Supporting Information

for

(Cross-linked Poly(ionic liquid) – Ionic Liquid – Zeolite) Mixed-Matrix Membranes for CO₂/CH₄ Gas Separations Based on Curable Ionic Liquid Prepolymers

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I. Materials

N-Vinylimidazole, and 4-chloromethylstyrene (CMS) were purchased from TCI America (Portland, OR). N-Methylimidazole, cyanomethyldodecyl trithiocarbonate (RAFT agent), azobis(isobutyronitrile) (AIBN), and 2-hydroxy-2-methylpropiophenone were purchased from Sigma-Aldrich (Milwaukee, WI). Lithium trifluoromethanesulfonimide (LiTf₂N) was purchased from 3M (St. Paul, MN). All reagents and solvents were obtained in the highest available purity. AIBN was dissolved in methanol, recrystallized under refrigeration, filtered, and dried before use. CMS was passed through a column of activated alumina to remove radical inhibitor compounds prior to use. All other reagents and solvents were used without additional purification. Cylinders of Ar, CO₂, N₂, and CH₄ gas were purchased from Airgas (Randor, PA) and were at least 99.99% pure. YMPZ3001 ultrafiltration membrane with a molecular weight (MW) cut-off of 30 kDa was purchased from Sterlitech (Kent, WA). The added free IL, 1-ethyl-3-methylimidazolium trifluoromethanesulfonimide [EMIM][Tf₂N], was synthesized according to previously reported literature.¹ SAPO-34 was synthesized at Nanjing Tech University, P.R. China, using a procedure reported in prior literature.² SAPO-34 crystals were observed to be square, flat crystals approximately 500 nm wide. FE-SEM images of these crystals are available in the Supporting Information. The zeolite powder was calcined at 600 °C for 24 h once it was received, held in a
100 °C oven between uses, and hand-ground to a very fine powder using a mortar and pestle prior to use in order to break up agglomeration.

II. Instrumentation

$^1$H NMR and $^{13}$C NMR spectra were acquired using a Bruker Avance-III 300 (300 MHz) NMR spectrometer. Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo TGA/DSC Star 1 System equipped with a GC200 Star gas controller, and the results were analyzed using Mettler-Toledo’s ‘StarE Software’. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra were acquired with a Nicolet 6700 FT-IR spectrometer equipped with a Pike MIRacle™ single-reflection horizontal ATR accessory. A UVP UV lamp producing wavelengths around 365 nm was used for radical photopolymerization and cross-linking. Gel permeation chromatography (GPC) for MW analysis of oligomers was performed on a Viscotek GPCmax™ VE2001 system equipped with a Viscotek Model 3580 Differential Refractive Index (RI) Detector and using THF as the eluent. The number-average MW ($M_n$) and weight-average MW ($M_w$) values obtained by GPC were based on monodisperse polystyrene MW standards purchased from Viscotek. Data on mechanical properties was obtained from a TA instruments Q-800 series dynamic mechanical analyzer. Single-gas (i.e., ideal) gas permeability and selectivity data were obtained using a time-lag apparatus previously described in literature.³ Experiments on this apparatus were conducted at 20 °C using 1 atm of transmembrane pressure. Field-emission scanning electron microscope (FE-SEM) images were obtained with a JEOL JSM-7401F Field Emission SEM. Cross-section images were taken using an FEI Nova 600 Nanolab focused ion beam (FIB) milling instrument equipped with a dual beam for electron imaging.
III. Synthesis of RAFT-polymerized poly(4-chloromethylstyrene) (PCMS) oligomers (2a–2d)

Figure S1. Synthesis scheme for producing RAFT-polymerized PCMS precursor oligomers 2a–2d and then converting them to the Tf$_2$N–substituted curable IL prepolymer 1a–1d.

