

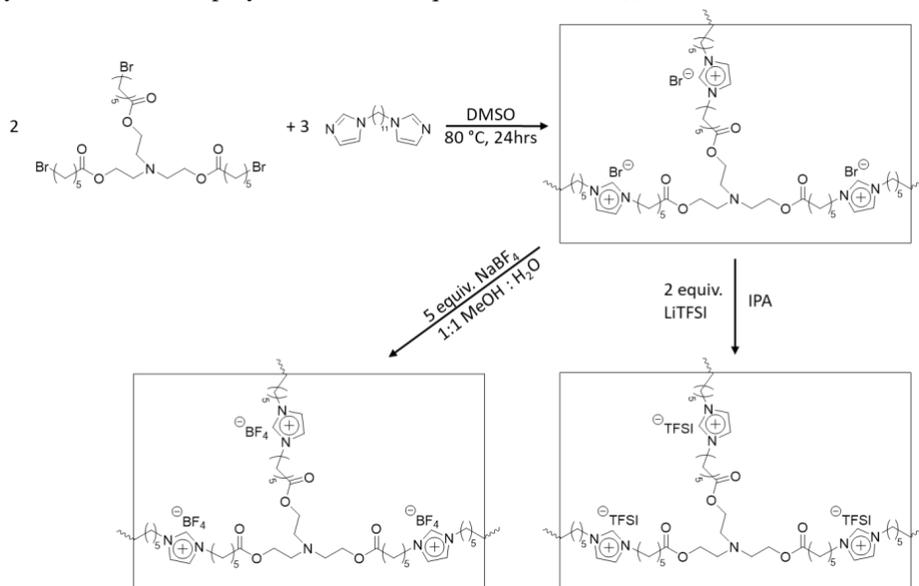
PRF Grant Number 58056

Understanding Organic Liquid Separations in Polymerized Ionic Liquid Networks and Blends
Christopher M. Evans, University of Illinois, Urbana-Champaign

Membranes are a promising route to energy efficient separations of species which require much less energy input than techniques such as distillation. Ionic liquids (ILs), composed entirely of molecular cations and anions, have recently shown promise as membranes for gas (CO₂) and liquid (hydrocarbon) separations. Typically, they are supported in a porous framework which can lead to leaching of the IL under pressure or due to solubility with a neighboring phase. Our project is focused on the molecular design and development of polymerized ionic liquid (PIL) membranes where one of the ions is tethered to a polymer network. This prevents ions from diffusing out of the separator and can lead to a more robust yet flexible membrane. Additionally, we are designing the cations (aromatic and nonaromatic), anions (hydrophilic vs hydrophobic, varying size and electrostatics), and network chemistry (silicone, hydrocarbon, ethylene oxide) to control interactions with penetrant liquid molecules. The first system of interest is toluene/heptane which both have seven carbons and similar boiling points. Thus, a passive membrane separation based on shape or aromaticity selectivity would be beneficial from an energy and cost standpoint.

A representative route to network PILs is shown in Scheme 1 via the step growth polymerization of a bisimidazole with a tribromo crosslinker to form an imidazolium bromide network. The reaction occurs between two glass slides separated by a 70 μm spacer. The anion is readily ion exchanged to BF₄ or TFSI (both bulky, hydrophobic species) and the cation can be ammonium or benzimidazolium depending on the starting monomer. The naming convention is ImC₁₁TFSI which indicates an imidazolium TFSI network with 11 carbons between crosslinks. For toluene/heptane, we anticipate stronger aromatic interactions with imidazolium networks and potential ion- π interactions depending on the anion in the system. In addition to controlling the ions, this synthetic route can control the linker length between charges to tune the crosslink and charge density which will impact the robustness and separation performance.

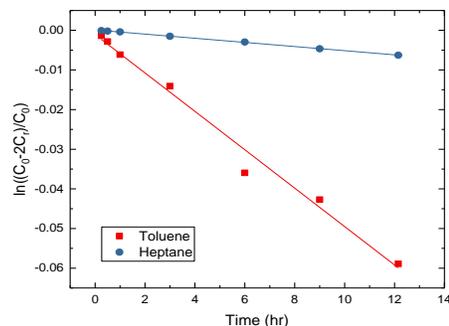
Scheme 1: Synthetic route for a polymerized ionic liquid network ImC₁₁Br.



To investigate the separation performance of network PILs, solubility and diffusion tests were conducted. Solubility tests were carried out by completely drying the membranes, immersing them in pure toluene and heptane, and monitoring the equilibrium mass uptake. For imidazolium networks, the TFSI anion provide better solubility than BF_4 anion, increasing the solubility selectivity from 2.6 to 9.0 as shown in Table 1. It is hypothesized that BF_4 is less selective because it has a stronger association with the imidazolium cation, limiting the aromatic interactions between imidazolium and toluene. Changing from imidazolium to benzimidazolium resulted in a decrease in the solubility selectivity of the membranes from 9.0 to 6.7. Preliminary diffusion experiments have also been carried out in a diaphragm cell where toluene and heptane were added at 100 mM concentration in dodecane. This solution was allowed to diffuse through the membrane into a pure dodecane phase with aliquots taken and analyzed via GCMS (Figure 1) for an $\text{ImC}_{11}\text{BF}_4$ membrane. Solving Fick's law for the diaphragm cell results in a solution which can be linearized as a plot of $\ln[(C_0 - 2C_r)/C_0]$ versus run time, where C_0 is the initial concentration and C_r is the receiving phase concentration. A permeability selectivity of 9.3 was obtained for toluene over heptane, and we anticipate even better performance in subsequent membranes based on solubility test. For reference, Matsumoto et al.¹ obtained a permselectivity of 11 separating toluene and heptane with free imidazolium PF_6 supported in a polymer indicating that our networks are promising for organic liquid separations. Continued work will focus on a broader range of precise networks as well as polymer blends.

Figure 1: Solubility tests of toluene and heptane in network PILs and diffusion cell measurement showing Fickian behavior and selective permeation of toluene.

	Solubility (mg solvent/mg membrane)		
	$\text{ImC}_{11}\text{BF}_4$	$\text{ImC}_{11}\text{TFSI}$	$\text{BzImC}_{11}\text{TFSI}$
Toluene	0.195 ± 0.022	0.415 ± 0.078	0.387 ± 0.065
Heptane	0.074 ± 0.030	0.046 ± 0.012	0.058 ± 0.024
Selectivity	2.6	9	6.7



Our work on this grant will provide a deeper understanding of how the molecular structure of polymers influences the transport of molecular penetrants. These insights are impactful across a number of fields including separations and ion transport which have major implications for society in terms of our future energy management. Molecular design of polymers for selective transport is a key focus of the Evans group, and this grant supports our liquid separations efforts. This grant has also supported a graduate student who has learned many skills related to synthesis and diffusion cell testing which will help in understanding membranes and preparation for an industry career. An undergraduate is also supported who has been developing polymer blends for separations, including understanding the synthesis and complicated phase behavior. This work has helped her understand the research process to prepare for graduate school.

References

- [1] M. Matsumoto, Y. Inomoto, K. Kondo, Selective separation of aromatic hydrocarbons through supported liquid membranes based on ionic liquids, *J. Membr. Sci.* 246 (2005) 77-81.