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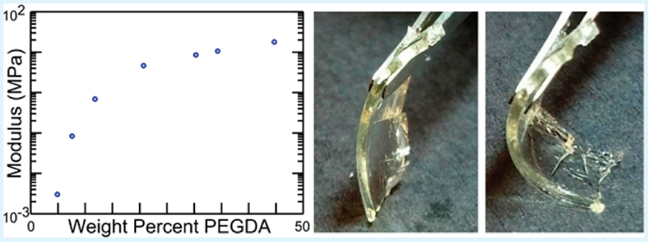
# Poly(Ethylene Glycol) Diacrylate-Supported Ionogels with Consistent Capacitive Behavior and Tunable Elastic Response

Adam F. Visentin and Matthew J. Panzer*

Department of Chemical & Biological Engineering, Tufts University, Medford, Massachusetts 02155, United States

*Supporting Information*



**ABSTRACT:** Harnessing the many favorable properties of ionic liquids in a solid electrolyte thin film form is desirable for a host of electrical energy storage applications, including electrochemical double layer capacitors. Using a cross-linked polymer matrix to provide structural support, freestanding ionogel materials can be achieved with a wide range of polymer weight fractions. Compression testing and impedance spectroscopy have been used to characterize the mechanical and electrical responses of ionogels containing between 4.9 and 44.7 wt % poly(ethylene glycol) diacrylate. Although the elastic modulus of these solid electrolyte materials is observed to vary by more than 4 orders of magnitude within the composition range studied, concomitant changes in gel ionic conductivity and double layer capacitance were much less dramatic.

**KEYWORDS:** *ionogel, ion gel, ionic liquid, electrochemical double layer capacitor, solid electrolyte, elastic modulus*

## 1. INTRODUCTION

Ionic liquids possess many attractive attributes that make them suitable for a wide range of electrical energy generation and storage applications. High ionic conductivities and wide electrochemical windows[1,2] have prompted investigations of their possible employment in solar cells,[3] fuel cells,[2] batteries,[2] transistors,[4−6] and electrochemical double layer capacitors (EDLCs).[7−10] In addition, ionic liquids are chemically inert, nonvolatile, nonflammable, and thermally stable, all of which suggest their use as a safer replacement for organic solvent-based electrolytes.[1,2]

To capitalize on the favorable electrochemical properties of ionic liquids in thin, flexible, and lightweight devices, it is desirable to develop solid electrolyte materials that can maintain the high performance of the neat ionic liquid. An ionogel (or "ion gel") is a solid or semisolid ionic liquid-based electrolyte containing a structural support matrix. The supporting matrix can be realized using different materials and formed by various processes. For example, the self-assembly of triblock copolymers,[4,5,8,11,12] thermal-[10,13−15] or UV-initiated[6,9,16,17] radical polymerization, copolymer gelation,[18,19] and sol−gel silica formation[2,20] have all been reported as viable methods to create ionogels. In situ free radical polymerization and/or cross-linking (e.g., of acrylate-functionalized monomers)[6,9,14,15] is a straightforward method to obtain ionogels over a wide range of polymer compositions.

Although several previous studies have focused on the electrical properties of ionogels with compositions near the minimum amount of support matrix required to generate a freestanding film, in this work we posed the question: do ionogels with compositions near the gelation point exhibit the dimensional stability required for their ultimate device application? Few studies have systematically investigated the mechanical rigidity of ionogels as a function of their composition, except for a small group that characterized dynamic gel rheological response.[12,14,21]

In this report, we examine the dependence of the ionic conductivity, double layer capacitance, and elastic modulus of polymer-supported ionogels on the weight fraction of polymer matrix in the gel. Our ionogels are formed via UV-initiated cross-linking of poly(ethylene glycol) diacrylate (PEGDA) inside an ionic liquid, which requires a low polymer weight percent to achieve gelation.[6] The ionic liquid used here is 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI TFSI), a hydrophobic electrolyte commonly investigated for use in EDLCs.[4,6,8,10,12,14] This is the first study, to the best of our knowledge, that examines the influence of PEGDA composition on both the electrical and mechanical properties of this type of ionogel. The goal is to obtain a better understanding of the trade-offs between a desired level of ionogel mechanical rigidity and corresponding electrical performance to guide the development of an ideal formulation for a flexible energy storage device, such as an EDLC.

