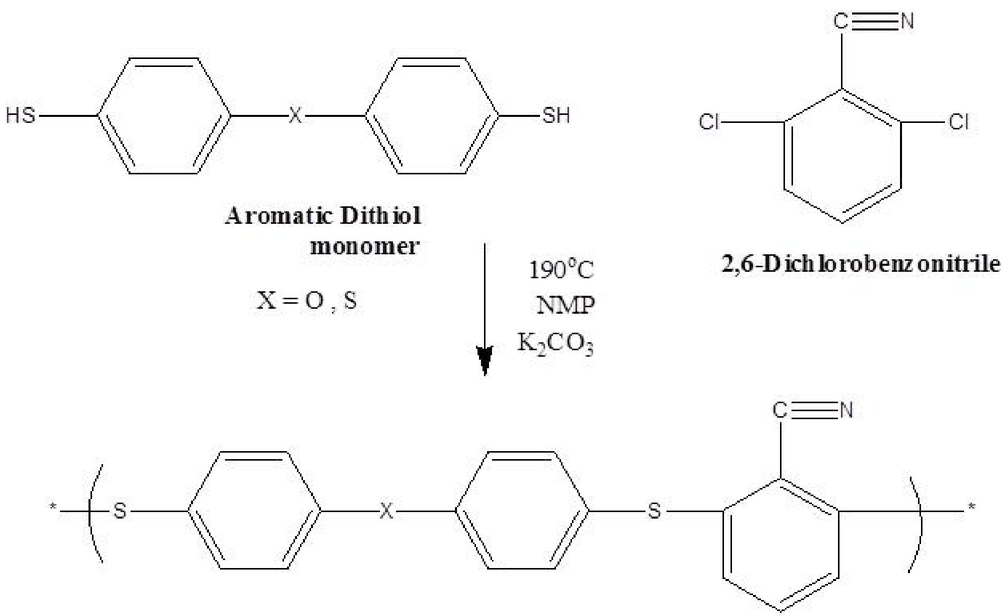
- Nitrogen (N and N-H) atoms in the polymer structure yield basic PBIs
  - Basic character allows for complexation to phosphoric acid
- Acid-Base membrane composites overcomes the dependence on water and/or humidification for conductivity
  - Capability of proton conductivity for fuel cell operation at temperatures greater than 100 °C
- Excellent conductivity up to 0.2 S/cm

Limitations of Phosphoric Acid-doped Polybenzimidazoles



- Difficult to solvate
- Reported pinhole formation and film thinning
- Operation: 140 to 180°C
  - Limited by acid leaching and phosphoric acid evaporation
- Mechanical property variations
- Water leaching of phosphoric acid
- Expensive

Synthesis and Properties of Poly(thioether benzonitrile)



Properties

- Noted thermal stability
  - High T_g and T_m
- Excellent oxidative stability
- Excellent hydrolytic stability
- Easy Processing
  - Thermal or solvent casting

