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Polymerized pyrrolidinium-based ionic liquid membranes for CO_2 capture

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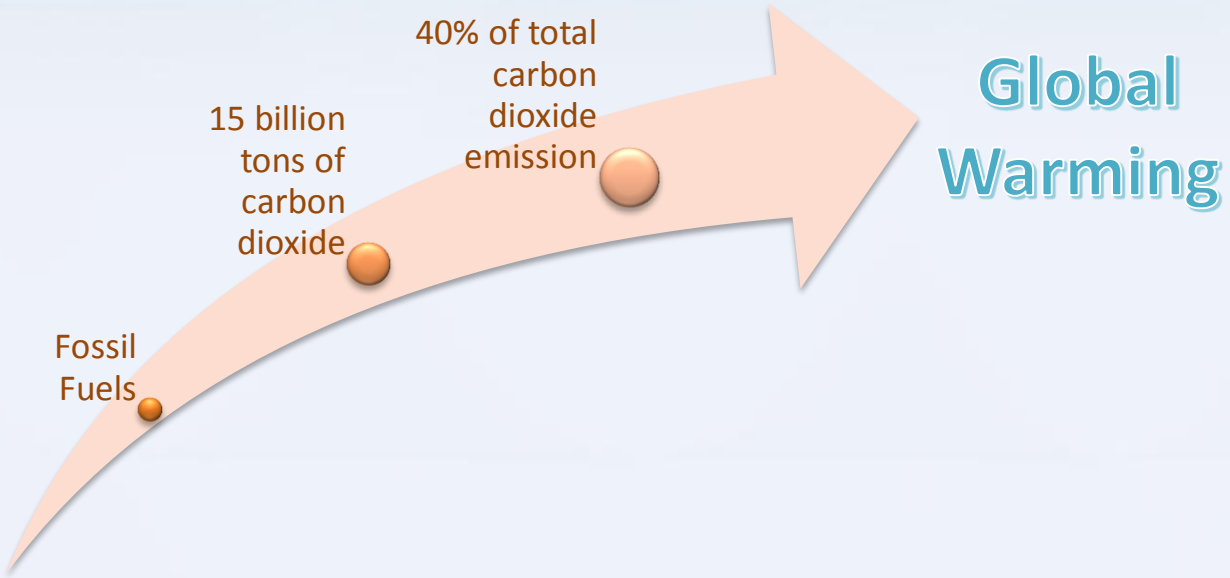
Background



- ***Post-combustion***: capture of CO_2 from flue gases created during fuel combustion with air.
- ***Pre-combustion***: capture of CO_2 from a synthesis gas before fuel combustion.
- ***Oxy-combustion***: capture of CO_2 from flue gases created during fuel combustion with oxygen.
- ***Chemical looping combustion***: capture of CO_2 from flue gases created during combustion with oxygen transported via a metal oxide.

1. Armaroli, N., Balzani, V., ***2011***. Energy for a Sustainable World From the Oil Age to a Sun-Powered Future. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
2. Brett P. Spigarelli, S. K. K., Opportunities and challenges in carbon dioxide capture. Journal of CO_2 Utilization ***2013***, 69-87.

Ionic Liquid Membranes

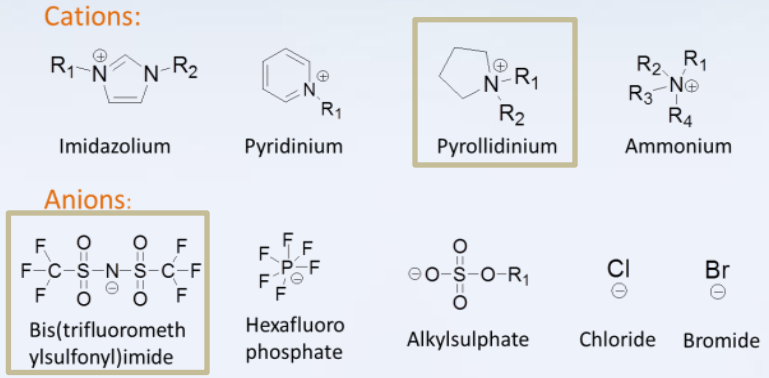
Ionic Liquid (IL)

Molten salt with melting point below 100 °C.

