Ionic liquid/polyether compatibility in cross-linked ion gel membranes

Megan Macala,[1,2] Victor Kusuma,[1,2], David Hopkinson[1]

[1]National Energy Technology Laboratory, U.S. Department of Energy, [2]AECOM,

Research & Innovation Center

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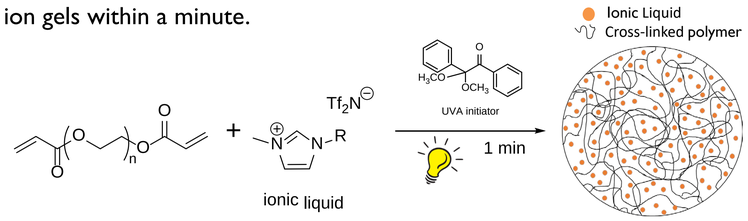
Introduction

- Ionic liquids (ILs) are attractive materials for gas separation due to their CO_2 selectivity over light gases, low vapor pressure, and tunable properties. Polyethylene oxide (PEO) is also an attractive material for gas separation membranes due to its high CO_2/light gas solubility selectivity. **Immobilizing ILs into polymers as ion gel membranes increases the gas permeability of the polymer.**
- A series of free-standing ion gel membranes have been prepared with PEO cross-linked polymers and a variety of commercial ionic liquids **to explore the cation and anion effect on the ion gel phase miscibility and CO_2/N_2 separation performance.**
- A second series of ion gels were prepared **utilizing the IL-PEO interaction to design miscible ion gels with excellent CO_2/N_2 gas separation properties**.

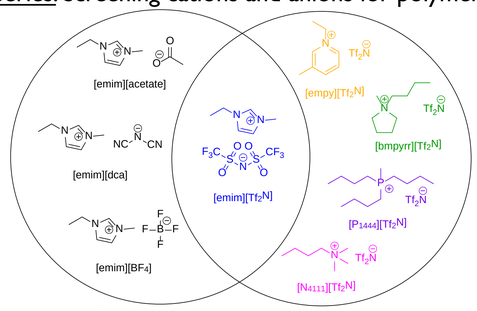
Film Fabrication

We mixed the ionic liquids (40 vol%) directly into the monomer mixture and exposed the reaction mixture to UVA (365 nm) irradiation to afford ion gels within a minute.

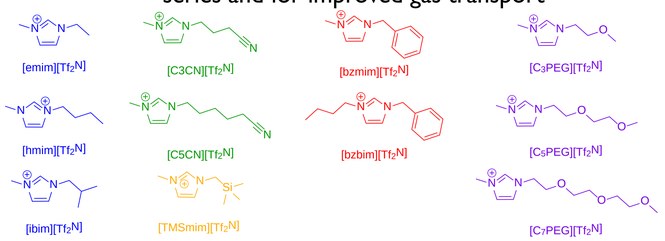


Ionic Liquids

Commercial Series: Screening cations and anions for polymer compatibility



Functionalized Series: Synthesized based on compatibility of commercial series and for improved gas transport

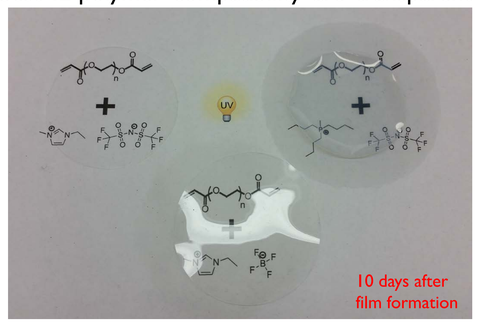


Evaluation of IL/polymer compatibility

Ion gel films with the best IL-polymer compatibility are transparent and completely dry.

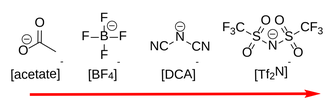
The 'greasy paper' test: observing IL wicking onto a dry, porous surface

- Oily surface or translucency indicates IL-polymer miscibility limit was reached



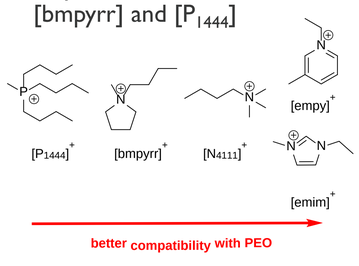
Anion Compatibility:

- Paired with $[emim]^+$ cation
- Completely dry film obtained with 40 vol% [emim][Tf_2N] or [emim][dca]
- [emim][acetate] is immiscible with monomer



Cation Compatibility:

