

# Poly(Ionic Liquid) Superabsorbent for Polar Organic Solvents

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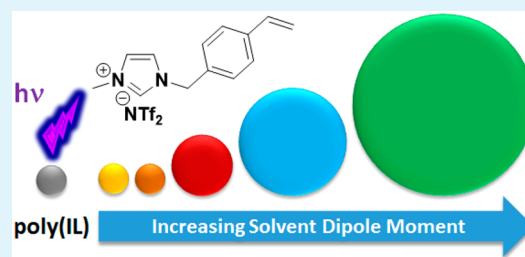
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## Supporting Information

**ABSTRACT:** A simple, polymerized ionic liquid (poly(IL)) based on methylimidazolium cations tethered to a polystyrene backbone exhibits superabsorbent behavior toward polar organic solvents, most notably propylene carbonate (PC) and dimethyl sulfoxide (DMSO), wherein the poly(IL) was observed to swell more than 390 and 200 times (w/w) its original mass, yet absorbs negligible quantities of water, hexanes, and other solvents, many of which were miscible with the IL monomer. Although solubility parameters and dielectric constants are typically used to rationalize such behaviors, we find that poly(IL)–solvent compatibility is most clearly correlated to solvent dipole moment. Poly(IL) superabsorbency is not reliant upon the addition of a cross-linking agent.

**KEYWORDS:** ionic liquid, polymer, absorbance, swelling, polar organic solvents, imidazolium



There is a large and growing number of papers in the literature relating to fundamental and applied studies on ionic liquids (ILs), yet there have been far fewer publications relating to poly(IL) materials. Ohno and co-workers produced many of the earliest works relating to the development of poly(IL) materials as mechanically stable ion conductors.<sup>1–4</sup> Other early applications of poly(ILs) focused on sorbents<sup>5–7</sup> and membranes for gas separations.<sup>8–14</sup> Mecerreyes and co-workers have published two review articles highlighting the history, applications, and progress of poly(IL) materials.<sup>15,16</sup> However, within the poly(IL) field of research, focus has yet to be devoted to understanding their bulk properties, with most reports tending to focus on specific applications where only small quantities of the poly(IL) are used, typically as thin films.

Although it is well-known that poly(IL) materials are capable of swelling/containing “free” ILs within their structures,<sup>13,17,18</sup> their ability to absorb neutral molecular solvents is virtually unexplored. Muldoon and Gordon first reported on cross-linked poly(IL) beads formed from imidazolium cations with vinyl groups that were able to swell in organic solvents such as acetone, but did not quantify the degree of swelling.<sup>19</sup> Firestone and co-workers demonstrated that amphiphilic poly(IL) materials produced from the photopolymerization of 1-octyl acrylate-3-methylimidazolium chloride in the presence of 23 wt % water were capable of forming hydrogels that swell to nearly 200 times (w/w) in water, with approximately 50 times (w/w) swelling in EtOH, DMSO, MeOH, and DMF.<sup>20</sup> Although the inclusion of water was necessary to solubilize the monomer, which was a waxy solid at ambient temperature, it is not clear as to whether the water already present within the poly(IL) structure promoted uptake of these polar organic solvents. Less

polar solvents such as 1-octanol, hexanes, EtOAc, and CHCl<sub>3</sub> had minimal or no swelling of the material.