- ✓ High viscosity
- ✓ Negligible vapor pressure
- ✓ Thermal and chemical stability
- ✓ Designable properties by the combination of cations and anions

Membrane technology

- ✓ Low energy consumption
- ✓ Easy to scale up
- ✓ High product purity
- ✓ environmental friendly impact

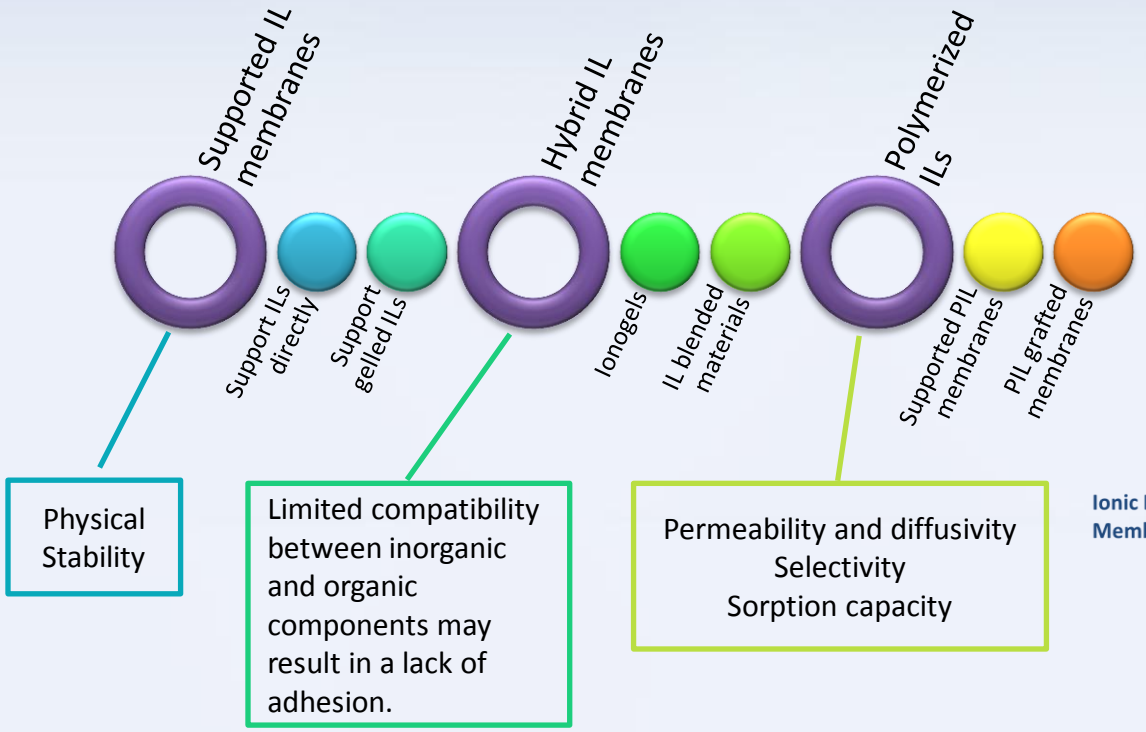


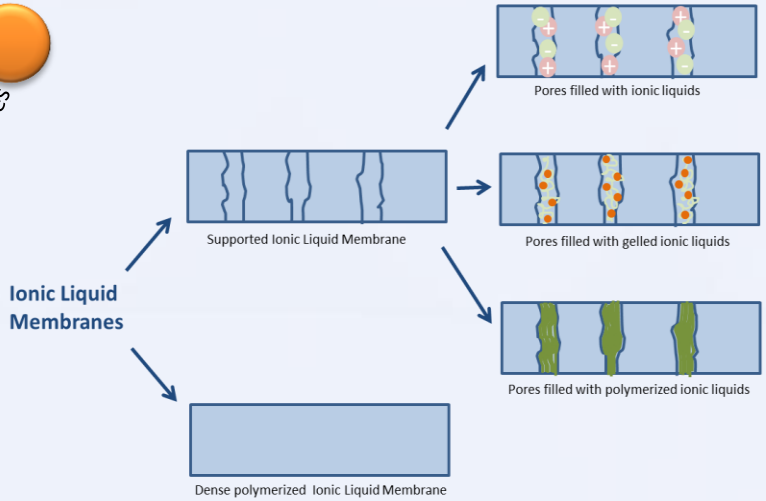
Commonly used cations and anions of ionic liquids.

An effective approach to highlight the properties of ILs and advantages of membrane technologies.

1. S. Heitmann *et. al*, Recovery of n-butanol using ionic liquid-based pervaporation membranes. Separation and Purification Technology ***2012***, 97, 108-114.
2. Bret A. Voss *et. al*, Physically Gelled Ionic Liquids: Solid Membrane Materials with Liquidlike CO2 Gas Transport. Chem. Mater. ***2009***, 21 (14), 3027-3029.
3. Mecerreyes, D., Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. Progress in Polymer Science ***2011***, 36, 1629-1648.