## 2. EXPERIMENTAL SECTION

EMI TFSI was purchased from EMD Chemicals Inc. Micro-90, PEGDA (average $M_n$ 575 g/mol), and 2-hydroxy-2-methylpropiophenone (HOMPP), the photoinitiator, were purchased from Sigma-Aldrich. Acetone and isopropanol were laboratory grade from Fisher Scientific. All materials were used as received. 50% w/v NaOH in

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water, from Sigma-Aldrich, was diluted as required with in-house deionized (DI) water.

Ionogel precursor solutions containing EMI TFSI, PEGDA, and HOMPP were prepared by weighing components on a balance. Precursor solution compositions ranged from 4.9 to 44.7 wt % PEGDA; each solution contained 2 wt % HOMPP, with the balance made up by EMI TFSI. The electrodes, tin-doped indium oxide (ITO) on glass (Thin Film Devices, Inc.), were cleaned by successive sonication in 2 vol % Micro-90 in DI water, DI water, and acetone, followed by immersion in boiling isopropanol. The cleaned substrates were finally submerged in 1 M NaOH for 30 min, then rinsed with DI water and dried under flowing $N_2$ gas. The ITO-coated glass substrates were clamped together in a parallel plate geometry using a circular poly(tetrafluoroethylene) spacer (PTFE, outer diameter 13.2 mm, inner diameter 6.35 mm, 1.58 mm thick). The spacer had a thin slit cut in its side to allow ionogel precursor solution to be injected via syringe into the cavity between the ITO electrodes. Figure 1 shows the chemical structures of PEGDA and the ionic liquid EMI TFSI, as well as a schematic of the architecture utilized for measuring ionogel impedance. The glass/ITO/precursor solution/ITO/glass assembly was exposed to longwave UV radiation at 365 nm (Spectronic Corp., 8 W) for 3 min to cross-link the acrylate functional groups. FT-IR spectroscopy was used to verify that this curing time is sufficient to achieve complete polymerization[22] (see Figure S1 in the Supporting Information).

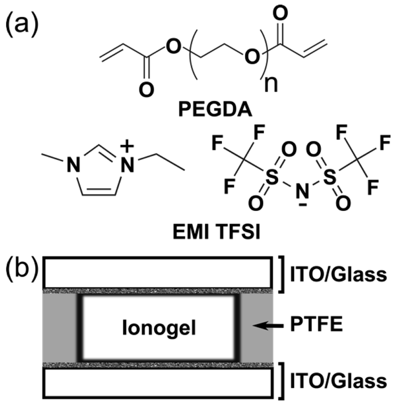

**Figure 1.** (a) Chemical structures of the ionogel components: PEGDA, the polymer support precursor, and EMI TFSI, the ionic liquid. (b) Cross-sectional schematic of the ITO electrode/ionogel/ITO electrode assembly (not to scale). The PTFE spacer is used to define the ionogel volume.

All impedance measurements were recorded at room temperature under ambient conditions using a Princeton Applied Research VersaSTAT 3 with a built-in frequency response analyzer. Two-electrode device impedance was measured over the frequency range 1 Hz to 100 kHz with a sinusoidal voltage amplitude of 10 mV superimposed on 0 V DC (vs open circuit).

Mechanical response data were acquired by unconfined compression testing using an Instron 3366 testing frame with a 100 N load cell. Each elastic modulus represents the average of at least 3 samples prepared with an aspect ratio of 2:1 (diameter: thickness). Samples were prepared between uncoated glass slides using the same method to fabricate ionogels for impedance testing. Free-standing ionogels were readily separated from the slides following UV-initiated cross-linking. The rate of strain applied was 0.1% strain per second to an upper limit of 40% strain. Best-fit lines to the resulting force-strain data were found for the two regions of 5−10% and 20−25% strain. The resulting slopes divided by the cross-sectional area yielded elastic modulus values. This assumed that the cross-sectional area did not expand with increased strain during testing.

