

Structural design of cross-linked polymer and ionic liquids for ion gel gas separation membranes

Victor Kusuma,^{1,2} Samir Budhathoki,^{1,2} James Baker,¹ Megan Macala,^{1,2} David Hopkinson¹

¹ U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA / Morgantown, WV

² Leidos Research Support Team, Pittsburgh, PA

Research & Innovation Center



Membranes for Carbon Capture

High performance membranes are needed to enable economical capture of CO₂ from large point sources such as coal-fired power plants. Any separation scheme involving flue gas treatment must contend with **large volumetric flow** (600 MW_e = 500 m³/s flue gas = 460 tons CO₂/h), **low CO₂ concentration** (<13 mol%) and low levels of **contaminants** (SO_x, NO_x and trace metals).¹ Membranes with higher permeances with reasonable CO₂/N₂ selectivity are required to reduce module size and reduce overall capture cost.

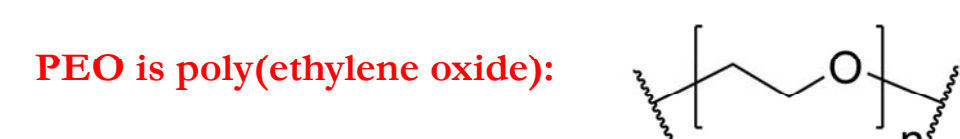
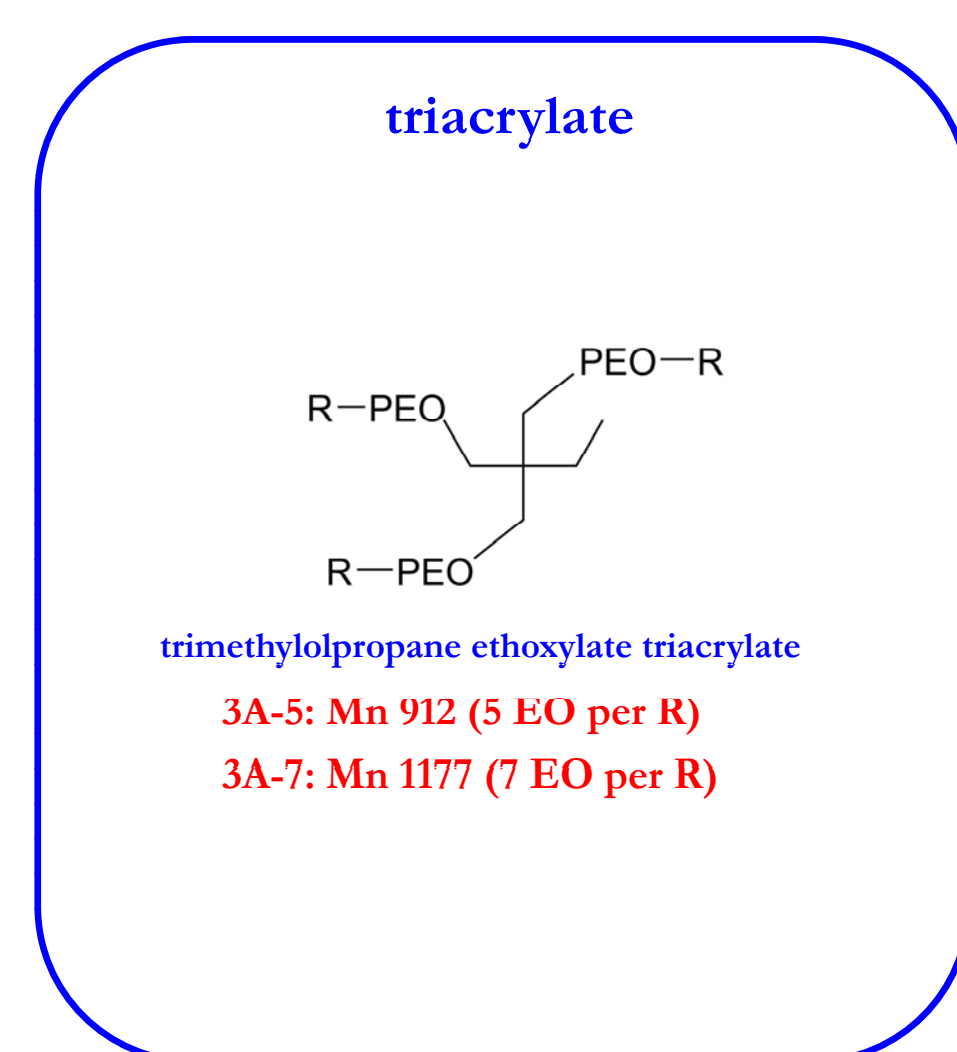
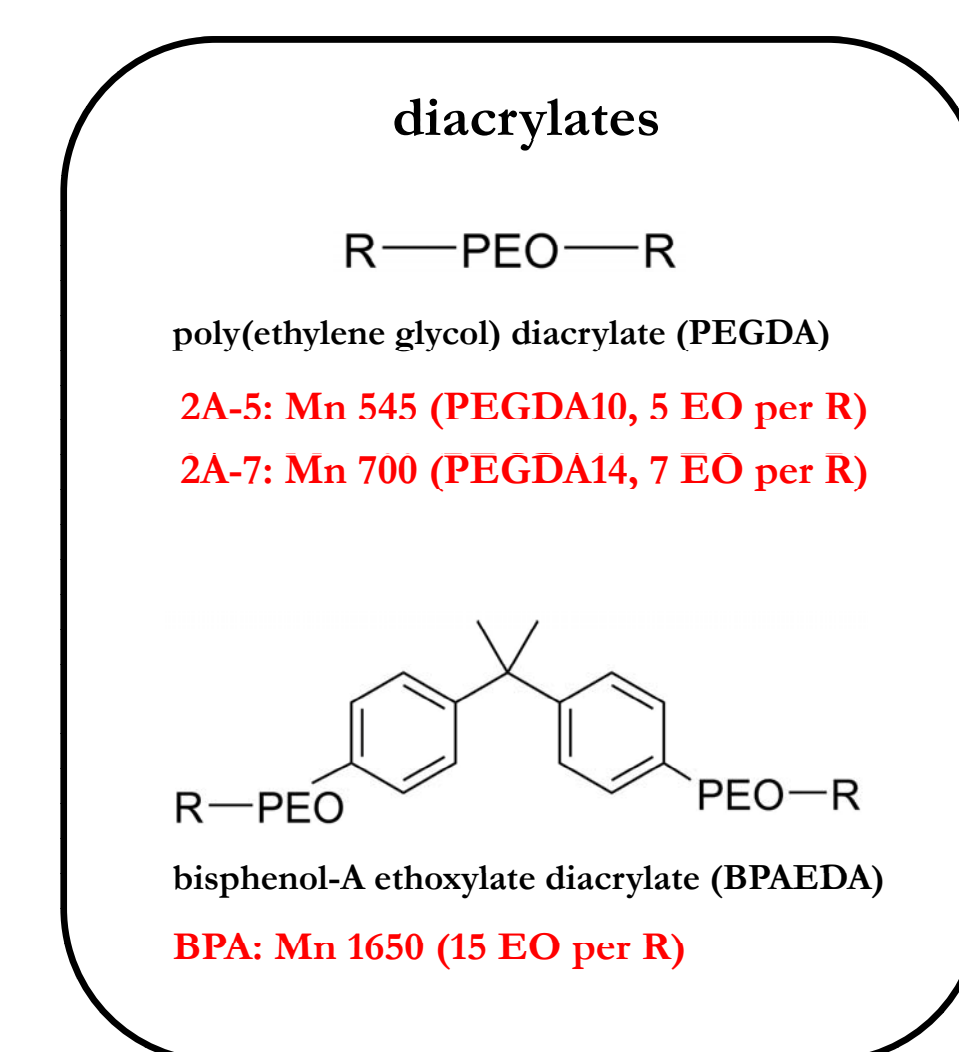
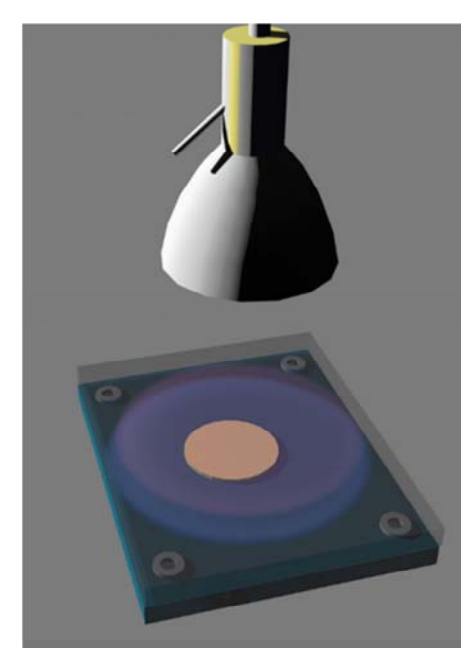


