

# The Effect of Poly(Ethylene Oxide) Cross-Linking Structure on the Mechanical Properties and CO<sub>2</sub> Separation Performance of an Ion Gel Membrane

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## Highlights

- Fabricated cross-linked poly(ethylene oxide) photopolymerized with ionic liquid
- Cross-link density varied by selection of polymer precursor
- Tensile and gas permeability tests performed on ion gel films
- Lower cross-link density can give better tensile properties and higher permeability

## Abstract

Ionic liquid gels of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide plasticizing a cross-linked poly(ethylene oxide) are high performance CO<sub>2</sub> separation membranes. Here, the effect of polymer cross-link density on the ionic liquid stability, on the mechanical properties of the resulting films, and on the gas separation properties were studied. Cross-link density was modified by changing the chain length of ethoxylated diacrylate and triacrylate monomers, and by incorporating small amounts of short, multifunctional acrylate monomers. Without the ionic liquid acting as permanent plasticizer, higher cross-link density is associated with higher yield strength but lower strain at break, as expected. In a plasticized network, however, the loss in flexibility is not accompanied by higher yield strength, leaving ion gels made from highly cross-linked network more fragile than those having longer, more flexible chains. Lowering cross-link density also allowed more ionic liquids to be incorporated as a phase stable gel and led to better CO<sub>2</sub> separation performance.

## 1. Introduction

Cross-linked poly(ethylene oxide) (PEO) is a class of promising polymer materials for CO<sub>2</sub> separations from light, permanent gases using membrane processes [1,2]. These polymers are amorphous rubbers which separate CO<sub>2</sub> principally through solubility selectivity [3]. Our interest in these materials is driven by the needs for better membrane performance in CO<sub>2</sub> capture from post-combustion flue gas processes. In our previous studies, we have demonstrated that certain classes of ionic liquids (ILs) can effectively plasticize these polymers, resulting in significant increases in gas permeability depending on the IL selection [4,5]. Owing to the good intermolecular interaction between the IL and the PEO chains and the low vapor pressure of the ILs, these ion gels are stable and homogeneous. In those studies, we focused on the IL selection by first determining the compatibility based on the choice of anions and cations [4], followed by focusing on cation functional groups on the gas separation properties of the ion gels [5]. In both cases, however, we kept the base polymers unchanged. In the first study, the network was formed by photopolymerizing polyethylene glycol (PEG) 600 diacrylate; in the second study, an ethoxylated triacrylate with 20:3 EO:acrylate ratio copolymerized with a dithiol. We recognize that just as much as incorporating IL can change the gas transport properties of the polymer, changing the polymer structural characteristics by changing the composition of the base monomer can also dramatically change the gas transport properties [6–8]. Exploring the effect of changing monomer compositions in an ion gel-forming network may lead to beneficial improvements to mechanical properties and/or gas transport properties.

The present work builds on cross-linked PEO design efforts to look specifically for strategies to improve mechanical and gas transport properties in an IL plasticized network by changing their cross-link density and chain length between cross-link bridges. Two principal strategies are pursued here. The first one modifies the chain length of network-forming ethoxylated diacrylate or triacrylate monomers. In effect, this is an extension of previous studies [9–11] applied to an IL plasticized network. The second strategy is to incorporate small amounts of short, multifunctional monomers to increase the cross-link density with a potentially large impact on mechanical properties without much sacrifice in gas permeability. The ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, is chosen based on its excellent compatibility with polymers containing ethylene oxide moieties; prior work has shown the identity

of similar ionic liquids has little effect on mechanical properties [12]. Differential scanning calorimetry (DSC) can probe the glass transition of the resulting networks and provide valuable insights into their structural details [6,7]; it is used extensively here. Dynamic mechanical analysis (DMA) can also probe the chain relaxation characteristics by performing variable frequency, temperature sweep experiments to construct modulus-frequency master curves [10,13]; however, given the number of films generated in this project, the DMA here is utilized only to probe the bulk mechanical properties by performing tensile tests at a fixed temperature. CO<sub>2</sub> and N<sub>2</sub> pure gas permeabilities of select polymers and gels, relevant to the needs for flue gas treatment, were measured to evaluate the effectiveness of various modification strategies on membrane separation performance. Finally, we also provided a direct comparison of the mechanical and gas transport properties of the ion gels to a cross-linked network copolymer of PEG diacrylate with PEG methyl ether acrylate, which is one of the most effective modifications for improving the gas permeability of cross-linked PEO.

## 2. Materials and Methods

### 2.1. Materials

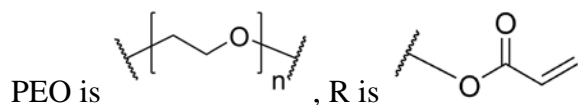
All materials used in this study were obtained from commercial sources and were used as received. The ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf<sub>2</sub>N]) was purchased from IOLITEC USA Inc. (Tuscaloosa, AL). Poly(ethylene glycol) 400 diacrylate,  $M_n=575$  and poly(ethylene glycol) 600 diacrylate,  $M_n=700$  were obtained from Sigma Aldrich. Bisphenol A ethoxylate diacrylate (30/2 EO/acrylate),  $M_n=1650$  (product number SR9038) was obtained from Sartomer, Inc. (Exton, PA). The trimethylolpropane ethoxylate triacrylate was obtained from two sources: the (14/3 EO/OH) ( $M_n=912$ ) was obtained from Sigma Aldrich whereas the (20/3 EO/OH) ( $M_n=1177$ ) was obtained from Sartomer (product number SR415). Two additional non-ethoxylated multiacrylate monomers, di(trimethylolpropane) tetraacrylate ( $M_n=466$ ) and dipentaerythritol penta-/hexa-acrylate ( $M_n=524$ ) were obtained from Sigma Aldrich. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was also obtained from Sigma Aldrich. The list of all monomers is shown in Table 1; the abbreviations given there will be used in all subsequent discussions. The numbers shown after the diacrylate and triacrylate (e.g. 2A-7) denote the approximate ratio of EO repeat units per acrylate unit of the monomer: i.e. 2A-7 has approximately 7 EO repeat units per acrylate, for an average of 14 EO repeat units per

molecule [2]. We note that the 2A-7 and 3A-7 as well as the 2A-5 and 3A-7 monomers have approximately similar EO chain length between acrylate groups.

**Table 1.** Chemical structure of all monomers in this study.

Abbreviation	Name	$M_n$	Structure
2A-7	Poly(ethylene glycol) diacrylate	700	
2A-5		545	
3A-7	Trimethylolpropane ethoxylate triacrylate	1177	
3A-5		912	
BPA	Ethoxylated bisphenol-A diacrylate	1650	
MEA or PEGMEA	Poly(ethylene glycol) methyl ether acrylate	480	
4A	Di(trimethylolpropane) tetraacrylate	466	
6A	Dipentaerythritol penta/hexa acrylate	524	

Note: the notation PEO and R indicate common elements to all monomers and represent poly(ethylene glycol) and acrylate segments, respectively:



Despite the notation, 6A has less than six acrylate substitution per molecule.

## 2.2. Film Fabrication

The film fabrication technique follows the same method as described in the previous works [4,5,14]. The monomers and ionic liquids were mixed together without solvent under magnetic stirring to form a transparent, homogeneous solution. 1 wt% of DMPA was introduced directly into the solutions and stirring continued until all crystals were dissolved. The monomer solution was then pipetted between two quartz plates with spacers of approximately 200 micron thickness to provide a controlled gap between the two plates. Photopolymerization was performed through exposure to a UVA source (Blak Ray B-100AP with exposure box from UVP, LLC – Upland, CA with a nominal intensity of  $12 \mu\text{W}/\text{cm}^2$  at the exposure distance) for 90 seconds. When present, the ionic liquid thus serves as a non-reactive diluent in the polymerization.

[emim][Tf<sub>2</sub>N] was introduced at either 40 vol% or 60 vol% loading by measuring the density of the base polymers and calculating the required amount of IL based on that and the density of [emim][Tf<sub>2</sub>N]. The wt% compositions of all polymers are given in the Supporting Information.

## 2.3. Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was performed on the polymerized films using a Bruker (Billerica, MA) Vertex 70 equipped with a Pike Technologies (Madison, WI) GladiATR™ ATR attachment. Density measurements were performed using a AccuPyc II 1340 (Micromeritics – Norcross, GA) helium pycnometer.

