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Gelation of Ionic Liquids Using a Cross-Linked Poly(Ethylene Glycol) Gel Matrix

Marc A. Klingshirn, Scott K. Spear, Raman Subramanian, John D. Holbrey, Jonathan G. Huddleston, and Robin D. Rogers*

Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Box 870336, Tuscaloosa, Alabama 35487-0336

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Conductive ionic liquid−poly(ethylene glycol) (IL−PEG) gels have been prepared by gelation of the hydrophobic ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_6mim][NTf_2]) by the cross-linking reaction of disuccinimidylpropyl PEG monomers with four-arm tetraamine PEG cross-linkers. This is the first time that a cross-linked PEG matrix, such as this, has been used to gel nonaqueous solvents. Initial studies screening other ionic liquids as solvents indicate that the gelation of the ionic liquid is both cation and anion dependent with smaller, coordinating cations disrupting or preventing gel formation.

Introduction

Organic hydrogels have many biological applications such as wound dressings, drug and protein delivery, and artificial tissue matrixes.[1−4] The gels generally exhibit a large degree of swelling in aqueous environments and show differential shrink−swell responses to different solvent environments including organics and salt solutions. Gelling of a range of aqueous and nonaqueous solvents is possible and desirable, and has particular applicability for the formation of polymer gel electrolytes for use in nonaqueous batteries, photovoltaic devices, and capacitors.[5−7] Ionic liquids (ILs) are one set of liquid electrolytes of interest for such devices.[8]

ILs have seen use as solvents for a range of chemical reactions, separations approaches, and liquid electrolytes for electrochemical applications.[9−13] Their unique utility comes from the tunability of physical and chemical properties to meet specific reaction criteria. One aspect is the ability to control water miscibility by simply changing the anion. Added advantages of some ILs include their nonvolatility, high conductivity, and large electrochemical windows. Their utility in the field of polymer gel electrolytes is not necessarily new, rather ILs possessing the tetrachloroaluminate, hexafluorophosphate, trifluoromethylsulfonate, tetrafluoroborate, and bis(trifluoromethanesulfonyl)imide anions have been studied,[14−18] typically as IL-in-polymer electrolytes prepared by in situ polymerization of oligomers (e.g., vinyl moieties).[19,20] Different compositions of polymer matrix, as well as incorporation of additional salts, have all been investigated as supported hybrid electrolytes.[21,22]

Recently, our group has studied a PEG hydrogel (Shearwater Polymers) that was found to have unique shrink−swell properties and the ability to take up dyes from aqueous salt solutions.[23] This gel was prepared (Scheme 1) in an aqueous phosphate buffer, which allows easy synthesis and a controllable rate of gel formation by adjusting solution pH.

Here we describe the formation of IL−PEG gels in an IL solvent and compare the characteristics of these gels with the corresponding aqueous PEG hydrogel

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* Corresponding author. E-mail: RDRogers@bama.ua.edu.

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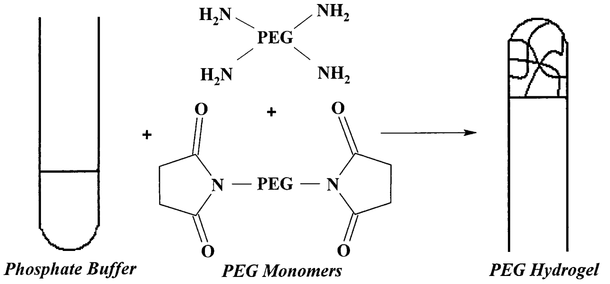
Scheme 1. General Synthesis of Poly(ethylene glycol) Hydrogel[a]



[a] PEG monomers are four-arm tetraamine PEG (MW 10 000 Da) and di-succinimidylpropyl PEG (MW 3400 Da).

formed from aqueous phosphate buffer. Shrink–swell studies of the IL–PEG gels in various solvents, partitioning of linear alcohols, and gel conductivity experiments were undertaken to determine the behavior of the gels and their utility as an extraction medium or as a polymer-gel electrolyte.

Experimental Section

PEG derivatives for the cross-linked hydrogel formation were obtained from Shearwater Polymers (currently Nektar of Huntsville, AL). Lithium bis(trifluoromethanesulfonyl)imide salt was provided by 3M Corp. (Minneapolis, MN). All other chemicals were purchased from Aldrich (Milwaukee, WI) and used as received. Deionized water was prepared using a Barnstead Nanopure system (Dubuque, IA). The carbon-14-labeled alcohols (methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol) used in partitioning studies were obtained from Sigma (St. Louis, MO). The radiotracers used as spikes in the partitioning experiments had individual activities between 0.06 and 0.08 μCi/μL.