Ionic Liquid Membranes



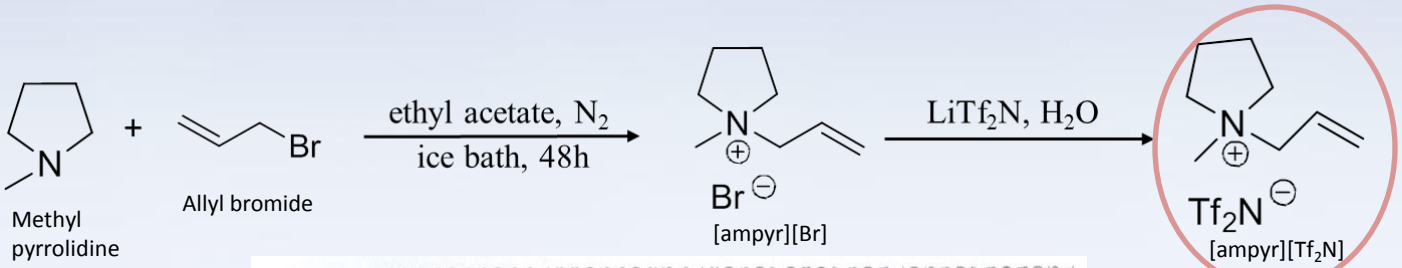


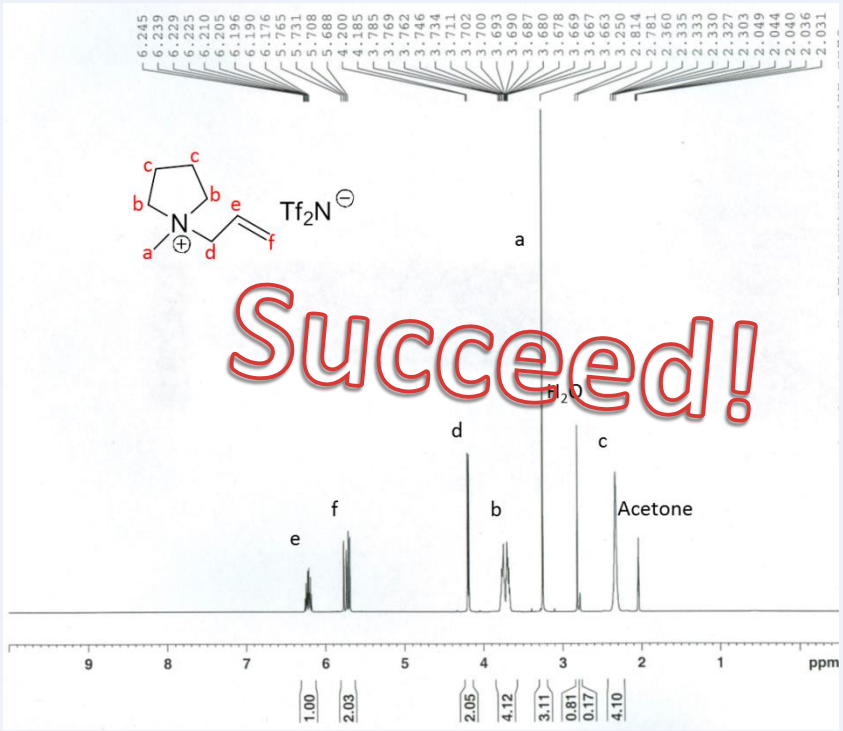
Some configurations of ionic liquid membranes.

❖ **Objective**: Fabricate the dense polymerized IL membranes with novel designed pyrrolidinium-based ILs proposed for CO_2 capture.

1. Paul Scovazzo *et. al*, Supported Ionic Liquid Membranes and Facilitated Ionic Liquid Membranes. In American Chemical Society In Ionic Liquids, ACS: Washingto, DC, **2002**.
2. Jianbin Tang *et. al*, Poly(ionic liquid)s: a new material with enhanced and fast CO_2 absorption. Chemical Comms **2005**, (26), 3325-3327.
3. Jason E. Bara *et. al*, Synthesis and Performance of Polymerizable Room-Temperature Ionic Liquids as Gas Separation Membranes. Ind. Eng. Chem. Res. **2007**, 46, 5397-5404.
4. Jean Le Bideau, L. V. a. A. V., Ionogels, ionic liquid based hybrid materials. Chemical Society Reviews **2011**, (2), 907-925.
5. Hang Zheng *et. al*, PVDF/ionic liquid polymer blends with superior separation performance for removing CO_2 from hydrogen and flue gas. International Journal of Hydrogen Energy **2012**, 37 (16), 11796-11804.
6. Won Seok Chi et. al,, Synthesis, structure and gas permeation of polymerized ionic liquid graft copolymer membranes. Journal of Membrane Science **2013**, 443, 54–61.