Different $M_n$ values were targeted by adjusting the molar ratio of monomer to RAFT agent. In order to afford a PCMS $X$-mer, $X$ moles of monomer were required for every one mole of chain-transfer agent and every 0.2 moles of initiator. As an example, the procedure for synthesizing a targeted 80-mer of PCMS oligomer, 2d, is provided below:

**Example procedure:** Purified CMS (5.00 g, 32.8 mmol) was dissolved in 5 mL of DMF and added to a 100-mL Schlenk flask equipped with a magnetic stir bar. The RAFT agent cyanomethyldodecyl trithiocarbonate (0.0885 g, 0.278 mmol) was then added to the flask. AIBN (0.0091 g, 0.0557 mmol) was then added to the flask, and stirring was started to mix the reagents. A blanket of Ar gas was passed into the flask to displace the outside atmosphere. The contents of
the reaction flask were then degassed by repeated free-pump-thaw cycles using liquid nitrogen until negligible pressure increase was detected on evacuation. Once the final thaw cycle was complete, Ar gas was flowed into the flask under positive pressure, and a reflux condenser was attached. The condenser was sealed, and the Ar flow shut off. The sealed reaction system then was placed in an oil bath set to a temperature of 70 °C, and the contents stirred rapidly. After stirring for 24 h at that temperature, Ar was flowed into the flask while the condenser was removed to add additional AIBN (0.0091 g) and 1 mL of DMF. Then, the condenser was replaced, and the argon flow stopped. This radical ‘re-initiation’ process was done a total of three times, allowing 24 h to pass before each one. 24 Hours after the last addition of AIBN and DMF, the reaction flask was removed from heat and allowed to cool to ambient temperature. The polymer solution was then added dropwise into 1-L Erlenmeyer flask containing 700 mL of rapidly stirred methanol. The precipitated PCMS oligomer appeared as light yellow ‘chips’ of solid matter. After the methanol was decanted and the PCMS oligomer was dried in a 40 °C in vacuo for 2 h, 10 mL of THF was added to re-dissolve the oligomer. The oligomer was then was re-precipitated into another 700 mL of methanol. This process was repeated a 3rd time, and the PCMS oligomer 2d was finally dried overnight in in vacuo at 40 °C. The final PCMS oligomer product was obtained as light-yellow solid chips (4.76 g, 95.2% yield). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 0.85 – 0.98 (br s, 0.048H) 1.03 – 2.46 (br m, 4H) 4.35 – 4.70 (br s, 2H) 6.20 – 6.80 (br m, 2H) 6.80 – 7.25 (br m, 2H) (see Figure S2). By comparing the integrated area of the $^1$H NMR signals associated with the 4 protons on the styrene ring with that of the 2 protons on the methylene unit adjacent to a sulfur atom in the RAFT endgroup ($\delta$ 3.2–3.35), oligomer $M_n$ determination by NMR endgroup analysis could be performed. GPC analysis was also used to acquire data about the degree of polymerization of the oligomers. However, the instrument was standardized using poly(styrene) standards. While CMS is relatively similar to styrene, the difference in hydrodynamic volume is sufficient to lead to slight inaccuracy when dealing with non-poly(styrene) solutions. The $M_n$, $M_w$, and polydispersity index (PDI) values of the prepared oligomers by GPC analysis, in addition to the degree of polymerization calculated from NMR and GPC data, are provided in Table S1. Given the close agreement in degree of polymerization between the two methods, the error from the use of the polystyrene instead of PMCS GPC MW standards appears to be small.
Figure S2. $^1$H NMR spectrum (300 MHz, CD$_2$Cl$_2$) of PCMS oligomer 2d.

Table S1. GPC-measured $M_n$ and PDI values of the RAFT-polymerized PCMS precursors, and degrees of polymerization based on $^1$H NMR endgroup and GPC analyses.

| PCMS Oligomer | DP (n) from $^1$H NMR from GPC | $M_n$ from GPC | PDI from GPC | DP (n) from GPC |
|---------------|--------------------------------|----------------|--------------|----------------|
| 2a            | 14.19                          | 2180           | 1.35         | 12.2           |
| 2b            | 16.98                          | 2389           | 1.41         | 19.93          |
| 2c            | 56.96                          | 8322           | 1.09         | 52.44          |
| 2d            | 86.97                          | 9192           | 1.19         | 80.44          |

$^a$After accounting for the mass of the RAFT endgroups on the oligomer chains.
IV. Synthesis of curable IL prepolymers 1a–1d from PCMS oligomers (2a–2d)

The following example procedure was followed for all the curable derivatization reactions for oligomers 2a–2d, differing only in quantity of reagents used. In all reactions, the molar mass contributions of the RAFT agent end groups were subtracted from the $M_n$ determined by GPC. This value was then divided by the $M_n$ to determine the percentage of the total mass that was due to repeat units.