Ionic Liquid Synthesis. The IL, 1-hexyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([C_6mim][NTf_2]), was synthesized by metathesis of 1-hexyl-3-methylimidazolium chloride (synthesized following literature procedures)[24] with lithium bis(trifluoromethanesulfonyl)imide in water. The IL separates as the dense lower phase and was washed thoroughly with deionized water until the aqueous phase showed no formation of silver chloride upon testing with a 0.1 M silver nitrate solution. This washing process was determined to be sufficient to substantially remove residual chloride from the ionic liquid. The IL was dried under vacuum with gentle heating, and characterized by ^{1}H and ^{13}C NMR and by melting point (−10 °C, ΔH_{fus} 11.8 J g^{-1}) determined by DSC. Residual water content of the IL, after drying in vacuo, as used in the gelation studies was 0.16 M determined by Karl Fisher (EM Science Aquastar, Milwaukee,WI) titration.

The hydrophobic *N*-hexylpyridinium bis(trifluoromethanesulfonyl)imide IL was prepared in an analogous manner starting from *N*-hexylpyridinium bromide. The other ILs investigated, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate, were prepared from 1-butyl-3-methylimidazolium chloride by metathesis with HPF_6 and HBF_4, respectively, in water following literature procedures.[13,25] 1-Butyl-3-methylimidazolium trifluoromethanesulfonate was synthesized by the direct alkylation of 1-butyl imidazole with methyl trifluoromethanesulfonate following the procedure described by Bonhôte and co-workers for the synthesis of 1-ethyl-3-methylimidazolium trifluoromethylsulfonate.[13] In each case, ^{1}H and ^{13}C NMR and melting points/glass transition temperatures for the ionic liquids were comparable with those from the literature. Water contents of all the ionic liquids used were less than 0.3 M, as determined by Karl Fisher titration.

Table 1. Gel Compositions Used in Partitioning and Conductivity Measurements

gel	PEG 1[a] (mg)	PEG 2[b] (mg)	IL vol (mL)[c]	buffer vol (mL)[c]	IL water content (mg)[d]
gel 1	25.0	37.5	1.2		3.5
gel 2	50.0	75.0	1.2		3.5
gel 3	100.0	150.0	1.2		3.5
PEG control	50.0	75.0		1.2	

[a] PEG 1 = disuccinimidylpropyl PEG. [b] PEG 2 = four-arm tetraamine PEG. [c] Each monomer is dissolved in 0.6 mL of IL or phosphate buffer independently and then combined and vortexed. [d] The determined water content of the IL was 0.16 M.

PEG Hydrogel Synthesis. Control PEG hydrogels were synthesized using the previously described procedure[23] of independently dissolving the PEG monomers disuccinimidylpropyl PEG (MW 3400 Da) (50 mg) [SPA-PEG] and four-arm tetra-amine PEG (MW 10 000 Da) (73.5 mg) in two 50 mM phosphate buffer (0.6 mL) solutions composed of K_2HPO_4 and KH_2PO_4 at pH 6.5. The two solutions were then combined, mixed, and then allowed to sit undisturbed at room temperature for 3–4 h to allow gelation. The resultant gels formed were washed with deionized water (3 × 25 mL) and stored in their swollen state under deionized water.

IL–PEG gels were prepared in an analogous manner; the two PEG monomers (SPA-PEG, 25–100 mg, and tetraamine-PEG, 27.5–150 mg) were dissolved directly into two ionic liquids samples (0.6 mL each), and the two solutions were then combined, mixed, and allowed to sit for 3–4 h to allow for gelation. Three IL–PEG gels were prepared, using different concentrations of PEG oligomers. The resulting nonhydrated gels were stored in their initial state, as synthesized, in sealed vials. Table 1 shows the amounts of monomer and IL or phosphate buffer used to synthesize each gel. No additional water was added to the ionic liquid to aid in monomer dissolution or formation of gels; only the trace levels of water initially present in the ionic liquid were present during the synthesis. Hydrated IL–PEG gels were then prepared by submersion of the gel samples in deionized water, and the hydrated IL–PEG gel samples were stored in sealed vials under deionized water.