20 ton/day CO₂ capture experimental membrane system installed by MTR, Inc. at the National Carbon Capture Center.³

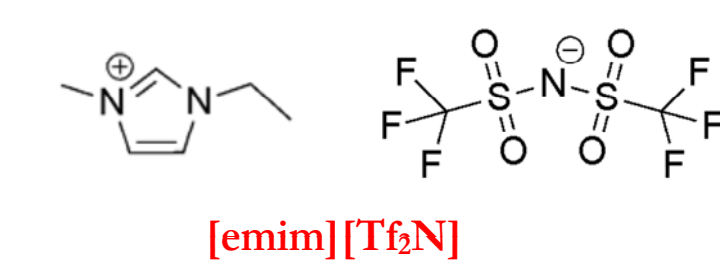
In the past few years, we have optimized ion gels by screening the ionic liquid plasticizers to increase gas permeability and modifying the cross-linked polyether host networks.² Some of our most useful findings are summarized here.

Polymer Design

The polymer in this study is a **cross-linked poly(ethylene oxide)** (XLPEO) which, as a class, has exceptional CO₂/N₂ selectivity with moderately high CO₂ permeability.⁴ PEO-based materials interact well with 1,3-substituted imidazolium cations. [emim][Tf₂N] is miscible with many PEGylated liquid acrylate monomers and can remain as permanent plasticizers in the networks obtained as these monomers are polymerized. Mixtures of polymer and ionic liquid can be fully cured within 30 seconds under low power UVA (λ=365 nm) source.



A 3A-7 ion gel containing 40 vol% [emim][Tf₂N].