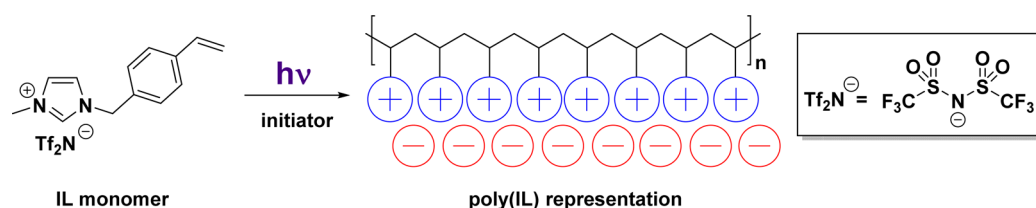
Other reports have focused on copolymers of ionic monomers with large, highly hydrophobic monomers and cross-linkers to produce polymers that swelled in nonpolar solvents. Sada et al. reported on a cross-linked copolymer gel network containing with ammonium cations or octadecyl groups attached the polyacrylate backbone.<sup>21</sup> The material was observed to swell over 120 times (w/w) in CH<sub>2</sub>Cl<sub>2</sub> and THF, 99 times in CHCl<sub>3</sub>, 70 times in chlorobenzene, and 11 times in hexane. Little or no swelling was observed for DMSO, DMF, MeOH, or CH<sub>3</sub>CN. More recently, polyelectrolyte gels containing a ternary mixture of vinyl imidazolium monomers, cross-linkable vinyl gemini imidazolium salts, and tetradecyl acrylate were shown to swell in solvents with low dielectric constants ( $\epsilon$ ) such as CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, and toluene at levels of ~10–50 times (w/w), yet had no absorption of solvents with larger  $\epsilon$  values such as CH<sub>3</sub>CN, DMSO, and DMF.<sup>22</sup>

These examples where poly(IL) materials were swollen by molecular solvents employ relatively sophisticated, highly tailored monomers, and cross-linkers. Furthermore, the swelling behavior is engineered based on a balance between long alkyl chains tethered to the imidazolium/ammonium cations as well as physical/chemical cross-linking. Given our experience in working with poly(IL) materials and reports on the swelling of other ionic polymers previously mentioned, we were interested as to whether a poly(IL) produced via the bulk

Received: March 3, 2015

Accepted: April 20, 2015

Published: April 20, 2015



**Figure 1.** Structure of IL monomer and representation of poly(IL) used in this work.



**Figure 2.** Digital photographs of 10 mm diameter pristine poly(IL) sample punched from the bulk (left); and the poly(IL) material fully swollen to ~89 mm diameter in DMSO (right).

photopolymerization of a “simple” styrene-based IL monomer, 1-[(4-ethenylphenyl)methyl]-3-methylimidazolium bistriflimide (Figure 1), without an added cross-linking agent would swell in various molecular solvents.

The IL monomer utilized in these studies (Figure 1) was synthesized and purified according to well-established procedures detailed by Bara and co-workers, and  $^1\text{H}$  NMR data were consistent with published values.<sup>14</sup>

A photoinitiator, 2-hydroxy-2-methylpropiophenone, was dissolved at 1–2 wt % in the IL monomer (4.00 g) using a vibrating mixer and mild heating ( $\sim 45^\circ\text{C}$ ) to ensure homogeneity. ATR-FTIR analysis showed that this amount of photoinitiator was sufficient to yield near quantitative (99%) conversion of styrene groups (see the Supporting Information). After cooling to room temperature, the IL + initiator solution was then pipetted onto a 5 in. diameter quartz plate, which was cleaned and coated in Rain-X, which is a commercially available, hydrophobic surface coating that aids in the release of the polymer film from the quartz surface postpolymerization yet is otherwise inert. An identical quartz plate, separated by 1 mm thick spacers, was then placed on top of the IL monomer, and the plates were placed inside a highly reflective chamber and exposed to 254 nm ultraviolet light for 4 h. After this time, the plates were pried apart using a clean razor blade and the large area film peeled easily from the lower quartz plate.

Uniform diameter samples were extracted from the poly(IL) disc by punching with a 10 mm diameter stainless steel die. The dry mass of each sample was recorded (typically  $\sim 150$  mg) and the sample was then placed in a sealed jar containing 60 mL of a solvent for and allowed to equilibrate for 36 h. After this time, the swollen polymers were removed from their containers, and excess (surface) solvent was removed using absorbent paper. The mass of the swollen sample was then recorded and the swelling ratio ( $Q$ ) was calculated according to eq 1