PEG Gel Characterization. Thermogravimetric analyses were performed on a TA Instruments 2950 Thermogravimetric Analyzer (New Castle, DE). Samples were heated under a nitrogen atmosphere from room temperature to 600 °C at 5 °C min^{-1}. Differential scanning calorimetry (DSC) experiments were carried out on a TA Instruments DSC 2920 Modulated DSC calorimeter (New Castle, DE). Samples were analyzed in aluminum pans (TA Instruments pt. 900793.901) with lids containing a pinhole (TA Instruments pt. 900860.901), initially cooling to −140 °C at 5 °C min^{-1}, followed by heating to 400 °C with ramping at 5 °C min^{-1}.

Shrinking and swelling of the initial and hydrated IL–PEG gels and the control (synthesized following IL–PEG gel 2 and control gel composition in Table 1) in contact with different solvents was investigated by placing gel disks (≈1 cm diameter and 1 cm thickness) or cubes (≈1 cm^3 in volume), formed by slicing the gels, into various organic solvents or salt solutions. Scintillation vials (25 mL volume) containing 20 mL of solvent were used. The samples were placed on a rotating wheel for 24 h to equilibrate. Upon equilibration, the gels were then removed from solution and slightly blotted dry. Sample dimensions, before and after contacting were measured and showed reproducibility generally within 10%. To ensure no further change in volume, measurements were taken again after an additional 24 h and compared. No further changes in volume were observed.

Alcohol Partitioning Experiments. Solid/liquid distribution ratios for linear alcohol solutes were determined by contacting a known mass of nonhydrated IL–PEG gel (follow-

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ing IL−PEG gel 2 formulation) that had previously been equilibrated with the required salt solution with 1 mL of salt solution containing tracer concentrations (1−4 μCi) of ^{14}C radiolabeled alcohols. Solids were stirred in the spiked solution magnetically for 1 h. An aliquot from the liquid phase (100 μL) was then mixed with 5 mL of scintillation cocktail (Ultima Gold) and counted using a scintillation counter (Packard Instruments, Downers Grove, IL). Weight distribution ratios (D_w) for the PEG hydrogels were calculated by difference using eq 1

$$D_w = \frac{A_o - A_f}{A_f}\,\frac{\text{contact volume (mL)}}{\text{mass of gel (g)} \times \text{dwcf}} \qquad (1)$$

where A_o and A_f are initial and final activities (in counts per minute) of the spiked solution, respectively, and dwcf is the dry weight conversion factor relating the mass of the hydrated IL−PEG gel to its dry weight.[26] The dwcf is equal to 1 for all IL−PEG gels studied, since weighed samples of the nonhydrated forms were used.

Conductivity Measurements. The ionic conductivity of [C$_6$mim][NTf$_2$] IL was measured using a Fisher-Accumet AR20 conductivity meter (Atlanta, GA). The cell constant was determined by calibration with 0.01 M KCl solution. Alternating current impedance spectroscopy (CH Instruments Model 660A, Austin, TX) was carried out to determine the conductivity of the initial IL−PEG gels prepared (see Table 1 for gel formulations). The nonhydrated IL−PEG gel was sandwiched between two parallel stainless steel rods (area = 0.5 cm^2) that were assembled in a plexiglass holder. Impedance measurements were made with a 5 mV excitation signal over a frequency range of 100 kHz to 0.1 Hz. The thickness of the gel was 0.2 cm. All experiments were carried out at a temperature of 293 K. The conductivity of the gel (σ) was calculated from the relationship in eq 2:

$$\sigma = \frac{l}{RA} \qquad (2)$$

where l is the thickness of the gel, R is the bulk resistance, and A is the cross sectional area of the stainless steel electrode (and consequently the area of the gel).

The control PEG hydrogel was investigated using the same procedure, after dehydrating the swollen PEG hydrogel overnight in a desiccator to remove water from the matrix. The resulting dehydrated gel formed a flat, opaque white disk that was nonconducting.

Results and Discussion

General Characteristics. IL−PEG gels were prepared by the gelation of the IL [C$_6$mim][NTf$_2$] by the cross-linking reaction of disuccinimidylpropyl PEG (SPA-PEG) and tetraamine PEG oligomers dissolved in the hydrophobic ionic liquid. The gels formed are resilient, rubbery, and transparent. On contacting the IL−PEG gels with water, the gels expand as water is absorbed and the gel changes in appearance from transparent to opaque white (Figure 1). The corresponding volume changes on expansion of the different gel compositions are given in Table 2.

