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Preparation of polymer protic ionic liquids to be used as membranes in proton exchange membrane fuel cells

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Background

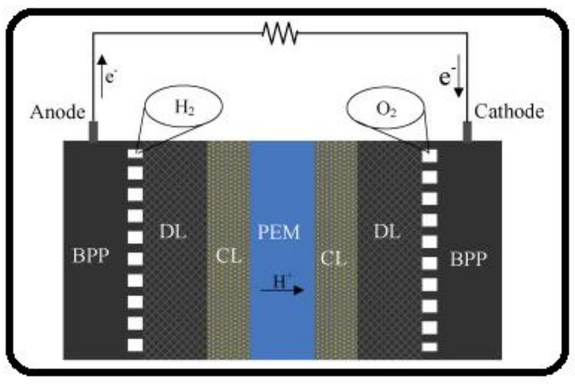


Figure 1. Diagram of proton exchange membrane (PEM) fuel cell, reproduced from [1]

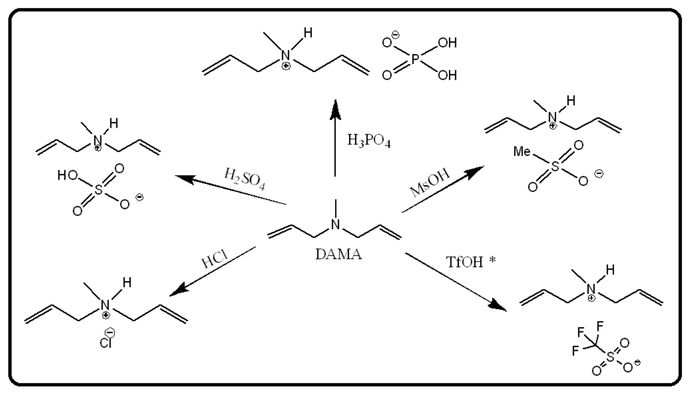
$$\text{Anode} : 2H_2 \rightarrow 4H^+ + 4e^-$$
$$\text{Cathode} : O_2 + 4H^+ + 4e^- \rightarrow 2H2O$$
$$\text{Fuel Cell} : 2H_2 + O_2 \rightarrow 2H_2O$$

Scheme 1. Half-cell and full-cell reactions in hydrogen fuel cell

- Fuel cells can be used to convert hydrogen and oxygen into electricity.
- Commercial fuel cells use perfluorinated membranes which are unsustainable and are not able to operate above 80 °C.
- Ionic liquids are being investigated as alternative components in fuel cells due to their low volatility and high conductivity.
- Polymerisation of protic ionic liquids can be used to produce single component membranes for intermediate-temperature fuel cells.

Methodology

- Synthesis of protic ionic liquid (PIL) monomers by Brønsted acid-base neutralisation with a small excess of base.
- Formation of PIL polymer was accomplished by thermal polymerisation using AIBA as a radical initiator.
- Methodology is based on recently published work [2].



*Scheme 2. Chemical structures of protic ionic liquid monomers synthesised in this work. *Note: [Hdama][TfO] kindly provided by Antonela Gallastegui (POLYMAT)*

PIL monomer purification: removal of excess base and residual water by rotary evaporation and Schlenk-line.
PIL monomer characterisation: $^1H/^{13}C$ NMR, ATR-FTIR, TGA, and CV to probe proton availability.
PIL polymer purification: cellulose dialysis bags OR solvent precipitation (cold acetone).

Figure 2. Dialysis bag containing PIL polymer mixture in deionised water.

PIL Monomer Synthesis

- Synthesising exact 1:1 acid : base ratio is challenging
- Excess of more volatile component used and later removed by rotavap
- Small residual traces were present in ^1H NMR