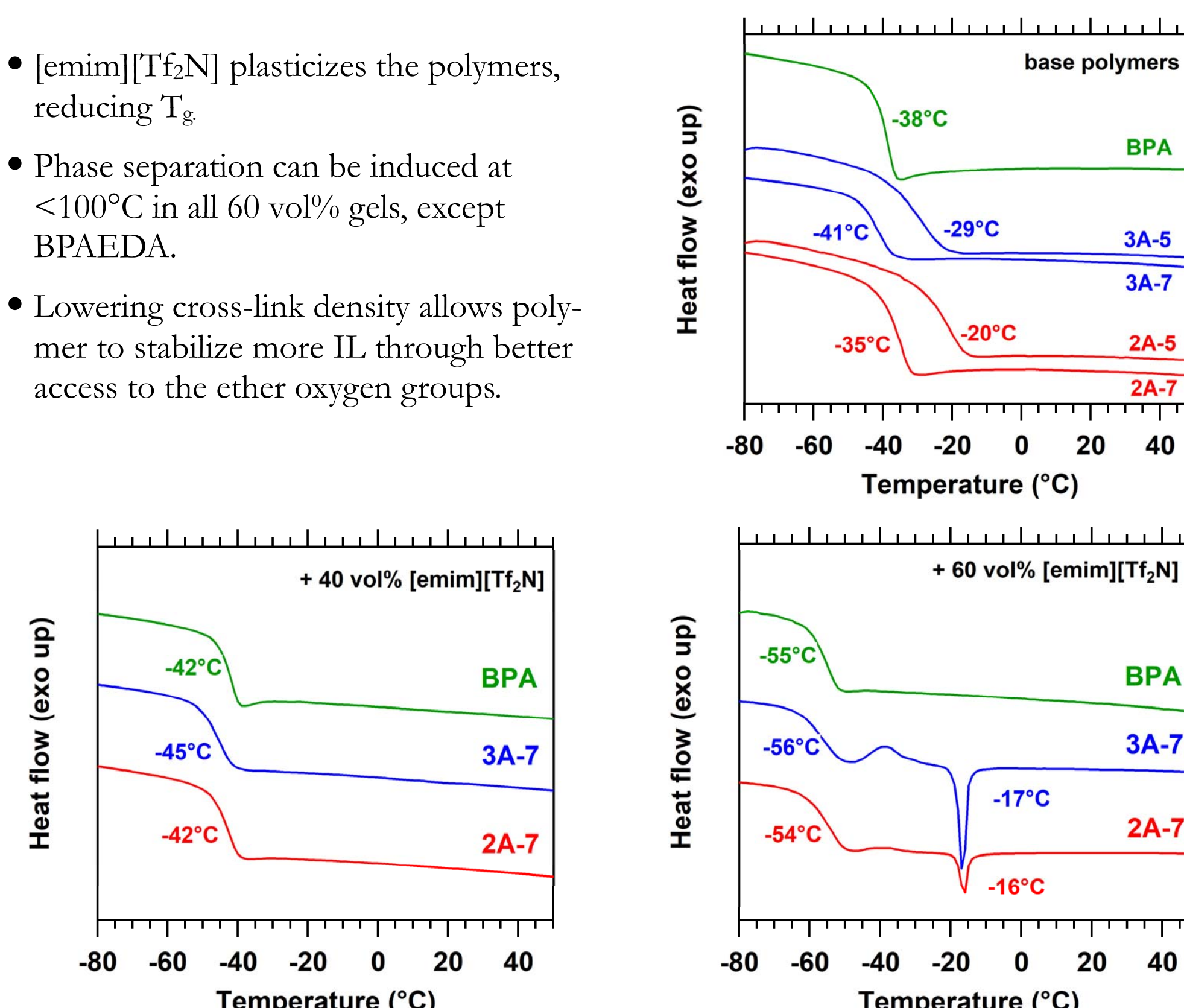


The study focuses on changing the chain length between cross-links by comparing polymers and ion gels made from **2A-5, 2A-7, 3A-5, 3A-7, and BPA**.

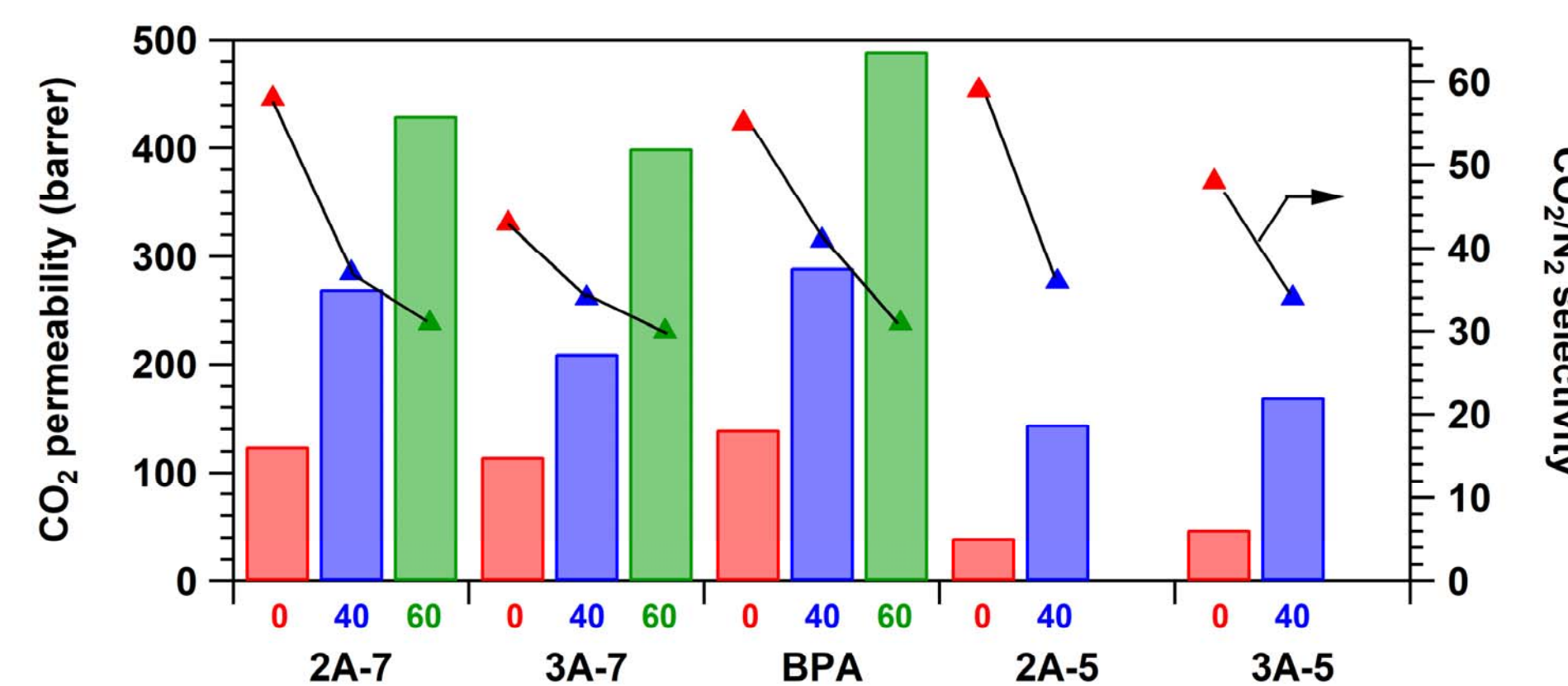
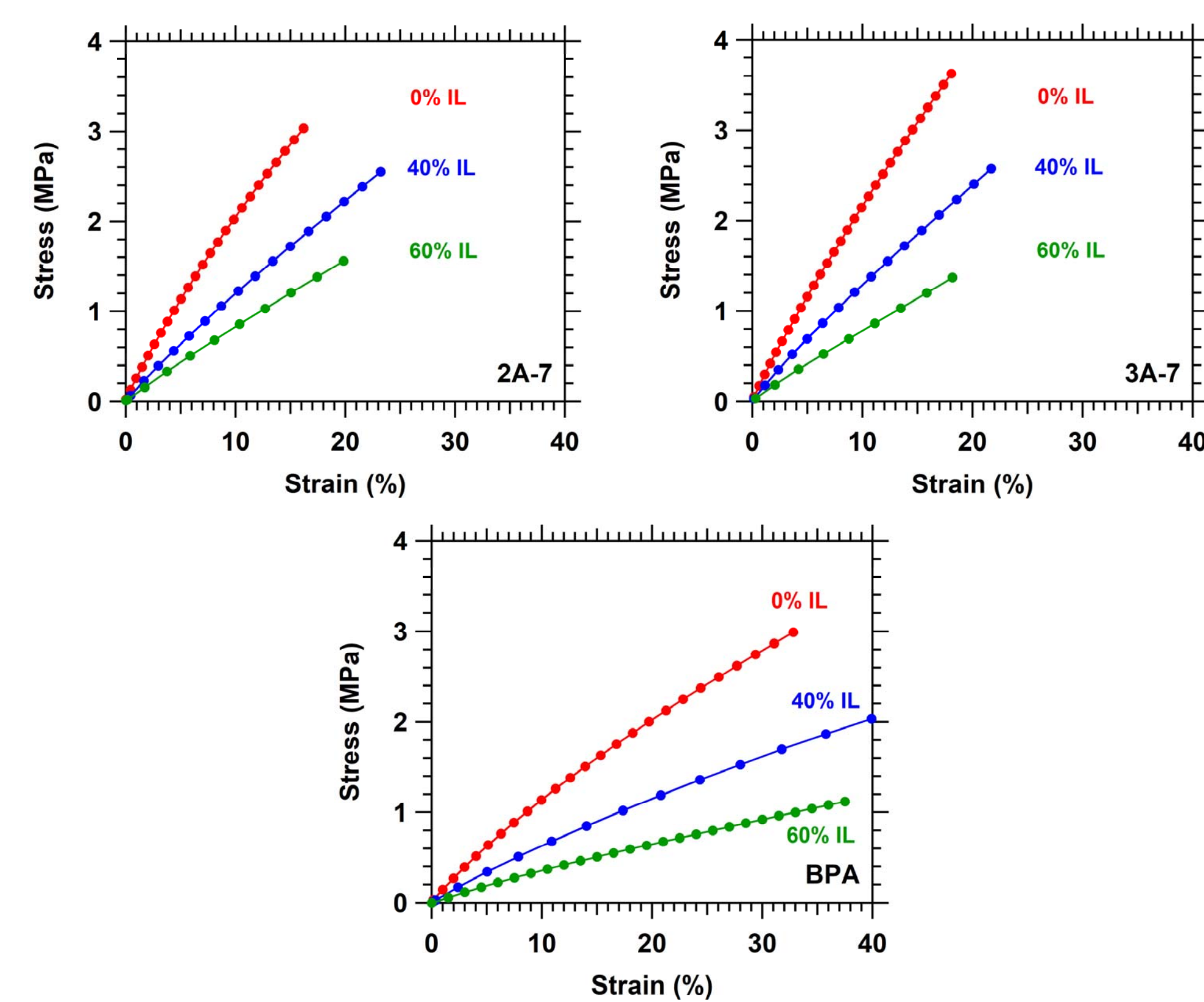
Wherever applicable, ion gels consisting of **40 vol%** and **60 vol%** [emim][Tf₂N] were fabricated. All diacrylate and triacylate networks containing 40 vol% IL are stable, transparent, dry films. 60 vol% IL films are also stable and dry except for the **2A-5** and **3A-5**, which have residual IL on the surface.