Since the IL held within the gel framework is hydrophobic and is not miscible with water, absorption of water into the gel must, necessarily, result in the formation of both hydrophilic and hydrophobic phase domains within the gel (Scheme 2). The low solubility of [C$_6$mim][NTf$_2$] in water prevents significant loss of IL from the gel matrix through dissolution in the bulk aqueous phase on hydration; however, this does not preclude mechanical loss of IL from the IL−PEG gels through diffusion. After storage of hydrated IL−PEG gel samples in water (50 mL volume) over a 2 week period, small droplets of IL were observed to coalesce in the flask and were collected. The total volume of IL isolated in each case was less than 20% of the total IL volume and indicates that at least approximately 80% of the IL is still retained within the matrix. Nonetheless, due to the hydrophilic nature of the PEG, inclusion of water does occur and resulting in expansion of the IL−PEG gels. There is presumably some interaction between the IL droplets formed, due to phase separation, and the PEG chains that entrain it within the gel matrix, although this is a subject of ongoing investigation.

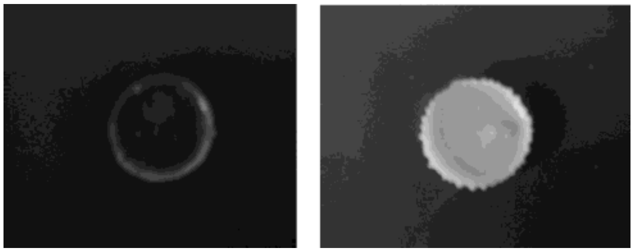


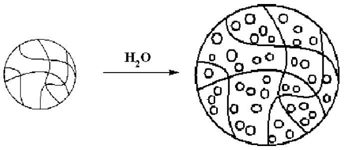
Figure 1. Original [C$_6$mim][NTf$_2$]−PEG gel (left) and after initial submersion in water (right).

Table 2. Shrink−Swell Behavior of [C$_6$mim][NTf$_2$]−PEG Gels and Control PEG Hydrogels

solvent	gel[a]	starting condition	% vol change	appearance (24 h)
water	IL	nonhydrated	485	opaque white
	IL	hydrated		
	control	nonhydrated	622	transparent
	control	hydrated		
dichloromethane	IL	nonhydrated	553	cloudy white
	IL	hydrated	71	cloudy white
	control	nonhydrated		
	control	hydrated	100	cloudy white
methanol	IL	nonhydrated	213	transparent
	IL	hydrated	−45	slight cloudy
	control	nonhydrated		
	control	hydrated	108	transparent
3.5 M $(NH_4)_2SO_4$	IL	nonhydrated	0	transparent
	IL	hydrated	−78	cloudy white
	control	nonhydrated		
	control	hydrated	−78	light yellow
2.5 M K_3PO_4	IL	nonhydrated	0	transparent
	IL	hydrated	−80	orange-brown
	control	nonhydrated		
	control	hydrated	−93	light yellow

[a] IL−PEG gels were synthesized following gel 2 formulation in Table 1. Control hydrogels were prepared following formulation for control PEG hydrogel in Table 1.

Scheme 2. IL Cross-Linked with PEG Chains (left) and IL Water Phase Separation and Gel Expansion (right) upon Gel Submersion in Water



To examine the reversibility of the hydration process, the behavior of the IL−PEG gel (gel 2, Table 1) was

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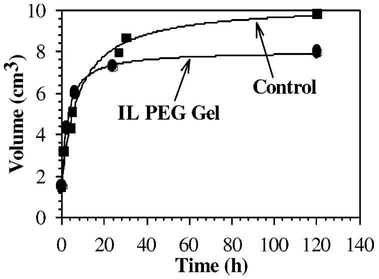

Figure 2. Swelling kinetics of the [C$_6$mim][NTf$_2$]−PEG gel (gel 2 formulation described in Table 1) and control PEG hydrogel in water.

observed when the gels were subjected to a range of dehydrating conditions. When the hydrated IL−PEG gels were removed from water and left in air under ambient conditions, the gels underwent slow dehydration, and the IL−PEG gel appearance changed back from opaque to the original, nonhydrated, transparent form. In contrast, it was found that when the IL−PEG gels were heated to 100 °C, the gel collapsed to form a residual liquid phase. Thermal dehydration of the IL−PEG gels reverses the formation of the amide bonds formed during gelation. Further submersion of the liquid residues in water does not cause the gel to re-form, indicating that the complete dehydration process under harsh conditions is irreversible. Excessive heating not only removes water from the matrix but also allows the activation energy of amide bond hydrolysis to be overcome, causing breakdown of gel structure.

