University of Reading

25.10.2010

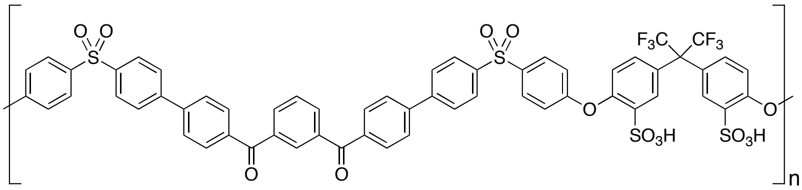
NEXPEL Programme: Work Package 02

Deliverable D2.1. Thermal and mechanical testing of PEEK-based polymeric ionic membranes with well-defined sequences of ionic and non-ionic groups (UoR).

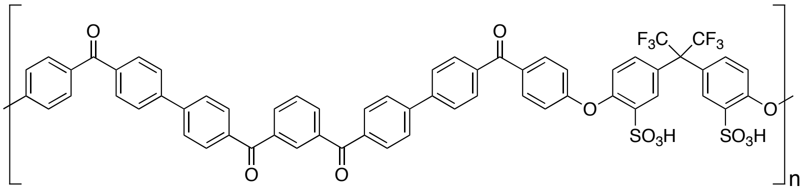
1. Membrane-ionomers designed, synthesised and tested in this work

Novel polyetherketone-type ionomers (**N1** to **N5**) investigated in this work-package are shown below. All five have fully-defined ionic/non-ionic sequence distributions.

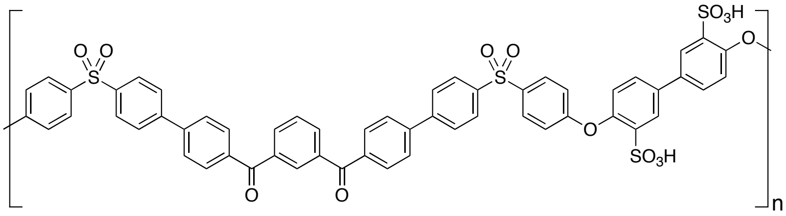
N1



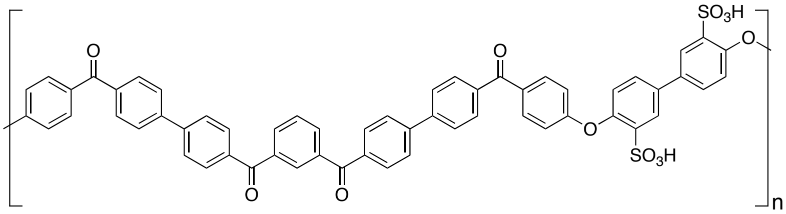
N2



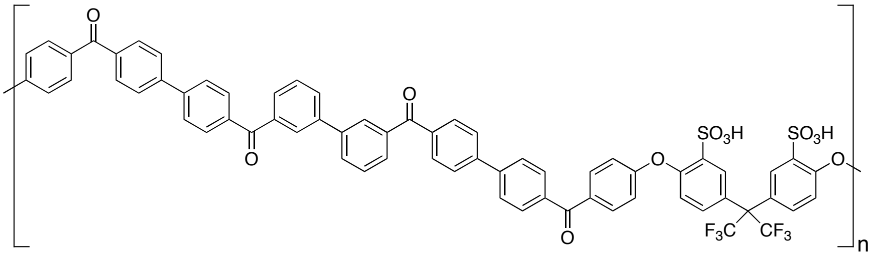
N3



N4



N5



2. Ionomer synthesis

The synthesis of ionomer **N1** is give here as an example. The other ionomers were obtained by analogous methods, except for **N4** where the unsulfonated prepolymer proved highly crystalline and required higher reaction temperatures – up to 320 °C – to maintain solubility.