**Example procedure:** Curable IL prepolymer 1d (targeted 25% vinyl-group substitution; actual substitution 34%) was prepared by reacting PCMS oligomer 2d with 0.25 equivalents of $N$-vinylimidazole, and the then reacting the resulting oligomer with an excess of $N$-methylimidazole to ensure all chloromethyl groups are substituted with IL moieties. PCMS oligomer 2d (4.00 g, $M_n = 12,595$, $n = 80.4$ repeat units of chloromethylstyrene, plus the mass of the RAFT endgroups) was added to a 50-mL round-bottom flask equipped with a magnetic stir bar. $N$-Vinylimidazole (0.613 g, 6.52 mmol) was then added to the flask, along with 10 mL of DMF. This mixture was stirred until the polymer completely dissolved. A reflux condenser was attached to the flask, and the flask was heated to 70 °C and held at that temperature for 24 h. $N$-Methylimidazole (2.38 g, 29.03 mmol) and 10 mL of methanol were then added to the flask, without letting it cool, so as to avoid irreversible gelation of the reaction mixture. This reaction was run under reflux at 70 °C for another 24 h to afford the Cl– intermediate curable polymer 3d.

The solution of 3d was added dropwise to 500 mL of rapidly stirred diethyl ether, and the polymer precipitated as a sticky, off-white solid. The ether was decanted and the solids dried with air hose before re-dissolving them in 10 mL of methanol. The precipitation was repeated in another 500 mL of ether, and the ether was decanted and the solids dried in a vacuum oven at 40 °C for 24 h. Intermediate polymer 3d, was dissolved in 50 mL of deionized (DI) H$_2$O. A 1.5 times molar excess of LiTf$_2$N (11.0 g, 38.32 mmol) was dissolved in 350 mL of DI H$_2$O. The aqueous solution of polymer 3d was added dropwise to the rapidly stirred LiTf$_2$N solution, and an off-white gum immediately formed. This new precipitate was the Tf$_2$N$^-$-substituted curable IL prepolymer 1d.

The H$_2$O was decanted, the polymer was washed with fresh DI H$_2$O, and the polymer was dried with an air hose. The polymer was re-dissolved into 10 mL of acetonitrile and precipitated into another aqueous solution of LiTf$_2$N, made as described above. The polymer was again decanted, washed, and dried. This process was repeated one more time.
The polymer was then dissolved in 10 mL of acetonitrile and precipitated into 600 mL of rapidly stirred DI H2O. The water was decanted, and the polymer was washed with fresh DI H2O and dried with an air hose. This process was repeated twice more. These precipitations were done to remove residual Cl ion. The polymer was dried in a 40 °C vacuum oven for 24 h, followed by drying at 50 °C under high-vacuum conditions for 12 h. This final product was a pale-yellow solid.

\(^1\)H NMR (300 MHz, CD\textsubscript{3}CN): \(\delta\) 0.80 – 0.94 (br s, 0.08H) 0.95 – 1.89 (br m, 3H) 2.05 – 2.20 (br s, 2H) 3.65 – 3.95 (br s, 1.65H) 4.97 – 5.55 (br d, 2H) 5.64 – 5.89 (br d, 0.20H) 6.20 – 6.80 (br m, 1.4H) 6.82 – 7.50 (br m, 4H) 7.56 – 7.79 (br s, 0.43H) 8.34 – 8.63 (br s, 0.61H) 8.65 – 8.90 (br s, 0.36H) (see Figure S3).