The control PEG hydrogels, prepared in aqueous buffer, swell in size and remain transparent on submersion in deionized water.[24] Heating of the control hydrogel to 100 °C produces a white solid, dehydrated PEG, which rehydrates on resubmersion in water, yielding a re-formed gel, although with smaller volume than the initial hydrogel. Damage to the gel matrix is apparent. These gels can also be dehydrated upon removal from water by simple drying in air at room temperature.

Swelling Kinetics. Figure 2 compares the rate of swelling and volume change of the IL−PEG gel (gel 2, Table 1) and control hydrogel when submersed in water and allowed to hydrate. The control hydrogel shows a greater overall volume change than the IL−PEG gel. This may be due to the presence of the hydrophobic ionic liquid in the gel that results in the formation of IL and aqueous pockets within the gel and reduces the overall concentration of water within the gel, as two different liquids are accommodated. Nonetheless, the rates of initial swelling are nearly identical, which suggests that the IL may migrate to the inner domains of the gel and then slowly move to outer domains as the PEG chains become fully hydrated, which allows for fast, initial swelling. The final differences in gel volume for the IL−PEG gel and PEG hydrogels may be attributed to the hydrophobicity of the [C$_6$mim][NTf$_2$] IL and, in addition, to the degree of PEG chain extension, or lack thereof, when the IL is incorporated in the gel matrix.

IL−PEG Gel Thermal Behavior. Thermal stability of the IL−PEG gel (gel 2, Table 1) was investigated by thermogravimetric analysis and differential scanning calorimetry. Thermogravimetric analysis of the IL−PEG gels shows two different weight losses on heating to high temperatures, for both the initial and hydrated gels. The first weight loss, at 380 °C (nonhydrated curve), corresponds to the degradation and breakdown of the PEG gel network, while the second, at 450 °C, is decomposition of the IL. The gel decomposition temperature depends on the treatment of the IL−PEG gel, particularly on whether the gel has been hydrated by contact with water or is in the initial nonhydrated form. The different decomposition temperatures are more readily seen in the derivative weight loss curves shown in Figure 3. Examination of the hydrated-IL PEG gel curve also shows resolution of unbound and bound water within the matrix as two peaks at approximately 100 and 110 °C, respectively, in the derivative weight loss curve.

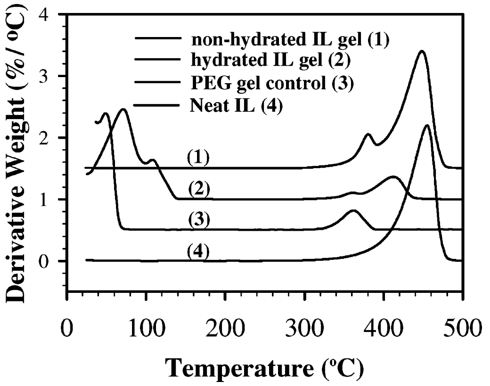

Figure 3. Derivative weight loss curves of [C$_6$mim][NTf$_2$]−PEG gels: (1) nonhydrated [C$_6$mim][NTf$_2$]−PEG gel, (2) hydrated [C$_6$mim][NTf$_2$]−PEG gel, (3) hydrated [C$_6$mim][NTf$_2$]−PEG gel control, and (4) neat [C$_6$mim][NTf$_2$]. Curves have been offset along the *y*-axis by 0.5%/°C for clarity. All IL−PEG gels were of gel formulation 2 described in Table 1.

Differential scanning calorimetry of the nonhydrated IL−PEG gel (gel 2, Table 1) (Figure 4a) shows a glass transition (1) (−85 °C) on cooling from room temperature and then on subsequent heating an exothermic first-order transition (2) (−36 °C) followed by an endothermic first-order transition (3) (−10 °C). These correspond to delayed crystallization of the glassy, supercooled IL followed by melting, are consistent with the transitions for the pure IL (Figure 4b), and indicate that the bulk IL within the gel is in an essentially free, unbound environment.

In contrast, thermograms for IL−PEG gels (gel 2, Table 1) after hydration in water, over the temperature range from −100 to 200 °C, show four different water transitions (Figure 5). The first peak (1) on initial cooling from room temperature represents the freezing of water within the matrix. No freezing or subsequent melting transitions for the IL were observed in the hydrated gels; suppression of crystallization of the ILs in the presence of a second solvent additive (for example water) is commonly observed. The decrease in freezing temperature is consistent with freezing point depression in the presence of salts.

