Ionic Liquid Compatibility in Polyethylene Oxide/Siloxane Ion Gel Membranes

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Abstract

Ion gel films were prepared by incorporating eight commercially available ionic liquids in two different cross-linked polymer matrices to evaluate their phase miscibility, gas permeability and ionic conductivity for potential applications as gas separation membranes and solid electrolyte materials. The ionic liquids cations were 1-ethyl-3-methylimidazolium, 1-ethyl-3-methylpyridinium, 1-butyl-1-methylpyrrolidinium, tributylmethylphosphonium, and butyltrimethylammonium with a common anion (bis(trifluoromethylsulfonyl)imide). In addition, ionic liquids with 1-ethyl-3-methylimidazolium cation with acetate, dicyanamide and tetrafluoroborate counterions were evaluated. The two polymers were cross-linked poly(ethylene oxide) and cross-linked poly(ethylene oxide)/siloxane copolymer. Differential scanning calorimetry, X-ray diffractometry and visual observations were performed to evaluate the ion gels' miscibility, thermal stability and homogeneity. Ionic liquids with the least basic anion (bis(trifluoromethylsulfonyl)imide) and aromatic cations containing acidic proton (e.g. imidazolium and pyridinium) gave the most stable and miscible ion gels. Phase stability was shown to be a function of both ionic liquid content and temperature, with phase separation observed at elevated temperatures. Gas permeability testing with carbon dioxide and nitrogen and ionic conductivity measurements confirmed that these ionic liquids increased the gas permeability and ionic conductivity of the polymers.

1. Introduction

Ionic liquids (ILs) have received considerable attention in gas separation membrane applications [1–3]. ILs, particularly room temperature ILs, which are organic salts with melting points around or below ambient temperature, exhibit many attractive features for membrane separation: very low vapor pressure, high gas diffusivity, high ionic conductivity, and structure customization that allows ILs to be tailored to a particular application [1]. For gas separation membranes, ILs were initially applied in the form of supported ionic liquid membranes (SILM). SILMs, in which the IL is held by surface tension and capillary forces in a microporous substrate [3,4], benefit from the IL's long-term stability conferred by its low vapor pressure, but suffer from two major shortcomings that prevent them from being practical for industrial membrane applications. First, the SILM mechanical robustness depends on the support having sufficient thickness, on the order of 100-200 μm, which leads to much lower gas permeance compared to commercial membranes, in which the separation layer is typically less than a micron thick [1]. Also, depending on the application, trans-membrane pressure may exceed the capillary pressure that retains the ILs within the porous network, which typically is only in the order of several bar, expelling the IL and resulting in the loss of membrane performance [5].

Recently, more attention was given toward incorporating ILs into a polymer, either by covalently binding ILs as part of a polymer network (forming poly ILs, or PILs) or by blending ILs with a polymer (forming IL gels, or ion gels) [1,6–8]. PILs generally have low gas permeability, comparable to those of conventional glassy polymers, since the strong ionic interactions within the network lead to low chain mobility that hampers gas diffusion [9,10]. Free ILs with matching structures can be blended into these PILs as plasticizers to help increase the gas permeability

[11–15]. For instance, Li et al. observed an increase in CO_2 permeability from 100 barrer to 560 barrer by introducing 60 wt% of a free IL into a PIL [15]. A drawback of this approach is the often highly specific nature of the polymer, which requires multi-step synthesis of new IL monomers having reactive groups (e.g. vinyl or styrene), with inherently longer path to commercial viability and higher cost [14].

Another promising approach is to create ion gels by mixing ILs with commercially available polymers that do not contain ionic groups. This approach was more prevalent in making solid electrolytes: poly(ethylene oxide) (PEO) electrolytes can incorporate not only lithium salts such as lithium bis(trifluoromethylsulfonyl)imide ($LiTf_2N$), but also a variety of ILs [8,16–19]. From a gas separations perspective, PEO-based polymers were also intensively studied for CO_2 separations in particular owing to its good CO_2/N_2 selectivity [20–22]. For instance, high molecular weight PEO has pure gas CO_2/N_2 selectivity around 55 at 35°C and 4.4 bar upstream pressure [23]. Its modest CO_2 permeability, 13 barrer at the same stated conditions [23], can be improved by reducing polymer crystallinity, for instance through the formation of cross-linked PEO from di-functionalized oligomers [24] or by using PEO-containing block copolymers [22]. Based on the same principles, ion gels comprising of IL and PEO can be engineered to have high gas permeability [25–28] while having reasonable mechanical integrity even at more than 90 wt% IL content [25,28]. For instance, Fujii et al. fabricated ion gels containing 94 wt% IL content that had elongation at break as much as 280% [29]. These ion gels employed a limited number of ILs, mostly those having alkyl imidazolium cations [1], which were known to have favorable interactions with PEO chains [30–34].

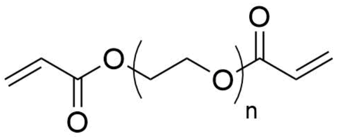
We are interested in developing materials that can be made into practical membranes for CO_2 separation from post-combustion flue gas, where not only high CO_2 permeability and high

CO_2/N_2 selectivity are desired, but also good cohesiveness and long term phase stability. For PEO-based ion gels to fully take advantage of the structure versatility of ILs, it is important to explore the stability of several classes of ILs beyond those with alkyl imidazolium cations. Even within this class of IL, we identified only one study in the literature where a series of PEO-based cross-linked ion gels was generated with imidazolium-based ILs with varying anions [35]. Predicting IL miscibility with a polymer is a difficult task: matching solubility parameters of ILs to the polymer does not always result in consistent solution behavior [36]. Specific Coulombic and hydrogen-bonding interactions between the polymers and ILs can influence the mixing entropy, making trial-and-error experiments important in establishing the compatibility of an IL with a particular polymer [36].

Thus, in this study, we have immobilized a variety of commercially available ILs at moderate loading (40 vol%) into two PEO-based cross-linked polymers to evaluate the ion gels' phase stability through visual observations and differential scanning calorimetry. The 40 vol% loading was chosen after initial experimentations showed it allowed the stability and properties of various ion gels to be readily differentiated while keeping the gels reasonably cohesive for membrane testing. We evaluated several ILs with a common anion (bis(trifluoromethylsulfonyl)imide, or $[Tf_2N]^-$) with differing cations having imidazolium, phosphonium, ammonium, pyrrolidinium and pyridinium core, representing major classes of IL cations that are currently commercially available. In addition, the effect of using several different anions ($[Tf_2N]^-$, dicyanamide, tetrafluoroborate and acetate) on ion gel stability was also evaluated through incorporating ILs with a common cation (1-ethyl-3-methylimidazolium, or $[emim]^+$). The list of ILs evaluated here is shown in Table 1. The two polymers selected are cross-linked poly(ethylene glycol) diacrylate (PEGDA), and a PEGDA copolymer with a thiol-functionalized polysiloxane (Scheme 1). Three of these ILs form miscible and dry ion gels with cross-linked PEGDA at 40 vol% IL loading when cast without solvent: they are [emim][Tf_2N], [empy][Tf_2N], and [emim][dca]. For these films, we also evaluated the stability of ion gels containing 60 vol% of the stated ILs. Two other ILs, [N_{4111}][Tf_2N] and [bmpyrr][Tf_2N], can also form dry ion gels with cross-linked PEGDA when cast with a co-solvent. Adding the polysiloxane, a strategy employed in our previous study to increase the base gas permeability of the PEGDA network [37], had a minimal effect on the ion gel phase stability as long as a co-solvent was employed during the casting process. The stable ion gels obtained were evaluated for pure gas CO_2 and N_2 permeability and ionic conductivity.