- Paired with $[Tf_2N]^-$ anion
- Aromatic cores gave dry films
- Oily surface obtained for [bmpyrr] and [P_{1444}]



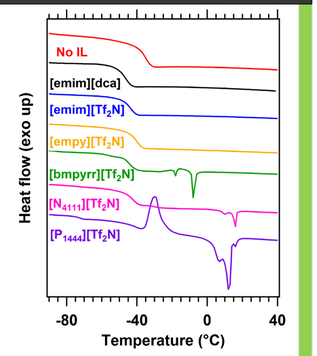
DSC for Evaluating Ion Gel Stability

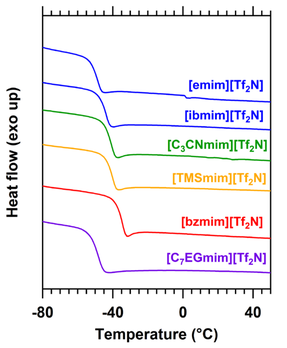
Commercial Series:

- The most stable ion gels were completely amorphous cross-linked polymers
- ↓ T_g with IL incorporation is due to plasticization/reduction in cross-link density
- Melting transitions are due to phase-separated ILs

Functionalized Series:

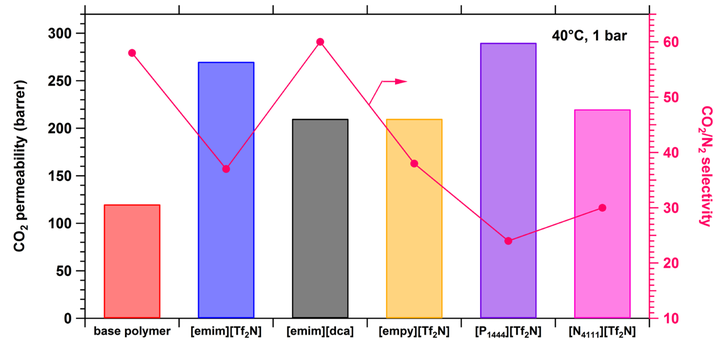
- Ion gel compatibility from commercial series led to development of functionalized imidazolium Tf_2N series
- All films were transparent, dry ion gel films with a single Tg
- ↑ Tg for terminal groups that may make additional non-covalent bonds





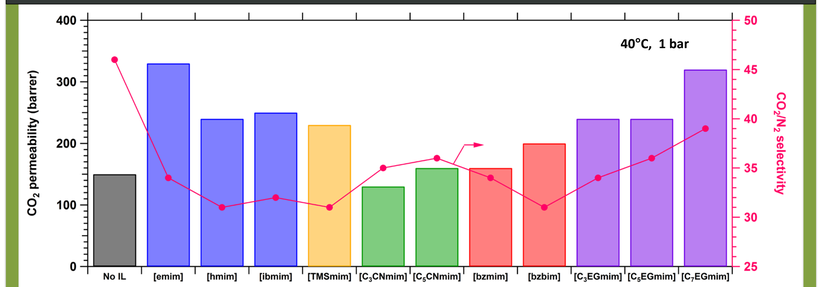
TA Q2000, +10°C/min, third heating scan shown

Commercial Series: Gas Transport Properties



- IL incorporation increases the gas permeability
- Property averaging: reduced CO_2/N_2 selectivity for [Tf_2N] ILs while [emim][dca] maintains high selectivity

Functionalized Series: Gas Transport Properties

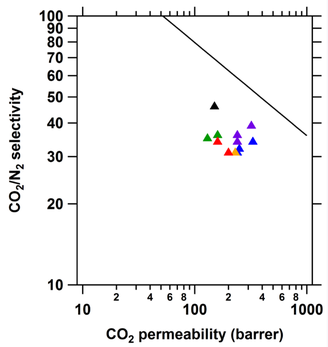


- Cation selection affects permeability and selectivity
- Most ILs have CO_2 permeability less than [emim][Tf_2N] gel
- CO_2/N_2 selectivity is best for nitrile and oligoethylene glycol functionalized ILs

[Tf_2N]$^-$ anion for all ILs

Conclusions

- The interaction of IL cation and anion with PEO determined the ion gel miscibility
- Less basic anions (i.e. Tf_2N, dca) and aromatic cations (imidazolium or pyridinium) provided dry, amorphous ion gel membranes.
- IL-PEO compatibility was used to synthesize functionalized imidazolium Tf_2N ILs that were incorporated into high performance ion gels with excellent phase stability, high gas permeability, and good CO_2/N_2 selectivity.



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