Dynamic Mechanical Analysis (DMA) was conducted using a TA Instruments Q800 in controlled force mode to evaluate the tensile properties of the films. All experiments were performed on strips of films 5.3 mm wide with the initial distance between clamp faces of approximately 11 mm. The sample was kept isothermal at 40°C for five minutes prior to the force ramp. A ramping tensile force of 1 N/min was applied to each strip until fracture is achieved. A minimum of three valid measurements were performed for each sample: a valid measurement is characterized by brittle fracture in the middle of the test strip. The Young's modulus is relatively consistent between the measurements, while yield strength typically has 5% standard deviation. For each sample, the measurement plotted here reflects one with a median observed yield strength.

Differential Scanning Calorimetry (DSC) was performed using a TA Instruments Q2000 MDSC equipped with liquid nitrogen cooling in conventional heating mode. The films were initially

cooled to -100°C and then thermally cycled three times between -100°C and +100°C with a heating rate of +10°C/min and a cooling rate of -10°C/min. The first heating run was discarded. The glass transition temperature ( $T_g$ ) is defined as the transition midpoint on the third heating cycle, which typically overlapped with the second. Melting temperature ( $T_m$ ) is defined at the trough of the transition, when applicable.

Pure gas permeability measurements were performed according to the constant volume method using equipment that we have utilized in other studies [4,5,14]. The films were masked using aluminum tape and epoxy to seal them within the membrane cell. Pure CO<sub>2</sub> or N<sub>2</sub> (research grade, obtained from Airgas via Butler Gas Company – McKees Rocks, PA) was introduced at 1 bar, 2 bar and 3 bar upstream pressure while the downstream is maintained under vacuum. To simplify discussion, only 1 bar data are reported in this work, but the CO<sub>2</sub> and N<sub>2</sub> permeability tend to be constant up to 3 bar. The temperature is kept constant at 40°C. Prior to the experiments, a low force micrometer (Mitutoyo VL-50B – Tokyo, JPN) was used to measure the film thickness. The CO<sub>2</sub>/N<sub>2</sub> pure gas selectivity is reported by taking the ratio of the CO<sub>2</sub> permeability to the N<sub>2</sub> permeability.

### 3. Results and Discussions

There were two principal strategies pursued in this study to improve the mechanical properties or gas transport properties of the ion gels. The first was to evaluate the networks of each ethoxylated diacrylate or triacrylate monomers (2A-7, 3A-7, 2A-5, 3A-5 and BPA) and their corresponding 40 vol% and 60 vol% [emim][Tf<sub>2</sub>N] ion gels. The second was to blend in small amounts of non-ethoxylated, multifunctional acrylates (4A or 6A) with either 2A-7 or 3A-7 to increase cross-link density and stiffness of the resulting gels. The results from each strategy are reported in separate sections below.

#### 3.1. Comparison of networks formed by diacrylate and triacrylate monomers

The PEG diacrylate crosslinker 2A-7 is one of the most common monomers employed in cross-linked PEO studies [2,3,6,7,9,10,14–18]. It is readily available from several commercial sources and can be easily polymerized using photo-catalyzed free radical polymerization in neat form to obtain an amorphous, rubbery cross-linked film [2]. All five diacrylate and triacrylate liquid monomers chosen here, however, can be polymerized just as readily into amorphous, rubbery

cross-linked films in neat form. FTIR showed complete conversion of the acrylate groups in the resulting polymers (Figure S1 in Supporting Information).

Cross-linked 2A-5 was previously shown to have higher  $T_g$  than 2A-7 due to higher cross-linking density, *i.e.* an average of 10 EO repeat units between acrylate groups vs. 14 for the latter [9,10]; this polymer was shown to have a lower water permeability as a result [9]. Cross-linked BPA, in contrast, has lower cross-link density than 2A-7 and showed higher gas permeability despite the similar  $T_g$  [11]. While there is on average 30 EO repeat units between acrylate groups, the bisphenol-A central linker prevented the long EO chain from forming crystal structures in the cross-linked network, which it would have otherwise done with an uninterrupted length of EO (e.g. PEG diacrylate with 23 EO between acrylates) [9]. The triacrylate monomers chosen here were rarely used in cross-linked PEO studies, because the diacrylate monomers were already effective in forming tough, fully cross-linked networks. Our recent ion gel work utilized 3A-7; however, it was in combination with a dithiol co-monomer to ensure sufficient cross-link density during network formation [5], a choice informed partly based on findings described here. With approximately 20 EO repeat units between three acrylate groups, 3A-7 effectively has similar chain length between cross-links as 2A-7 under complete conversion.

DSC traces shown in Figure 1 confirmed that five base polymers are amorphous cross-linked rubbers with  $T_g$  between  $-45^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$ , which varied based on the cross-link density and the presence of the bulky bisphenol-A spacer. The networks with higher cross-link density (*i.e.* 2A-5 and 3A-5) have higher  $T_g$  than the longer analogs as the network has lower chain mobility. Despite the longer distance between cross-links, cross-linked BPA has similar  $T_g$  to 2A-7 and 3A-7, consistent with the result observed in a previous study [11].



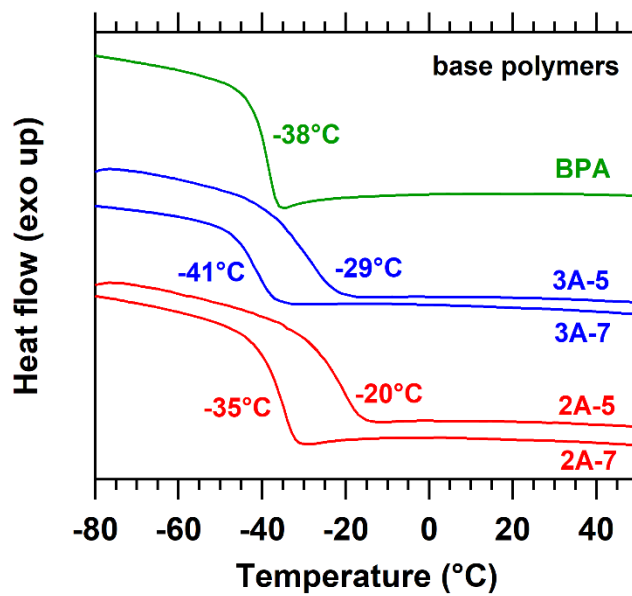


Figure 1. DSC heating traces of cross-linked diacrylate and triacrylate monomers, displaced vertically for clarity. No other transition was observed above 50°C.

[emim][Tf<sub>2</sub>N] is highly miscible with PEO-based networks: it was the ionic liquid of choice not only in our previous works but also in other recent ion gel studies [4,5,15,19,20]. Here, [emim][Tf<sub>2</sub>N] can be incorporated into all polymers to form phase stable ion gels at room temperature with 40 vol% loading. DSC analysis, shown in Figure 2a, showed a lack of characteristic [emim][Tf<sub>2</sub>N] melting transition (a prominent sharp trough at -9°C) [4] in most of the 40 vol% ion gels. The presence of [emim][Tf<sub>2</sub>N] as a non-reactive diluent during polymerization acts to reduce the cross-link density because it reduces the concentration of the double bonds in the prepolymer, as was also shown in studies using water as diluent for 2A-7 [2,10,21]. The presence of non-reactive diluents during polymerization led to decreased interconnectivity of the polymer network through the formation of more linear chains, wasted cross-links and chain cyclization, resulting in a looser polymer network. Unlike in those previous studies, here the [emim][Tf<sub>2</sub>N] remains in the polymer as a plasticizer, reducing the  $T_g$  relative to the base polymers (cf. Figure 1) [5].

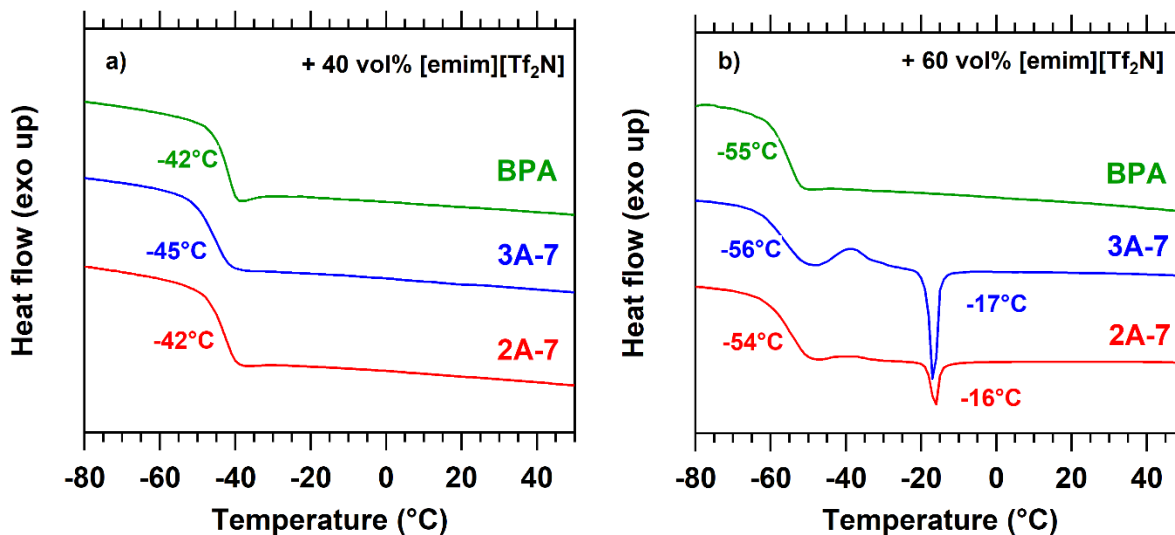


Figure 2. DSC heating traces of ion gels based on 2A-7, 3A-7 and BPA, containing a) 40 vol% [emim][Tf<sub>2</sub>N] and b) 60 vol% [emim][Tf<sub>2</sub>N].