2. Material Fabrication

All chemicals used in this work were obtained from commercial sources and used as received. Poly(ethylene glycol) diacrylate, Mn=700 (PEGDA), 2,2-dimethoxy-2-phenylacetophenone (DMPA, the photoinitiator), 1-ethyl-3-methylimidazolium acetate ([emim][ac] – 97%) and ACS Reagent grade 2-butanone (methyl ethyl ketone; MEK) were obtained from Sigma-Aldrich. This PEGDA has been employed by previous studies [20,21,24,37] for its ability to form rubbery cross-linked polymer with high acrylate conversion and has the highest Mn currently commercially available to maximize ether content while keeping the polyether segments short enough to inhibit crystallization [38]. (Mercaptopropyl) methyl siloxane homopolymer, 75-150 cSt ("thiosiloxane") was obtained from Gelest, Inc. (Morrisville, PA) (catalog number SMS-992). All other ILs were obtained from IOLITEC USA Inc. (Tuscaloosa, AL). Scheme 1 shows the monomer structures for the two cross-linked polymers, and Table 1 shows the list of all ILs examined in this study. Ultra high purity grade carbon dioxide and nitrogen (99.999%) were obtained from Airgas through Butler Gas Company (McKees Rocks, PA).



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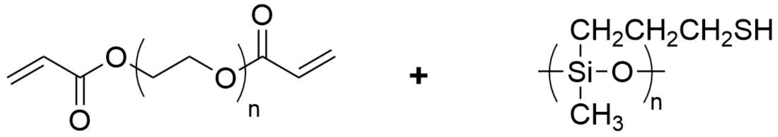

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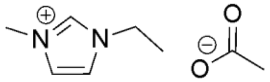
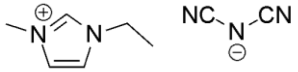
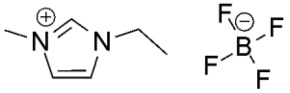
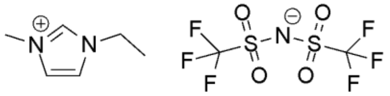
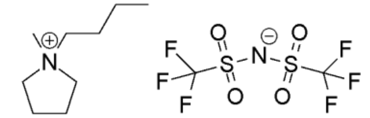
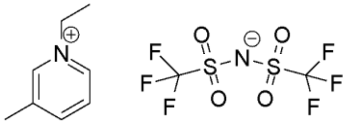
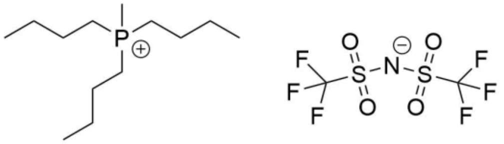
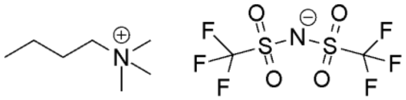
Scheme 1. Constituent monomers for the two cross-linked polymers in this study: poly(ethylene glycol) diacrylate, Mn=700 (PEGDA) and poly(mercaptopropyl)methyl siloxane, Mn=4000 to 7000 (thiosiloxane)

Table 1. Ionic liquids abbreviation and structure

Abbreviation	Full name	Structure
[emim][ac]	1-ethyl-3-methylimidazolium acetate	
[emim][dca]	1-ethyl-3-methylimidazolium dicyanamide	
[emim][BF$_4$]	1-ethyl-3-methylimidazolium tetrafluoroborate	
[emim][Tf$_2$N]	1-ethyl-3-methylimidazolium bis(triflouromethylsulfonyl)imide	
[bmpyrr][Tf$_2$N]	1-butyl-1-methylpyrrolidinium bis(triflouromethylsulfonyl)imide	
[empy][Tf$_2$N]	1-ethyl-3-methylpyridinium bis(triflouromethylsulfonyl)imide	
[P$_{1444}$][Tf$_2$N]	tributylmethylphosphonium bis(triflouromethylsulfonyl)imide	
[N$_{4111}$][Tf$_2$N]	butyltrimethylammonium bis(triflouromethylsulfonyl)imide	

The desired reagents were mixed together at room temperature using magnetic stirring for at least 15 minutes with a typical batch size of 1 g. To make polymer **2** (cf. Scheme 1), the ratio of PEGDA to thiosiloxane was set at a 1:1 acrylate to thiol functional group ratio following our previous work [37]. Unless stated otherwise, ILs were added to the liquid monomer at approximately 40 vol% of the overall mixture based on the measured liquid densities. DMPA was added at 1 wt% of total monomers and IL. For most ion gels based on polymer **2**, MEK was added as a co-solvent to comprise 55 wt% of the total solution to improve compatibility. Detailed compositions are available in Table S1 in the Supporting Information.

Following the previous study [37], the mixture was pipetted into a gap formed by two quartz plates separated by four 200 μm thick stainless steel washers placed in the corners (Figure S1 in the Supporting Information). The plates were placed inside an exposure box under a Blak-Ray B-100AP high intensity lamp (UVP, LLC – Upland, CA). After 90 seconds cross-linking time, careful separation of the quartz plates yielded films with typical thicknesses of 230 μm. FTIR spectra confirmed that 90 s cross-linking was enough to ensure essentially complete acrylate reaction, consistent with previous studies (Figure S2 in the Supporting Information) [24,37]. When present, MEK was removed by placing the ion gel film in a fume hood at ambient conditions for 15 minutes. Complete removal of MEK was also confirmed by FTIR. Ion gel films were assessed for the presence of surface exudate immediately after casting: some films had slick surfaces with removable liquid residue, whereas others were completely dry to touch.

Detailed descriptions of the material characterization methods performed in this work can be found in the Supporting Information.