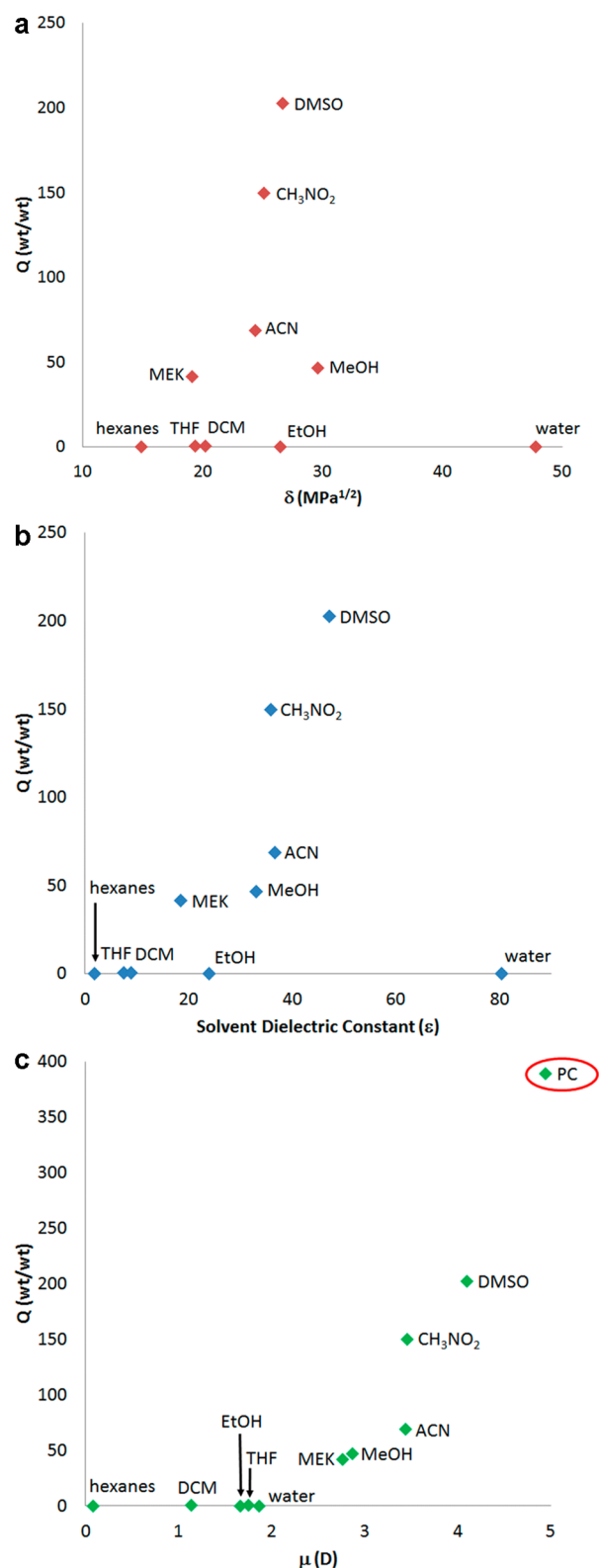
$$Q = (m_{\text{wet}} - m_{\text{dry}}) / m_{\text{dry}} \text{ (wt/wt)} \quad (1)$$

All experiments were performed in triplicate at ambient temperature ( $\sim 20^\circ\text{C}$ ). A list of the solvents examined and their relevant properties are provided as Supporting Information with respective values for solubility parameter ( $\delta$ ),  $\epsilon$ , and dipole moment ( $\mu$ ).

Investigation of the swelling behavior of the poly(IL) focused on variety of organic solvents with a wide range of solubility parameters. As expected, solvents that were completely immiscible with the IL monomer (e.g., hexanes, water) were incapable of swelling the poly(IL). Yet, we also observed that some solvents that were fully miscible with the IL monomer such as dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), tetrahydrofuran (THF), and ethanol (EtOH) had virtually no ability to swell the poly(IL). Furthermore, there was no apparent mass loss from the poly(IL) into these solvents, indicating that any soluble fraction of the poly(IL) sample is essentially nondetectable (or nonexistent). Other solvents that were known to be fully miscible with the monomer such as acetonitrile (ACN), methanol (MeOH), and dimethyl sulfoxide (DMSO) did exhibit varying degrees of swelling. The largest swelling capacity initially observed was for DMSO where the swelling capacity ( $Q$ ) was measured to be 202 times the initial sample mass, or approximately a 20 000% increase in mass. Figure 2 provides an example of the difference in size between a “dry” poly IL sample and the fully swollen sample in DMSO. An image of the bulk poly(IL) material edge-on displaying the uniformity of the material obtained using scanning electron microscopy (SEM) is provided as Supporting Information.