Isophthaloyl[bis(4-fluorobenzoyl)-4,4'-biphenyl](3.86 g, 5.56 mmol), 4,4'-hexafluoroisopropylidenediphenol (1.9 g, 5.56 mmol), potassium carbonate (0.820 g, 5.93 mmol) and diphenyl sulfone (32.7 g) were placed in a tubular reaction vessel fitted with an overhead stirrer. Nitrogen was purged through the vessel for 20 minutes, and it was then immersed in a metal bath and heated to 190 °C. Once the diphenyl sulfone had melted, mechanical stirring was started and the temperature was raised progressively to 290 °C over 7 hours. The reactor was held at this temperature for a further hour until the polymer had become visibly viscous upon which it was poured onto a metal tray and allowed to cool. This "toffee" was then broken up, milled to a fine powder, extracted with refluxing methanol (x 3) to remove diphenylsulfone, then with boiling water to remove salts, and finally vacuum- dried at 100 ºC to give the prepolymer as a white powder.

To a 250 mL, three-necked, round-bottomed flask, fitted with a mechanical stirrer and PTFE paddle, was added 98% sulfuric acid (70 mL), followed by the unsulfonated prepolymer (5 g), which was added in portions with continuous stirring over *ca.* 5 minutes. The mixture was stirred at room temperature for 20 min, then brought to 65 °C on an oil bath and left stirring for *ca.* 16 h. The resulting viscous red solution was cooled and added slowly to stirred deionised water (*ca.* 2 L) through a PTFE colander with 1 mm holes. This gave uniform bead formation on coagulation in the water. The ionomer beads were washed with deionised water on a coarse glass sinter, then stirred again in deionised water (*ca.* 1 L) and re-filtered, and this washing process was repeated (typically 5 or 6 times) until the conductivity of the washings was less than 10 μS cm^{-1}. The final ionomer beads (**N1**) were dried in a vacuum oven at 110 °C. Yield was 4.8 g, (91%).

3. Ionomer characterisation

Ionomer N1: η_{inh} (NMP) = 1.38 dL/g; GPC M_n = 97,900 g mol^{-1}, PD = 1.58; ^{1}H NMR (d_6-DMSO) δ (ppm) 6.99-7.12 (6H, m, $H_{c,d}$), 7.25 (2H, d, J_{bc}= 8.0 Hz, Hb), 7.79 (t,J_{lk}= 7.5 Hz, H_l), 7.88-8.07(24H, m, $H_{a,e,f,g,h,i,k}$), 8.12 (br, s, H_j); ^{13}C NMR (d_6-DMSO) δ (ppm) 118.9, 122.6, 127.9, 128.3, 128.8, 129.4, 130.1, 130.5, 130.9, 132.7, 133.9, 134.7, 136.6, 137.5, 140.4, 141.5, 142.9, 144.0, 152.5, 162.2, 194.9 (C=O); IR (film) 1026 cm^{-1} ($\nu_{sym}SO_3H$).

Ionomer N2: η_{inh} (NMP) = 1.36 dL/g; GPC M_n = 86,500 g mol^{-1}, PD = 2.88; ^{1}H NMR (d_6-DMSO) δ (ppm) 7.14- 7.19 (6H, m, $H_{c,d}$), 7.37 (2H, br, d, J_{bc} = 9.25 Hz, H_b), 7.82-8.06 (21H, m, $H_{e,f,g,h,i,j}$), 8.12-8.15 (4H, m, $H_{a,k}$) 8.20 (1H, br, s, H_l); ^{13}C NMR (d_6-DMSO) δ (ppm) 118.5, 121.6, 127.5, 127.6, 129.3, 130.6, 131.0, 131.7, 132.4, 132.6, 133.8, 136.3, 137.3, 137.6, 140.0, 142.7, 143.5, 153.2, 161.4, 194.3 (C=O), 194.6 (C=O); IR (film) 1027cm^{-1} ($\nu_{sym}SO_3H$).