3. Results and Discussions

3.1. Characterization of PEO ion gels (polymer 1)

Polymer **1** ion gel films were prepared by mixing PEGDA with one of the eight ILs shown in Table 1 at 40 vol% loading. A moderate IL loading was selected to ensure the resulting films were sufficiently robust for gas permeability measurements, since adding ILs reduces the mechanical integrity of the ion gels due to the decreasing cross-link density [29]. Volumetric basis was chosen because it allowed good prediction for the gas permeability of binary polymer/IL mixtures [21] and allowed fair comparison between ion gels made from ILs with different densities. Most ILs examined in this study were completely miscible at room temperature with liquid PEGDA, as evidenced by the complete optical transparency of their mixtures. However, [emim][ac] is only partially miscible with PEGDA and is thus excluded from further consideration here.

Table 2 summarizes the visual observations for all ion gels we evaluated based on polymers **1** and **2** – in this section, we start by describing neat-cast polymer **1** ion gels in greater detail. For the ILs with a common [emim] cation and different anions, we obtained a transparent [emim][BF_4] ion gel film having copious liquid exudate on the surface, suggesting that [emim][BF_4] was not completely miscible at this 40 vol% composition with polymer **1**. In contrast, cohesive, tough, optically transparent ion gels with a completely dry surface and no distinguishing defects were obtained by incorporating [emim][Tf_2N] or [emim][dca] into the ion gel (Figure S3a in the Supporting Information). The remaining ILs studied had a common [Tf_2N]$^-$ anion. In addition to [emim][Tf_2N], ([empy][Tf_2N] and [N_{4111}][Tf_2N]) also produced dry ion gel films with polymer **1** similar in appearance. Ion gel films of [bmpyrr][Tf_2N] and

$[P_{1444}][Tf_2N]$, however, developed exudate within an hour of casting. Curiously, the $[P_{1444}][Tf_2N]$ film turned translucent after polymerization (Figure S3b in the Supporting Information) despite its mixture with liquid PEGDA monomer being completely transparent.

Table 2. Summary of visual observations for as-cast ion gel films made for all combinations of polymers and ionic liquids in this study, at room temperature.

Ionic liquid	**Polymer 1**	**Polymer 2**
[emim][ac]	IL immiscible with monomer – no cohesive film can be obtained	
[emim][dca]	Dry (neat-cast)	Slick (solvent-cast); self-polymerizes
$[emim][BF_4]$	Slick (neat-cast); dry (solvent-cast)	Slick (solvent-cast)
$[emim][Tf_2N]$	Dry (neat-cast)	Dry (solvent-cast)
$[bmpyrr][Tf_2N]$	Slick (neat-cast); dry (solvent-cast)	Dry (solvent-cast)
$[empy][Tf_2N]$	Dry (neat-cast)	Dry (solvent-cast)
$[P_{1444}][Tf_2N]$	Slick, translucent (neat-cast); dry (solvent-cast)	Slick (solvent-cast); dry, opaque (neat-cast)
$[N_{4111}][Tf_2N]$	Dry (neat-cast)	Dry (solvent-cast)

All films were transparent unless otherwise noted. "Slick" indicated the presence of liquid exudate on film surface that can be removed by wiping.

The miscibility of an IL with its host polymer matrix was evaluated using differential scanning calorimetry (DSC) by comparing the heat flow curve of the ion gel to its constituents [26]. Figure 1 shows the heat flow curves for the series **1** ion gels, with transition temperatures numerated in Table 3. Cross-linked PEGDA was a rubbery, amorphous polymer with a single glass transition temperature at -35°C and no melting transitions, consistent with previous studies [24,37]. Plasticization due to IL incorporation was expected to reduce cross-link density and increase overall polymer chain mobility. At the same time, a well dispersed IL will be strongly associated with the polymer chains and therefore should not be present in domains large enough to exhibit crystal melting behavior akin to the bulk IL. Thus, complete IL miscibility is indicated by a lower ion gel glass transition temperature (T_g) relative to cross-linked PEGDA and the absence of thermal transitions attributable to the free IL. DSC analysis on [emim][Tf_2N], [emim][dca], [empy][Tf_2N] were consistent with complete miscibility of the ILs with the polymer by fulfilling the aforementioned criteria (Figure 1). The most significant T_g decrease occurred in the case of the [emim][dca] ion gel, from -35°C to -46°C (cf. Table 2). In contrast, the ion gels with surface exudate, i.e. [emim][BF_4], [bmpyrr][Tf_2N] and [P_{1444}][Tf_2N], showed lower T_g relative to cross-linked PEGDA but also additional melting transitions roughly similar to their corresponding free ILs, even on the first heating scan. This observation is consistent with these ILs having miscibility threshold lower than 40 vol% in the polymer **1** network at room temperature. Interestingly, despite [P_{1444}][Tf_2N] free IL having two distinct melting transitions, the [P_{1444}][Tf_2N]/**1** gel exhibited a more complex melting transition. This result suggests the [P_{1444}][Tf_2N] gel had a less homogeneous molecular arrangement than the other gels: [P_{1444}][Tf_2N] was dispersed in the polymer matrix in a separate phase where they can still exhibit short range order, as opposed to being present only in the liquid exudate.

The [N_{4111}][Tf_2N]/**1** ion gel is an interesting case where visual observations suggested that it was a stable and miscible gel at room temperature, but DSC trace showed additional melting transitions on the third heating scan. However, we note that the first heating scan of this ion gel did not show these melting transitions, which emerged only in the second and subsequent heating scans in the DSC (see Figure S5 in the Supporting Information). The result suggests that phase separation occurred during the first heating cycle, when the sample was first heated to 150°C, and the subsequent heating scans picked up on this biphasic behavior. As others have discovered, DSC analysis could be useful for discerning ion gel phase stability at elevated temperatures [26].

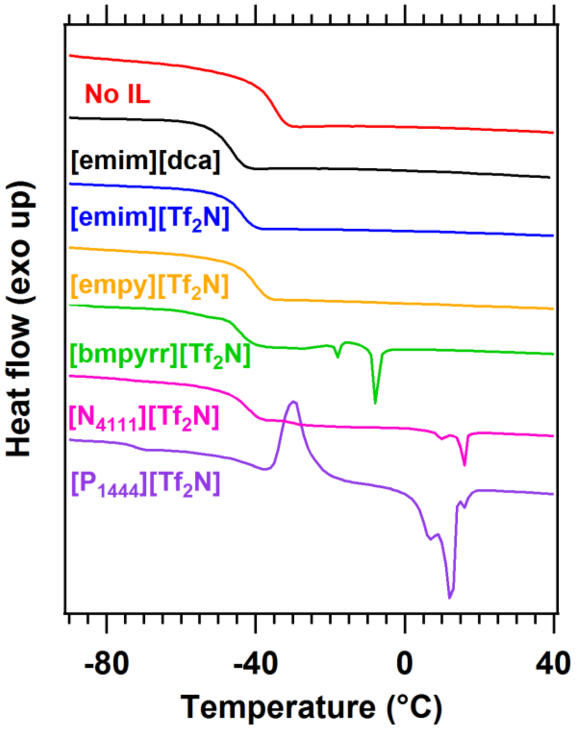


Figure 1. Second scan DSC heating curves for neat-cast ion gels based on polymer **1**. Annotation designates the IL contained within the PEGDA network present at 40 vol%. Curves were shifted vertically for clarity.