Polymer Cross-link Density Study

- [emim][Tf₂N] plasticizes the polymers, reducing T_g
- Phase separation can be induced at <100°C in all 60 vol% gels, except BPAEDA.
- Lowering cross-link density allows polymer to stabilize more IL through better access to the ether oxygen groups.



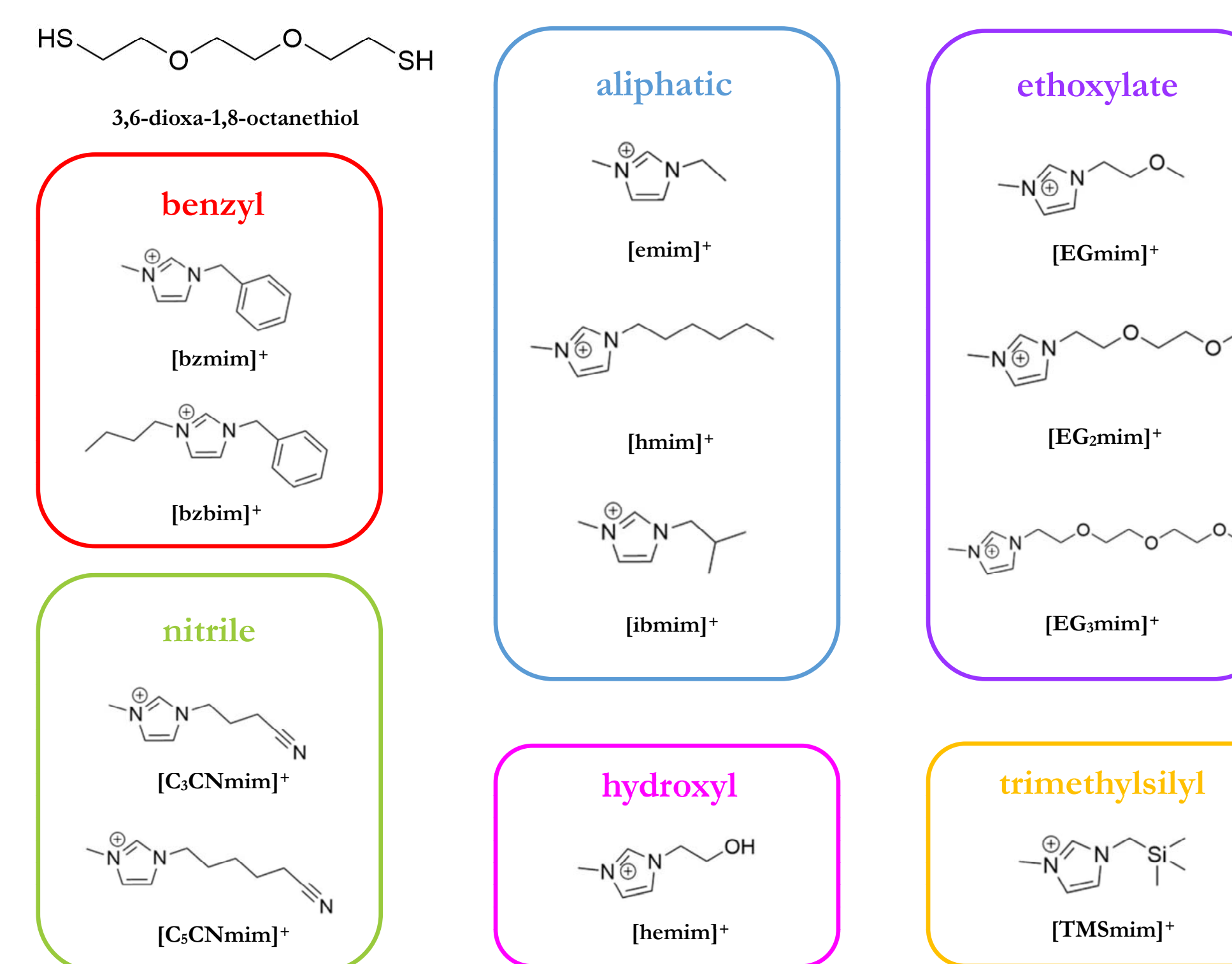
- No difference in mechanical properties between diacrylate and triacylate polymers with same distance between cross-links (e.g. 2A-7 with 3A-7).
- IL plasticized networks have slightly better flexibility at 40 vol%. Yield strength and Young's modulus are reduced by IL incorporation.
- The BPAEDA networks are more flexible than PEGDA due to lower cross-link density.