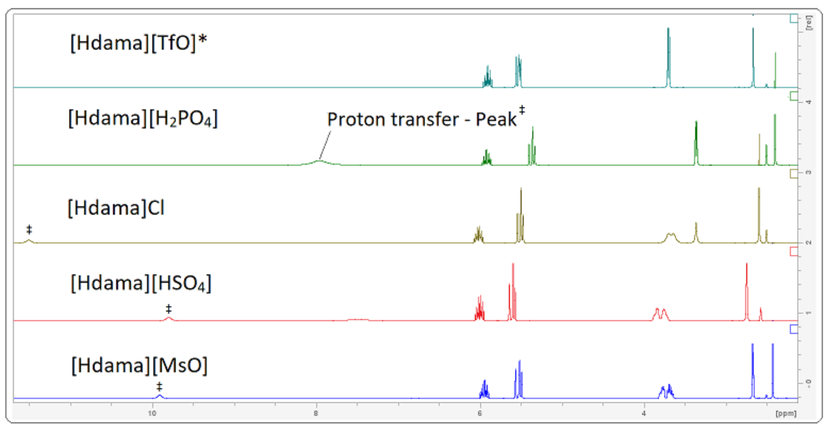
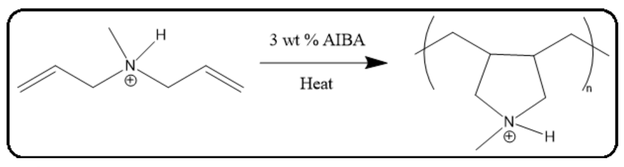


*Figure 2. ^1H NMR spectra of PIL monomers. *[Hdama][TfO] from POLYMAT*

PIL polymer synthesis

- Thermal polymerisation explored in aqueous solution at 70 °C after N_2 purge



Scheme 3. Polymerisation of PIL monomers using 2,2-azobis(2-methylpropionamidine) and heat

ATR-FTIR

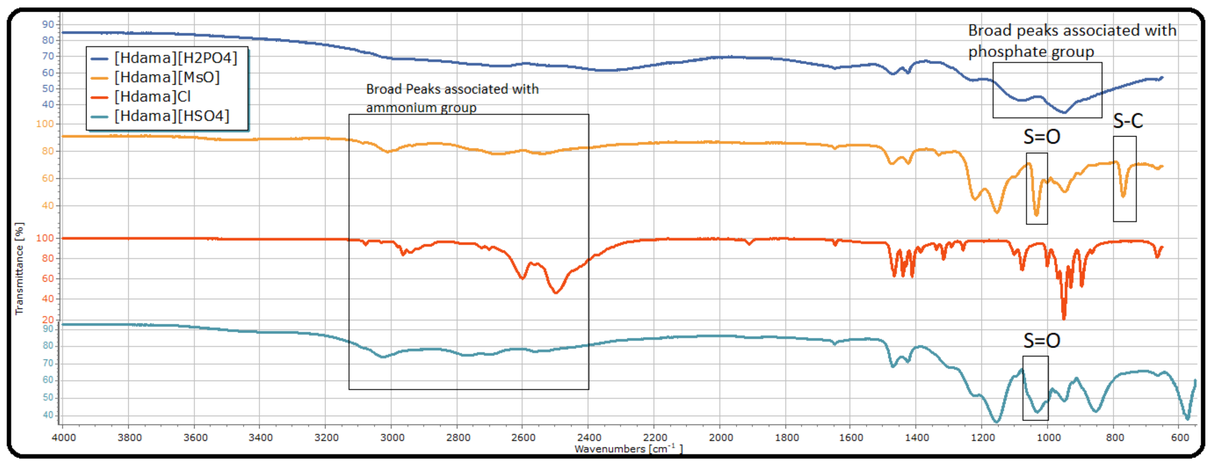


Figure 3. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum of PIL monomers

- FTIR shows that proton transfer was successful due to the presence of broad peaks in the region between 3000 – 2500 cm^{-1} (N^+-H)
- $[Hdama][H_2PO_4]$ spectrum is less resolved, potentially due to high viscosity and/or water content.