Table 3. Glass transition (T_g) and melting (T_m) temperatures observed for polymer **1**-based ion gels containing 40 vol% of listed IL (cf. Figure 1), and the T_m of its corresponding ionic liquids.

Ionic liquid		**Ion gel 1**	
Identity	**T_m (°C)**	**T_g (°C)**	**T_m (°C)**
No IL	--	-34	--
[emim][dca]	-3.6	-46	--
[emim][Tf_2N]	-9.7	-44	--
[empy][Tf_2N]	+1.3	-40	--
[N_{4111}][Tf_2N]	+9.1, +17.3	-42	+9.0, +16.0 (post second scan only)
[bmpyrr][Tf_2N]	-25.0, -15.8	-45	-17.5, -7.5
[emim][BF_4]	-18, +13 (lit) [39]	around -40	+13
[P_{1444}][Tf_2N]	+10.4, +18.7	around -40	+6 to +12

X-ray diffraction (XRD) analysis provides additional test for the phase homogeneity of the ion gels. The XRD patterns of polymer **1** and two of its ion gel derivatives are shown in Figure 2. The amorphous cross-linked PEGDA exhibited a broad peak centered around 21.7° due to short range order, consistent with the observation from a previous study [24]. The [emim][Tf_2N]/**1** gel, which was representative of most other ion gels in the series, exhibited a similar amorphous peak with only a slight peak shift (21.0°). The peak angle is inversely correlated with the average spacing between polymer chains [24], and so the [emim][Tf_2N]/**1** results suggested that the IL plasticizes but does not fundamentally change the polymer network and the IL was well incorporated as a homogeneous blend. In contrast, the [P_{1444}][Tf_2N]/**1** ion gel exhibited a primary peak with a more significant peak shift at 20.2°, as well as a weaker secondary peak centered around 11.4°. This result suggested the presence of a second phase where the polymer chains are much further apart, consistent with the hypothesis suggested by the DSC scan that some [P_{1444}][Tf_2N] may be present in an IL-rich phase within the ion gel network.

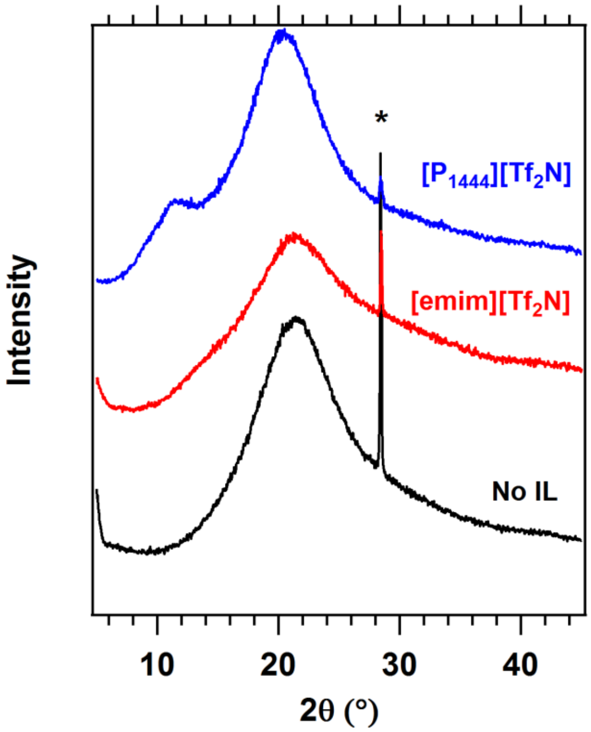


Figure 2. XRD patterns for polymer **1** and its derivative ion gels containing [emim][Tf_2N] or [P_{1444}][Tf_2N]. Curves were shifted vertically for clarity. * denotes the peak attributed to a Si standard that serves as an internal reference (see Supporting Information).

The phase behavior of the ion gels observed here can be explained in terms of IL interaction with the ether oxygen moieties in the polyether backbone. Mixtures of liquid polyethers with ILs were previously found to exhibit lower critical solution temperature (LCST) behavior, which provides a convenient measure for phase compatibility [31]. The key to an IL's compatibility with polyether lies in the hydrogen bonding interaction between the ether oxygen in the polyether and the acidic hydrogen in the IL's cation [40]. Miscibility is thus increased with greater accessibility to the ether oxygen, increasing Lewis acidity of the cation, and decreasing Lewis basicity of the anion (which provides competitive interaction for the cation) [31]. Solidifying the liquid polyether through cross-linking reduces access to its ether oxygen, thereby decreasing the cross-linked network's miscibility with ILs in general. Comparing across the ILs containing the $[Tf_2N]^-$ anion, ILs with aromatic cations possessing acidic protons (i.e. imidazoliums and pyridinium) exhibited the best miscibility here, consistent with the study performed by Kodama et al. [31]. The non-aromatic cations (ammonium, phosphonium and pyrrolidinium) were less miscible, with phase separation of $[P_{1444}][Tf_2N]$ and $[bmpyrr][Tf_2N]$ observed at room temperature after photopolymerization, and the $[N_{4111}][Tf_2N]$ likely exhibiting a LCST-type behavior due to phase separation at higher temperatures. The $[Tf_2N]^-$ anion itself proved to be a good anion to promote miscibility as it is the least basic out of the four chosen in this study [41]. The miscibility of the ILs containing more basic anions such as the acetate are poor, again consistent with the observation made in the previous study [31]. Nonetheless, basicity alone does not provide a complete prediction as the $[BF_4]$ anion, despite its apparent low basicity, is less soluble in polymer **1**, a contrary behavior it also displayed in other polymer systems [31,42].

As a final note, we observed that the IL miscibility with polymer **1** can be improved by casting the ion gel film using a co-solvent. MEK-cast films containing 40 vol% $[emim][BF_4]$, $[N_{4111}][Tf_2N]$, $[bmpyrr][Tf_2N]$ or $[P_{1444}][Tf_2N]$ had completely dry surface, and the $[P_{1444}][Tf_2N]$ film was optically transparent after solvent removal. DSC heating scans did not show evidence of IL release from these films after heating to 150°C (see Figure S6 in the Supporting

Information) and XRD analysis of the solvent-cast $[P_{1444}][Tf_2N]$/**1** film did not show a second peak in a manner shown by Figure 2 above (cf. Figure S7). In these cases, having a co-solvent during photopolymerization resulted in a lower cross-link density [43] which in turn increased the accessibility of the ether oxygen moieties for interactions with the IL. For 40 vol% loading of $[emim][BF_4]$, $[N_{4111}][Tf_2N]$, $[bmpyrr][Tf_2N]$ or $[P_{1444}][Tf_2N]$, decreasing the cross-linked density in this manner was sufficient to make these ion gels completely stable.