Synthesis of IL Monomers

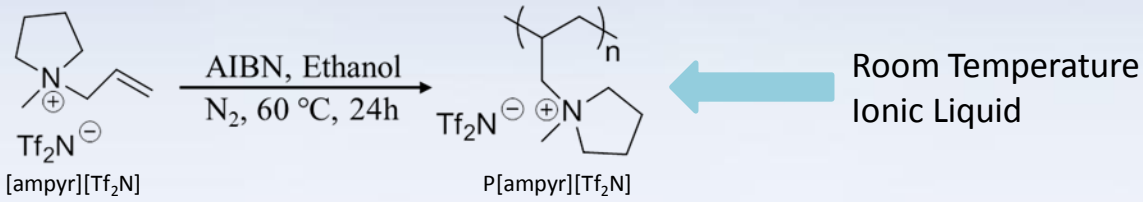




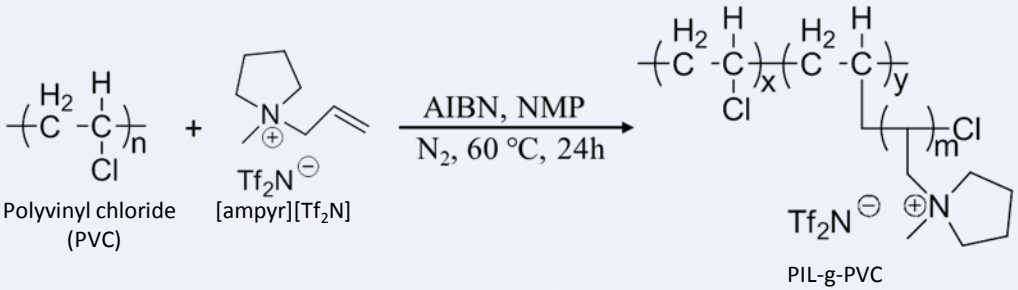
^{1}H NMR spectra of [ampyr][Tf_2N].

1. Anthony K. Burrell, R. E. D. S., Sheila N. Baker, T. Mark McCleskey and Gary A. Baker, The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids. *Green Chem.* **2007,** *9*, 449-454.

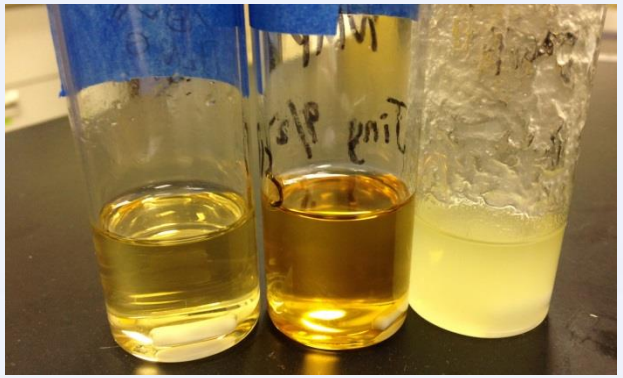
IL Polymerization



[ampyr][Tf_2N] P[ampyr][Tf_2N]



Polyvinyl chloride (PVC) [ampyr][Tf_2N] PIL-g-PVC



From left to right: (1) Ionic liquid [ampyr][Tf_2N], (2) PVC-g-P[ampyr][Tf_2N] in NMP, (3) PVC-g-P[ampyr][Tf_2N] in DMF.

Atom transfer radical polymerization (ATRP)

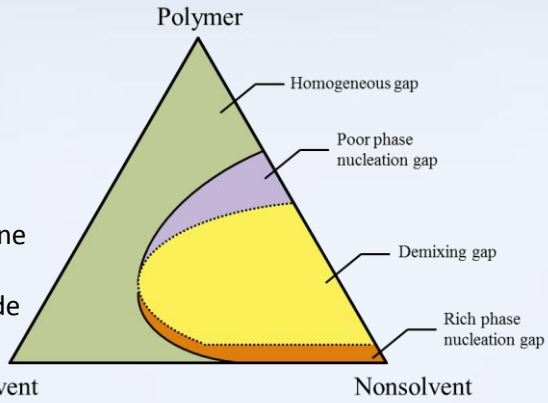
Initiator: azobisisobutyronitrile (AIBN)