- Gas permeability is increased with lower cross-link density. This holds true for the ion gels as well as the base polymers.
- CO₂/N₂ selectivity decreases with increasing IL content. The reduction in EO content reduces CO₂/N₂ solubility selectivity: [emim][Tf₂N] is less CO₂-selective than PEO.

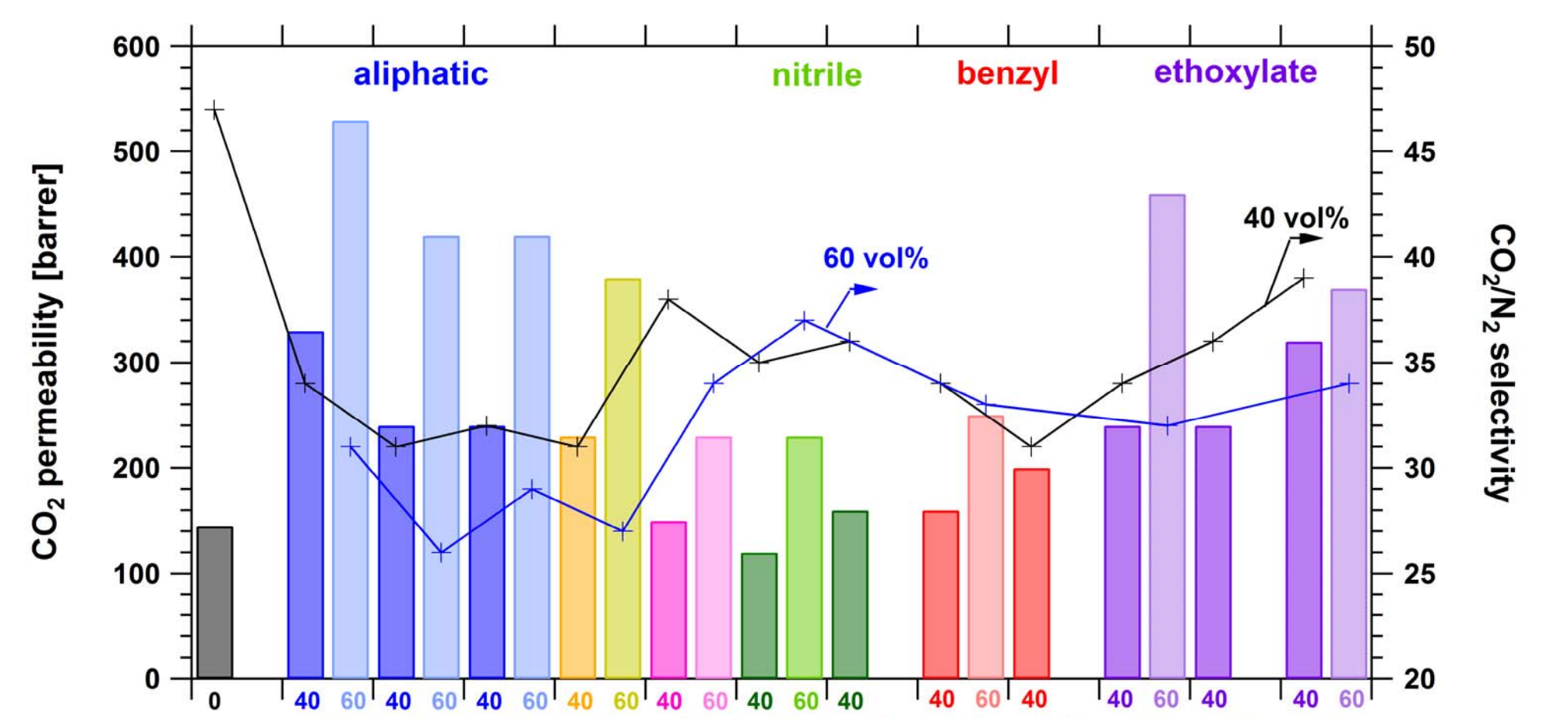
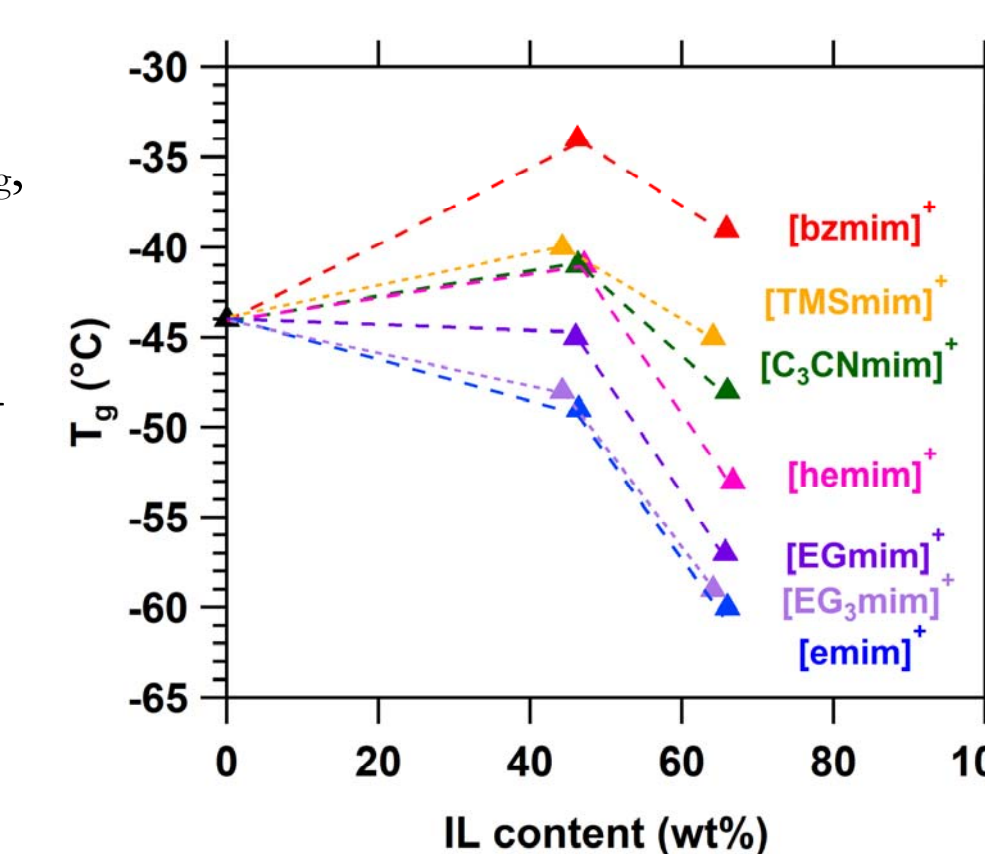
Ion Gels with [Rmim][Tf₂N]