3.2. Characterization of PEO/siloxane ion gels (polymer 2)

Polysiloxanes have several unique properties that make them desirable for gas separation membrane applications. For example, poly(dimethylsiloxane) is a tough, highly flexible material with very high gas permeability owing to the exceptional flexibility of the silicon-oxygen backbone [44]. They are not as CO_2-philic as PEO-based materials, but the high permeability of siloxane polymers nevertheless made hybrid siloxane/EO materials attractive membrane candidates [45,46]. However, PEO and siloxane moieties exhibit a miscibility gap that must be overcome to create viable membranes. In our previous work, we reported an effectively homogeneous cross-linked blend of thiol-functionalized polysiloxane (thiosiloxane) with PEGDA that can be cast with or without solvent [37]. Compared to cross-linked PEGDA (i.e. polymer **1**), incorporating the polysiloxane to make polymer **2** (cf. Scheme 1) increased its CO_2 permeability from 150 barrer to 255 barrer at 40°C, while decreasing its CO_2/N_2 pure gas selectivity from 53 to 43. The development of ion gels based on polymer **2** were aimed to confer the siloxane's benefit of higher gas permeability in a similar fashion.

The ILs evaluated in this study were immiscible with thiosiloxane at room temperature, and the ternary mixtures of IL/PEGDA/thiosiloxane at the compositions studied here formed colloids. To improve mixture compatibility, MEK as a common solvent must be added to reduce the monomer solution's turbidity. Photopolymerizing these solutions yielded dry ion gel films after solvent removal for most of the ILs examined (cf. Table 2). However, in addition to being immiscible with the monomer solution, adding [emim][ac] led to instantaneous gelation of the monomer solution. [emim][dca] can also catalyze polymerization reaction but at a slower rate, with gelation onset approximately five minutes after mixing, allowing ion gel films to be obtained. We posit that this catalytic behavior was a result of these ILs, which had basic anions, serving as a base catalyst for thio-Michael addition between the electron-deficient acrylate groups with the thiols in the siloxane [47].

Of the ILs with [emim] common cation, only [emim][Tf_2N] formed a dry ion gel with polymer **2**. As shown in Figure S9 in the Supporting Information, the ion gel is less stiff and has poor tear resistance compared to its neat-cast polymer **1** analog because casting with MEK reduces its cross-link density [43]. The [emim][dca] gel initially had a dry surface after solvent removal; however, over the course of several hours developed a small amount of surface exudate. Polymer **2** overall has less ether oxygen content than polymer **1**, which reduced the miscibility of these $[emim]^+$ ILs as the anion basicity increases, to the point only the least basic [emim][Tf_2N] remained completely miscible in polymer **2**. For the five ILs containing the $[Tf_2N]^-$ anion, four of them ([emim][Tf_2N], [empy][Tf_2N], [N_{4111}][Tf_2N] and [bmpyrr][Tf_2N]) also formed dry ion gel films with similar appearance as the film depicted in Figure S9. Ion gel precursor mixture with the other IL, [P_{1444}][Tf_2N], developed copious surface exudate upon casting, indicating a solubility limit in polymer **2** was reached. While the neat-cast version of this film is unexpectedly stable, its physical appearance suggested internal phase separation and defect formation (see Supporting Information). Thus, ion gel based on $[P_{1444}][Tf_2N]$ is excluded from further consideration here.

DSC scans of the ion gels based on polymer **2** are shown in Figure 3, with notable thermal transitions summarized in Table 4. The cross-linked PEGDA/polysiloxane (i.e. polymer **2**) itself was completely amorphous at room temperature but exhibited a cold crystallization and melting transition. This behavior arose due to the reduced cross-link density from introducing the solvent during polymerization, making the network sufficiently loose to allow the PEO chains to crystallize [37,48,49]. Once made into an ion gel, however, this melting transition disappeared and all the dry series **2** ion gels exhibited only a single glass transition, suggesting the ILs occupied the space between the polymer chains. Melting transitions attributed to residual $[N_{4111}][Tf_2N]$ or [bmpyrr]$[Tf_2N]$ observed in the neat-cast series **1** ion gels were not observed for the solvent-cast series **2** – the miscibility is instead more similar to their solvent-cast versions of series **1** ion gels. In addition, despite having a surface exudate, the [emim][dca]/**2** gel also did not show melting transitions attributable to the free IL, suggesting that the exudate amount was relatively small.

Table 4. Glass transition (T_g) and melting (T_m) temperatures observed for polymer **2**-based ion gels containing 40 vol% of listed IL (cf. Figure 3), and the T_m of its corresponding ionic liquids.

Ionic liquid		**Ion gel 2**	
Identity	**T_m (°C)**	**T_g (°C)**	**T_m (°C)**
No IL	--	-52	+7.1

[emim][dca]	-3.6	-50	--
[emim][Tf_2N]	-9.7	-55	--
[empy][Tf_2N]	+1.3	-52	--
[N_{4111}][Tf_2N]	+9.1, +17.3	-53	--
[bmpyrr][Tf_2N]	-25.0, -15.8	-58	--

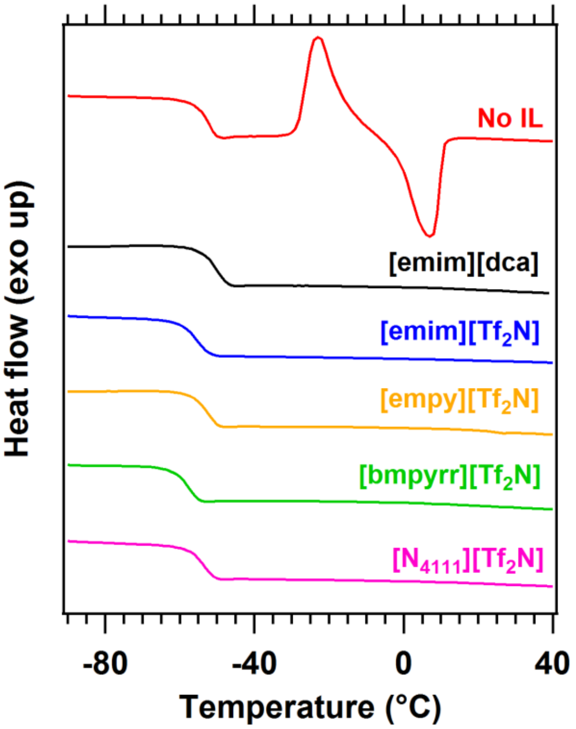


Figure 3. Third scan DSC heating curves for solvent-cast ion gels based on polymer **2.** Annotation designates the IL identity which are present at 40 vol%. Curves were shifted vertically for clarity.