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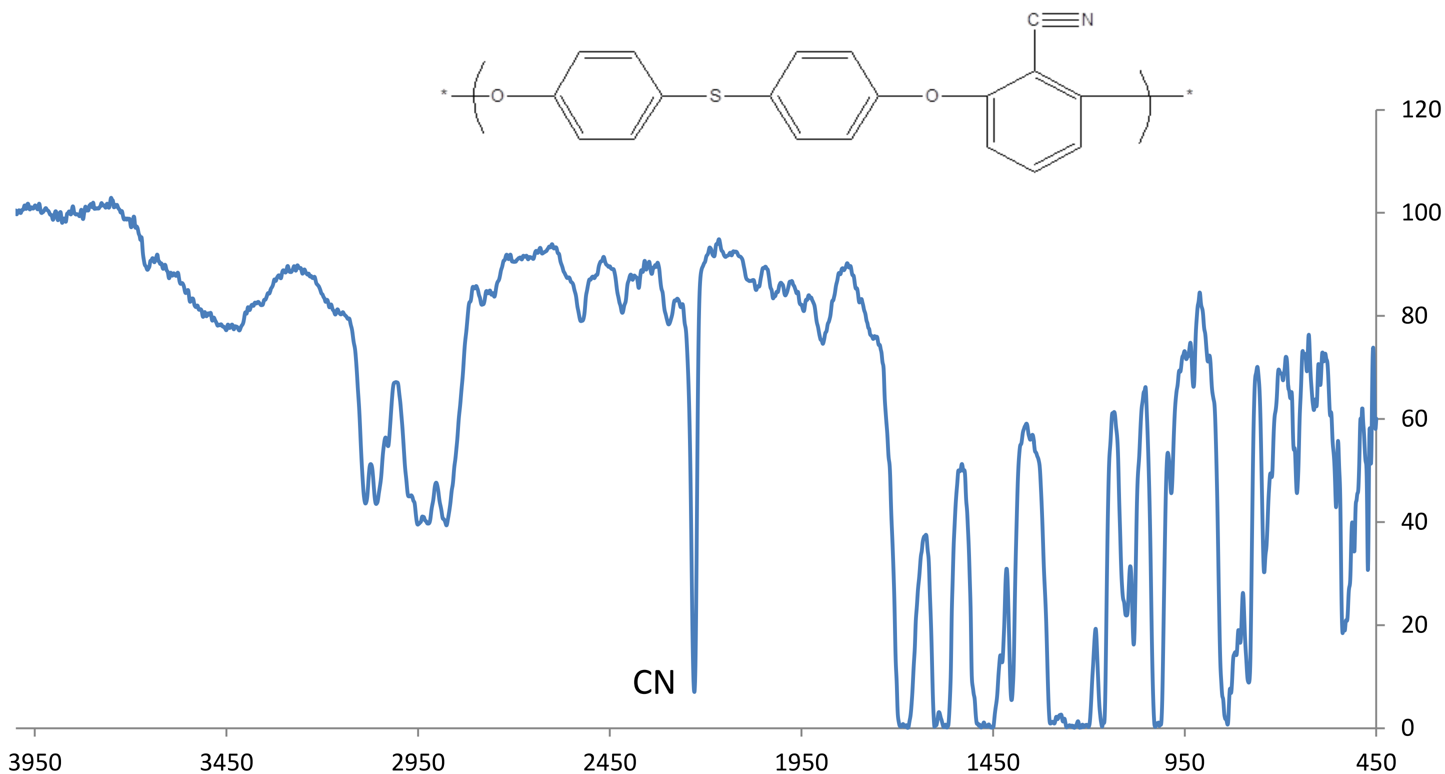
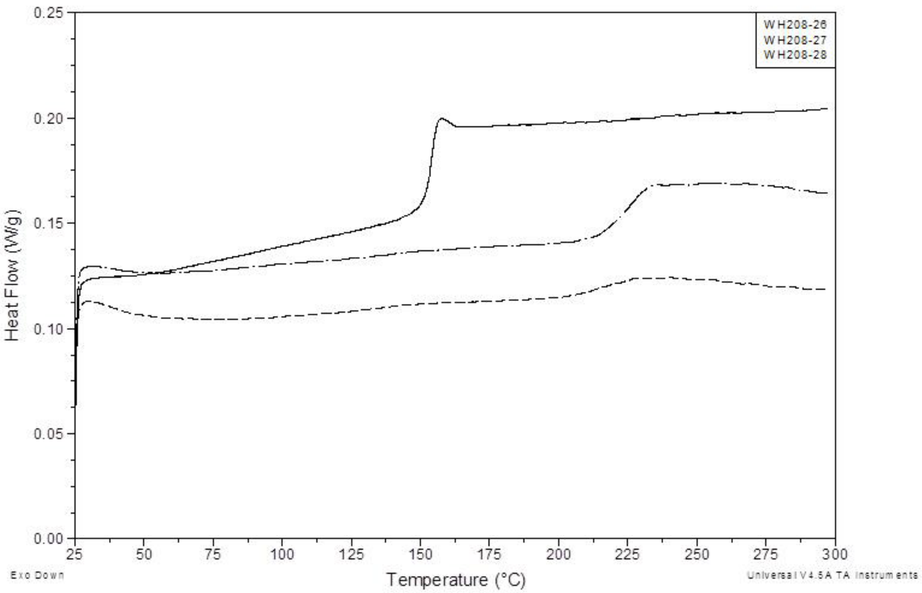
Poly(thioether ether benzonitrile) FTIR Spectrum