Using **3A-7** and an ethoxylated dithiol co-monomer to reduce cross-link density, a series of 40 vol% and 60 vol% ion gels were made by incorporating 1-substituted-3-methyl imidazolium [Tf₂N] ionic liquids⁵ to evaluate the effect of incorporating alkyl, benzyl, hydroxyl, nitrile and alkoxy tails into the plasticizers. All films were stable, transparent and dry.

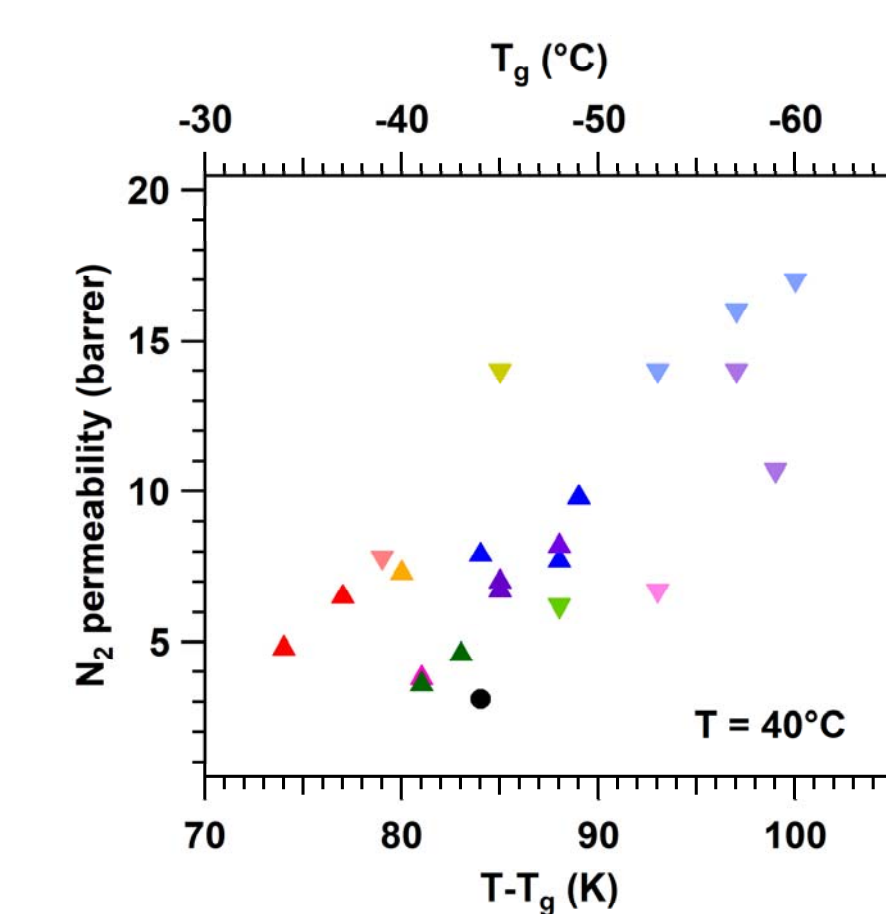


Effect of IL Functional Group

- T_g is affected by the IL present. ILs with aliphatic and ethoxylate tails effectively lower T_g, whereas ion gels with benzyl, nitrile and hydroxyl tails have higher T_g.
- The functional group may influence intermolecular interactions within the ion gel, affecting overall polymer chain mobility.