As before, XRD analysis proves useful in evaluating the phase distribution in the [emim][Tf_2N] and [bmpyrr][Tf_2N] gels made with polymer **2**. As shown in Figure 4, both the [emim][Tf_2N]/**2** and [bmpyrr][Tf_2N]/**2** gels were sufficiently homogeneous to show only one amorphous peak. Relative to the baseline, however, these ion gels did appear to have a broader peak than polymer **2**, indicating a greater distribution of polymer chain order as a result of IL incorporation. Due to the similar physical appearance and lack of additional melting transitions shown by the DSC, the other ion gels should have similar XRD patterns to these two representative ion gels.

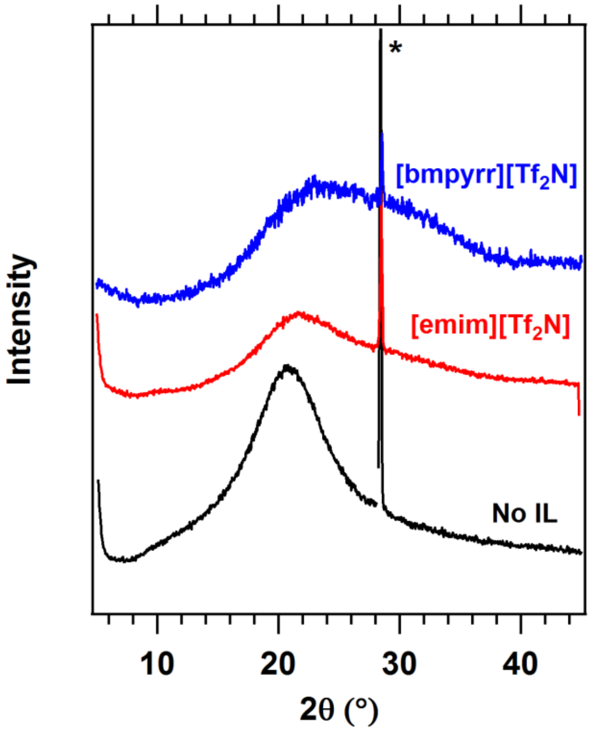


Figure 4. XRD patterns for polymer **2** and its derivative ion gels containing [emim][Tf_2N] or [bmpyrr][Tf_2N]. Curves were shifted vertically for clarity. * denotes the peaks attributed to the internal Si standard reference.

From observing the polymer **2** ion gels, we conclude that incorporating siloxanes into the network has minimal effect on IL miscibility; where the changes occurred, they were in favor of less IL miscibility due to the lower ether oxygen content. The most obvious difference with the polymer **1** gels was the miscibility of the non $[Tf_2N]^-$ ILs: ion gels based on the $[BF_4]^-$ and $[dca]^-$ ILs showed surface exudate even when cast with a co-solvent, and the more basic anions (e.g. $[dca]^-$) could result in undesirable polymerization catalysis that affects the shelf life of the monomer mixture. Within the $[Tf_2N]^-$ ILs, the miscibility were largely unchanged except for $[P_{1444}][Tf_2N]$, which was markedly less miscible in polymer **2**, probably because the tributyl chains in $[P_{1444}]^+$ cation make it less polar than the other cations considered in this study.

3.3. Stability of ion gels with higher IL content

While the discussions thus far have focused on ion gels having moderate IL content (i.e. 40 vol%), the novelty of ion gels lies in their ability to immobilize large amounts of IL to confer IL-like properties to a solid polymeric network. Having now identified that an all-PEO base polymer is a better host matrix than a PEO/siloxane copolymer in terms of conferring good IL-polymer miscibility, the most stable ion gels based on polymer **1** can be modified by incorporating a higher IL content to further differentiate the IL miscibility. The three ion gels that exhibited the best stability contained $[emim][Tf_2N]$, $[empy][Tf_2N]$ or [emim][dca] (cf. Figure 1). Ion gels containing 60 vol% of these ILs were cast and evaluated visually and using the DSC in a similar manner as above.

Ion gel films containing 60 vol% of either $[emim][Tf_2N]$ or $[empy][Tf_2N]$ were completely dry as cast, showing that these ILs are still completely miscible with polymer **1** at this higher concentration at room temperature. In contrast, the [emim][dca] film was cohesive but has a wet surface indicating that the miscibility limit of [emim][dca] has been exceeded in this film. The lower miscibility threshold for [emim][dca] was already expected from the studies using polymer **2** (cf. Table 2) but here it was made more apparent. However, DSC measurements revealed that 60 vol% is close to the room temperature miscibility limit for [emim][Tf_2N] and [empy][Tf_2N] in polymer **1**. While these two gels exhibited one glass transition on their initial heating scan, subsequent scans revealed an upward primary T_g shift accompanied by the appearance of melting transitions, as shown in Figure 5. This behavior suggests that the temperature stability limit for these 60 vol% ion gels are less than 100°C. In contrast, the [emim][dca] exhibited increasing T_g and melting transition from the first scan and with each subsequent heating scans, indicating continuing phase separation during the experiment. These experiments clearly showed that the ion gel phase stability is a function of both IL concentration and temperature.

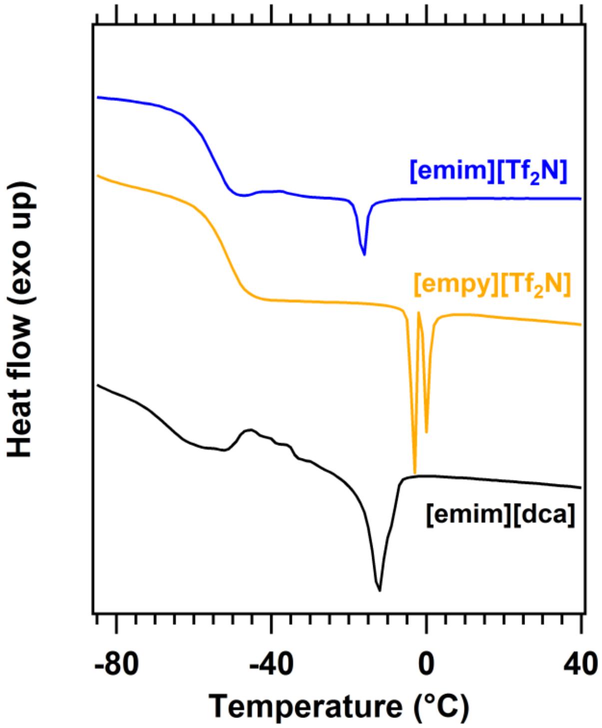


Figure 5. Third scan DSC heating curves for neat-cast ion gels based on polymer **1**, containing 60 vol% of the stated IL. Curves were shifted vertically for clarity.