Previously, we showed that [emim][Tf<sub>2</sub>N] can be incorporated to at least 60 vol% into cross-linked 2A-7 at room temperature to give a phase-stable, dry ion gel [4]. Heating this 60 vol% gel to 100°C in the DSC, however, revealed an increasingly prominent melting transition close to the bulk [emim][Tf<sub>2</sub>N]  $T_m$  upon thermal cycling (around -16°C, vs -9°C for [emim][Tf<sub>2</sub>N]). This was attributed to the emergence of an IL rich phase within the PEO network at higher temperature, a behavior which is well known from experiments between [emim][Tf<sub>2</sub>N] and low molecular weight PEO [22]. In this study, both the 60 vol% gels of 2A-7 and 3A-7 exhibited the same phase instability that was first observed in that previous study as evidenced by the emerging melting transition peak. Interestingly, the 60 vol% BPA gel remained phase stable after three heating cycles in the DSC, suggesting that the cross-linked BPA network can stabilize higher IL content than the 2A-7 or 3A-7 networks. This behavior is likely due to the lower cross-link density of the BPA network: in our previous study, decreasing cross-link density of the 2A-7 by way of incorporating additional diluent improved phase stability with ILs by making the polymer chains more accessible for interactions with IL [4]. This observation was also supported by Li et al. in a study that shows ionic liquid uptake into cross-linked poly(methyl methacrylate) is highly sensitive to cross-link density [23]. The 60 vol% ion gels with all three polymers exhibited significantly lower  $T_g$  compared to their 40 vol% counterparts.

The networks with the highest cross-link density, 2A-5 and 3A-5, exhibited visible phase separation upon casting with the 60 vol% ILs, suggesting that the miscibility limit has been exceeded even at room temperature. The surface of the films was wet with IL, and the films left visible imprints of free IL when placed on a piece of office paper. DSC results reported by Visentin and Panzer for [emim][Tf<sub>2</sub>N] gels in cross-linked 2A-5 confirmed that this loading is about maximum at room temperature [15]. The 60 vol% films were not considered further for gas separations in this study due to this behavior. Interestingly, DSC suggested some phase separation can occur when performing a heating cycle on the 40 vol% IL gel of 3A-5 (Figure S2 in the Supporting Information) due to the high cross-link density of this network.

While decreasing cross-link density may improve the network's ability to stabilize IL, cross-link density also influenced the mechanical properties of the network: the lower the cross-link density, the more flexible the polymer becomes, but yield strength typically also decreases. Figure 3 shows the stress-strain curve for the tensile tests performed on the 2A-7, 3A-7 and BPA base polymers. All three polymers exhibited brittle failure at the end of the test, with minimal plastic deformation, which is a typical thermosetting behavior. The cross-link density of 2A-7 and 3A-7 networks are almost identical: 3A-7 has only slightly higher stiffness (quantified by Young's modulus) and yield strength due to the higher network interconnectivity. Because of its lower cross-link density, the BPA network is more flexible, but it also retained similar yield strength as the 2A-7 network, and so it possessed superior toughness over the other two networks.

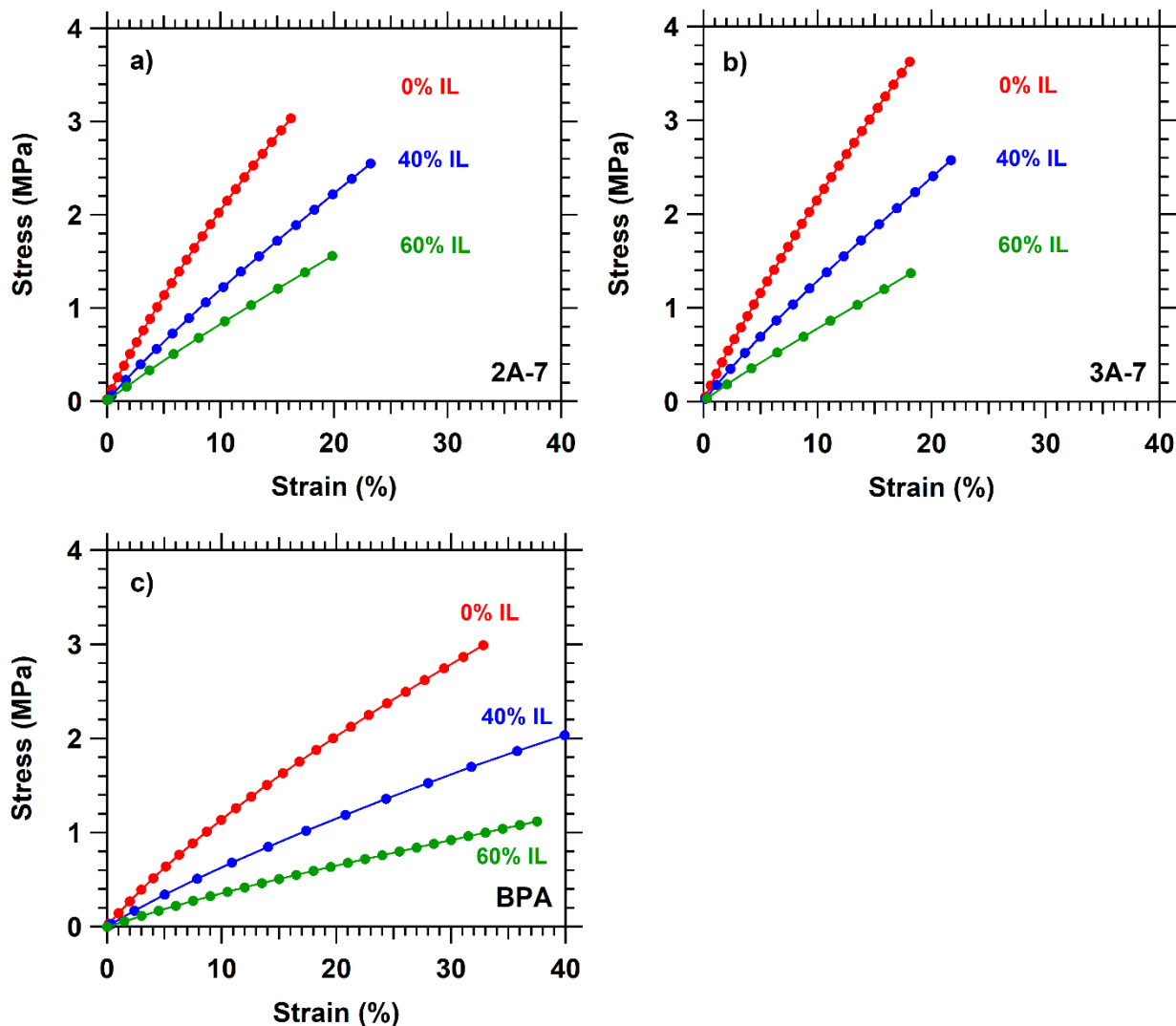


Figure 3. Stress-strain curves for the cross-linked polymers and ion gels as measured by the DMA tensile test at 40°C: a) 2A-7, b) 3A-7 and c) BPA.

Introducing the IL into the polymer networks reduced the cross-link density of the resulting ion gels compared to the base polymers. The stiffness, as characterized by Young's modulus, and yield strength were thus reduced with increasing IL content. In all the polymers studied, incorporating 40 vol% IL in the network improves the flexibility (i.e. higher strain at failure) only slightly, and increasing the content to 60 vol% reduced the strain at failure back to the same level as the base polymer. Despite the lower cross-link density in the ion gel, the polymer chains still possessed the same chain length between cross-links. As a result, the swollen networks are less interconnected than the unfilled network, and are more likely to form looser overall structures [10]. However,

they are still sufficiently interconnected as to not allow significant additional freedom of movement upon strain application. A similar observation was noted for 2A-5 and 3A-5 and their 40 vol% IL gels (Table S2 in Supporting Information), where the IL reduces the Young's modulus and yield strength while failing to improve flexibility. Thus, incorporation of ionic liquid into the network reduced the toughness relative to the base polymer.