Due to the charged character of these curable polymers, GPC analysis was not possible and had to be limited to the uncharged oligomeric PCMS precursors. Additionally, the peak used to perform NMR end group analysis on the PCMS oligomers could not be differentiated from a separate, overlapping peak present in both 1d and 3d.

**Figure S3.** \(^1\)H NMR spectrum (300 MHz, CD\textsubscript{3}CN) of curable IL prepolymer 1d, derived from PCMS oligomer 2d.
V. TGA of curable IL prepolymer 1d and a (64-16-20) MMM made using curable IL prepolymer 1d – [EMIM][Tf2N] – SAPO-34

TGA was performed on the longest curable IL prepolymer produced as well as on the MMM made using it. The protocol was as follows: Heating to 850 °C at 5 °C/min, followed by holding at 850 °C for 1 h, all under nitrogen gas flowed at 2 mL/min. This protocol was run on the empty alumina sample pans to remove any left-over matter, and then the pans were weighed so that their mass could later be removed from that of the samples in the pans to get a true sample mass. The protocol was then run on approximately 20 mg of each sample loaded into alumina pans. Decomposition onset temperature was determined by taking the first derivative of the mass vs. time curve, identifying the inflection point, and the finding the intersection of the tangents at the inflection point and at the initial section of the curve. The final decomposition temperature was determined by locating the intersection of the tangents at the inflection point and at the final, decomposed, section of the curve. The decomposition temperature of curable IL prepolymer 1d was found to be 428 °C. The decomposition temperature of the (64-16-20) MMM based on this polymer was found to be 418 °C.

VI. ATR-FTIR spectroscopy of pre-cross-linked and post-cross-linked curable IL prepolymer films

ATR-FTIR spectroscopy was used to observe the loss of the vinyl CH2 peak (920–960 cm\(^{-1}\)) associated with the reactive vinyl groups on the curable polymer. The degree of vinyl conversion was calculated by taking the ratio of the integrated area underneath the vinyl peak to the area underneath a (non-reactive) internal reference peak (1000–1070 cm\(^{-1}\)). The equation is as follows:

\[
\left(1 - \frac{[A_{\text{viny}l}]_{\text{cured}}}{[A_{\text{ref}}]_{\text{cured}}} \right) \frac{[A_{\text{viny}l}]_{\text{uncured}}}{[A_{\text{ref}}]_{\text{uncured}}} \right) \ast 100 = \% \text{ vinyl conversion}
\]
Uncured and cured indicate measurements taken with and without a 15-min exposure to UV light, respectively. Samples from the films were placed directly on the ATR crystal.

Two neat 1d samples were produced for this spectroscopy experiment by co-dissolving curable IL prepolymer 1d (0.25 g) with 5 wt % 2-hydroxy-2-methylpropiophenone (0.013 g, 0.083 mmol) in acetonitrile (0.25 g). This pair of solutions were stirred with a vortex mixer for 5 min to completely dissolve the polymer. The solutions were poured onto circular quartz plates coated with RainX™, two 150-µm-thick microscope slides were laid onto each plate as spacers, and a second RainX™ coated plate was laid on top of each to create a sandwich. These assemblies were clamped together with 3 binder clips. One was placed underneath a 365 nm UV lamp for 15 min to trigger cross-linking, while the other was kept away from UV light. The measured UV intensity at the distance to the plates was 4.3 mW/cm². The clips were removed from both sets of plates, and both sets of plates were separated and loaded into a 40 °C vacuum oven for 1 h to remove solvent. Both films were then analyzed by ATR-FTIR spectroscopy as explained above. Based on these measurements, 99.95% of the vinyl groups present had been reacted in the cured film.