- ✓ Direct functionalization
- ✓ No post-polymerization modification required
- ✓ Yields α-telechelic polymers
- ✓ Multiple applicable functionalities (more than those attainable via nucleophilic substitution of ω-end halogen atom)

1. Won Seok Chi *et. al*,, Synthesis, structure and gas permeation of polymerized ionic liquid graft copolymer membranes. Journal of Membrane Science ***2013***, 443, 54–61.
2. NIYAZI BICAK, M. O., Graft Copolymerization of Butyl Acrylate and 2-Ethyl Hexyl Acrylate from Labile Chlorines of Poly(vinyl chloride) by Atom Transfer Radical Polymerization. Journal of Polymer Scienc Part A: Polymer Chemistry ***2003***, 41 (21), 3457-3462.
3. http://www.sigmaaldrich.com/materials-science/polymer-science/atrp.html

Membrane Fabrication

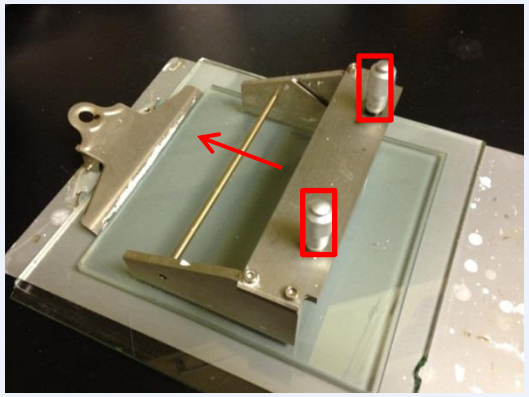
Theory: Phase Inversion



n-methylpyrrolidone (NMP), Dimethylformamide (DMF).

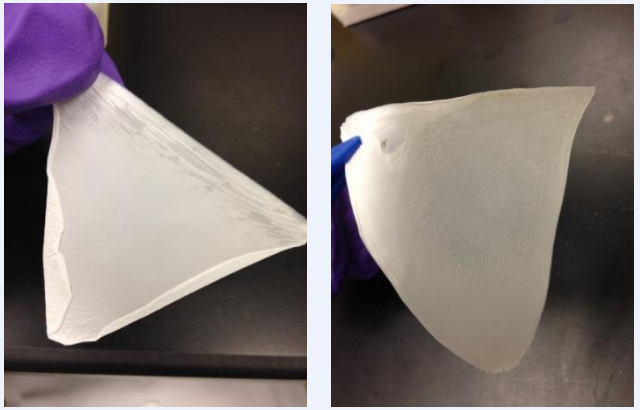
Ternary phase diagram of polymer–solvent–nonsolvent.

Method: Casting Solution



Casting knife for membrane fabrications.

Membrane fabrication using NMP (left) and DMF (right) as solvent.