The appeal of incorporating IL into these cross-linked polymers is primarily to increase gas permeability. As a permanent plasticizer, [emim][Tf<sub>2</sub>N] is particularly effective in doing so, leading to an increase of CO<sub>2</sub> permeability from 120 barrer for the cross-linked 2A-7, to 270 barrer for the 40 vol% gel and 430 barrer for the 60 vol% gel [4]. As shown in Figure 4, not surprisingly [emim][Tf<sub>2</sub>N] is equally effective in increasing the gas permeability of the gels using 3A-7 and BPA cross-linked polymers. 3A-7 base polymer has similar CO<sub>2</sub> permeability to 2A-7 with slightly lower CO<sub>2</sub>/N<sub>2</sub> selectivity, while BPA has slightly higher CO<sub>2</sub> permeability and similar CO<sub>2</sub>/N<sub>2</sub> selectivity, which was in line with the previous study. The permeability increase as a result of incorporating [emim][Tf<sub>2</sub>N] into 3A-7 is less than in 2A-7. This result is likely due to the more interconnected network achieved with the trifunctional monomer, which renders it more resistant to IL plasticization effects. On the other hand, the BPA network is readily plasticized, achieving 490 barrer CO<sub>2</sub> permeability at 60 vol% IL incorporation. All three 60 vol% IL networks have the same CO<sub>2</sub>/N<sub>2</sub> selectivity (31±1). The shorter acrylate networks, 2A-5 and 3A-5, have much lower base gas permeability than the other three networks. Incorporating 40 vol% [emim][Tf<sub>2</sub>N] into these networks increase their gas permeability, but not to the same extent achieved by the other ion gels.

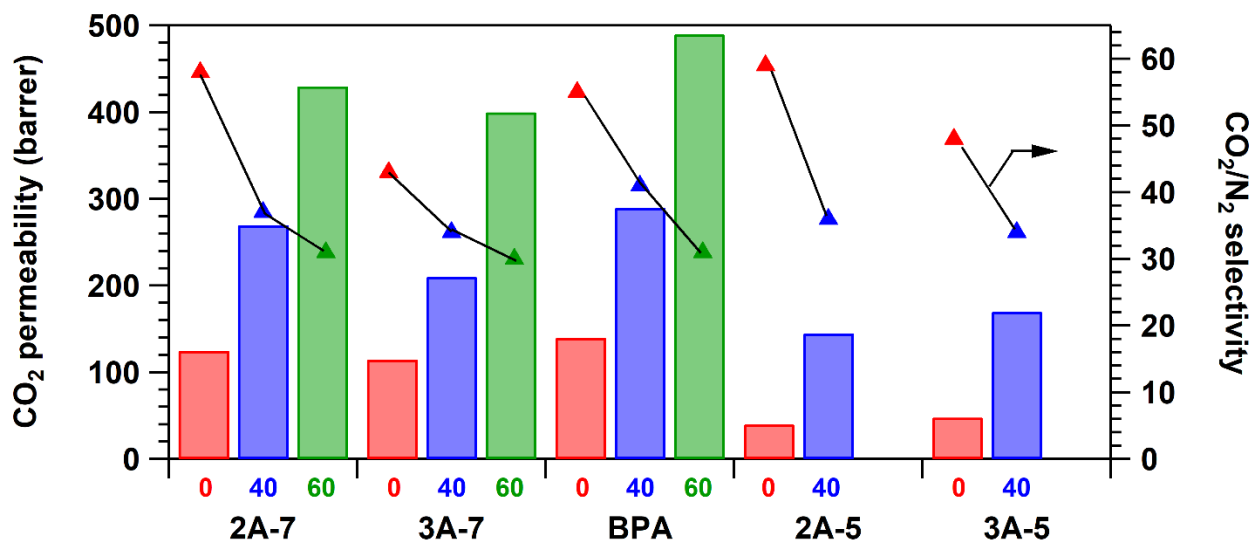


Figure 4. CO<sub>2</sub>, N<sub>2</sub> permeability (vertical bars) and selectivity (filled triangles) of the base polymers and its associated ion gels. The numbers above the cross-linker denoted [emim][Tf<sub>2</sub>N] content in vol%. Lines on selectivity data added to guide the eye.

### 3.2. Blending higher functional monomers into triacrylate network

The second strategy we pursued was to incorporate short monomers in 3A-7 containing four or more acrylate functional groups to add cross-linking bridges, with the goal of increasing cross-link density and improving the tensile properties. Increasing cross-link density increases the cohesive energy density of the network, which tends to reduce gas permeability [7]. Furthermore, incorporation of monomers not containing EO moieties is also expected to reduce CO<sub>2</sub>/N<sub>2</sub> selectivity. Hence, this strategy may be beneficial only when confined to using small amounts of these monomers. We chose to incorporate 5 wt%, 10 wt% or 20 wt% of either 4A or 6A into 3A-7 prepolymer mixtures.

Acrylate conversion is a concern with utilizing multifunctional monomers: as the polymerization reaction proceeds and chain mobility decreases, the probability of a monomer having unreacted double bonds increases. The presence of unreacted double bonds can be evaluated using FTIR. As shown in Figure 5, the characteristic acrylate peaks belonging to unreacted monomer (such as 6A shown here) appear at 812, 1190 and 1410 cm<sup>-1</sup> [2]. For the triacrylate network 3A-7, the overall network remained sufficiently mobile that the network achieved essentially complete double bond conversion as characterized by complete disappearance of these peaks. Even with 20 wt% of either

4A or 6A, where the FTIR spectra suggest the presence of some unreacted double bonds, the overall conversion remains high with few unreacted monomers. (More comparison between polymers and respective monomers are also given in Figure S3 in Supporting Information.) The network appears to have retained relatively high chain mobility to allow sufficient conversion of all acrylate groups, even those attached to these multifunctional monomers, because the network retained low  $T_g$  throughout.

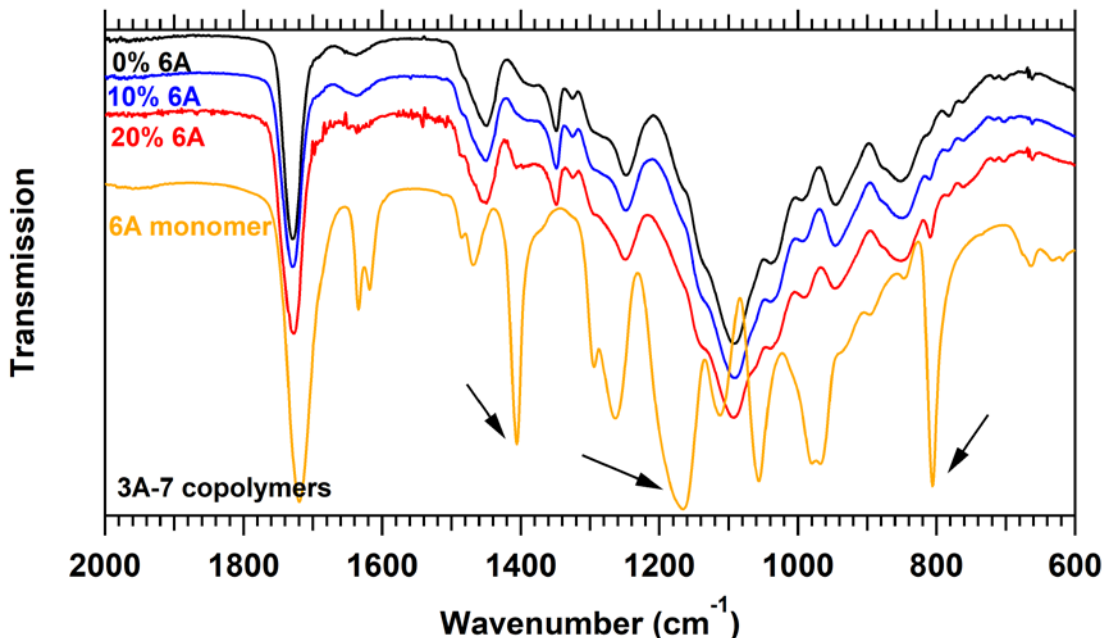


Figure 5. FTIR spectra of cross-linked 3A-7 (black), 90/10 wt% 3A-7/6A (blue) and 80/20 wt% 3A-7/6A base polymers (red). Arrows indicate acrylate characteristic peaks that were readily identified on the uncross-linked 6A monomer spectrum (orange). Spectra were displaced vertically for clarity.