VII. Synthesis of free standing (cross-linked PIL – IL – zeolite) MMMs using 64 wt % curable IL prepolymer, 16 wt % [EMIM][Tf₂N], and 20 wt % SAPO-34

The following procedure was used to synthesize all (64-16-20) MMMs in this work, and a procedure using curable IL prepolymer 1d will be used as an example. Previously calcined SAPO-34 powder (0.100 g) was removed from its 100 °C storage oven and added to a ceramic mortar and manually ground with a pestle until no grit or resistance could be felt (approximately 15 min of grinding). The ground zeolite was added to a small glass vial equipped with a micro stir bar. Curable IL prepolymer 1d (0.320 g) and [EMIM][Tf₂N] (0.080 g, 0.205 mmol) were added to this vial, along with 0.250 g of acetonitrile. This vial was then submerged in an ultra-sonication bath for 1 h, before being transferred to a stir plate, and rapidly stirred for 24 h to ensure maximum particle wetting and dispersion. 5 wt % (0.020 g, 18.57 µL) of the radical photo-initiator 2-hydroxy-2-methylpropiophenone was added to the vial via micropipette and the solution was stirred for another 15 min.
The contents of the vial were poured onto the center of a quartz plate treated with RainX™. A glass pipette was used to manually remove any visible bubbles from the mixture on the plate. Two 150-µm-thick glass microscope slides were placed at the edge of the plate to act as spacers, and a second RainX™-coated plate was laid on top of the first to create a ‘sandwich’. Three (3) evenly spaced binder clips were attached to the edge of this sandwich to secure it together. This assembly was then placed under a UV lamp emitting 365 nm light at an intensity of 4.3 mW/cm² for 2 h. After irradiation, the binder clips were removed to release compression on the plates, and solvent was allowed to slowly evaporate from the edges of the assembly for 24 h. The plates were then taken apart, and the membrane, still on its plate, was placed into a 40 °C vacuum oven for at least 4 h. Once dried, the membrane was peeled from its plate and stored in a plastic Petri dish. ATR-FTIR spectroscopy was used to qualitatively check for the stretch associated with the C-N triple bond in acetonitrile to ensure solvent removal and adequate drying. A digital micrometer was used to measure film thickness, with membrane thickness ranging from 90–150 µm.

VIII. Synthesis of free standing (cross-linked PIL – IL – zeolite) MMMs using 80 wt % curable IL prepolymer, 20 wt % [EMIM][Tf₂N], and 0 wt % SAPO-34

The following procedure was used to synthesize all (80-20-0) ion-gel membranes in this work, and a procedure using curable IL prepolymer 1d will be used as an example. Curable IL prepolymer 1d (0.400 g) and [EMIM][Tf₂N] (0.100 g, 0.256 mmol) were added to a small glass vial equipped with a micro stir bar, along with 0.250 g of acetonitrile. This vial was then transferred to a stir plate, and rapidly stirred for 24 h. 5 Wt % (0.025 g, 23.21 µL) of the radical photo-initiator 2-hydroxy-2-methylpropiophenone was added to the vial via micropipette, and the solution was stirred for another 15 min.

The contents of the vial were poured onto the center of a quartz plate treated with RainX™. A glass pipette was used to manually remove any visible bubbles from the mixture on the plate. Two 150-µm-thick glass microscope slides were placed at the edge of the plate to act as spacers, and a second RainX™-coated plate was laid on top of the first to create a ‘sandwich’. Three (3) evenly spaced binder clips were attached to the edge of this sandwich to secure it together. This assembly was then placed under a UV lamp emitting 365 nm light at an intensity of 4.3 mW/cm²
for 2 h. After irradiation, the binder clips were removed to release compression on the plates, and solvent was allowed to slowly evaporate from the edges of the assembly for 24 h. The plates were then taken apart, and the membrane, still on its plate, was placed into a 40 °C vacuum oven for at least 4 h. Once dried, the membrane was peeled from its plate, and stored in a plastic Petri dish. ATR-FTIR spectroscopy was used to qualitatively check for the stretch associated with the C-N triple bond in acetonitrile to ensure solvent removal and adequate drying. A digital micrometer was used to measure film thickness, with membrane thickness ranging from 110–140 µm.