Ionomer N3: η_{inh} (NMP) = 1.35 dL/g; GPC M_n = 118,100 g mol^{-1}, PD = 1.53; ^1H NMR (d_6-DMSO) δ (ppm) 7.03-7.07 (4H, AA'XX'system, H_d), 7.11 (4H, d, J_{cb} = 8.3 H_z, H_c), 7.66 (2H, dd, J_{bc} = 8.3 Hz, J_{ba} = 1.6 Hz), 7.79 (1H, t, J_{lk} = 8.3 Hz, H_l), 7.90-8.08 (22H, m, $H_{a,d,e,f,g,h,i,k}$), 8.14 (1H, s, H_j); ^{13}C NMR (d_6-DMSO) δ (ppm) 118.3, 123.4, 127.3, 127.9, 128.2, 128.8, 129.1, 129.4, 129.9, 130.6, 130.9, 133.9, 135.9, 136.6, 137.5, 141.0, 141.6, 142.9, 143.9, 150.9, 163.0, 194.9 (C=O); IR (film) 1022 cm^{-1} ($\nu_{sym}SO_3H$).

Ionomer N4: η_{inh} (H_2SO_4) = 1.70 dL/g; GPC M_n = 51,500 g mol^{-1}, PD = 3.66; ^1H NMR (d_6-DMSO) δ (ppm) 7.06-7.09 (4H, AA'XX'system, H_d), 7.13 (2H, d, J_{cb} = 8.5 H_z, H_c), 7.71 (2H, d, J_{bc} = 8.5 H_z, H_b), 7.80-8.02 (21H, m, $H_{e,f,g,h,i,l}$), 8.08-8.11 (2H, d, J_{kl} = 7.75 H_z, H_k), 8.13-8.14 (3H, m, $H_{a,j}$); ^{13}C NMR (d_6-DMSO) δ (ppm) 117.8, 122.8, 127.3, 127.5, 127.6, 128.9, 129.4, 130.6, 131.0, 132.3, 133.9, 135.4, 136.3, 137.5, 137.6, 140.8, 142.6, 143.6, 151.6, 162.5, 194.4 (C=O), 194.9 (C=O); IR (film) 1023 cm^{-1} ($\nu_{sym}SO_3H$).

Ionomer N5: η_{inh} (NMP) = 1.32 dL/g; GPC M_n = 72,600 g mol-1, PD = 1.80; ^1H NMR (d_6-DMSO) δ (ppm) 7.08-7.12 (6H, m, $H_{c,d}$), 7.27-7.31 (4H, d, J_{bc} = 7.6 Hz, H_b), 7.66-8.07 (30H, m, $H_{a,e,f,g,h,i,j,k,l,m}$); ^{13}C NMR (d_6-DMSO) δ (ppm) 118.5, 121.6, 127.5, 128.0, 129.8, 130.6, 131.0, 131.5, 131.7, 132.4, 136.6, 137.3, 138.2, 139.8, 139.4, 142.8, 143.4, 161.4, 194.4 (C=O), 195.5 (C=O); IR (film) 1024 cm^{-1} ($\nu_{sym}SO_3H$).

4. Membrane fabrication

All five ionomers were soluble in N-methylpyrrolidinone (NMP) containing 1% water, in which solvent 15% w/v solutions were made up in a round-bottomed flask. A clear viscous solution was obtained by magnetically stirring for several hours. A glass plate (20 x 25 cm^2) was rigorously degreased with a fine abrasive cleaner, rinsed copiously with deionised water, then with acetone, and allowed to air-dry. A Gardner casting knife was then set with a blade height of 300 mm above the glass plate. The casting dope was spread evenly in front of this, and a uniform film was produced by drawing the blade carefully across the plate. The film was then dried in a vacuum oven by slowly increasing the temperature over 48 hours from room temperature to 105 °C. After solvent removal and equilibration with atmospheric water vapour overnight, the membrane could be peeled easily from the glass-plate.

Notes: If the solvent is allowed to evaporate too quickly, bubbles can form in the film and poor, brittle membranes are the result. Also, the glass-plate must be set exactly horizontal while the film is in its liquid state, otherwise flow of the liquid film will lead to formation of membranes with non-uniform thickness.