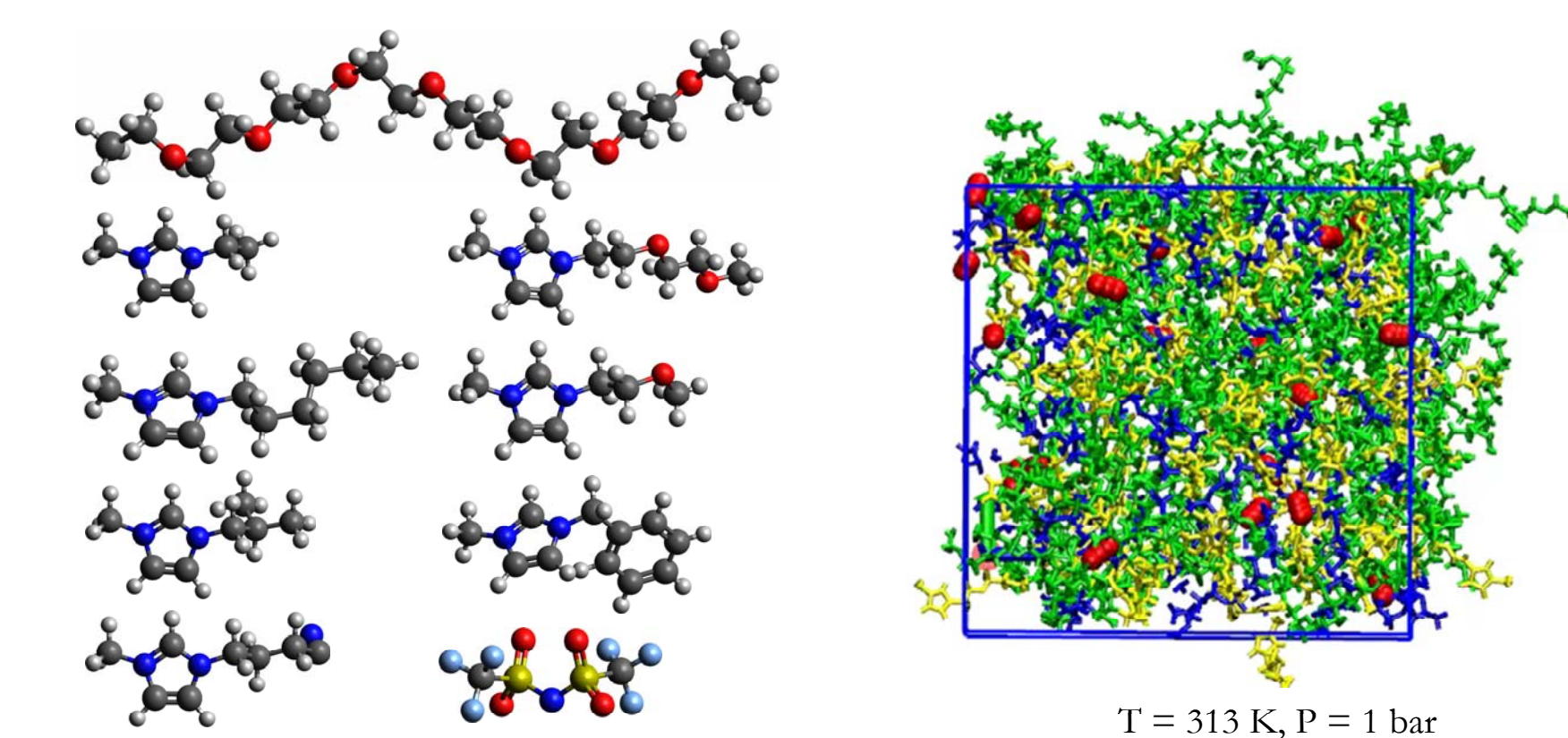


- [emim][Tf₂N] is most effective in increasing gas permeability among the alkyl ILs.
- Ethoxylated ILs do not increase permeability as much as the alkyl. At higher IL content, IL cation head-to-tail interactions become increasingly significant, increasing cohesive energy density (CED).
- Benzyl, nitrile and hydroxyl groups also increase CED through additional interactions within the network. These ion gels have the lowest gas permeability.
- The T_g strongly predicts gas permeability but is not the only determining factor.