IX. Modulus of elasticity comparisons between curable IL prepolymer-based systems and curable IL monomer-based systems.

In order to demonstrate the difference in mechanical properties observed between MMMs made with uncontrolled radical polymerization of IL-monomer (viz. [1-vinyl-3-methylimidazolium][Tf2N]) versus those made with cross-linking of curable IL prepolymer, a DMA instrument was employed to determine the modulus of elasticity for films of both the neat polymers, and (64-16-20) MMMs made from these polymers containing [EMIM][Tf2N] and SAPO-34. The instrument was run in constant-strain mode, with an elongation rate of 0.1% strain/min, automatically adjusted based on the dimensions of the sample coupon. Stress vs. strain data was recorded, and the onboard software was used to determine the modulus of elasticity as the slope of the initial linear section of the stress vs. strain curve. It should be noted that even though all samples were over 100 µm thick, the neat [VMIM][Tf2N] films were so fragile that only 1 out of 16 attempts to measure the modulus of elasticity actually yielded data. All other attempts resulted in fracture of the film on loading, or fracture upon application of initial stress. For all other samples, data was obtained in triplicate and the mean value was reported. For all samples except [VMIM][Tf2N], the error represents the standard deviation in the values.

Neat films were prepared by combining 0.25 g of curable IL polymer or IL monomer in a vial equipped with a stir bar with 5 wt % 2-hydroxy-2-methylpropiophenone (0.0125 g, 11.6 µL) and 0.25 g acetone. To allow the IL monomer to cross-link, 2 wt % of divinylbenzene (DVB) was added to the vial. These vials were stirred for 1 h and poured onto quartz plates coated in RainXTM. The UV polymerization and drying procedure was the same as given in section VII. MMMs were
produced using the same procedure reported in section VIII, with the difference that 2 wt % divinylbenzene was added to the IL-monomer-based MMM along with the photo-initiator to facilitate cross-linking.

Table S2. Modulus of elasticity comparison between neat films and MMMs made with curable IL prepolymer and curable IL monomer casting solutions.

| Sample ID | Modulus of elasticity (MPa) |
|-----------|-----------------------------|
| Curable IL prepolymer 1d | 490 ± 80 |
| [VMIM][Tf2N] + 2 wt % DVB | 858 |
| (64-16-20) MMM with IL prepolymer 1d | 70 ± 20 |
| (64-16-20) MMM with IL monomer | 170 ± 50 |

These results suggest that there are large differences in the elasticity of the cured IL prepolymer compared to the polymerized monomer. The MMMs show substantial decreases in their modulus, likely due to the plasticizing effects of free ionic liquid in the polymer matrix. These effects are more pronounced in the MMM synthesized using curable IL prepolymer 1d.

X. Comparative support penetration evaluations for neat solutions of curable IL prepolymer 1a and 1d and IL monomer [VMIM][Tf2N]

To evaluate the ability of curable IL prepolymer to resist penetrating into an ultra-filtration support, several 50 wt% solution of neat polymer and monomer were prepared. 0.15 g of [VMIM][Tf2N] and curable IL prepolymer 1a and 1d were added to vials equipped with stir bars. 1 Wt % 2-hydroxy-2-methylpropiophenone (0.0015 g, 1.39µL) was added to the monomer vial along with 2 wt % divinylbenzene (0.003 g, 3.28 µL). 5 Wt % 2-hydroxy-2-methylpropiophenone (0.0075 g, 6.96 µL) was added to the prepolymer vials. 0.15 g of acetone was added to all 3 vials, which were all stirred on a vortex mixer until all solids had dissolved.
The solutions were added dropwise to separate, pre-weighed pieces of a UF membrane with a MW cut-off of 30 kDa (Sterlitech PZ series). Half of the samples were exposed to 365 nm UV light for 15 min. All samples were then dried in a 40°C vacuum oven for 1 h. The dry masses of the samples were recorded, with the difference between these masses and the initial support masses being equal to the total amount of polymer present. A razor blade was then used to carefully peel and scrape away as much of the added polymer as possible without damaging the UF support. The samples were then weighed a third time, and the fraction of added polymer that could not be removed was calculated and is given as ‘% mass penetrated’. The reported values are averages of three experiments, with error given by the standard deviation in the values.