5. Membrane characterisation

Membranes were characterised in terms of film-thickness, equivalent weight/ion-exchange capacity, water-uptake at up to 90 °C, proton conductivity, thermal analysis (DSC) and thermomechanical performance (TMA). Not all membranes have yet been characterised by all these techniques. Results are shown in Table 1, on p.4, and in Figures 1 and 2.

Table 1. Membrane Characterisation Data

Ionomer Code	Equivalent Weight Theory/Expt. (Da)	Proton Conductivity (mS cm^{-1})	Water Uptake at 80 °C (wt% on dry membrane)	Tg (°C)*
N1	608/637	70	60%	230
N2	537/568	60	56%	199
N3	529/500	70	68%	247
N4	494/461	61	61%	N/D
N5	607/590	57	38%	195

* Glass transition temperature of the unsulfonated prepolymer

Thermomechanical analysis (TMA) of ionomer N3: In TMA analysis the position of a weighted probe in contact with the sample is monitored as a function of temperature. Membrane samples were equilibrated at room temperature and ambient relative humidity before being analysed. The data given below were obtained with a hemispherical tip probe and a 79.0 g load, and the samples were heated from 20 to 180 °C at 10 °C/min.

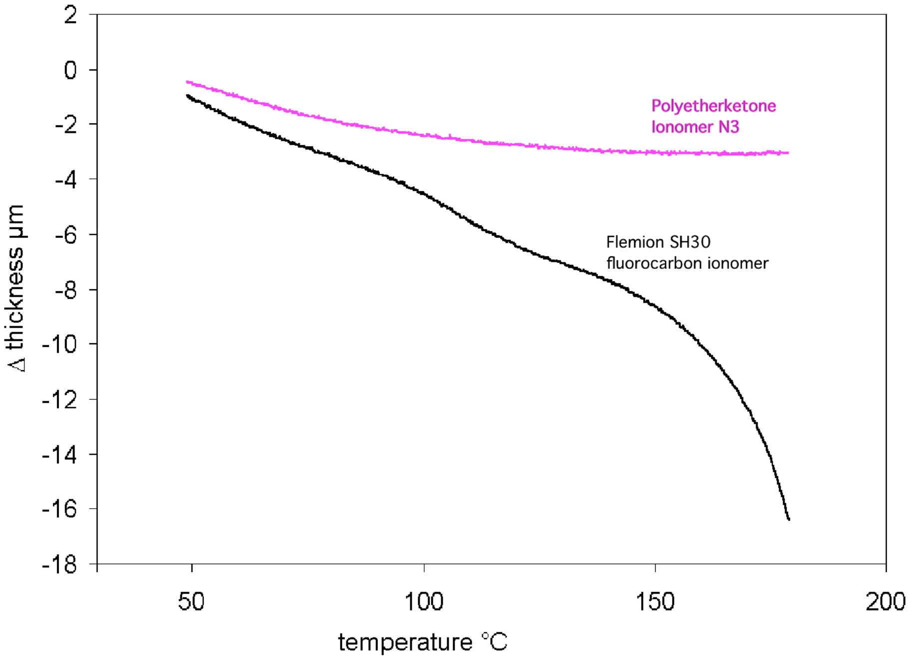


Figure 1: Thermomechanical analysis of ionomer **N3** and the fluorocarbon ionomer Flemion SH30