## 3. RESULTS AND DISCUSSION

AC impedance spectroscopy was performed on optically transparent ionogels of constant geometry (area ≈ 0.317 $cm^2$ ± 0.026 $cm^2$, thickness ≈ 0.158 cm ±0.004 cm) formed in situ against ITO electrodes. Figure 2 displays the impedance response of PEGDA-supported ionogels with polymer contents ranging from 4.9 wt % (approximate minimum amount required for gelation) to 44.7 wt %. Corresponding data for the neat EMI TFSI ionic liquid (0 wt % PEGDA) is also shown for comparison. The magnitude of the impedance response, |Z|, is a reflection of both the capacitive and resistive behavior of the gel electrolyte, as expressed in eq 1.

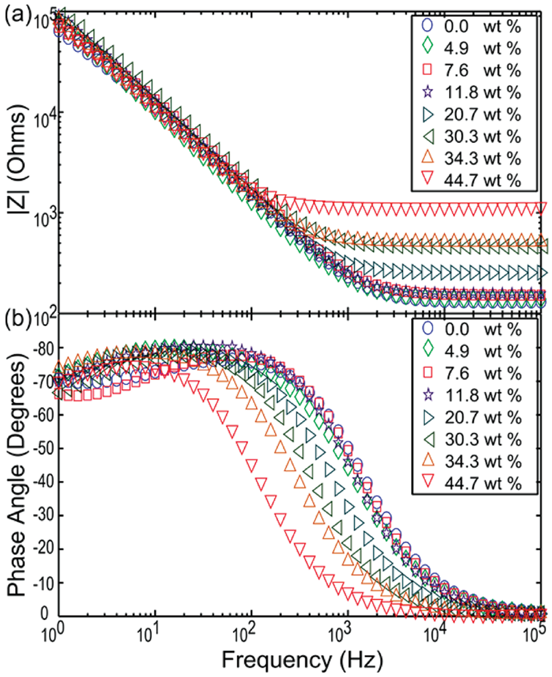

**Figure 2.** Impedance behavior of PEGDA-supported EMI TFSI ionogels with varying polymer weight fractions: (a) magnitude of impedance versus frequency, (b) phase angle versus frequency.

$$|Z| = [(Z')^2 + (Z'')^2]^{1/2} \tag{1}$$

At high frequencies, the behavior of each device is dominated by a resistive response, as characterized by the real component of impedance ($Z'$), and is independent of the frequency. At low frequencies, capacitive behavior (which can be strongly frequency-dependent) dominates, and is characterized by the value of the imaginary component of the impedance ($Z''$). The formation of the capacitive electrostatic double layers depends on electric field-driven ion rearrangement near the electrodes; at very high frequencies, this is not possible. As seen in Figure 2, our devices show primarily resistive behavior above 1 kHz. In this region, the influence of the supporting polymer matrix is clearly observed; as the amount of PEGDA increases, so does the impedance. Initially, the increase is gradual, but by 44.7 wt % PEGDA, the impedance has increased from 131 Ω for neat EMI TFSI to 1131 Ω for the ionogel. Importantly, the data show that the polymer support matrix does not dominate ionogel electrical properties at low PEGDA content (11.8 wt % polymer or less).

Figure 2b, the Bode phase plot, clearly shows the transition from primarily resistive to capacitive response as the frequency is decreased. The phase angle of impedance, $\theta$, is expressed as