In the study of superabsorbent materials, swelling behavior is typically rationalized in terms of solubility parameters and dielectric constants.<sup>20,21</sup> On the basis of well-known thermodynamic relationships for solvent–solute interactions, a “match” between polymer and solvent solubility parameters (i.e.,  $(\delta_2 - \delta_1)^2 = 0$ ) should result in maximum swelling. Furthermore, solvents with high  $\epsilon$  values should have an affinity for charged/ionic groups. Analysis of the relationship between  $Q$  and  $\delta$

(Figure 3a) appears to reveal that there is “sweet spot” with regard to poly(IL) swelling behavior, but there is not an overall defining trend. On the basis of the large degree of swelling ( $Q =$



**Figure 3.** Relationship between poly(IL) swelling ( $Q$ ) and (a) solvent solubility parameter ( $\delta$ ), (b) solvent dielectric constant ( $\epsilon$ ), (c) and solvent dipole moment ( $\mu$ ) with data point for propylene carbonate (PC) appended.

202.4) in DMSO ( $\delta = 26.7 \text{ MPa}^{1/2}$ ), it can be inferred that DMSO is the most well-matched solvent in terms of solubility parameter to the poly(IL). Interestingly, this value is nearly identical to that calculated by Bara et al. via group contribution methods for a structurally similar, nonpolymerizable IL, 1-benzyl-3-methylimidazolium bistriflimide ( $\delta = 27.2 \text{ MPa}^{1/2}$ ).<sup>23,24</sup>

However, not all solvents with solubility parameters near  $27 \text{ MPa}^{1/2}$  resulted in a high swollen poly(IL) (i.e.,  $Q > 40$ ). For example, EtOH ( $\delta = 26.5$ ) had a value of  $Q = 0.11$ , indicative of nearly zero swelling. Contrastingly, exposure of the poly(IL) to methyl ethyl ketone (MEK) ( $\delta = 19.1$ ) resulted in  $Q = 41.5$ . These distinctly different behaviors indicate that for a poly(IL) system,  $\delta$  cannot be taken as the sole predictor of swelling and a more obvious/direct relationship between other solvent properties and swelling might exist.

On the basis of observations reported in other works, we then examined correlations between poly(IL) swelling and  $\epsilon$ , which is considered to be a measure of the solvent's ability to screen charges (Figure 3b). Here, the organic solvent with the greatest  $Q$  value, DMSO, also has a large value for its dielectric constant ( $\epsilon = 47.2$ ). Figure 3b illustrates a distinct tendency of the poly(IL) to swell more in organic solvents with increasing dielectric constant, although the near-zero swelling in EtOH ( $\epsilon = 24.3$ ) compared to that in MEK ( $\epsilon = 18.5$ ) is anomalous. As also can be seen in Figure 3b, there is a poor correlation between  $Q$  and  $\epsilon$  when the solvent with the largest dielectric constant, water ( $\epsilon = 80.4$ ) is considered. Experimental results thus suggest that solvents with high dielectric constants that also have solubility parameters near that of the poly(IL) will yield greater swelling.

Still, we endeavored to find a more intuitive correlation by which to rationalize the swelling behavior of the poly(IL). Solvent dipole moment ( $\mu$ ) was selected because the dipole moment represents the distance between centers of charge on the solvent and may be a more appropriate metric by which to rationalize solvent-poly(IL) interactions as  $\mu$  may effectively describe the ability of the solvent to align itself with the charges present on cation and anion of the poly(IL).  $Q$  values for the solvents were then plotted against solvent dipole moment ( $\mu$ ) (Figure 3c), resulting in a much more obvious trend between swelling and an intrinsic physical property of the solvent itself. Solvents with dipole moments  $< 2 \text{ D}$  are observed to have no ability to swell the poly(IL), whereas those with dipole moments  $> 2.5 \text{ D}$  result in highly swollen materials. Figure 3c also illustrates a nearly exponential increase in swelling as dipole moment increases, with the large degree of swelling in DMSO again correlated with the largest dipole moment. This result led us to search for at least one additional solvent with a larger dipole moment than DMSO. We selected propylene carbonate (PC) ( $\mu = 4.94$ ), which has a solubility parameter in the “sweet spot” ( $\delta = 27.1 \text{ MPa}^{1/2}$ ) and a larger dielectric constant ( $\epsilon = 64.9$ ) than DMSO. Confirming the hypothesis, PC was observed to be absorbed by the poly(IL) in larger quantity than any other solvent tested, resulting in  $Q = 390$ . The PC-swollen poly(IL) was quite fragile in this state, any significant motion or pressure would cause the gel to separate into pieces.