3.4. Membrane properties of ion gels

Incorporating ILs into the cross-linked PEO polymers was expected to increase their gas permeability and ionic conductivity [15,50,51]. Plasticization of the polymer network by IL allows faster gas diffusion through the network, which correlates to increased gas permeability [1]. The high CO_2/light gas selectivity in cross-linked PEO is driven primarily by solubility difference between the gases, instead of the size-sieving ability of the polymer; thus, plasticization by small molecules has less effect on selectivity compared to conventional glassy polymers [52]. Therefore, ion gels of both polymers have solubility-driven separation like their parent materials. In addition, due to good ion mobility in a liquid state, free ILs have ionic conductivity in the order of 10^{-4} to low 10^{-2} S/cm around room temperature [19,53]. Incorporating free ILs into polyelectrolytes such as PILs, which have an upper limit of around 3 x 10^{-5} S/cm [8], was a proven strategy to help increase their ionic conductivity.

As part of the initial ion gel evaluation to establish the optimum IL loading for a comparative study, we cast a series of [emim][Tf_2N]/**2** ion gels with varying [emim][Tf_2N] content. The ion gel gas permeability increased with IL loading as expected. As shown in Figure 6, the CO_2 permeability of the [emim][Tf_2N]/**2** ion gel at 40°C and 1 bar upstream pressure increased from 240 barrer to 390 barrer as the IL content is raised from 25 vol% to 54 vol%. However, N_2 permeability also increased, and the net effect is a systematic reduction of CO_2/N_2 selectivity with increasing [emim][Tf_2N] content. The permselectivity trend is in line with the additive model prediction: however, the actual permeability values fall below the prediction line, similar to a result recently obtained by Fam et al. with another ion gel series [54]. The strong polymer-IL interaction which restricts the IL mobility could explain the lower-than-expected gas permeability. The apparent deviation in CO_2/N_2 selectivity, however, is within the measurement uncertainty.

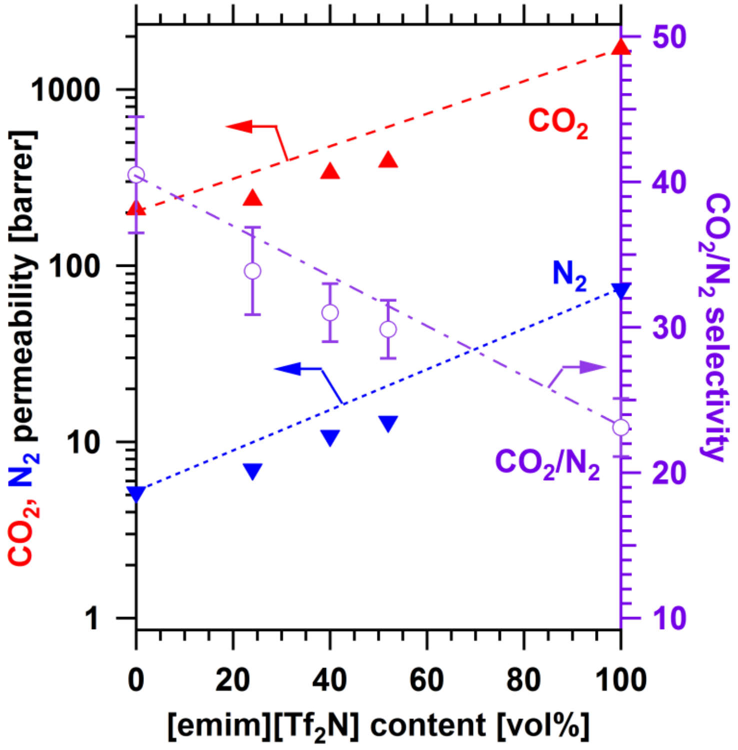


Figure 6. Gas transport properties of polymer **2** ion gels containing [emim][Tf_2N] at different loadings taken at 1 bar upstream pressure and 40°C. The 100 vol% data point (i.e. free [emim][Tf_2N]) was Scovazzo's estimate at 30°C [55]. Lines represent the log average model prediction based on the two endpoints [48]. Error bars for permeability were small in this scale and were thus omitted for clarity.

The pure gas CO_2 and N_2 permeability comparison for the ion gels containing various IL at 40 vol% loading is summarized in Table 5. All ILs increased both CO_2 and N_2 permeability of the two polymers due to successful plasticization of the networks. The ion gels containing the [Tf_2N]$^-$ ILs had similar CO_2/N_2 selectivity at equal IL loading, consistent with the observation that the anion plays the primary role in determining CO_2 solubility in ILs, which in turn influences CO_2/N_2 solubility selectivity [56]. The CO_2/N_2 selectivity of these ion gels were lower than the base polymers, reflective of the low CO_2/N_2 selectivity of the $[Tf_2N]^-$ ILs. For instance, Scovazzo estimated [emim][Tf_2N] has CO_2/N_2 selectivity of 23 at 30°C, and 21 for [N_{4111}][Tf_2N] [55]. On the other end, the high CO_2/N_2 selectivity of the [emim][dca] ion gels (e.g. 54 for the polymer **2** gel) was also not unexpected, given that the free [emim][dca] CO_2/N_2 selectivity was estimated around 57 at 30°C [55]. The ion gel gas permeability coefficients were pressure independent within the narrow pressure range tested, i.e. up to 3 bar.

Table 5. Pure gas CO_2 and N_2 permeability of ion gels containing 40 vol% IL measured at 40°C and upstream pressure of 1 bar, plus ionic conductivity values measured at 25°C under nitrogen atmosphere.

Series	**IL**	**Permeability (barrer)**		**CO_2/N_2 selectivity**	**Ionic conductivity (S cm^{-1})**
		CO_2	**N_2**		
PEO-only (1)	**No IL**	120 ± 10	2.1 ± 0.2	58 ± 3	4.0×10^{-8}
	[emim][Tf_2N]	270 ± 10	7.4 ± 0.2	37 ± 1	8.6×10^{-5}
	[emim][dca]	210 ± 10	3.4 ± 0.2	60 ± 3	2.0×10^{-3}
	[P_{1444}][Tf_2N]	290 ± 20	12 ± 1	24 ± 2	3.4×10^{-5}
	[N_{4111}][Tf_2N]	220 ± 10	7.4 ± 0.2	30 ± 1	4.2×10^{-5}
	[empy][Tf_2N]	210 ± 10	5.8 ± 0.2	38 ± 2	1.0×10^{-5}
PEO/siloxane (2)	**No IL**	210 ± 20	5.2 ± 0.5	40 ± 4	5.9×10^{-8}
	[emim][Tf_2N]	340 ± 20	11 ± 1	31 ± 2	1.3×10^{-4}
	[emim][dca]	240 ± 10	4.6 ± 0.3	54 ± 3	5.6×10^{-4}

	$[N_{4111}][Tf_2N]$	310 ± 30	9.2 ± 0.8	33 ± 3	6.3×10^{-5}
	$[empy][Tf_2N]$	300 ± 20	9.7 ± 0.8	31 ± 2	1.2×10^{-4}
	$[bmpyrr][Tf_2N]$	310 ± 30	10 ± 1	31 ± 3	1.5×10^{-4}

Ionic conductivity measurement standard deviation was 2% for base polymers, <1% for ion gels.

