Tunable Networks from Thiolene Chemistry for Lithium Ion Conduction

Catherine N. Walker,[†] Craig Versek,[‡] Mark Touminen,[‡] and Gregory N. Tew*,[†]

[†]Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States
[‡]Department of Physics, University of Massachusetts, Amherst, Massachusetts 01003, United States

S *Supporting Information*

ABSTRACT: End-functionalized poly(ethylene glycol) (PEG) and polydimethylsiloxane (PDMS) were cross-linked by a thiolene reaction with a tetra-functional thiol to create robust, tunable networks. These networks were loaded with increasing amounts of lithium bis(trifluoromethane sulfonyl imide) (LiTFSI), and their ion conductivity was measured. A wide range of salt loading was achieved, allowing the investigation of both salt-in-polymer and polymer-in-salt regimes. Thermal, mechanical, and ion conductivity properties of LiTFSI-loaded PEG and PEG-PDMS networks were measured. Even at high salt loadings, both networks maintained rubber-like characteristics, which were stable over a range of temperatures (30−90 °C). The PEG network with the highest salt loading showed the greatest ion conductivity, 6.7×10^{-4} S cm^{-1} at 30 °C, as measured by impedance spectroscopy. This system provides a route to optimize lithium ion conduction and mechanical properties.
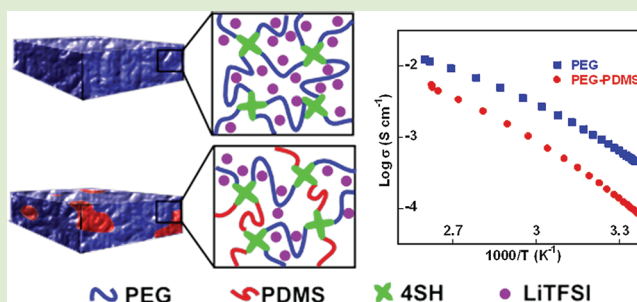
Access to affordable, clean energy is a well-recognized scientific and technical challenge of this century.[1] Although many different opportunities are being investigated, every solution involves better batteries, as they represent the main energy storage device.[2] Despite widespread use, current batteries are far from their theoretical storage potential, and significant improvements can be made (up to 95% of theoretical values) by eliminating components such as the separator.[3] Among commercially available batteries, lithium ion batteries are attractive because they have the highest energy density.[4,5] One important area of research focuses on replacing the current liquid or gel electrolyte of these batteries with a solid material. This is expected to double the energy density and eliminate the volatile organic solvents, which pose a fire hazard.[4,6] For a solid material to replace liquid and gel electrolytes, it should have a minimum ion conductivity of 10^{-3} S cm^{-1} throughout the expected range of operating temperatures.[2,4] At the same time, solid electrolytes should have enough mechanical integrity to replace separators currently used in the liquid electrolyte design. While many material systems have been examined,[4−7] few exhibit the necessary conductivity or mechanical properties; simultaneously improving both remains a challenge. Soft materials enable rapid chain-relaxation and thus higher conductivity, while stiffer materials, which yield more appropriate mechanical properties, generally have a lower conductivity.[8] A notable exception is the poly(ethylene glycol) (PEG)−polystyrene block copolymer system reported by Balsara and co-workers that showed ion conducting properties decoupled from the mechanical properties without a large decrease in ion conductivity, yielding

materials with a high shear modulus, 10−100 MPa, and ion conductivity of 3.6×10^{-4} S cm^{-1} at 90 °C.[9]