DSC heating scans confirmed that incorporating these multifunctional monomers up to 20 wt% did not significantly affect the primary  $T_g$  of the networks. Figure 6 shows the DSC traces for the 3A-7/4A polymers; the 3A-7/6A polymers were shown in Supporting Information. The  $T_g$  of cross-linked 3A-7 was  $-41^{\circ}\text{C}$ ; incorporating 20 wt% 4A only raised it to  $-39^{\circ}\text{C}$ , and it remained unchanged with incorporation of 6A. The most notable difference is instead the *breadth* of the glass transition: the polymers containing 20 wt% 4A or 6A underwent glass transition over a wider temperature range. A broadening glass transition in highly cross-linked rubbers is characteristic of increasing heterogeneity of the polymer segments [10], which makes sense when considering that

short, highly branched segments were added to the network with incorporation of 4A or 6A. At the same time, the overall  $T_g$  is minimally affected because these new segments are short and have a relatively small effect on the overall segmental motions during the glass transition, which is dominated by the longer EO chains. The 40 vol% [emim][Tf<sub>2</sub>N] gel of 3A-7/4A exhibited similar behavior: relatively similar  $T_g$  as the 3A-7 gel (-45°C) while the glass transition broadened with increasing incorporation of 4A, indicating that adding the plasticizer did not fundamentally change the cross-linked network's segmental characteristics despite acting as a diluent during photopolymerization.

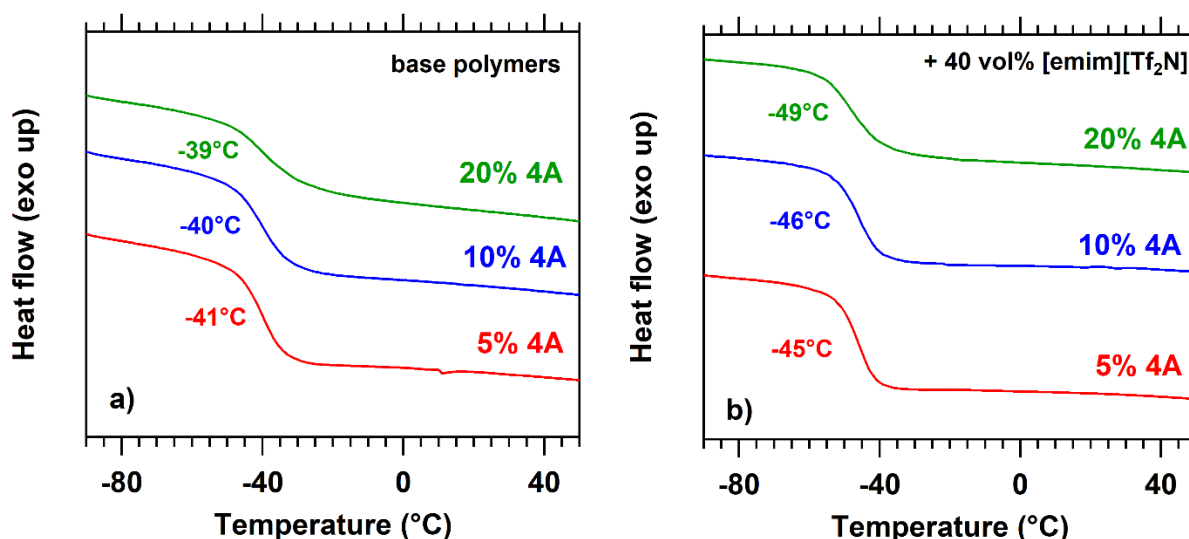


Figure 6. DSC heating scans of a) 3A-7/4A base polymers, and b) corresponding 40 vol% [emim][Tf<sub>2</sub>N] ion gels.

Tensile tests performed on the DMA confirmed the qualitative observations that incorporating these short, multifunctional monomers increased the stiffness of the resulting polymers. As shown in Figure 7, we observed a systematic increase in Young's modulus with increasing 4A or 6A content. The loss in flexibility, however, is generally not compensated by an increase in yield strength. A significant increase in yield strength was only observed in the network containing the highest loading of each of the short monomers. This observation agreed with the DSC results that in these polymers, the overall segmental motion is dominated by the longer EO chains of 3A-7. In a network with heterogeneous chain length, the short strands tend to break at lower strain, reducing the yield strength relative to a more monodisperse network [24]. This effect is amplified when plasticizers such as [emim][Tf<sub>2</sub>N] were added to the prepolymer mixture – the dilution further



increases the heterogeneity of the plasticized polymer. Figure 7c shows that the yield strength of the ion gels was virtually the same regardless of the 4A content (at least up to 20 wt%). We did not analyze the 6A ion gels but we expect the behavior to also be observed in these networks.

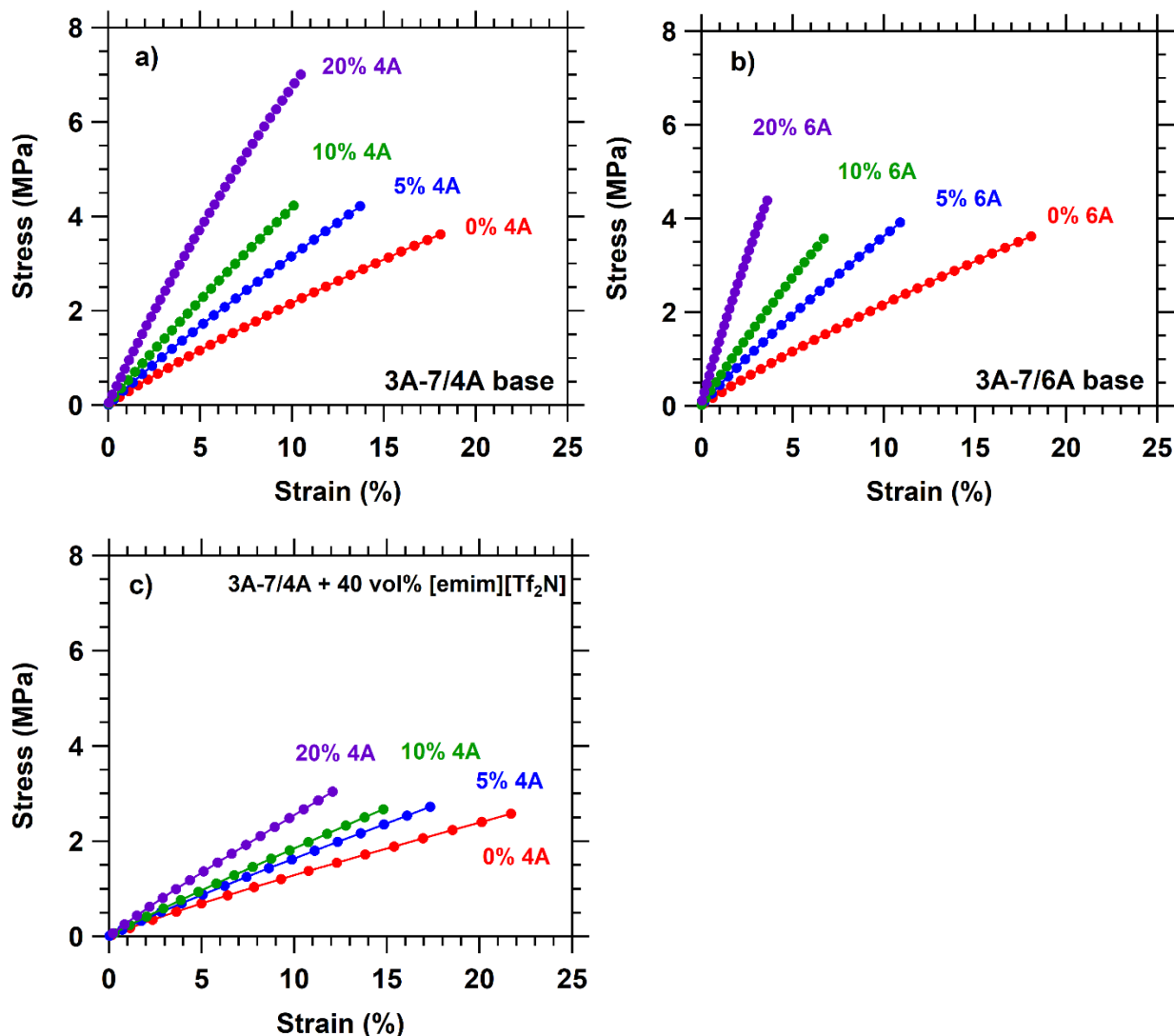


Figure 7. Stress-strain curves of the a) 3A-7/4A base polymers, b) 3A-7/6A base polymers, and c) 40 vol% [emim][Tf<sub>2</sub>N] ion gels of 3A-7/4A.