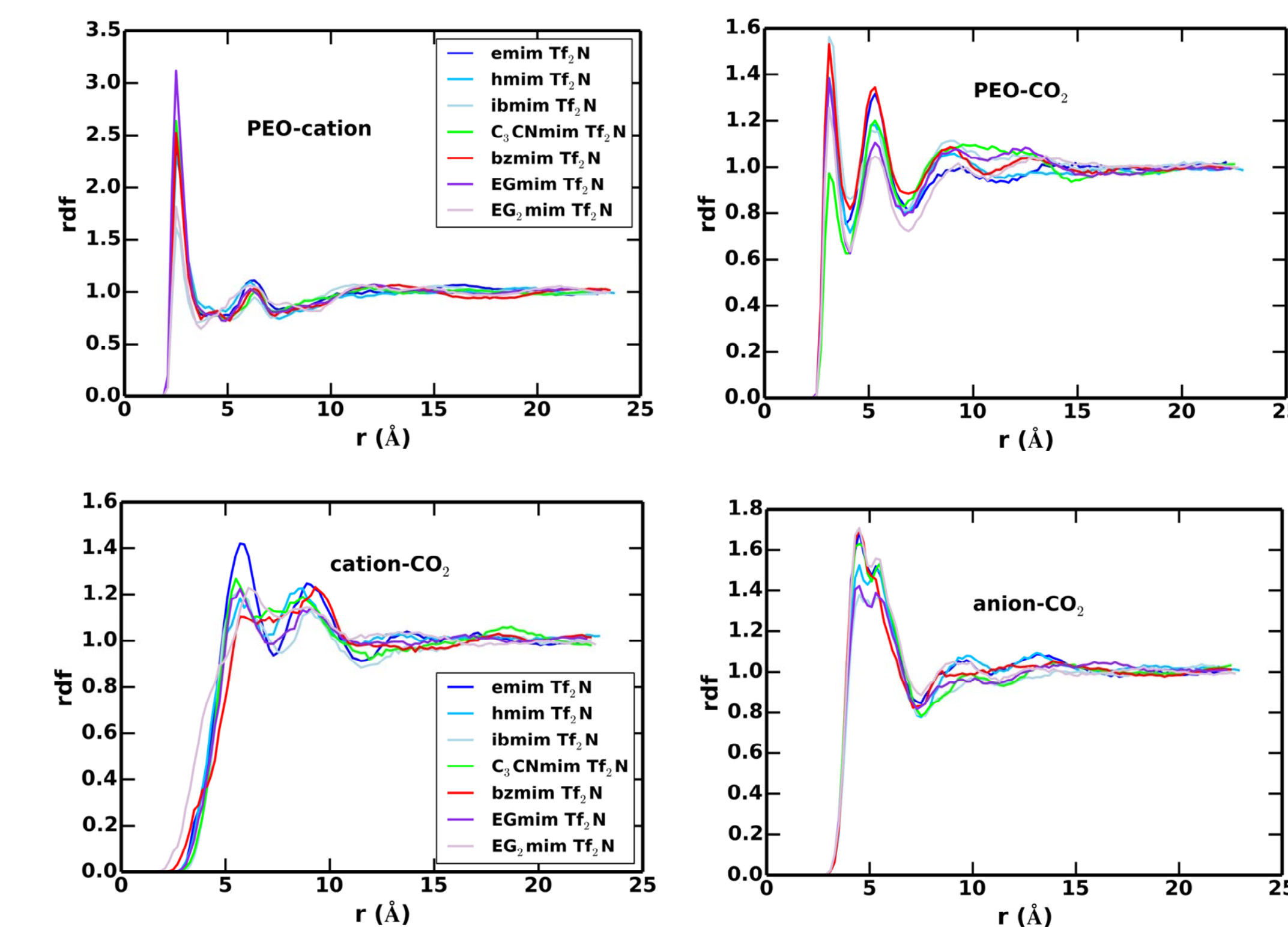
Molecular Dynamics of IL+PEO+CO₂

MD simulation helps shed light on the IL-PEO interactions with each other and CO₂. We initially simplify the cross-linked polymer as an **uncross-linked, low M_n PEO** (7 repeat units) with alkyl end-caps (a.k.a. heptaglyme) to focus on the different interactions.

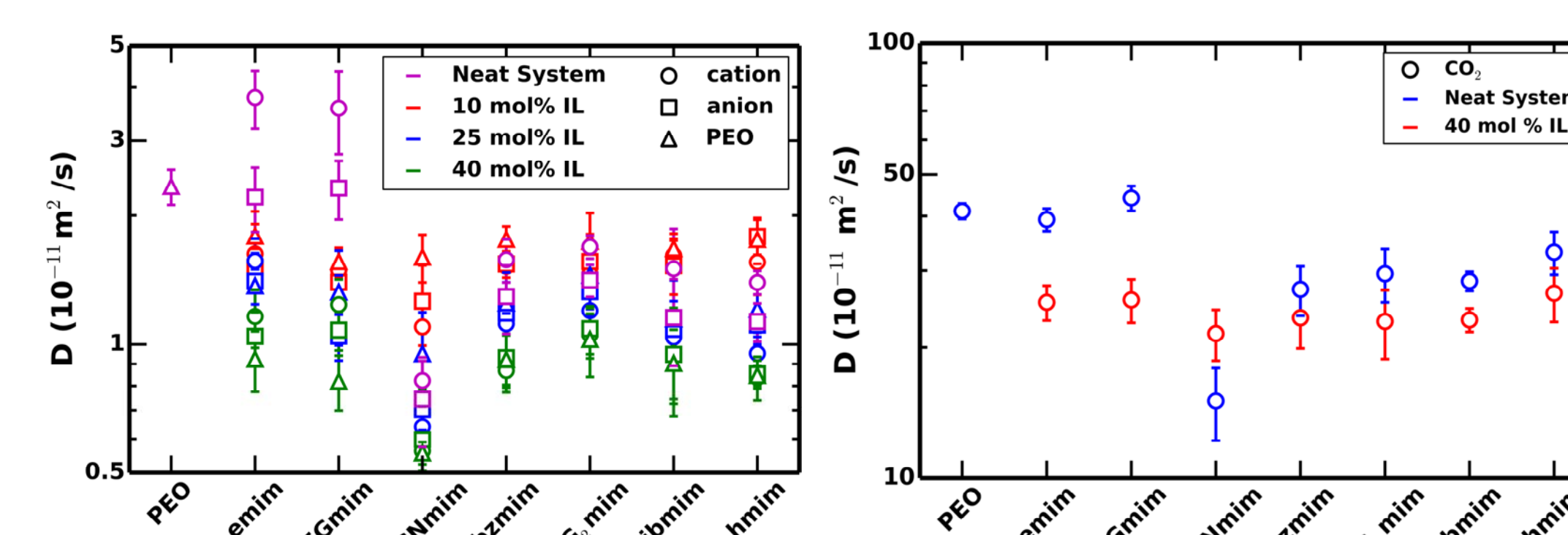


IL + PEO + CO₂ Interactions

- All imidazolium cations show strong interactions with PEO through H-bonding on the imidazolium core C-2 proton, regardless of the tail identity.
- CO₂ interactions is in the order PEO > anion > cation in the mixtures, except in [C₂CNmim][Tf₂N] where CO₂ favors the IL.
- ILs with benzyl and longer tails (e.g. EG₂mim and hmim) show smaller CO₂-cation peaks due to steric hindrance effects.



- Due to strong PEO-cation interactions, the diffusion coefficient differences between cations, anions and PEO across all mixtures tend to disappear. All components diffuse as a cohesive unit.
- Due to increasing CED in an IL+PEO mixture, CO₂ diffusion coefficients are lower than in neat systems, and become similar across all mixtures regardless of IL identity.
- These analysis may not apply to cross-linked networks where PEO is much less mobile



¹Merkel, T.C.; Lin, H.; et al. *J. Membr. Sci.* **350**, 126 (2010); ²Kusuma, V.N.; Macala, M.K.; et al. *J. Membr. Sci.* **545**, 292 (2018); *Ind. Eng. Chem. Res.* **57** (34), 11658 (2018); *Polymer* **180** doi:10.1016/j.polymer.2019.121666 (2019); ³Merkel, T.C. DE-FC0005795 Final Report (2016); ⁴Lau, J.; Hou, X.; et al. *Chem. - A Eur. J.* **22** (43), 15980 (2016); ⁵[Bara, J]; Gabriel, C.J.; et al. *Ind. Eng. Chem. Res.* **46** (16), 5380 (2007); [Bara, J]; Gabriel, C.J.; et al. *J. Membr. Sci.* **321**, 3 (2008); [Bara, J]; Carlisle, T.K.; et al. *Ind. Eng. Chem. Res.* **48** (6), 2736 (2009); [Horec, W]; [Andrews, M.A]; et al. *Sep. Purif. Technol.* **155**, 89 (2015)

DSC: TA Instruments Q2000, +10°C, heat/-10°C, cool between -85°C and 100°C, third scan shown. DMA: TA Instruments Q800, controlled force mode (tensile test), 40°C, 1 N/min ramp until fracture. Gas permeation: Pure gas/constant volume, 40°C, data shown at 1 bar.

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