Three peaks are seen in the heating portion of the curve. These represent the melting of water (2) and the boiling of unbound (3) and bound (4) water. The symmetric peak at 0 °C may indicate that free and bound water melt simultaneously. Alternatively, it is possible that bound or interstitial water is not frozen within the matrix. Discrimination of water types is seen and is consistent with TGA data, in the boiling portion, as the water of solvation is removed at higher temperatures.

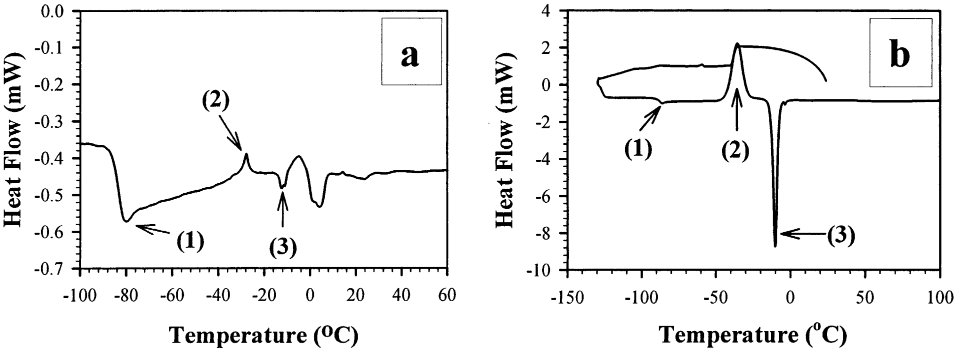

Figure 4. (a) DSC of nonhydrated [C_6mim][NTf_2]−PEG gel (gel formulation 2 in Table 1) and (b) neat [C_6mim][NTf_2].

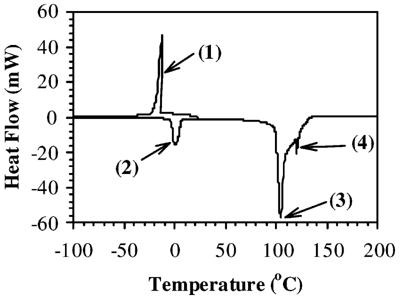

Figure 5. DSC of hydrated [C_6mim][NTf_2]-PEG gel (gel formulation 2 in Table 1).

Shrink−Swell Behavior. When contacted with different solvent systems, the IL−PEG gels exhibit responses that are similar to, but uniquely different from, the PEG hydrogels previously studied.[23] Shrinking and swelling of the IL−PEG gels were studied with aqueous salts that are known to salt-out (phase separate) hydrophilic ILs[27] and PEG polymers from aqueous solution[28] and with the organic solvents dichloromethane and methanol, both of which are completely miscible with [C_6mim][NTf_2]. Both nonhydrated and hydrated IL−PEG gels (gel 2, Table 1) were tested and compared to PEG hydrogels with the same weight composition of PEG that were prepared in aqueous phosphate buffer. Table 2 shows the systems investigated and the volume changes determined in each case in the presence of each solvent, relative to the initial volume of the gel. As a general trend, both the IL−PEG gels and PEG hydrogels swell in organic solvents, whereas a volume loss is observed when contacted with salt solutions. These general observations indicate that the organic solvents studied show solvation of the PEG chains while the salts, as a result of the water-structuring ability, are able to remove or dehydrate the PEG chains within the gel. Further comparison of the organic solvents indicates that dichloromethane solvates the PEG chains better than methanol, which is in turn better than water, when the IL−PEG gel is not hydrated. However, in the hydrated IL−PEG gels, the order of preferred PEG solubility is dichloromethane, water, and methanol. A decrease in volume is seen when the hydrated IL−PEG gel is placed in methanol. Presumably, this shrinkage is linked to the possible complete comiscibility of the three components, IL/water/methanol, in the phase regime. A similar comiscibility of ethanol and water mixtures with 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids has been reported, despite only partial miscibility of each or the two molecular solvents (water and ethanol) with the ionic liquid.[29,30]

In the presence of $(NH_4)_2SO_4$ and K_3PO_4, dehydration of the water-swollen hydrated IL−PEG gels is seen. This phenomenon is analogous to the salting-out of PEG polymers from water, where as the amount of salt is increased, the concentration of free water becomes smaller and the PEG phase becomes more “organic” and the salt phase more “aqueous”.[28] This is in contrast to the nonhydrated IL−PEG gel in which no volume change is seen. No visible volume change is evident due to the low water content (0.16 M) of the IL, which was determined prior to gel formation using Karl Fisher analysis.