The incorporation of 4A into the 3A-7 network led to a systematic reduction in gas permeability, as expected from the increasing cohesive energy density. The CO<sub>2</sub> permeability decreased from 120 barrer to 37 barrer with addition of 20% 4A, as shown in Figure 8. This trend was reflected in the corresponding ion gel as well: the 40 vol% [emim][Tf<sub>2</sub>N] gel CO<sub>2</sub> permeability decreased from 210 barrer to 160 barrer with incorporation of 20% 4A. The % reduction in CO<sub>2</sub> permeability

is not as severe in the ion gel as it was in the base polymer, since the network is still highly plasticized. Nonetheless, since 4A addition is characterized by both the loss in polymer flexibility and a reduction in gas transport performance, the strategy of incorporating short multifunctional monomers does not improve these ion gels.

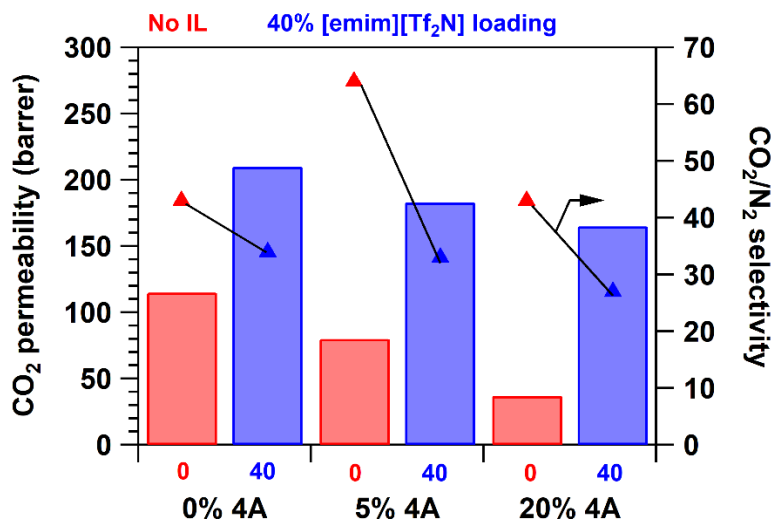


Figure 8. CO<sub>2</sub>, N<sub>2</sub> permeability (vertical bars) and selectivity (filled triangles) of the 3A-7/4A base polymers and their associated 40 vol% [emim][Tf<sub>2</sub>N] ion gels. Lines on selectivity data added to guide the eye.

### 3.3. Mechanical properties comparison with a monoacrylate copolymer

In this final section, we want to compare the tensile properties and gas transport properties of the best performing ion gels to those of the covalently-bonded network formed by 2A-7 and MEA, a methyl ether monoacrylate. It is well established that incorporating MEA significantly increases the gas permeability of 2A-7. The MEA forms pendant groups which significantly reduce the cross-link density because it does not form cross-link bridges, greatly reducing  $T_g$  of the resulting networks [16,21,25]. While this strategy results in much higher gas permeability, it came with a tradeoff in mechanical properties as the resulting network became more fragile with the reduced extent of covalent cross-linking. In the ion gels, while the presence of [emim][Tf<sub>2</sub>N] during polymerization reduces cross-link density of the network, the hydrogen bonding between [emim][Tf<sub>2</sub>N] and EO chains in the network should act to increase intermolecular interactions which would help improve the mechanical properties.

For this study, we incorporated MEA in three compositions in 2A-7: 25 wt%, 50 wt% and 75 wt%. The DSC heating scans for these films are given in Figure S5 in the Supporting Information, showing a progressive decrease in  $T_g$  as more MEA is incorporated, in line with prior studies. Lin et al. reported at higher MEA content, the network became loose enough that the EO chains can start forming crystals at certain temperatures [6,16], which we observed here for the network incorporating 75 wt% MEA.

The tensile test results for the 2A-7/MEA copolymers are shown in Figure 9. The incorporation of MEA progressively reduces the Young's modulus of the 2A-7/MEA network, but the yield strength was not impacted at 25 wt% MEA. Beyond that, however, yield strength decreased to as low as 1 MPa for the 75 wt% MEA film. The data shows that the 2A-7/[emim][Tf<sub>2</sub>N] ion gels have comparable tensile properties to the networks containing MEA. The 40 vol% gel has similar tensile properties as the 50 wt% MEA base polymer, while the 60 vol% gel has higher yield strength (1.5 MPa) compared to the 75 wt% MEA (1.0 MPa). Indeed, the 75 wt% MEA film was fragile and difficult to handle.

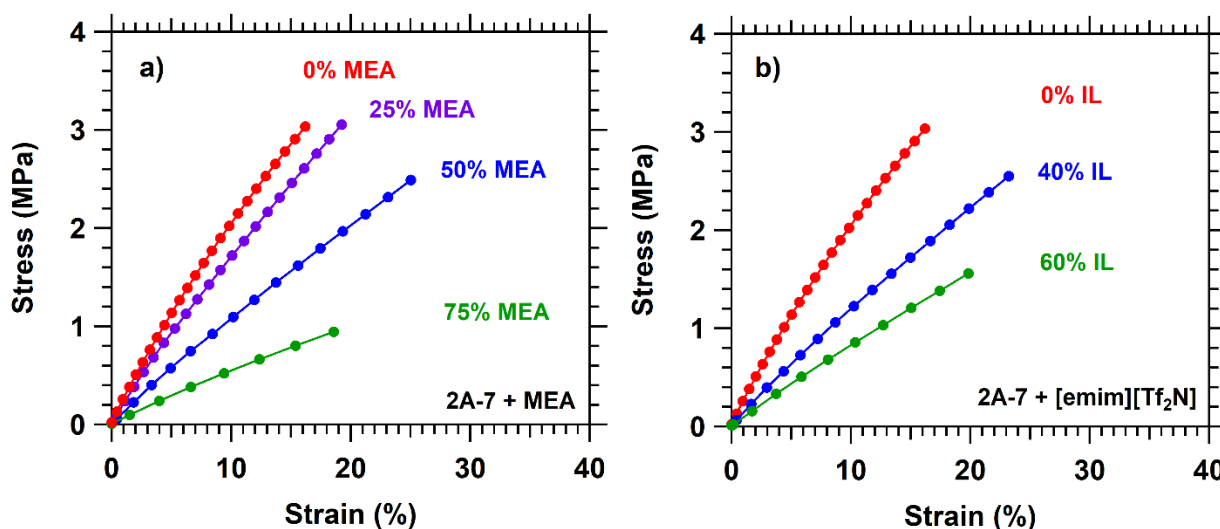


Figure 9. Stress-strain curves of a) 2A-7/MEA base polymers and b) 2A-7/[emim][Tf<sub>2</sub>N] as obtained through DMA tensile test. Figure 9b is identical to Figure 3a to facilitate direct comparison with Figure 9a.

Figure 10 shows the gas permeability comparison between the two proven strategies to modify 2A-7. The CO<sub>2</sub> permeability of the 40 vol% [emim][Tf<sub>2</sub>N] is 270 barrer, comparable to the CO<sub>2</sub>

permeability of 50 wt% 2A-7/MEA (240 barrer). Both polymers also have comparable CO<sub>2</sub>/N<sub>2</sub> selectivity at 40°C: 36 for the former, 38 for the latter. The biggest difference between the two strategies is the CO<sub>2</sub>/N<sub>2</sub> selectivity continued to decrease with increasing [emim][Tf<sub>2</sub>N] content in the ion gel, whereas it tended to stay constant around 40 at higher MEA loading. The difference is because MEA kept the EO content of the polymer high, which was the key feature to retain high CO<sub>2</sub>/N<sub>2</sub> solubility selectivity in these networks [6]. [emim][Tf<sub>2</sub>N], in contrast, introduces the [Tf<sub>2</sub>N]<sup>-</sup> anion which has much lower CO<sub>2</sub>/N<sub>2</sub> solubility selectivity than EO moieties [26].

