

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

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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 CO₂ 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 nucleophilic 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][NTf₂] (Sigma Aldrich, Ireland).

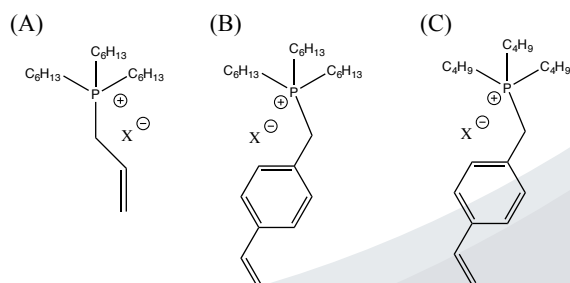


Fig. 1: PILs synthesised (A) Trihexylphosphonium-allyl [x]⁻ ([P_{6,6,6,allyl}][x]) (B) Trihexylphosphonium-4-benzylvinyl [x]⁻ ([P_{6,6,6,₄VB}][x]) and (C) Tributylphosphonium-4-benzylvinyl [x]⁻ ([P_{4,4,4,₄VB}][x]) where X = [Cl]⁻, [Br]⁻, [dca]⁻ or [NTf₂]⁻

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Results & Discussion

- Table 1 presents early thermal characterisation various PIL. Interestingly the [P_{6,6,6,₄VB}][Cl] PIL shows crystallisation / 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) complements the rheometry (decrease in C=C bonds @ 1650 cm⁻¹).

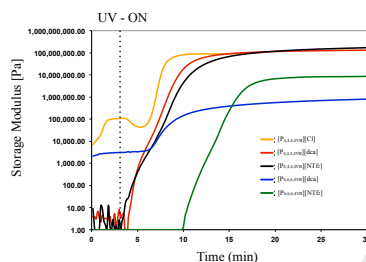


Fig 2: Storage modulus during UV polymerisation of PILs.

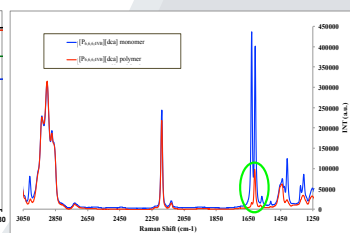


Fig 3: Raman spectroscopy of [P_{6,6,₄VB}][dca].

- Tan δ vs Temp. experiments show a large difference between [P_{6,6,6,₄VB}][NTf₂] and [P_{6,6,6,₄VB}][Cl] (Fig 4). We observe a smaller plasticizing effect with the Cl anion (Smaller hydrodynamic radius).

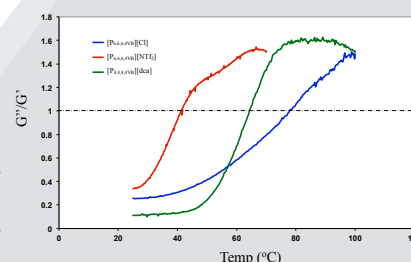


Fig 4: Tan δ vs Temp for [P_{6,6,₄VB}][Cl], [P_{6,6,₄VB}][NTf₂], [P_{4,4,4,₄VB}][dca] PILs.

Conclusions

- Nine PILs have been successfully synthesised, with characterisation ongoing.
- [P_{6,6,6,₄VB}][NTf₂] shows promise as a platform for further development for use in μ fluidic devices.

References

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