Thermogravimetric analysis

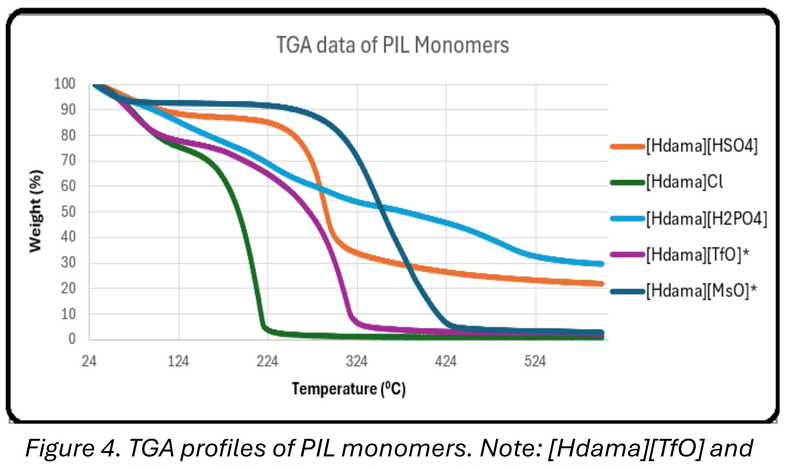


Figure 4. TGA profiles of PIL monomers. Note: [Hdama][TfO] and [Hdama][MsO] samples provided by POLYMAT

- TGA presented a challenge due to the hygroscopic nature of the PIL monomers,
- High moisture content observed in most cases.
- Obtaining ideal 1:1 stoichiometry for the reaction was difficult; excess of either component gives artefacts in data.

- Nonetheless, the data appears to show the main $T_{degradation}$ of the PIL monomers $[HSO4]^-$, $[TfO]^-$, $[MsO]^-$ are 200 °C or above. Cl^- is a solid at RT.
- The highly hygroscopic, viscous $[H_2PO_4]^-$ monomer behaved erroneously.

Cyclic Voltammetry

- Cyclic voltammetry confirms that there is a labile proton in both PIL monomers that can in theory conduct protons in a fuel cell system.
- [Hdama][TfO] has a more available proton, in keeping with the higher ΔpKa of this PIL

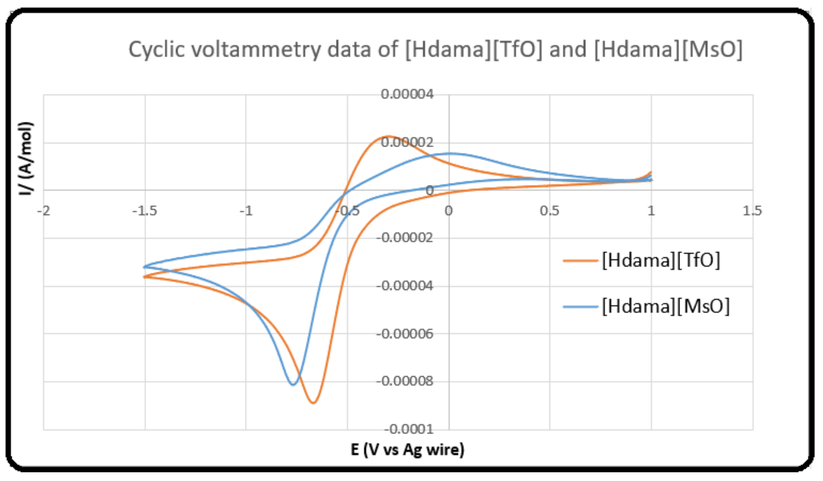


Figure 7. Cyclic voltammograms of [Hdama][TfO] (orange) and [Hdama][MsO] (blue). Data was produced with a scan rate of 250 mV s^{-1}. Data was obtained from samples provided by POLYMAT.

- Aqueous CVs of the $[HSO_4]^-$ and $[H_2PO_4]^-$ systems are on-going to inspect if the trend with ΔpKa is also present.

References

[1] Shao, Y., Yin, G., Wang, Z. and Gao, Y., 2007. Proton exchange membrane fuel cell from low temperature to high temperature: material challenges. *Journal of Power Sources, 167*(2), pp. 235-242
[2] Gallastegui, A., Foglia, F., McMillan, P.F., Casado, N., Gueguen, A. and Mecerreyes, D., 2023. Poly (diallylmethylammonium) proton conducting membranes with high ionic conductivity at intermediate temperatures. *Polymer, 280*, p.126064

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Conclusions

- PIL monomers were successfully produced by acid-base neutralisation.
- Attaining the ideal 1:1 stoichiometry is synthetically challenging, bespoke apparatus needed.
- Polymer purification: cellulose dialysis *versus* solvent precipitation methods explored.
- Future work will develop membrane casting, membrane characterisation by electrochemical impedance spectroscopy and membrane-electrode-assembly fabrication for fuel cell testing.