Table S3. Percentage mass of polymerizable monomer and curable IL prepolymer that penetrated into an UF support membrane.

| Monomer or curable IL prepolymer | Mass% penetrated into support |
|---------------------------------|-----------------------------|
| [VMIM][Tf₂N], uncured          | 70 ± 20                     |
| [VMIM][Tf₂N], cured            | 67 ± 9                      |
| Curable IL prepolymer 1a,      |                             |
| uncured                        | 7 ± 1                       |
| Curable IL prepolymer 1a,      |                             |
| cured                          | 6 ± 2                       |
| Curable IL prepolymer 1d,      |                             |
| uncured                        | 11 ± 8                      |
| Curable IL prepolymer 1d       |                             |
| cured                          | 3.7 ± 0.9                   |

These results suggest that even short-chain curable IL prepolymer solutions are more capable of resisting support penetration than a solution of IL monomer.
XI. Qualitative comparative gelation study of ion-gels made with IL monomer [VMIM][Tf$_2$N] and curable IL prepolymers 1a and 1d

In order to better understand the relationship between polymer chain length and the time required to ‘set’ or form an immobile gel, a series of gelation experiments were carried out between the curable IL prepolymers ($x = 14$ and $x = 87$) and compared to that performed with a cross-linkable, low-MW IL monomer as a reference system. Three solutions containing 40 wt % [EMIM][Tf$_2$N] were prepared by the following method. Either the monomer or curable IL prepolymer (0.395 g) was added to a vial equipped with a stir bar. [EMIM][Tf$_2$N] (0.595 g), along with 1 wt % (0.010 g, 9.19 µL) 2-hydroxy-2-methylpropiophenone, were added to the vial. In order to completely dissolve the curable IL prepolymer and monomer components into the free IL, 0.200 g of acetone was added to the vial, followed by vortex mixing. The vials were then placed in a 40 °C vacuum oven for 3 h to remove the acetone. This resulted in a highly viscous solution of curable IL prepolymer or IL monomer dissolved in [EMIM][Tf$_2$N].

4–5 Drops of these solutions were added to separate cuvettes made of UV transparent plastic. These small containers have a narrow, rectangular cavity that allows for convenient observation of the solution inside. Multiple cuvettes were prepared for each solution, and exposed to 365 nm UV light for different lengths of time. After UV exposure, the cuvettes were turned on their sides and photographed. Solutions that have completely gelled will not flow from the bottom of the cuvette when turned, and more completely gelled solutions will be more resistant to flow than less completely gelled solutions.

In the images in Figure S3, the cuvettes are ordered from top to bottom as curable IL prepolymer 1d, curable IL prepolymer 1a, poly([VMIM][Tf$_2$N]). Starting from the top left and moving right, the images show vials exposed to UV light for 5 s, 25 s, 90 s, and 300 s. In the 300 s image, the vials were left on their sides for 1 hour before being photographed to ensure that an immobile gel had formed. Even in images where all three solutions are flowing, it is clear that solutions of curable IL prepolymer 1d are more viscous and resistant to flow compared to solutions of curable IL prepolymer 1a, which in turn are more viscous than solutions of [VMIM][Tf$_2$N]. These results suggest that polymer chain length has an effect on the speed of gelation, and that longer-chain curable IL prepolymers form immobile ion-gels more rapidly than shorter-chain variants.
Figure S4. Cuvettes containing curable IL prepolymer–IL solutions after UV light exposure. From the top left to right, UV exposure time is 5 s, 25 s, 90 s, and 300 s.
XII. Ideal (i.e., single) gas permeability time-lag measurements

Previous literature in this group has described the construction and operation of the time-lag gas permeation apparatus in more detail than is needed here. Membranes made using the technique detailed in sections VII and VIII were ‘masked’ by cutting out defect free regions with a razor, placing the section on a circular piece of aluminum backed tape with a ¼ inch or ½ inch diameter hole punched into it, and then covering the piece of membrane with a second circular piece of tape with a hole punched into it. These masks were loaded into a cell with an internal diameter of 40 mm. The cells were screwed shut and vacuum was applied to both the feed and permeate sides to degas the membrane for 12 h and remove any residual solvent or gas adsorbed from the environment. Degassing was done before all gas permeation test runs. One (1) atm of the test gas was introduced into the evacuated feed volume, and the permeate side of the apparatus was kept under vacuum. A valve was opened to connect the feed volume to the feed side of the membrane chamber and data recording began for feed and permeate side pressure. Details of the calculations used to convert the pressure vs. time data into permeated volume vs. time data, and ultimately into permeability, solubility, and diffusivity values can also be find in prior literature.

