Exploring The Behavior Of *In-Situ* Polymerised Ionogel Thermal Actuators

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INTRODUCTION

- Poly-(N-isopropylacrylamide) (pNIPAM) is a thermo responsive polymer gel that displays an inverse solubility of aqueous solutions upon heating above its Lower Critical Solution Temperature (LCST).
- Below the LCST, the gel becomes solvated by water molecules through hydration of aliphatic groups and hydrogen bonding with the amide group.
- Above the LCST (31 – 32 ºC)[1], the gel collapses along the polymer backbone before water molecules are expelled. This process is driven by the conversion from polymer-solvent bonds to polymer-polymer and solvent-solvent bonding.[2]
- Ionic liquids (ILs) / ionogels have evolved as a new type of material for actuators, mainly due to their unique and tunable physical properties.[1]

AIMS

- To investigate the physicochemical interactions that occur between A) IL B) Water C) Polymer as a result in a change in temperature .
- Examine the macro actuator effect as a result of these interactions

EXPERIMENTAL

- ILs of interest in this study are; 1-ethyl-3-methylimidazolium ethyl sulfate [C_2mIm][$EtSO_4$] and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) [C_2mIm][NTf_2] (Figure 1).

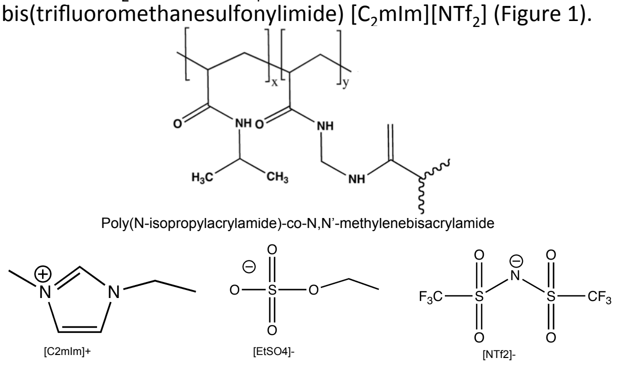


Fig 1: Ionic Liquids of interest and repeating unit of the polymer.

- The thermo-physical properties of these pure water-saturated ILs were investigated using density, viscometry, and rheometry.
- All measurements were performed in temperature range corresponding above and below the LCST (20 – 35 ºC).
- Storage modulus was measured using an Anton-Paar MC301 rheometer, where the temperature was ramped 5 ºC / min above and below the LCST of the ionogel.
- Hydrated gels were gold sputtered using a Polaron® SC7640 Auto/ Manual High Resolution Sputter coater, and SEM measurements were performed on a ZEISS ® microscope instrument.

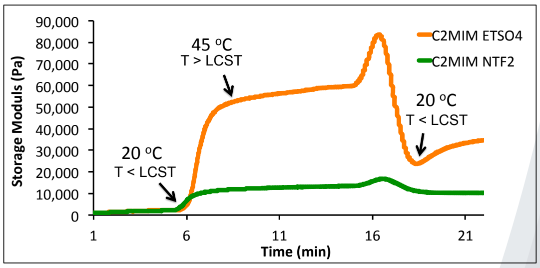
RESULTS AND DISCUSSION

- Swelling and contracting properties of the ionogel were found to differ depending on the variation and hydrophobicity of the anion.

References
1. Benito-Lopez, Fernando and Byrne, Robert and Raduta, Ana Maria and Vrana, Nihal Engin and McGuinness Garrett and Diamond Dermot (2010) Lab on a Chip, 10 (2). pp. 195-201.
2. *H.G Shild, Prog. Polym. Sci., Vol. 17, 163-249, 1992*

RHEOMETRY

- Storage modulus, measuring the elastic energy of the hydrated gel.



- Clear difference observed between the storage modulus of [C_2mIm][$EtSO_4$] and [C_2mIm][NTf_2] ionogels when passed through the LCST threshold.
- At the phase transition, when the polymer backbone of pNIPAM collapses and expels water, the hydrophilic [C_2mIm][$EtSO_4$] leaves with the expelled water, producing a more compact, condensed and stiffer gel.

ACTUATION

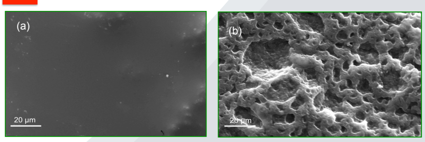
- Actuation properties of ionogel are found to differ according to anion hydrophilicity.

IL	LCST (ºC)	Diameter (mm)	Hydration diameter mm (% change)	Contraction diameter mm (% change)
[C_2mIm][$EtSO_4$]	24	12.00	15.7 (30.42)	11.2 (28.47)
[C_2mIm][NTf_2]	24	12.00	13.8 (15.83)	11.8 (13.67)

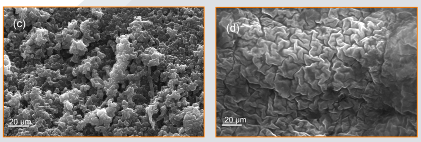
- Viscosity values measured were found to correlate with previous actuation measurements.

IL	IL viscosity 20 ºC m.Pas	Viscosity of IL/Water below LCST m.Pas (% change)	Viscosity of IL / Water above LCST m.Pas (% change)
[C_2mIm][$EtSO_4$]	93.60	3.43 (96.33)	2.42 (97.40)
[C_2mIm][NTf_2]	32.49	23.93 (26.34)	12.78 (60.60)

SEM



[C_2mIm][NTf_2]
Shows polymer networks only in the hydrated phase (a & b)



[C_2mIm][$EtSO_4$] display distinct porous morphology in both states (c) dry and hydrated (d) states.
It shows the hydrophobicity of the anion has effect on the formation of the polymer network.

CONCLUSIONS

- The storage modulus of the ionogels are found to change significantly according to the hydrophobicity of the anion.
- The actuation properties of the ionogels correlate with the trend of viscosity values of the ILs when saturated with water.
- SEM images clearly display differences between ionogels when dry and when submerged in water.
- It is clear that the nature of the IL employed dictates the actuation properties of the ionogel.

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