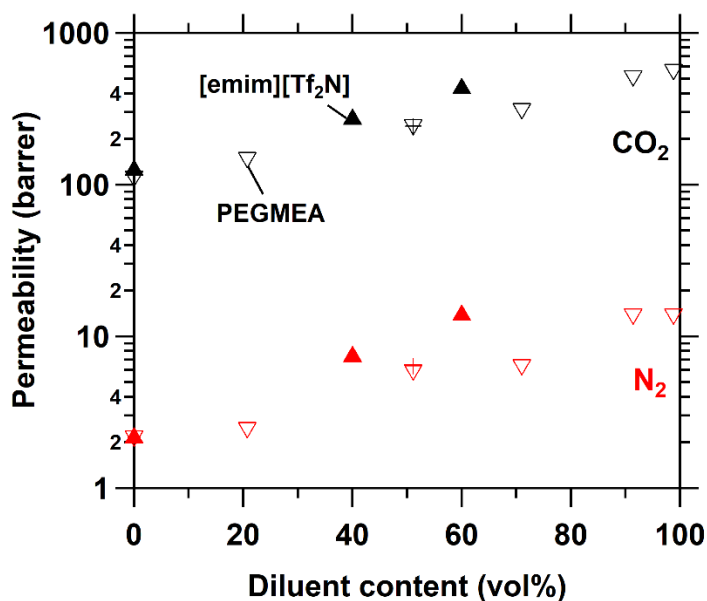


Figure 10. Comparison of CO<sub>2</sub> and N<sub>2</sub> permeability of 2A-7/MEA base polymers (inverted open triangles) to the 2A-7/[emim][Tf<sub>2</sub>N] ion gels (upright filled triangles). 2A-7/MEA data was taken from ref. [6] and measured at 35°C, compared to 40°C for the ion gels. In addition, the 50/50% 2A-7/MEA data denoted as + were measured in our laboratory at 40°C.

#### 4. Conclusion

In this work, we evaluated two different strategies to improve the mechanical properties of PEO-based cross-linked ion gels with [emim][Tf<sub>2</sub>N]: changing the EO-containing cross-linker and blending these cross-linkers with small amounts of short, multifunctional monomers. Changing the average chain length between cross-links, achieved by changing the primary di- or tri-functional monomer, had the greatest impact on the properties of the resulting ion gels. The PEG diacrylate and triacrylate we utilized in our previous work have similar mechanical properties, but

the less interconnected nature of the diacrylate allowed the ion gels to have higher CO<sub>2</sub> permeability. The shorter PEG monomers led to a stiffer network and higher tensile yield strength, but the tighter network cannot stabilize as much ionic liquid as the longer analogues. A particularly promising cross-linker is bisphenol A ethoxylate diacrylate, which not only exceeded the high gas separation performance of the PEG diacrylate but also improved the flexibility of the resulting gels due to the longer distance between cross-link segments, which could be critical when considering device fabrication. We also showed that incorporating small amounts of short multifunctional segments into the PEG network was detrimental to the film's mechanical properties and gas separation performance. The short segments reduced the film flexibility but were not numerous enough to affect yield strength significantly. The strategy of increasing chain length heterogeneity in the network should be avoided for future polymer network design.

We took the opportunity to compare the mechanical properties of these ion gels with a covalently bonded PEGDA copolymer with PEGMEA. These were the two successful strategies for increasing the gas permeability of cross-linked PEO in the literature, and we were interested to evaluate whether the ion gel route offers better mechanical properties despite the lower CO<sub>2</sub>/N<sub>2</sub> selectivity. We showed that these two strategies result in films with comparable mechanical properties with each other. For the same gas separation performance, the ion gel route did not offer a clear advantage on mechanical properties. It is perhaps helpful to treat the plasticization strategy with [emim][Tf<sub>2</sub>N] as part of a strategy to design a better membrane rather than the superior route for membrane modification. As we have mentioned in our previous work, the major drawback of the ionic liquid chosen here is the [Tf<sub>2</sub>N]<sup>-</sup> anion, with its poor CO<sub>2</sub>/N<sub>2</sub> selectivity, and while research may continue to find a better ionic liquid plasticizer, the PEGDA/PEGMEA copolymer remains the benchmark to beat for both mechanical and gas separation properties. A different polymer design strategy will be needed to further improve this class of materials.

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# The Effect of Poly(Ethylene Oxide) Cross-Linking Structure on the Mechanical Properties and CO<sub>2</sub> Separation Performance of an Ion Gel Membrane

**Victor A. Kusuma, Christina Chen, James S. Baker, Megan K. Macala, David Hopkinson**

Table S1. Density of base polymers and its resulting calculations for IL content in wt% for the corresponding ion gels in this study

<b>Polymer base</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>40 vol% IL (wt%)</b>	<b>60 vol% IL (wt%)</b>
<b>2A-7</b>	1.22	45.4	65.3
<b>3A-7</b>	1.21	45.7	65.5
<b>BPA</b>	1.20	46.0	65.7
<b>2A-5</b>	1.26	44.8	64.6
<b>3A-5</b>	1.24	45.1	64.8
<b>3A-7 + 5% 4A</b>	1.23	45.3	
<b>3A-7 + 10% 4A</b>	1.23	45.3	
<b>3A-7 + 20% 4A</b>	1.23	45.3	
<b>3A-7 + 5% 6A</b>	1.24	45.1	
<b>3A-7 + 10% 6A</b>	1.25	45.0	
<b>3A-7 + 20% 6A</b>	1.26	44.8	

Density of [emim][Tf<sub>2</sub>N] is 1.53 g/cm<sup>3</sup> at 23°C. All polymer density data taken at 23°C. Blank cells designate ion gels not fabricated. The content for 4A and 6A were given in wt% relative to 3A-7.

SUPPORTING INFORMATION

Table S2. Tensile properties of the cross-linked polymers and their gels: Young's modulus (E), yield strength ( $\sigma_y$ ), and strain at break ( $\epsilon_y$ ). Errors are standard deviations based on 3 to 5 measurements. Abbreviations follow Table 1. All %IL are in vol%; %4A or %6A are in wt% relative to 3A-7; %MEA are in wt% relative to 2A-7.

Sample	E (MPa)	$\sigma_y$ (MPa)	$\epsilon_y$ (%)
2A-7	21.9 ± 0.7	3.1 ± 0.2	16 ± 2
3A-7	23.5 ± 0.7	3.3 ± 0.4	17 ± 2
BPA	11.9 ± 0.3	2.8 ± 0.2	30 ± 4
2A-5	40.6 ± 0.9	4.4 ± 0.5	13 ± 2
3A-5	42.3 ± 0.3	4.2 ± 0.7	12 ± 2
2A-7 + 40% IL	13.0 ± 0.1	2.6 ± 0.2	24 ± 1
3A-7 + 40% IL	13.9 ± 0.1	2.6 ± 0.1	22 ± 1
BPA + 40% IL	6.3 ± 0.4	2.0 ± 0.1	41 ± 1
2A-5 + 40% IL	21.6 ± 0.1	2.2 ± 0.1	11 ± 0.4
3A-5 + 40% IL	22.1 ± 0.4	2.8 ± 0.1	15 ± 0.4
2A-7 + 60% IL	8.6 ± 0.1	1.5 ± 0.1	20 ± 2
3A-7 + 60% IL	8.5 ± 0.2	1.4 ± 0.1	18 ± 0.6
BPA + 60% IL	3.8 ± 0.1	1.0 ± 0.1	34 ± 2
3A-7 + 5% 4A	35.0 ± 0.8	4.2 ± 0.2	14 ± 1
3A-7 + 10% 4A	49.3 ± 2.2	4.4 ± 0.2	10.0 ± 0.6
3A-7 + 20% 4A	80.9 ± 2.6	7.2 ± 0.8	7.2 ± 1.2
3A-7 + 5% 4A + 40% IL	17.8 ± 0.2	2.5 ± 0.3	15 ± 2
3A-7 + 10% 4A + 40% IL	19.4 ± 1.2	2.7 ± 0.2	15 ± 2
3A-7 + 20% 4A + 40% IL	28.2 ± 0.3	3.1 ± 0.2	12.5 ± 0.6
3A-7 + 5% 6A	39.2 ± 1.1	4.3 ± 0.4	12.5 ± 1.4
3A-7 + 10% 6A	60 ± 1	5.0 ± 0.2	9.7 ± 0.4
3A-7 + 20% 6A	124 ± 1	7.6 ± 0.9	7.0 ± 1.0
2A-7 + 25% MEA	18.7 ± 0.4	3.0 ± 0.2	19 ± 1
2A-7 + 50% MEA	11.6 ± 0.4	2.4 ± 0.1	25 ± 2
2A-7 + 75% MEA	5.5 ± 0.2	0.97 ± 0.09	20 ± 2