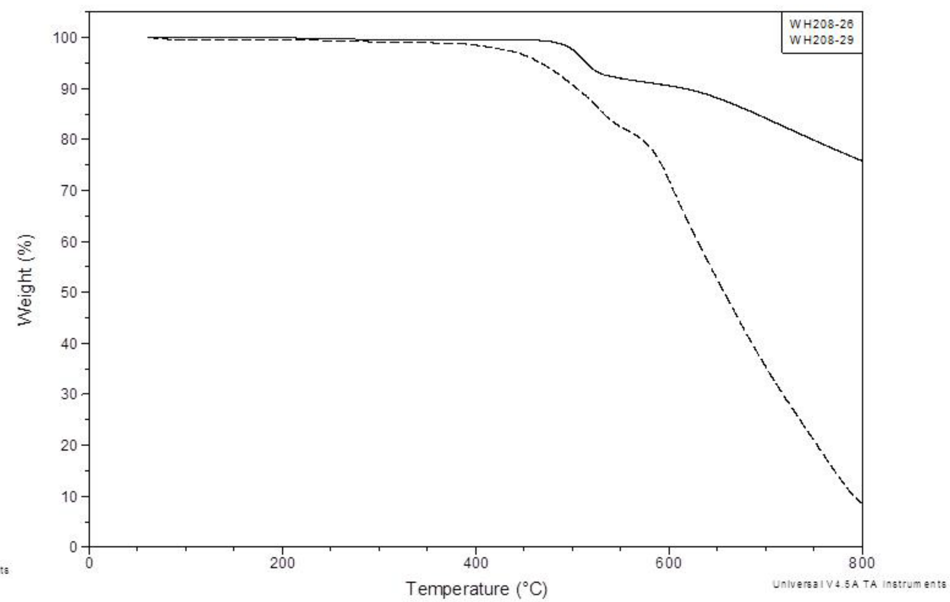


Poly(thioether benzonitriles) Films Thermal Analysis

Differential scanning calorimetry scan of select thioether benzonitrile copolymers

Thermogravimetric analysis displaying excellent thermo-oxidative stability of representative thioether benzonitrile polymers in air





Glass transition temperature of copolymer depend on comonomer selection and ratio. Some polymers are semi-crystalline.

5% Weight loss of all benzonitrile copolymers exceed 350 ^{o}C in air.

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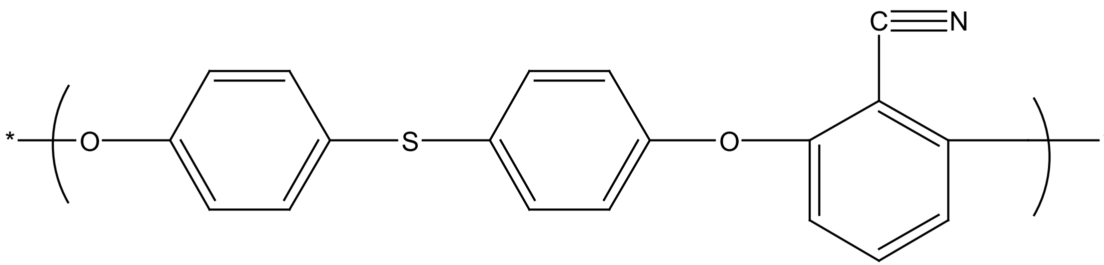
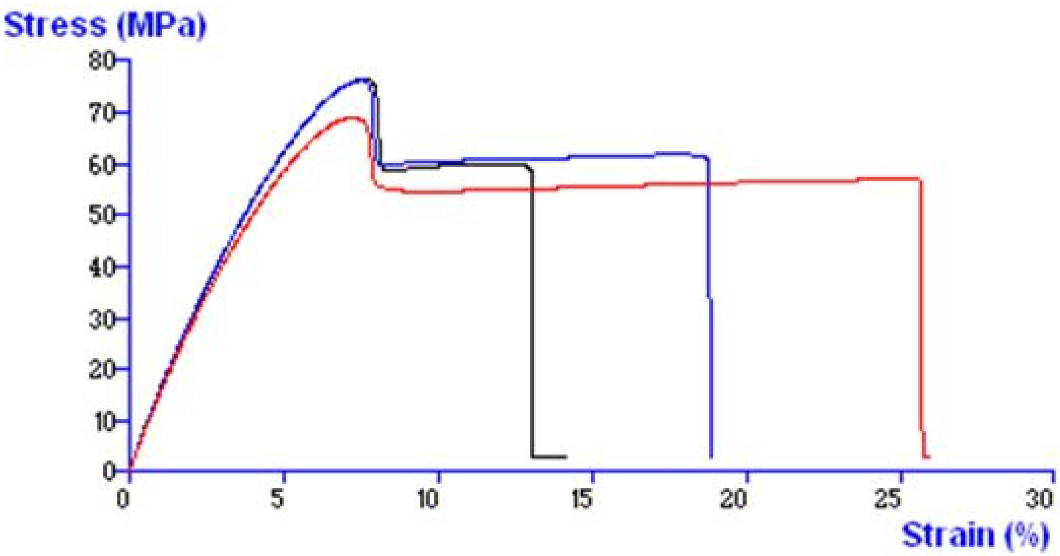
Poly(thioether ether benzonitrile) Copolymers Tensile Properties