The general appearance of the gels (after salt equilibration) ranges from cloudy to yellow in color. While the cause of the color is not known, the general cloudiness is due to solvent immiscibility, similar to a cloud point.[28] The cloudiness is believed to be due to microdroplet formation, while the observed color is due to small impurities within the contact salt, rather than due to an impure IL. The immiscibility observed is known in aqueous biphasic systems (ABS), since PEG and salts of the same concentration and type salt-out PEG, forming a biphasic system.[26]

Alcohol Partitioning. Partitioning studies of linear alcohols to the IL−PEG gel (gel 2, Table 1) from various concentrations of K_3PO_4 were carried out (Figure 6) in order to investigate the potential for the gels to partition organic solutes from solution. (This technique has been used to determine relative hydrophobicity between PEG-rich and salt-rich phases in ABS.)[31] Prior to measuring the distribution ratios, the initial IL−PEG gels were equilibrated overnight with 5 mL of the respective salt solution to ensure no further volume change during the studies. All the gels show preferential uptake of the linear chain alcohol tracers from aqueous K_3PO_4 solutions. The distribution ratio of the alcohols to the IL−PEG gels from aqueous salt solution increases with increasing concentration of salt, suggesting a salting-out effect as the concentration of K_3PO_4 is increased.

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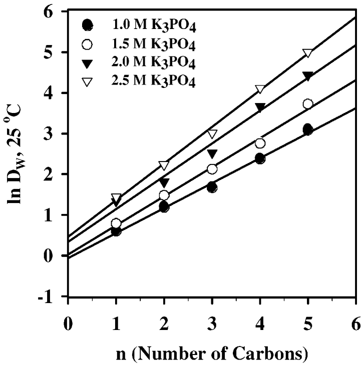

Figure 6. Natural logarithm (ln) of the weight distribution ratio of linear aliphatic alcohols to the [C$_6$mim][NTf$_2$]−PEG gel from various K$_3$PO$_4$ solutions. IL−PEG gel was prepared by following gel formulation 2 described in Table 1. n = number of carbons in alcohol chain.

Table 3. Conductivities of the Cross-Linked [C$_6$Mim][NTf$_2$]-PEG Gels and ILs

material	monomer	conductivity (mS cm^{-1})
gel 1[g]		2.14
gel 2[g]		1.87
gel 3[g]		1.88
control PEG gel[g]		
[C$_1$mim][NTf$_2$]		8.4[d]
[C$_2$mim][NTf$_2$]		8.8[d]
[C$_4$mim][NTf$_2$]		3.9[d]
[C$_6$mim][NTf$_2$]		2.7
[DMPI][NTf$_2$][b]		5.3[e,f]
[DMPI][NTf$_2$] gel	PVdF-HFP[a]	3.9[e,f]
[DMBI][NTf$_2$][c]		4.4[e]
[DMBI][NTf$_2$] gel	PVdF-HFP	3.5[e,f]

[a] PVdF-HF = polyvinylidenedifluorohexafluoropropylene. [b] DMPI = 1,2-dimethyl-3-propylimidazolium. [c] DMBI = 1,2-dimethyl-3-butylimidazolium. [d] From ref 14. [e] From ref 33. [f] 75% IL/25% polymer composite. [g] See Table 1 for gel compositions. C1, C2, and C4 correspond to linear alkyl chain analogues of the methylimidazolium cation.

In addition, the distribution ratios increase as the hydrophobicity of the alcohol increases, suggesting that the IL−PEG gel is more hydrophobic than the salt solutions, just as the PEG-rich phase is more hydrophobic than the salt-rich phase in ABS. It is clear from the slope of the lines in Figure 6 that as the salt concentration is increased, the resolution (or differences in alcohol distribution ratios) between the alcohols increases. We are currently exploring the alcohol partitioning between the IL and aqueous ABS systems but anticipate the same trends seen in PEG−salt systems.

The salting-out effect observed in the partitioning of linear alcohols between the K$_3$PO$_4$ and the IL−PEG gel phase is similar to that found in ABS composed of pure poly(ethylene) glycol and salt.[31] The hydrophobicity of these liquid−liquid systems can be altered by changing the concentration of polymer or salt. It appears that the same can be said for the IL−PEG gel systems presented here, and it is significant, since a desired separation can be achieved by simple changes to the solution phase.