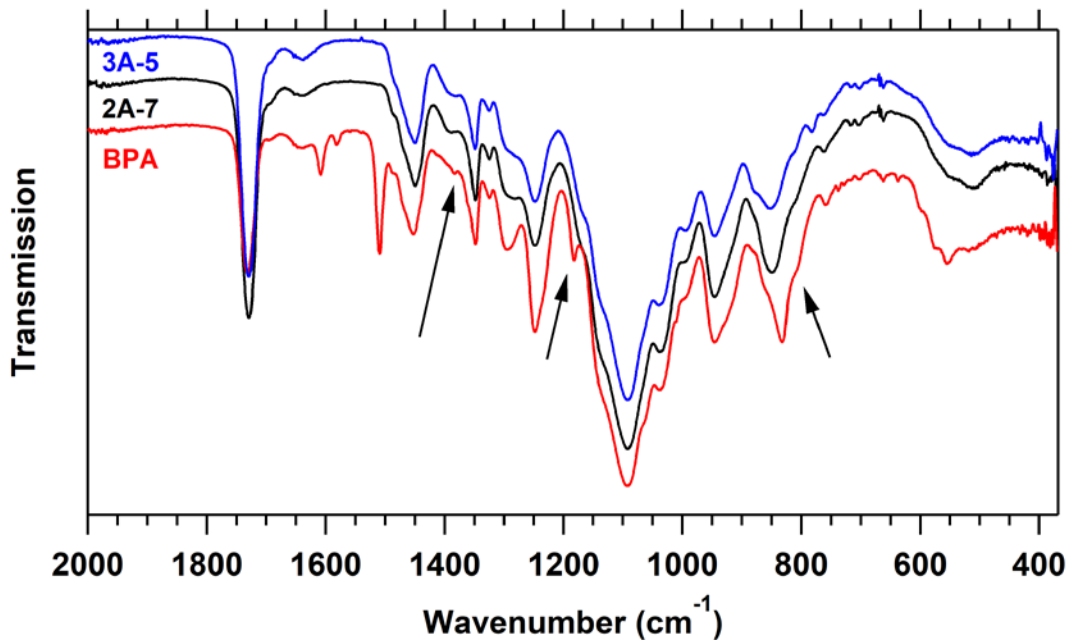


Figure S1. FTIR spectra of 2A-7, 3A-5 and BPA base polymers. Expected locations of acrylate characteristic peaks were indicated by arrows.

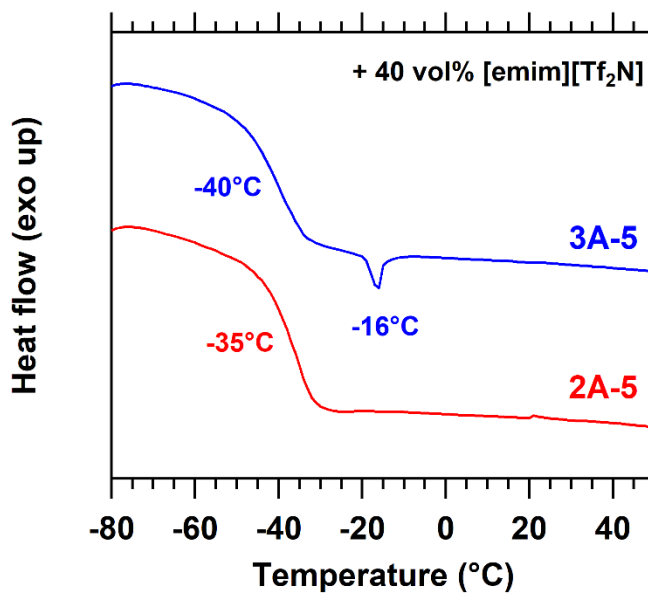


Figure S2. DSC traces of 40 vol% ion gels of 2A-5 and 3A-5.

SUPPORTING INFORMATION

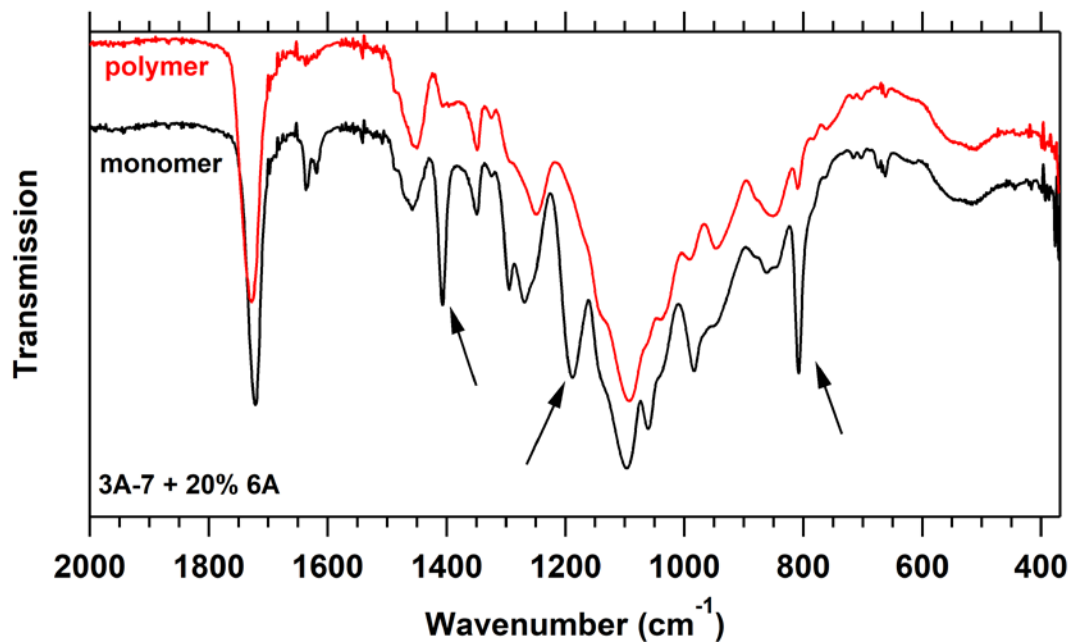


Figure S3. FTIR spectra of 3A-7/20% 6A polymer and monomer. Characteristic acrylate peaks, readily identified in the monomer, are denoted with arrows.

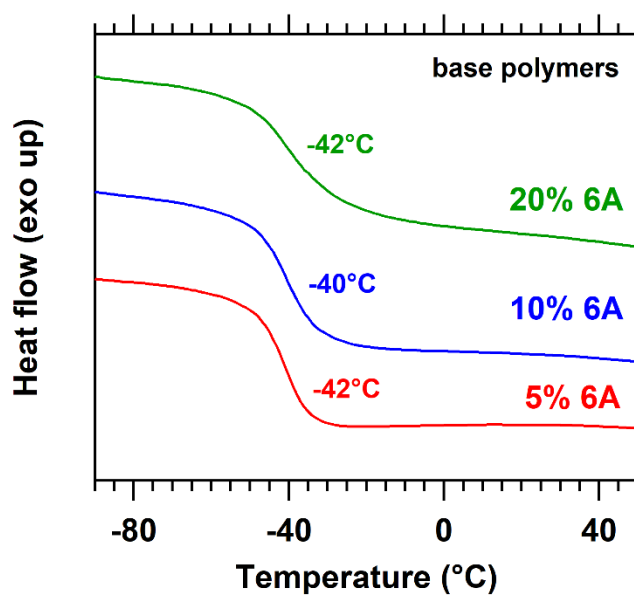


Figure S4. DSC traces of 3A-7/6A polymers.

SUPPORTING INFORMATION

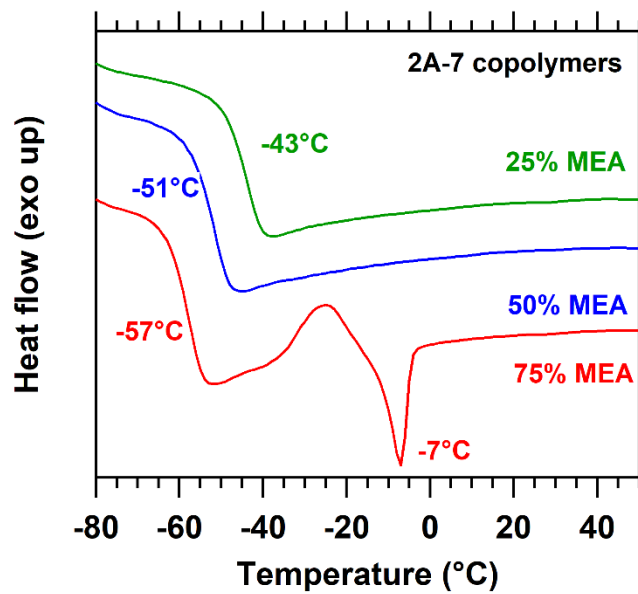


Figure S5. DSC traces of 2A-7/MEA polymers.