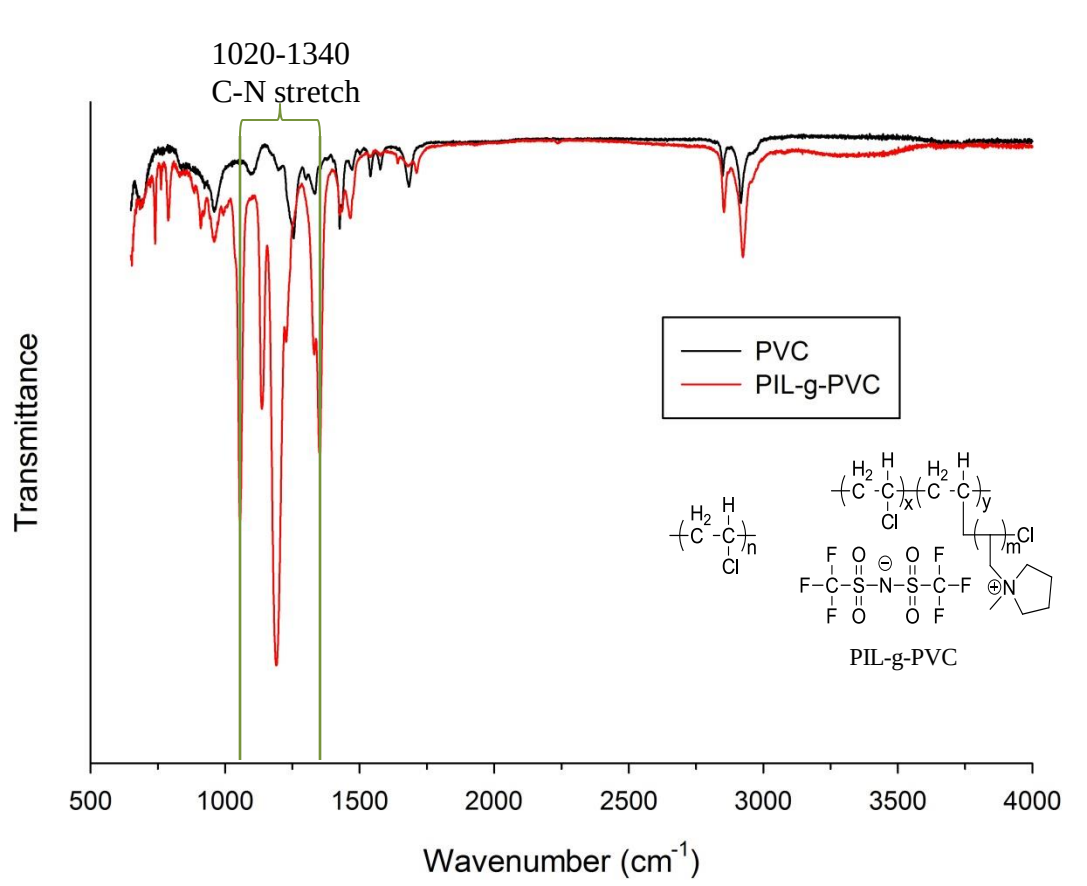


Pure PVC membrane (left) and PVC-g-P[ampyr][Tf_2N] membrane (right).

1. Yan Ren, F. L., Yan Wen, Hong-Yan Guan, A novel PVFM based membranes prepared via phase inversion method and its application in GPE. Polymer ***2013***, 54 (18), 4807-4813.
2. Katrien Hendrix, M. V., Guy Koeckelberghs, Ivo F.J. Vankelecom, Synthesis of modified poly(ether ether ketone) polymer for the preparation of ultrafiltration and nanofiltration membranes via phase inversion. Journal of Membrane Science ***2013***, 447, 96-106.