The polymer upper bound performance curve, identified by Robeson, is a convenient yardstick against which the gas separation performances for our membranes are compared [57]. Figure 7 shows the performance of these ion gels against the CO_2/N_2 upper bound. The loss in CO_2/N_2 selectivity from incorporating the $[Tf_2N]^-$ ILs affected both polymers, moving these ion gels away from the upper bound. [emim][dca] provided the only movement toward the upper bound thanks to its high CO_2/N_2 selectivity – despite the more modest CO_2 permeability, these ion gels essentially reside on the upper bound curve.

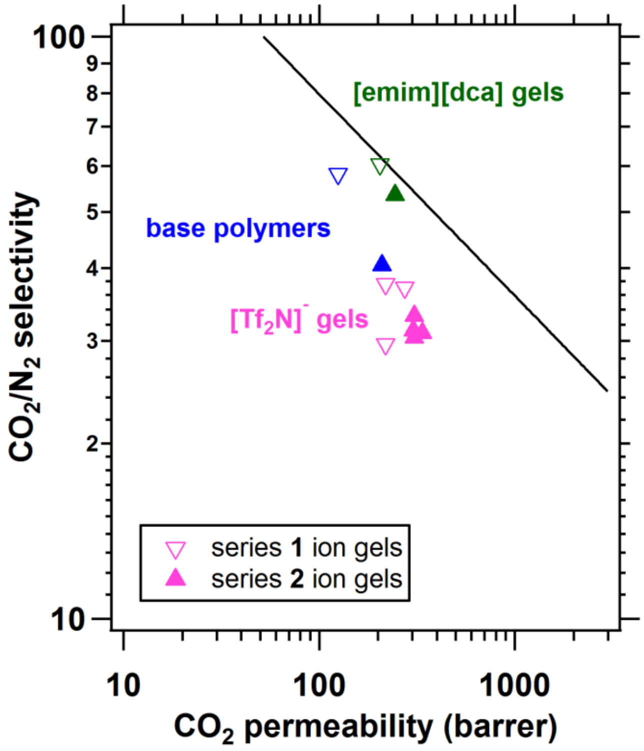


Figure 7. CO_2 permeability and CO_2/N_2 selectivity of the ion gels based on polymer **1** (open symbols) and polymer **2** (closed symbols) at 1 bar and 40°C (cf. Table 5) compared with the performance upper bound curve [57]. Error bars are omitted for clarity.

Finally, we measured the membranes' ionic conductivity. The base polymers were not conductive, with ionic conductivity of 4.0 x 10^{-8} S/cm for polymer **1** and 5.9 x 10^{-8} S/cm for polymer **2** at room temperature (cf. Table 5). Incorporating 40 vol% IL increased their ionic conductivity to approximately 10^{-5} to 10^{-4} S/cm for the $[Tf_2N]^-$ ion gels, with no significant difference between individual ILs in this class. The [emim][dca] ion gels exhibited the highest ionic conductivity in their respective series: 2.0 x 10^{-3} S/cm for series **1** and 5.6 x 10^{-4} S/cm for series **2**. However, ionic conductivity measurement is very sensitive also to external factors such as water content of the polymer. Compared to the $[Tf_2N]^-$ based ILs, dicyanamide based ILs are more hygroscopic – [emim][dca] is water miscible at all compositions and water as an impurity can be particularly difficult to remove from this IL [58]. Despite our care in ensuring dry conditions during ionic conductivity measurement, by allowing a minimum 12 hours equilibration in nitrogen, the [emim][dca] ion gels nevertheless retained more water than the $[Tf_2N]^-$ ion gels. We think the primary reason [emim][dca]/**1** has higher ionic conductivity than [emim][dca]/**2** is because polymer **2** has lower equilibrium water content due to its siloxane moieties.

The ionic conductivity values reported here are lower than the ion gels' conductivity values typically reported in the literature, which is in the order of 10^{-3} to 10^{-2} S/cm [59,60]. However, those ionic conductivity values were reported for gels containing higher IL loadings, in some cases more than 90 wt%. Since the primary determinant for ionic conductivity is the IL loading in the ion gel, not all ILs identified in this study could be made into cross-linked PEO ion gels with ionic conductivity approaching those of free ILs.

4. Conclusions

In this study, we explored the ionic liquid (IL) compatibility and miscibility with two cross-linked PEO ion gels, drawing from a wider variety of commercially available ILs than has been examined in the literature to date. The ion gel films with the best IL-polymer compatibility are dry, transparent and thermally stable, suitable for membrane applications. In agreement with previous studies, we showed that ILs consisting of an aromatic cation with available acidic proton (such as 1,3-substituted imidazolium) and a low basicity anion (such as bis(trifluoromethylsulfonyl)imide) provided the best miscibility and thermal stability with a cross-linked polyether network. Other ILs with non-aromatic cations or a more basic anion (such as dicyanamide) can be incorporated but at lower IL loading, or requiring a lower polymer cross-link density. Incorporating a less polar polysiloxane in the polyether network via thiol-ene polymerization, which in our previous work led to increased gas permeability, reduced the miscibility of ILs with the resulting polymer. These ion gels also must be cast with a co-solvent, which weakened the film mechanically, and the lower ether oxygen content also limited the amount of IL that can be stabilized within the ion gel. The PEO/siloxane as formulated also could not be used to incorporate ILs containing a basic anion (e.g. acetate, and to a lesser extent dicyanamide) as the IL can prematurely catalyze the polymerization. Differential scanning calorimetry was successfully utilized to probe IL miscibility in the polymer network, showing that the phase stability of these gels depends on the temperature and IL content, noting that phase separation could happen at elevated temperatures. X-ray diffraction studies helped confirm the phase homogeneity of the ion gels. Gas permeability and ionic conductivity measurements confirmed that the ILs can be well incorporated into the polymers to confer the expected benefits of higher gas permeability and ionic conductivity. On the balance, we think the drawbacks of incorporating siloxanes into ion gels outweighed the potential benefits in terms of increasing gas permeability and ionic conductivity. We hope this study provide practical considerations to help guide future work to incorporate other ILs into different polymers.

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