To gain further insight into the interactions of a solvent within the highly swollen poly(IL),  $^1\text{H}$  NMR spectra of the IL monomer in DMSO- $d_6$  were compared to the poly(IL) swollen in DMSO- $d_6$ . Our analysis focused on the chemical shift of the C(2)-H proton in the IL monomer (pink) to that in the

poly(IL) swollen in DMSO- $d_6$  (see Supporting Information for figure). The observed chemical shift of the IL monomer ( $\sim 9.21$  ppm) in DMSO- $d_6$  is identical to that reported in the literature.<sup>14</sup> However, in the swollen poly(IL) sample, a broadening is observed along with a simultaneous upfield shift to  $\sim 9.09$ . Although the broadening of  $^1\text{H}$  NMR signals is certainly expected in a polymer sample, the upfield shift observed here indicates a weakening cation–anion interaction that may be associated with cation interactions with a neighboring  $\pi$  system (e.g., the aromatic benzene rings).<sup>25</sup>

The imidazolium C(2)-H proton chemical shift can be taken as an indicator of H-bonding strength, with signals further downfield indicative of stronger cation–anion interactions. However, here we observe an apparent weakening of these interactions in the poly(IL) relative to the IL monomer, suggesting that the imidazolium cation is a weaker H-bond donor in the poly(IL), or that DMSO is able to effectively “pull” the bistriflimide anion further from the polystyrene-bound imidazolium cation. Furthermore, there may be large steric effects due to the orthogonal arrangement of the imidazolium and benzene rings along the polymer backbone. Although we cannot completely discount the possibility of a small amount of cross-linking of the polystyrene segments induced by UV radiation,<sup>26</sup> any significant amount of ionic or covalent cross-linking of the polymer chains would be expected to dramatically limit the ability of the poly(IL) to swell. Furthermore, cross-linked polystyrene would also be expected to swell in solvents with lower values of  $\epsilon$  or  $\mu$ .<sup>26</sup> Yet, we observe that the swelling of this poly(IL) is limited to polar organics such as PC, DMSO, and others. A value of  $\mu > 2$  D appears critical to separate cations and anions and this may be the key mechanism driving the exponential increases in poly(IL) swelling associated with increasing  $\mu$ . Simulations performed by others suggest that effective dipole moment of the IL, 1-hexyl-3-methylimidazolium bistriflimide ( $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ ) (which has a composition similar to that of the IL monomer used in this study) is  $5.7 \pm 0.9$  D,<sup>27</sup> which is comparable to the dipole moment of PC.

In this study, we have shown that a simple poly(IL) material is prone to exponential swelling in neutral molecular solvents that have dipole moments  $> 2$  D. Unexpectedly, the poly(IL) absorbed nearly 400 times its initial mass in PC and more than 200 times in DMSO. Poly(IL) swelling also shows a somewhat less direct relationship to solvent solubility parameter and dielectric constant. Yet, not all solvents that were miscible with the IL monomer could swell the poly(IL). On the basis of  $^1\text{H}$  NMR evidence, weakened cation–anion interactions were observed that may be due to sterics surrounding the poly(IL) chain and/or  $\pi$ –cation interactions between the benzene and imidazolium rings. Only solvents with relatively large dipole moments appear to be able to compete with these interactions, which in turn causes the poly(IL) to swell. These behaviors provide useful insight into poly(IL)–solvent interactions and may be used to design functional or responsive materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

Statement of materials, Table S1, Figures S1–S3, and  $^1\text{H}$  NMR (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for partial support of this work; partial support from the National Science Foundation (EEC-1358750) is gratefully acknowledged.

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