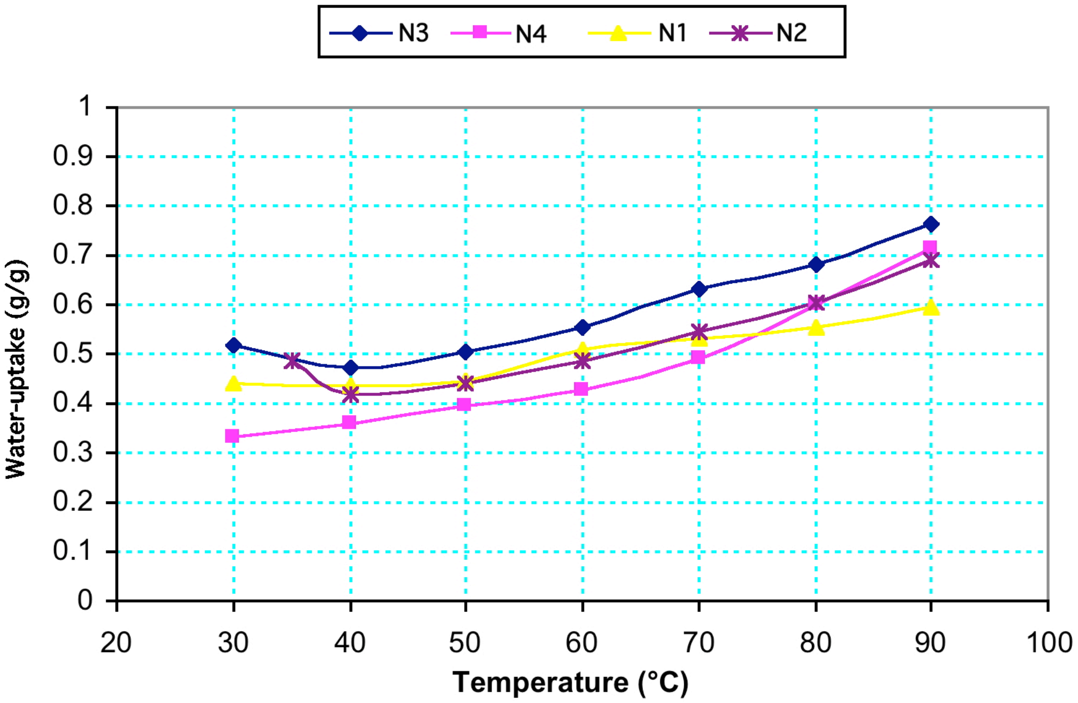
The analysis (Figure 1) showed that, as the samples were heated, the probe penetrated further into the membrane, as expected, for both the control material (a perfluorinated ionomer; Flemion SH30, from Asahi Glass) and the aromatic ionomer **N3**. Up to 100 °C, both membranes show reasonably good resistance to deformation. However, when the temperature was raised above 100 °C pronounced differences between the different membranes emerged. Softening greatly increased in the Flemion sample, as would be expected if the ionomer glass transition temperature had been reached. This is consistent with literature data for perfluorinated ionomers, whose T_g's are typically in the range 80 - 100 °C. The aromatic ionomer **N3** (T_g = 247 °C in unsulfonated form) is however relatively unaffected up to 200 °C. In operational terms, this would suggest aromatic ionomers of the type described in this report would be less likely to distort at high temperatures in an electrolyser, so avoiding shorting caused by electrode penetration of the membrane. They should also possess good mechanical strength for high temperature operation. Conversely, lamination of the membranes as a means of assembling the MEA may prove problematic for high-T_g ionomers as it is clear that they do not soften and flow so easily as perfluorinated materials.

Water-uptake of ionomers: A 5 cm x 5 cm square of membrane was dried under vacuum at 120 °C for 2 hours and weighed immediately to give the dry mass of the membrane (m_{dry}). The membrane was then immersed in a beaker of deionised water and placed in a water bath held at a fixed temperature for 1 hour to equilibrate, before being quickly pressed dry in absorbent paper, and weighed to give the mass of membrane (m_{wet}). The immersion step was then repeated with 10 °C increments in water bath temperature up to 90 °C.

The water uptake was calculated as:

$$wateruptake = \frac{m_{wet} - m_{dry}}{m_{dry}}$$

Water-uptake values as a function of temperature for four of the ionomer membranes described in this report are shown in Figure 2 (below).



6. Conclusions

All five membrane ionomers described in this report show good mechanical stength, realtive ease of fabrication, good levels of proton conductivity and very good resistance to water-swelling up to 90 °C. The hoped-for advantages of aromatic ionomers over fluorocarbon materials in terms of thermomechnical stability above 100 °C have been confirmed.

In terms of their balance of properties, ease of scale-up and synthetic reproducibility, ionomers **N1** and **N2** have been selected to go forward for evaluation in MEA form and ultimately in electrolyser operation.