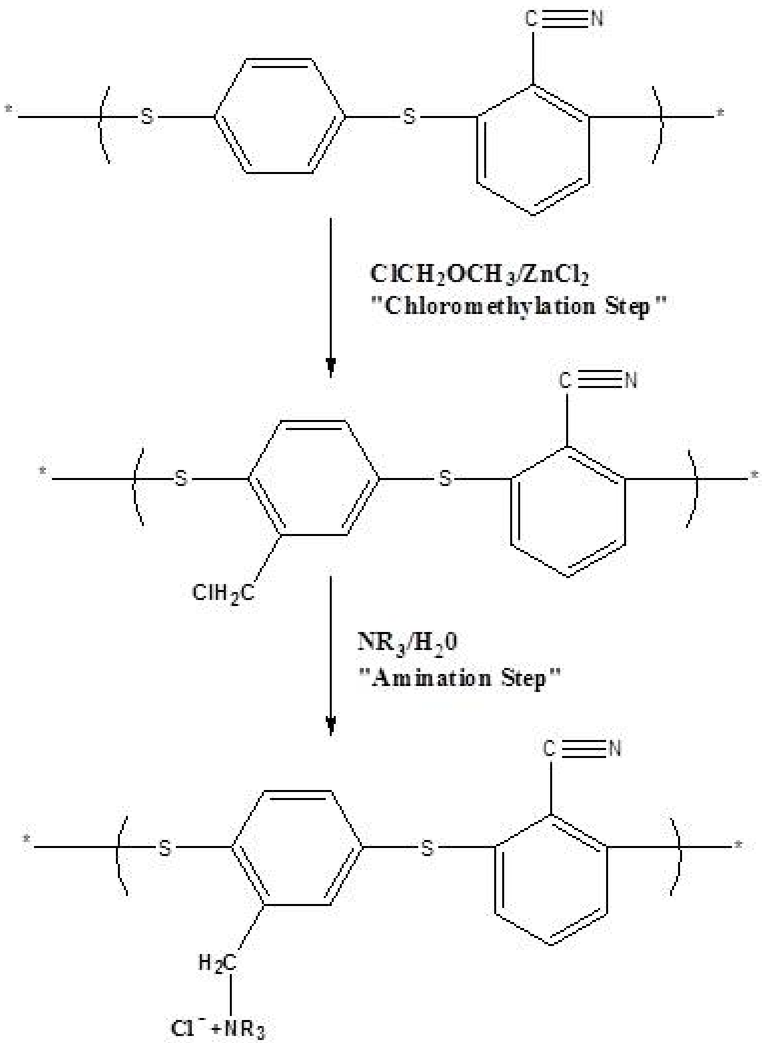


Modulus: 1600-2800 MPa

Tensile Strength: 70-90 MPa

Percent Elongation: 3-10

Introduction of Pendant Quaternary Ammonium as Phosphoric Acid Complex Site



- Ion exchange capacity control
- Quaternary ammonium has strong affinity for phosphoric acid