Conductivity Determination. The conductivities of the initial nonhydrated IL−PEG gels were measured to determine their possible utility as polymer-gel electrolytes. Conductivities of the gels are given in Table 3 and are compared to the literature conductivities of typical bulk phase ionic liquids. The incorporation of a gelling agent into nonaqueous batteries, photovoltaic devices, and capacitors aids in the inhibition of electrolyte leakage by immobilizing the electrolyte within the vessel. Conductivity of the IL−PEG gel was compared to that of the neat IL. The dehydrated PEG hydrogel control displayed no measurable conductivity. Conductivities of hydrated IL−PEG gels were not determined; in these cases, it would be impossible to distinguish between IL−PEG gel conductivity and that of the aqueous electrolyte in the systems.

The change in conductivity of the IL−PEG gels with various concentrations of PEG oligomers indicated that upon addition of the PEG network, only a small decrease in conductivity is seen. This drop in conductivity is consistent with that seen in other IL-in-polymer gel electrolyte systems resulting from incorporation of the cross-linking network and its interruption of electrical flow.[32,33] These values along with the conductivities of similar ILs are shown in Table 3.

Preliminary Studies Utilizing Other ILs. The results discussed above all originate from the gelation of a single hydrophobic ionic liquid, [C$_6$mim][NTf$_2$], with amide cross-linking of disuccinimidylpropyl PEG and tetraamine-derived PEG oligomers. This IL produced robust, good-quality gels with the formulation of gel 1, containing only 52 mg/mL of gelling agent, being sufficient to form a free-standing IL−PEG gel.

A series of other common ionic liquids containing 1-butyl-3-methylimidazolium and *N*-alkylpyridinium cations were screened using the same experimental gelation procedure and oligomer concentrations used to prepare gels of formulation 2 in Table 1. The only examples for which firm, self-supporting gels could be prepared were with the ionic liquids with bis(trifluoromethanesulfonyl)imide anions. In these cases, with both imidazolium and pyridinium-based ILs, rigid gels were obtained, from which the IL did not readily leach. However, it was not possible to gel a 1 M Li[NTf$_2$] solution.

When the hydrophobic IL 1-butyl-3-methyl-imidazolium hexafluorophosphate was used, a soft gel was formed; however, the gels readily leached the IL on standing in water. Rigid gels were not obtained with the hydrophilic ILs 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate, tetrafluoroborate, or molten 1-butyl-3-methylimidazolium chloride. In each case, a paste or free flowing liquid was obtained. Similarly, it was not possible to gel 1 M solutions of NaCl or LiOTf.

The IL purity (residual chloride halide) does not seem to play a role in the gelation process, since 1-butyl-3-methylimidazolium trifluoromethanesulfonate, which was prepared by direct alkylation, did not result in gel formation. It is believed that hydrophobicity or polarity effects are the main thrusts for allowing for gelation to occur. This, however, is paradoxical in that water is a much more polar solvent than the ILs.

The anion of the ionic liquid is often thought to control the gross physical and solvent properties of ILs[25] and here, as well, we have observed the major influence of the IL anion. ILs with noncoordinating, hydrophobic IL

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anions can be gelled under the conditions utilized here, while coordinating, more hydrophilic anion-based ILs cannot.

Conclusions

This work has shown that gelation of hydrophobic ILs by the cross-linking of tetra-armed PEG amine and bifunctional PEG succinimide oligomers is possible, yielding IL−PEG gels. The general behavior and physical properties (e.g., shrink−swell upon hydration) of the IL−PEG gels formed are generally comparable to those of the analogous PEG hydrogels. Partitioning data of linear alcohols for the IL−PEG gel/K_3PO_4 system suggest that the systems can be fine-tuned to meet a specific hydrophobicity or separation need, and conductivity measurements show the potential utility for forming IL−polymer gel electrolytes containing only relatively low concentrations of polymer.

These systems provide a novel method for gelling ILs and, to our knowledge, represent the first time that this cross-linked PEG matrix has been used to gel liquids other than water. Future interest in these gels lies in controlling the effects of the IL on properties of the gels, such as in partitioning of metals and organics, and as gel electrolytes. Further studies to characterize these gels and expand the range of ILs that can be gelled in this fashion are currently underway.

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