$$\tan(\theta) = Z''/Z' \qquad (2)$$

where a phase angle of −90° signifies a purely capacitive response and 0° corresponds to a pure resistor. Frequently, a phase angle equal to −90° is not obtained in EDLC structures due to factors such as atomic and/or macroscale electrode inhomogeneity, as well as the adsorption of impurities at the electrolyte/electrode interface. As a result, the impedance behavior of EDLCs is commonly modeled by an equivalent circuit that includes a constant phase element.[23,24] The observed shift in the onset of capacitive response to lower frequency with increasing PEGDA weight fraction suggests that the polymer may hinder ion diffusion or lower the availability of EMI TFSI free ions. This retardation of gel switching ability demonstrates the influence of the polymer matrix on bulk ionogel conductivity. In contrast, the observed capacitance is a result of a surface phenomenon between gel and electrode, and is not significantly impacted by the presence of the polymer support (see Figure 2a). The slope of a best-fit line in the capacitive region of Figure 2a (frequency <100 Hz) is one indicator of capacitive performance; an average slope of −0.84 is obtained for this region, confirming the capacitive nature of these ionogels.

Ionogel conductivity (Figure 3) was determined by

$$\sigma = t(AR_{\text{gel}})^{-1} \qquad (3)$$

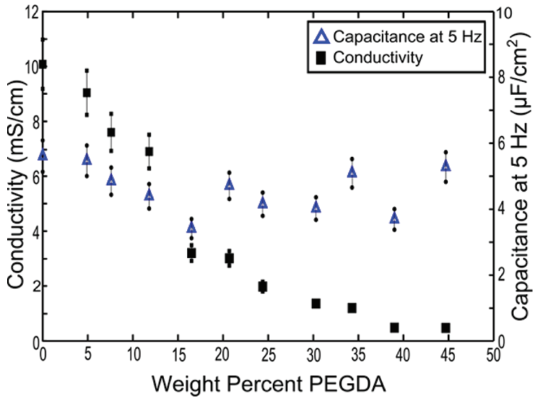

**Figure 3.** Calculated ionic conductivity and specific capacitance values for ionogels with varying PEGDA content.

where $t$ is the thickness of the gel, $A$ is the cross-sectional gel area, and $R_{\text{gel}}$ is the resistance of the gel. $R_{\text{gel}}$ was found by subtracting the resistance of the test setup (79 Ω, including the ITO electrodes; see Figure S2 in the Supporting Information) from the $Z'$ value measured at approximately 40 kHz. As seen in Figure 3, ionogel conductivity decreases with increasing PEGDA content. We note, however, that the decrease in conductivity is relatively gradual with increasing amounts of PEGDA. Furthermore, the relative ionic conductivity decrease (compared to the neat EMI TFSI ionic liquid) for a given weight percentage of polymer support appears to be less than for the case of triblock copolymer-based ionogels.[12] The ionic conductivity of the 44.7 wt % ionogel (0.47 mS/cm) is approximately a factor of 20 times lower than that of the neat ionic liquid. Ionic conductivity values were measured at room temperature (~22 °C), significantly above the glass transition temperature of these ionogels. Differential scanning calorimetry indicates that the glass transition for all ionogels studied lies below −55 °C (see Figure S3 in the Supporting Information).

Figure 3 also displays the specific capacitance of ionogels containing different amounts of PEGDA, along with that of neat EMI TFSI, measured at 5 Hz. This frequency was selected based upon the behavior illustrated in the Bode phase plot (Figure 2b); at 5 Hz, all gels exhibit strongly capacitive behavior. The specific capacitance ($C'$) was calculated by:

$$C' = (2\pi f|Z''|A)^{-1} \qquad (4)$$

where $f$ is the frequency (in Hz). As noted previously, the slope of the low-frequency data in Figure 2a (where $|Z| \approx |Z''|$) is not equal to −1; therefore, calculated capacitance values are frequency-dependent. Importantly, the capacitance of our ionogels is largely unaffected by an increase in PEGDA weight percentage; this is possibly due to the formation of a thin "skin" of neat EMI TFSI adjacent to the ITO electrodes during the ionogel cross-linking step. This hypothesis is supported by observations of a small amount of EMI TFSI liquid residue remaining on the ITO upon physically disassembling the two-electrode device. A thin layer of unentangled ionic liquid could explain the ability of all gels to form a consistent double layer at the electrode/gel interface, regardless of polymer content within the bulk of the gel.