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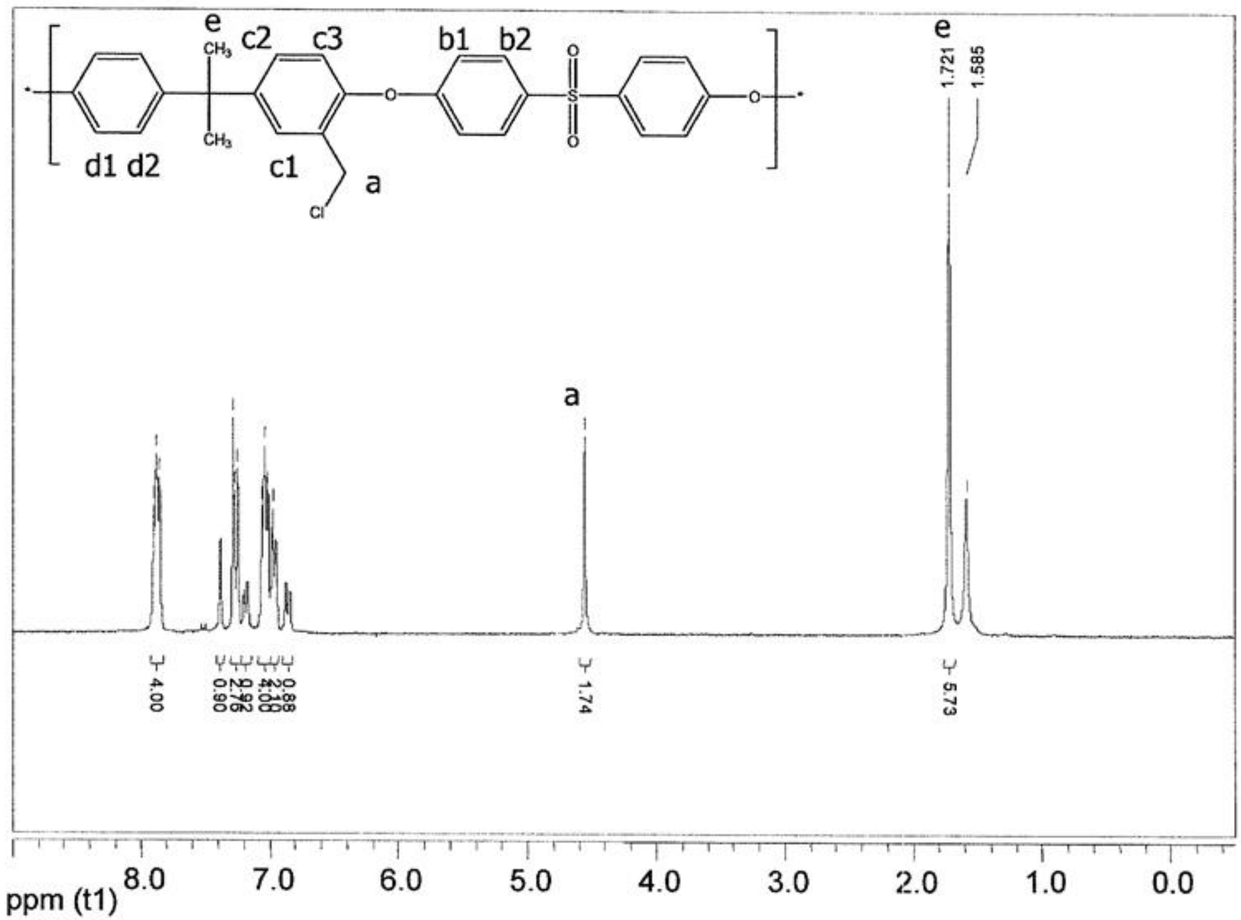
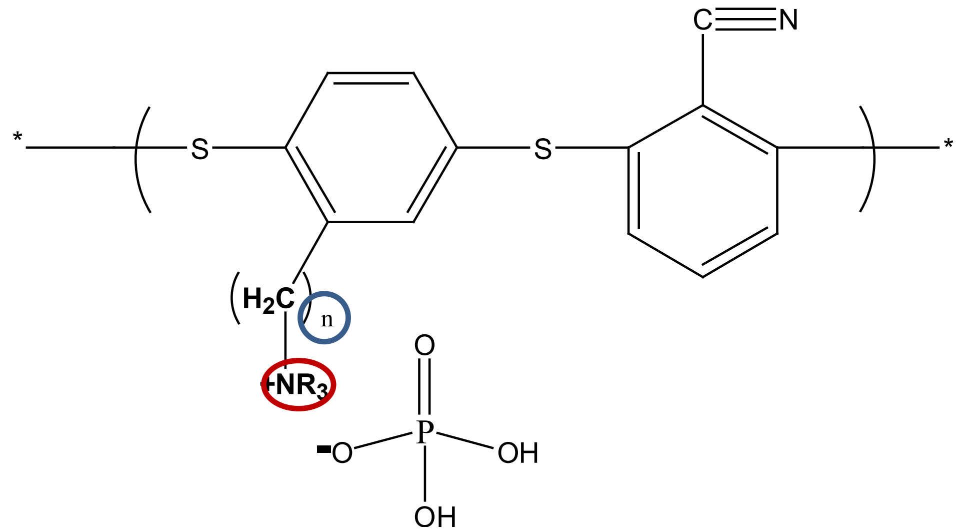
^{1}H-NMR Spectra of Chloromethylation of Polysulfone as Model Reaction