Membrane Characterizations

1. Fourier transform infrared spectroscopy (FT-IR).

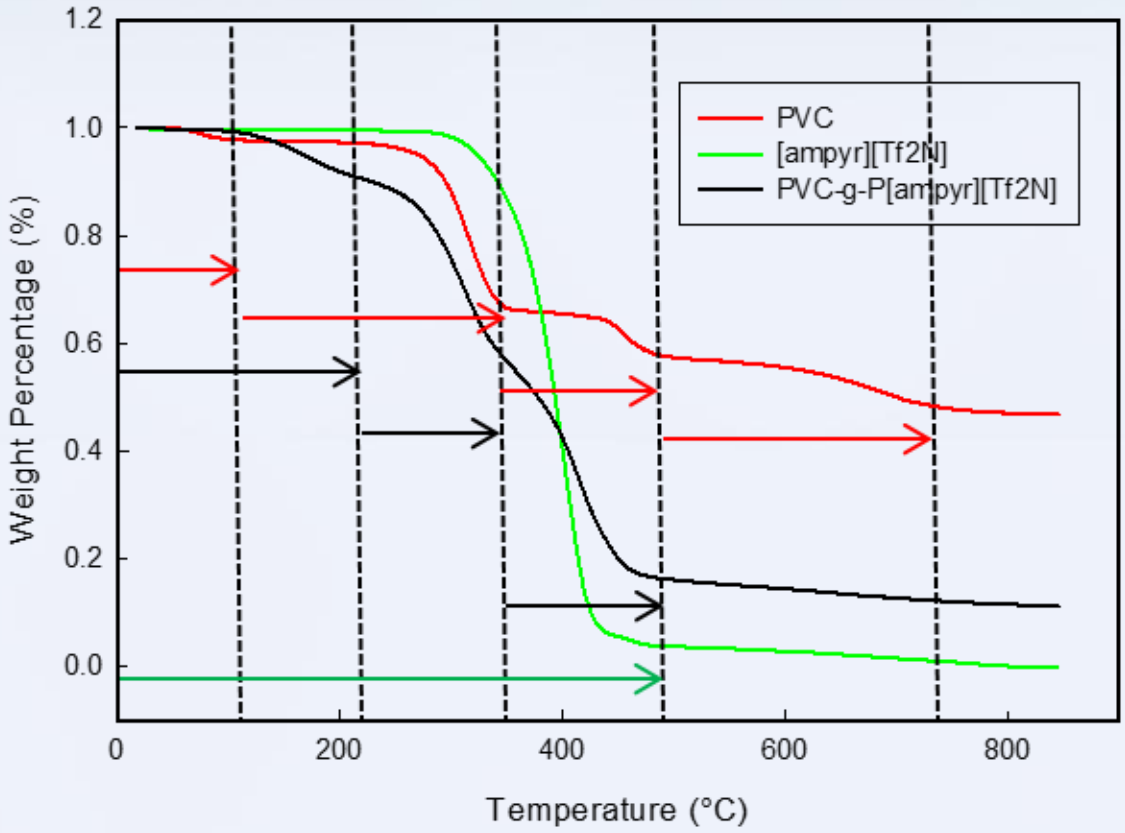


FT-IR spectrum of the PVC and IL membranes.

1. http://wwwchem.csustan.edu/Tutorials/INFRARED.HTM

Membrane Characterizations

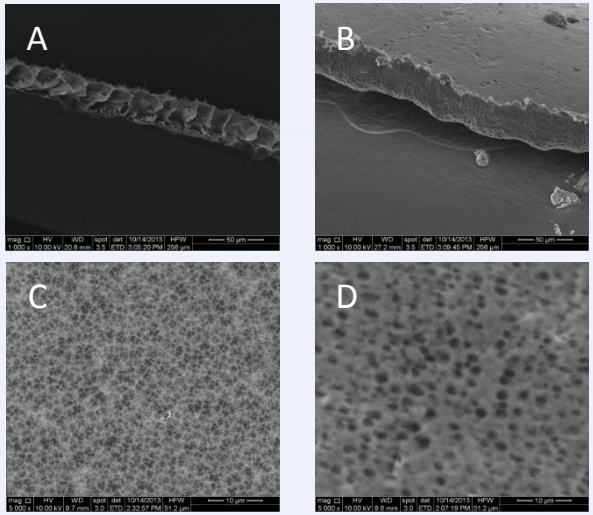
1. Thermo gravimetric analysis (TGA).



TGA analysis of IL, PVC and IL membranes.

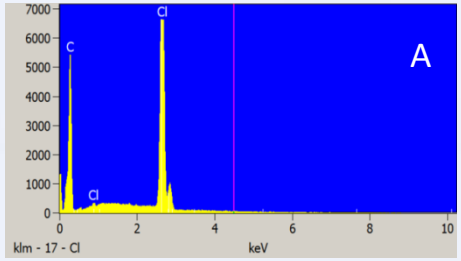
Membrane Characterizations

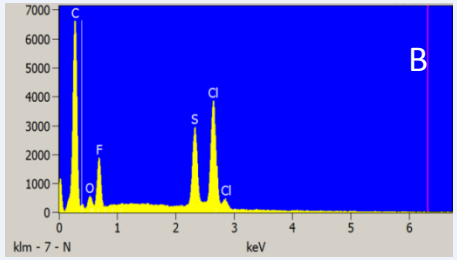
2. Scanning electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS).



SEM spectra of (A) cross section of pure PVC membrane, (B) cross section of PVC-*g*-P[ampyr][Tf_2N] membrane, (C) surface of pure PVC membrane, (D) surface of PVC-*g*-P[ampyr][Tf_2N] membrane.

- Thickness: 20 µm.
- Pore sizes: PVC < PVC-g-IL.
- Solid part, PVC-g-IL is denser than PVC.





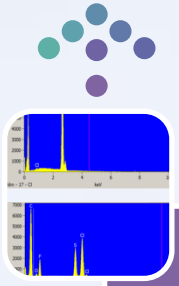
EDS spectra of (A) pure PVC membrane, (B) PVC-*g*-P[ampyr][Tf_2N] membrane.

- Pure PVC: C, Cl.
- PVC-g-IL: C, O, F, S. Cl.

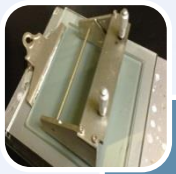
Conclusions

CO_2 Capture Performance?

- Membrane characterization with FT-IR, TGA, SEM and EDS. Successfully have the IL component added in the membranes.
- Fabricate the PVC-*g*-P[ampyr][Tf_2N] membranes with casting solution method based on the phase inversion theory.
- Synthesized the PVC-*g*-P[ampyr][Tf_2N] copolymer in NMP/DMF solvent with AIBN as initiator through ATRP.
- Succeed on synthesis of IL with doubld bond ([ampyr][Tf_2N]), proposed to have ILs task specific.