The relationship between ionogel composition and mechanical rigidity is more dramatic than the corresponding variation in electrical properties for low PEGDA weight percent gels. Figure 4 shows the elastic modulus of our ionogels within two strain regimes, 5−10% and 20−25% strain. The modulus obtained in the higher strain regime was approximately twice the value of that observed in the 5−10% strain regime for all ionogels containing less than 30.3 wt % PEGDA. Most notable is the greater than 3 orders of magnitude increase in elastic modulus between 4.9 wt % (near the gelation point) and 20.7 wt % PEGDA. The modulus of the 7.6 wt % ionogel (~50 kPa) is comparable to gelatin (0.01−0.018 g/mL in water);[25] the 11.8 wt % gels display a modulus comparable to the widely used

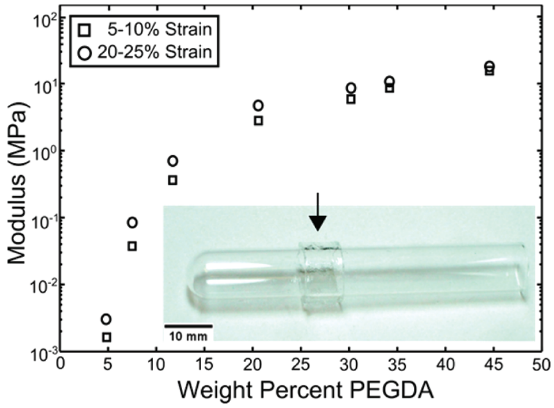

**Figure 4.** Elastic modulus of ionogels with varying PEGDA weight percentage for two different strain regimes: 5−10% and 20−25% strain. The inset image illustrates the flexibility of an ionogel film, approximately 2 mm thick (8 wt % PEGDA), which was wrapped by hand around a glass test tube of outer diameter 9.5 mm after being formed as a rectangular strip. The arrow indicates the position of the gel (see Figure S4 in the Supporting Information for representative compressive stress−strain data).

elastomer poly(dimethylsiloxane), PDMS.[26] Remarkably, while the elastic modulus of ionogels containing 4.9−11.8 wt % PEGDA varies by more than two hundred-fold, the ionic conductivity and capacitance values change by less than 30%. At the highest polymer content studied here (44.7 wt %), the elastic modulus at 5−10% strain (15 MPa) corresponds to an approximate molecular weight between cross-links (entanglements) of 850 g/mol and a cross-link density of 0.80 $nm^{-3}$ (see the Supporting Information).

The dramatic increase in ionogel elastic modulus with increasing polymer content slows above 20.7 wt % PEGDA. This can be observed physically, as all gels at and above this weight percentage polymer are hard and brittle. Mechanical failure (fracture) of the gels upon loading was observed to occur between 30 and 40% strain for all samples with PEGDA content greater than 11.8 wt %. None of the EMI TFSI was visibly squeezed out of the gels during compression. With a maximum strain imposed of 40%, failure points for the 4.9 and 7.6 wt % PEGDA gels were not observed. Ionogels of these two compositions were not permanently deformed by testing, and returned to their original dimensions upon unloading.

## 4. CONCLUSIONS

In conclusion, we have observed that the low-frequency capacitive behavior of PEGDA-supported ionogels is not strongly influenced by polymer content within the composition range examined (4.9 to 44.7 wt % PEGDA). However, increasing PEGDA content reduces the ionic conductivity and response speed of these ionogels, which may be an important consideration for ionogel-based EDLC charge and discharge rate capabilities. The elastic modulus of PEGDA-supported ionogels depends strongly on polymer content, especially at low polymer weight fractions. At 11.8 wt % PEGDA and below, flexible and compliant ionogels were obtained; gels containing higher polymer content were hard and brittle. These findings suggest that ionogels with polymer contents greater than the minimum amount required for gelation may be appropriate for device applications where greater mechanical rigidity is necessary without sacrificing significant electrical performance.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

FT-IR data, determination of the experimental setup resistance, differential scanning calorimetry measurements, sample mechanical compression force-strain data, and determination of cross-link density details. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: matthew.panzer@tufts.edu.

