Mechanical Stability of aryl-ether polymeric materials for use in Proton Exchange Membranes

The current commercial and academic drive towards cheap and durable materials of low toxicity for use in proton exchange membranes (PEM) has resulted in a range of materials being investigated. Most prominent of these has been the use of polymeric aryl-ether-ketone materials which have glass transition temperatures much higher than the operating temperatures of the PEMs. These materials, such as PEEK (Victrex®), have been shown to retain, if not improve, their mechanical properties after sulfonation due to increased ionic interaction creating a physical form of crosslinking. Increasing the nanophase separation between the ionic and non-ionic regions of the ionomer materials has been further investigated through the use of block co-polymerisation. The result of this provides a bi-phasic system where the hydrophilic domain provides the high physical and mechanical properties required to withstand the operating conditions during PEM electrolysis. The second domain provides the hydrophilic properties required for proton conductivity, which crucially must provide a continuous network throughout the membrane morphology.

In our current work into the investigation into microblock polymer synthesis, poly aryl-ether systems have been used for their properties in both mechanical and chemical stability. The novel design of a 7-aromatic ring monomer bound together via ketone linkages provides the high structural stability required for PEM material.

The 7 aromatic-ring monomer has a high melting point (310 °C) and a highly crystalline nature arising from the molecules rigidity, resulting from the ketone linkages, and the planar conjugated properties of extended pi system. This crystalline nature will provide semi-crystalline properties within the resulting polymer, providing it with greater mechanical stability, such as higher glass transition temperatures and melting points. Through the tailoring of similar monomer units, specific equivalent weights can be achieved.

Scheme 1, Synthesis of 7 aromatic –ring fluorine terminated monomer via Friedel-Crafts Acylation at both synthetic steps.
Incorporation of the 7 aromatic-ring monomer with Hexafluoro Bisphenol A provides high molecular weight polymeric systems, required for materials of high strength and toughness.

Figure 1, 7 aromatic-ring monomer polymerised with Hexafluoro Bisphenol A via step growth condensation in DPS with a K$_2$CO$_3$ initiator.

The polymer showed an initial high melting point at 210 °C which was not reproduced upon the second heat, possibly showing a partially crystalline nature. The polymer also displayed a high glass transition temperature of 194 °C making the material highly suited to the working conditions of PEM electrolysis. A higher $T_g$ could be achieved with the removal of the hexafluoro methyl side groups to reduce steric hindrance, but this may also provide processing problems with reductions in solubility and solvent interaction.

Conversion of the polymer to its ionomer form by the addition of sulfonic acid groups would be expected to increase the $T_g$ even with the addition of sterically large ionic groups. The ionic acid groups provide additional non covalent bonding interactions causing an increase in the ionomers glass transition state (238 °C).
Figure 3, DSC thermogram of ionomer displaying an increase in $T_g$ at 238 °C as a result of additional ionic interactions from the bound sulfonic acid groups.

TGA analysis displays the thermal stability of the ionomer with the sulfonic acid groups, showing resistance up to 300 °C and polymeric back bone, >450 °C. The ionomer also displays a water content of ~5 % from atmospheric hydration of the hydrophilic domain.

Figure 4 TGA thermogram of Ionomer 7 aromatic-ring-Hexafluoro Bisphenol A displaying mechanical stability of sulfonic acid groups up to 300 °C.
Once cast into membranes from aprotic organic solvents such as DMAc and NMP the material shows a lower glass transition temperature, 156 °C NMP, 179 °C DMAc. Deviations in the $T_g$ could be a result of residual solvent interactions within the membrane.

Figure 5, DSC thermogram of ionomer membranes cast from DMAc and NMP displaying glass transitions at 179 °C and 156 °C respectively.

Mechanical and structural stability has also been displayed in the low swelling properties (18-23 % increase in volume) during increased hydration temperature. The membranes also showed a high level of water content (~14 % NMP and 5-11 % DMAc) over the hydration temperatures 20 °C -90 °C.

Figure 6, Membranes cast from DMAc and NMP displaying the volume increase with increase hydration over the temperature range 20 °C to 90 °C.
Figure 7, Membranes cast from DMAc and NMP displaying the mass increase with increased hydration over the temperature range 20 °C to 90 °C.

Further analysis of the ionomer membrane via DMTA analysis displays consistent tensile strength with reproduced material and with little fluctuation displayed over a range of thicknesses (20-80 µm).

Figure 8, DMTA analysis of sulfonated 7-aromatic-ring - Hexafluoro Bisphenol A cast from NMP. Left hand thermogram shows reproducible data of the same sample. Right hand thermogram displays data for varying membrane thickness. Blue 70-80 µm, Red 60-70 µm, Green 20-30 µm

From this data, it has been shown that the sulfonated 7-aromatic-ring - Hexafluoro Bisphenol A ionomer has highly suitable mechanical and chemical properties for use in PEM electrolysis. The membranes produced have glass transitions sufficiently higher than the working temperatures of a PEM electrolysis cell (120 °C) and high mechanical stability under hydrated conditions. From this analysis it has been shown that no additional strengthening through crosslinking or reinforcement is required for efficient use in an electrolysis cell.