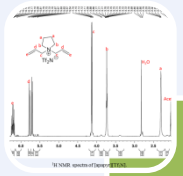


Membrane Characterizations



Membrane Fabrication

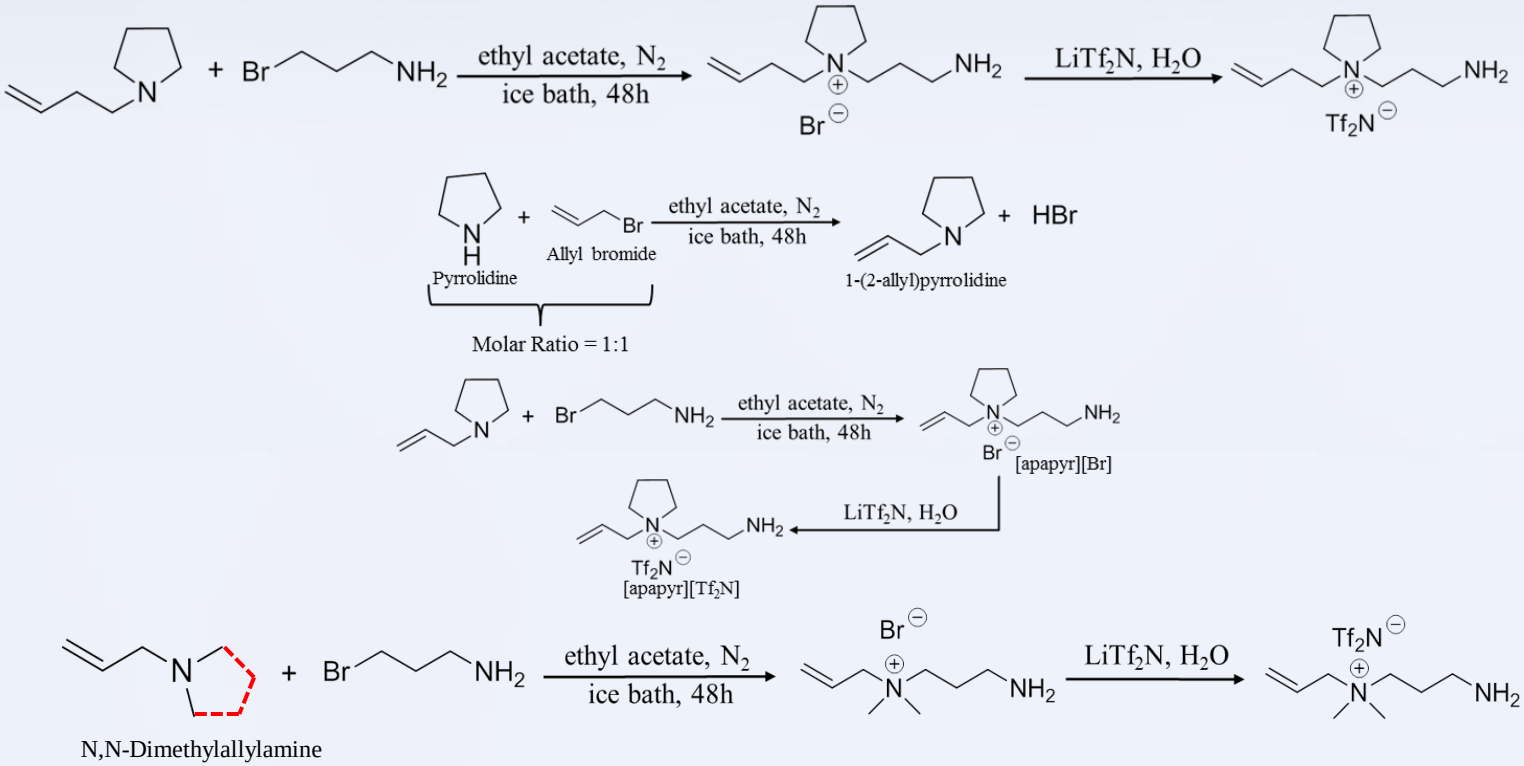
IL Polymerization



Ionic Liquid Synthesis

Future Works

1. Synthesis of pyrrolidinium-based IL with $-NH_2$ functional group.



2. Membrane CO_2 performance test.

1. Shannon M. Mahurin, J. S. Y., Sheila N. Baker, De-en Jiang, Sheng Dai, Gary A. Baker, Ring-opened heterocycles: Promising ionic liquids for gas separation and capture. Journal of Membrane Science ***2012***, 401-402, 61-67.

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Thank you!

Questions or Comments?