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083.
(2) Bideau, J. L.; Viau, L.; Vioux, A. *Chem. Soc. Rev.* **2011**, *40*, 907−925.
(3) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Gratzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 1166−1167.
(4) Lee, J.; Kaake, L. G.; Cho, J. H.; Zhu, X. Y.; Lodge, T. P.; Frisbie, C. D. *J. Phys. Chem. C* **2009**, *113*, 8972−8981.
(5) Lee, J.; Panzer, M. J.; He, Y.; Lodge, T. P.; Frisbie, C. D. *J. Am. Chem. Soc.* **2007**, *129*, 4532−4533.
(6) Choi, J.; Lee, S. W.; kar, J. P.; Das, N. S.; Jeon, J.; Moon, K.; Lee, T. I.; Jeong, U.; Myoung, J. *J. Mater. Chem.* **2010**, *20*, 7393−7397.
(7) Lewandowski, A.; Swiderska, A. *Solid State Ionics* **2003**, *161*, 243−249.
(8) Lee, K. H.; Zhang, S.; Lodge, T. P.; Frisbie, C. D. *J. Phys. Chem. B* **2011**, *115*, 3315−3321.
(9) Yang, C.; Ju, J. B.; Lee, J. K.; Cho, W. I.; Cho, B. W. *Electrochim. Acta* **2005**, *50*, 1813−1819.
(10) Isshiki, Y.; Nakamura, M.; Tabata, S.; Dokko, K.; Watanabe, M. *Polym. Adv. Technol.* **2011**, *22*, 1254−1260.
(11) He, Y.; Boswell, P. G.; Buhlmann, P.; Lodge, T. P. *J. Phys. Chem. B* **2007**, *111*, 4645−4652.
(12) Zhang, S.; Lee, K. H.; Frisbie, C. D.; Lodge, T. P. *Macromolecules* **2011**, *44*, 940−949.
(13) Jiang, J.; Gao, D.; Li, Z.; Su, G. *React. Funct. Polym.* **2006**, *66*, 1141−1148.
(14) Susan, Md. Abu Bin Hasan; Kaneko, T.; Noda, A.; Watanabe, M. *J. Am. Chem. Soc.* **2005**, *127*, 4976−4983.
(15) Noda, A.; Watanabe, M. *Electrochim. Acta* **2000**, *45*, 1265−1270.
(16) Delaney, J. T., Jr.; Liberski, A. R.; Perelaer, J.; Schubert, U. *Macromol. Rapid Commun.* **2010**, *31*, 1970−1976.
(17) Stepniak, I.; Andrzejewska, E. *Electrochim. Acta* **2009**, *54*, 5660−5665.
(18) Pandey, G. P.; Hashmi, S. A.; Kumar, Y. *Energy Fuels* **2010**, *24*, 6644−6652.
(19) Pandey, G. P.; Hashmi, S. A.; Yogesh, K. *J. Electrochem. Soc.* **2010**, *157*, A105−A114.
(20) Gayet, F.; Viau, L.; Leroux, F.; Monge, S.; Robin, J. J.; Vioux, A. *J. Mater. Chem.* **2010**, *20*, 9456−9462.
(21) Hanabusa, K.; Fukui, H.; Suzuki, M.; Shirai, H. *Langmuir* **2005**, *21*, 10383−10390.
(22) Kalakkunnath, S.; Kalika, D. S.; Lin, H.; Freeman, B. *J. Polym. Sci., Polym. Phys.* **2006**, *44*, 2058−2070.
(23) Pajkossy, T. *Solid State Ionics* **2005**, *176*, 1997−2003.
(24) Kerner, Z.; Pajkossy, T. *Electrochim. Acta* **2000**, *46*, 207−211.
(25) Markidou, A.; Shih, W. Y.; Shih, W. *Rev. Sci. Instrum.* **2005**, *76*, 064302.
(26) Cheng, Q.; Sun, Z.; Meininger, G. A.; Almasri, M. *Rev. Sci. Instrum.* **2010**, *81*, 106104.