Physical and Mechanical Properties of Phosphonium Based Poly(ionic liquids)

Kevin J. Fraser, Andrew Kavanagh, Bartosz Ziółkowski , Simon Gallagher & Dermot Diamond.

CLARITY: Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland

Introduction

- Currently for applications in materials science, there is a growing interest in Ionogels i.e. polymers with incorporated ionic liquids (ILs).
- However one disadvantage of ionogels is the leaching of the IL in the liquid phase. To overcome this, "poly ionic liquids" (PILs), are gaining momentum in the literature[1].
- Interesting applications for the incorporation of PILs into polymers have been published such as ultrasensitive and selective chemiresistive CO_2 sensors[1]. PILs have also found applications in fuel cell technology as some reported PIL films display very high ionic conductivities (exceeding 90 mS cm^{-1} at 100 °C and 75 % relative humidity)[2].
- However the range of possible monomeric IL structures is far greater than has so far been explored[3].

Aim

- Synthesise and characterise new PIL's based on the phosphonium cation.
- Expand the existing potential of "*Ionogels*" as a platform to develop stimuli responsive materials.

Experimental

- Nine polymeric ILs were synthesised through direct nucleophillic addition of a trialkylphosphine, **Cytop 360 ($[P_{6,6,6}]$) & Cytop 340 ($[P_{4,4,4}]$)** (Cytec Industries, Ontario Canada) using allyl bromide or 4-benzylvinyl chloride .
- Metathesis reaction once halide salt was formed with sodium dicyanamide [Na][dca] or lithium bis(trifluoromethylsulfonyl)amide [Li][NTf_2] (Sigma Aldrich, Ireland).

(A) (B) (C)

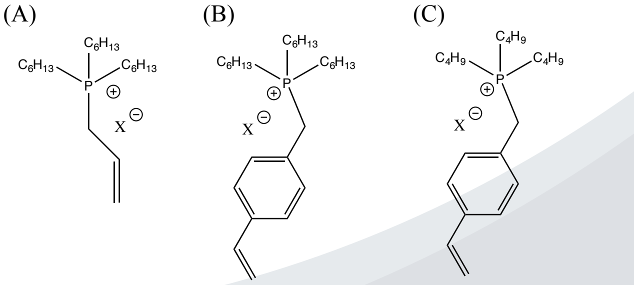

Fig. 1: PILs synthesised (A) Trihexylphosphonium-allyl [x]⁻ ($[P_{6,6,6,allyl}][x]$) (B) Trihexylphosphonium-4benzylvinyl [x]⁻ ($[P_{6,6,6,4VB}][x]$) and (C) Tributylphosphonium-4benzylvinyl [x]⁻ ($[P_{4,4,4,4VB}][x]$) where X = [Cl]⁻, [Br]⁻, [dca]⁻ or [NTf_2]⁻

Results & Discussion

- Table 1 presents early thermal characterisation various PIL. Interestingly the $[P_{6,6,6,4VB}]$[Cl] PIL shows crystalisation / melting behavior whereas $[P_{4,4,4,4VB}]$[Cl] does not.

Table 1: Thermal behavior of PILs synthesised. T_m relates to the glass transition. T_{dec} is the decomposition temperature measured using the onset.

PIL	T_m (°C)	T_{dec} (°C)
$[P_{6,6,6,4VB}]$[Cl]	79	365
$[P_{6,6,6,4VB}][NTf_2]$		449
$[P_{4,4,4,4VB}]$[Cl]	-	382
$[P_{4,4,4,4VB}]$[dca]		376
$[P_{4,4,4,4VB}][NTf_2]$		479

- Fig 2 shows the storage modulus for various PIL during UV curing (DMPA photo initiator added). Polymerisation occurs after 20 min in all cases (modulus plateau reached). Raman spectroscopy (Fig 3) compliments the rheometry (decrease in C=C bonds @ 1650 cm^{-1}).

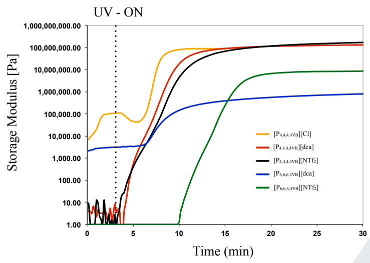

Fig 2: Storage modulus during UV polymerisation of PILs.

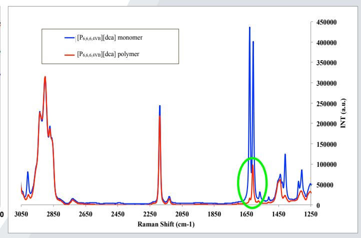

Fig 3: Raman spectroscopy of $[P_{6,6,6,4VB}]$[dca].

- Tan δ vs Temp. experiments show a large difference between $[P_{6,6,6,4VB}][NTf_2]$ and $[P_{6,6,6,4VB}]$[Cl] (Fig 4). We observe a smaller plasticizing effect with the Cl anion (Smaller hydrodynamic radius).

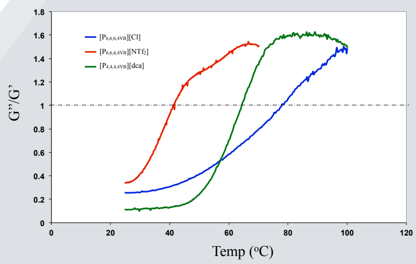

Fig 4: Tan δ vs Temp for $[P_{6,6,6,4VB}]$[Cl], $[P_{6,6,6,4VB}][NTf_2]$, $[P_{4,4,4,4VB}]$[dca] PILs.

Conclusions

- Nine PILs have been successfully synthesised, with characterisation ongoing.
- $[P_{6,6,6,4VB}][NTf_2]$ shows promise as a platform for further development for use in µFluidic devices.

References

[1] Y. Li, G. Li, X. Wang, Z. Zhu, H. Ma, T. Zhang and J. Jin, Chem. Commun., 2012, 48, 8222-8224.
[2] T. J. Wood, W. C. E. Schofield, P. Lund, M. J. Larsen and J. P. S. Badyal, Chem. Commun., 2012, 48, 10201-10203.
[3] J. Lu, F. Yan and J. Texter, Prog. Polym. Sci., 2009, 34, 431-448.

Funding Acknowledgement

This work is supported by a Marie Curie Actions International Re-integration Grant (IRG) (PIRG07-GA-2010-268365) and the Irish Research Council. D. D. acknowledges funding from Science Foundation Ireland (SFI) under the CLARITY CSET award (Grant 07/CE/I1147)

SEVENTH FRAMEWORK PROGRAMME

UNIVERSITY COLLEGE DUBLIN • DUBLIN CITY UNIVERSITY • TYNDALL NATIONAL INSTITUTE