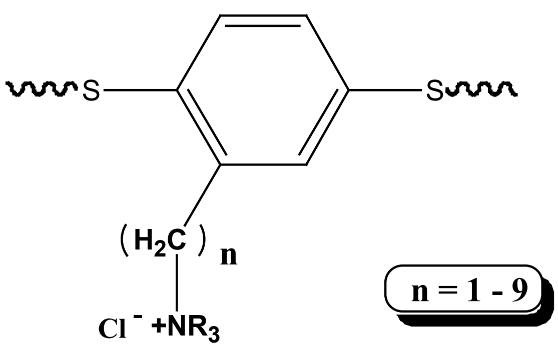


Ratio of “a” to “e” allows degree of chloromethylation

Influence of Side Chain Length and Quaternary Structure



Influence of "n" Chain Length on Quaternary Amine



- Packing/Phase Separation

Influence of "R" Group on Quaternary Amine

- Alkyl or Aryl or Mixed
- Basicity
- Stability

Ongoing and Future Characterize and Optimization of PEM Composites

- Titration (Ion Exchange Capacity)
- Molecular Weight
  - GPC and Intrinsic Viscosity
- Spectroscopic Analysis
  - FTIR
  - NMR
- Mechanical Testing
- Thermal Characterization
  - DSC
  - TGA
- Water Uptake
- Proton Conductivity

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Project Summary

- Several high molecular weight poly(thioether benzonitrile) copolymers with tailored compositions have been synthesized
- Tough, ductile films have been solution cast
- Polymers are thermally and thermo-oxidatively stable
- High glass transition temperatures are obtained
- Chloroacylation modification of polymers have successfully been demonstrated
- Polymer characterization is ongoing

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IP and Awards

- NanoSonic has exclusively licensed nine patents covering electrostatic self-assembly (ESA) processing and use from Virginia Tech and is establishing its own intellectual property portfolio to enable process, material, and device commercialization
- R&D 100 Award for Metal Rubber™
- R&D 100 Award for HybridSil® Fire Blast
- Metal Rubber was recognized as one of NASA's top 13 nanotechnology products
- Micro Nano 25 Award for flexible electronics

R&D 100

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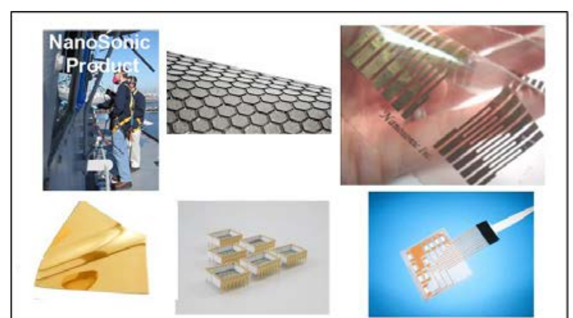

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