Permeability was calculated from the linear section of a permeated volume vs. time graph, where the slope provides flux and the intercept is related to \( \Theta \), the time lag. Permeability is the product of gas diffusivity and solubility, which themselves can be expressed by the following equation:

\[
\frac{V_{perm} \Delta P}{A_t RT \Phi} \frac{l}{\Delta p_i} = D_l S_l = P_l
\]

Where \( l \) is the membrane thickness in cm, \( A_t \) is the membrane area exposed by the mask in cm\(^2\), \( t \) is the elapsed time in minutes, \( \Delta p \) is average pressure drop in cm Hg, \( T \) is temperature in K, \( \Phi \) is the porosity fraction of a support (set to 1 for a bulk film), and \( V_{perm} \) is the permeated volume given in L. Diffusivity can be calculated based on the time lag from the following equation:

\[
D_l = \frac{l^2}{6\Theta}
\]

Once diffusivity and permeability are known, solubility can be obtained trivially, assuming that the solution-diffusion mechanism is valid. Ideal gas pair selectivity is calculated by taking the ratio of the permeability of the fast gas to the slow gas.
XIII. SEM imaging of MMMs.

Dual-beam focused ion beam (FIB) SEM instruments combine an ion beam with an electron microscope. This allows for controlled milling into a sample surface to reveal a smooth cross-section several microns deep. In the following images, a 6.5 nA cutting beam was used to create a cleaning cross-section 10 µm wide by 10 µm long, to a depth of 8 µm. The perspective of the electron beam images is at an angle of 52 degrees from perpendicular, so that images of the cross-section may be obtained. In all of the MMM samples imaged, zeolite particles are visible dispersed in the cross-linked PIL-IL matrix. There are no visible void defects either in the bulk of the PIL-IL matrix or near the zeolite interfaces common to MMMs without an IL interfacial agent present. This is consistent with the relatively low reported permeabilities.
Figure S5. Surface SEM image of an (80-20-0) MMM based on curable IL prepolymer 1d.
Figure S6. Cross-section SEM image of an (80-20-0) MMM based on curable IL prepolymer 1d.
Figure S7. Surface SEM image of a (64-16-20) MMM based on curable IL prepolymer 1d.
Figure S8. Cross-section SEM image of a (64-16-20) MMM based on curable IL prepolymer 1d.
Figure S9. Surface SEM image of a (64-16-20) MMM based on curable IL prepolymer 1b.
**Figure S10.** Cross-section SEM image of a (64-16-20) MMM based on curable IL prepolymer 1b.
Figure S11. Surface SEM image of a (64-16-20) MMM based on curable IL prepolymer 1a.
Figure S12. Cross-section SEM image of a (64-16-20) MMM based on curable IL prepolymer 1a.
**Figure S13.** CO$_2$/CH$_4$ Robeson plot$^4$ that includes data points for the curable oligomer-based MMMs synthesized and tested in the current study. Partially reproduced from Reference 4 with permission. Copyright Elsevier, 2008.
XIV. References for the Supporting Information:

(1) Bara, J. E.; Hatakeyama, E. S.; Gin, D. L.; Noble, R. D. Improving CO$_2$ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid. *Polymers for Advanced Technologies* 2008, 19, 1415–1420.

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(3) Bara, J. E.; Lessmann, S.; Gabriel, C. J.; Hatakeyama, E. S.; Noble, R. D.; Gin, D. L. Synthesis and Performance of Polymerizable Room-Temperature Ionic Liquids as Gas Separation Membranes. *Industrial & Engineering Chemistry Research* 2007, 46, 5398–5404.

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