Since Wright discovered the ion conducting properties of PEG,[10] this material has been extensively studied as the main component of solid electrolytes and remains one of the best lithium ion conductors known. However, PEG conducts lithium ions through chain relaxation, which typically creates a trade-off between robust mechanical properties and high ion conductivity.[7,11] In addition, the crystallinity of PEG reduces its ion conductivity. Efforts to limit this crystallization have included numerous branch polymers with reported conductivities of 7×10^{-5} to 10^{-3} S cm^{-1} at 90 °C.[12,13] Similarly, cross-linking can reduce crystallinity while increasing mechanical stability,[2] giving materials with moduli on the order of $10^{4}−10^{6}$ Pa and ion conductivity on the order of 10^{-5} S cm^{-1} at 25 °C.[14−16] However, the cross-linking must be efficient since loops, dangling ends, or other defects compromise the mechanical properties.[5] It has also been shown that materials with low T_g generally have better ion conductivities.[17−19] This leads to the study of PDMS-based materials including comb-like polymers consisting of a polymethylhydrosiloxane (PMHS) backbone with oligo(ethylene glycol) side chains. These polymers alone did not have sufficient mechanical properties to yield free-standing films so they were entrapped in cross-linked PEG-dimethacrylate. The resulting semi-interpenetrating
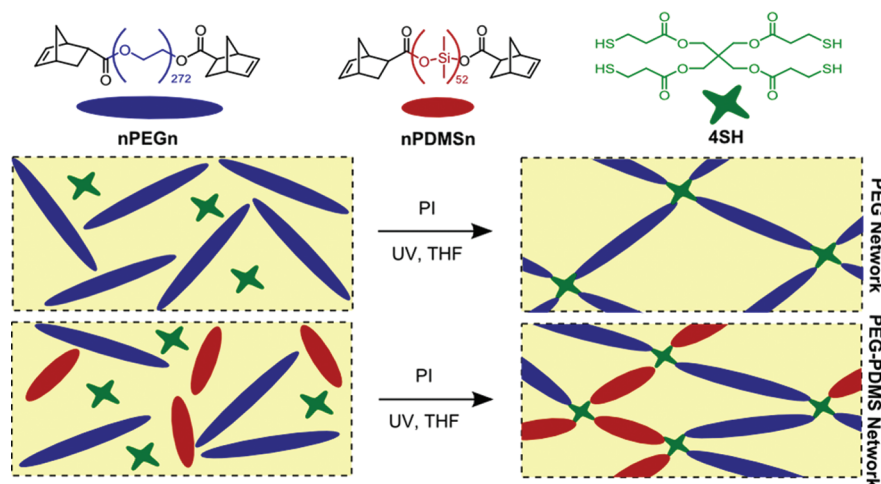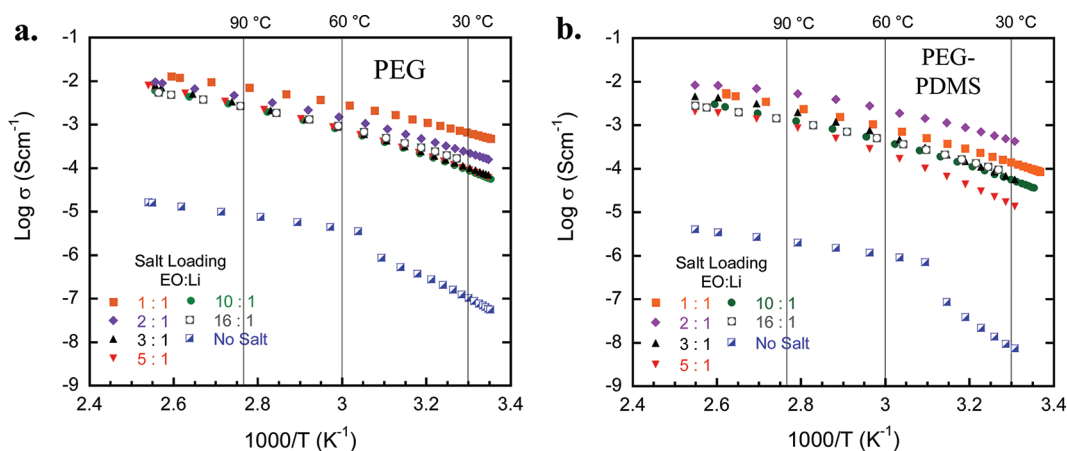
Figure 1. End-functionalized precursors and synthetic conditions for the formation of PEG and PEG-PDMS cross-linked networks. The structure of nPDMSn as been abbreviated for space and clarity; the full structure can be found in the SI.

Figure 2. Ion conductivity of (a) PEG networks and (b) PEG-PDMS networks in Arrhenius plots. Approximate temperatures in °C are given as a reference at the top of the plot. The salt loadings, EO/Li, are given in the legend.

networks were free-standing and exhibited an ion conductivity of approximately 10^{-4} S cm^{-1} at 37 °C.[17]

The amount of salt dissolved in the polymer electrolyte also affects ion conductivity.[4] Generally, PEG-based polymer electrolytes exhibit a maximum conductivity at fairly low salt loadings such as a molar ratio of ether oxygens to lithium ions (EO/Li) of 16. This trend is due to the lithium ions acting as additional physical cross-links between polymer chains, increasing the T_g and reducing the molecular mobility.[9,20,21] At significantly higher salt loading, the polymer T_g decreases, causing conductivity to increase. This regime has been dubbed "polymer-in-salt" as opposed to the conventional "salt-in-polymer" example described above.[20] Provided the molecular weight of the linear, noncross-linked polymer is high ($>8 \times 10^6$ g mol^{-1}), it takes as little as 10 wt % to give the material rubbery properties (shear modulus of 10^4 Pa) despite the high salt content.[22] Because networks have an infinite molecular weight, they should also be able to exhibit rubbery properties at high salt loading, for example EO/Li = 1.

In this report, hydroxyl-terminated, narrow polydispersity polymers were quantitatively end-functionalized with reactive norbornene end groups by the highly efficient Mitsunobu reaction. Figure 1 shows the cross-linking chemistry used to synthesize the two types of networks investigated in this study.

The telechelic polymer precursors were cross-linked by a tetra-functional thiol in a photoinitiated thiolene reaction to create a well-defined network. This chemistry is an attractive method for solid electrolyte preparation because it is known to be highly efficient, yield networks with few defects[23,24] and can accommodate a wide variety of precursor polymers. In the PEG-PDMS networks, the molar ratio of PEG to PDMS is 1:1. As the PDMS degree of polymerization is much less than the PEG, their volume fractions are approximately 0.3 and 0.7, respectively, before salt loading. Once the networks were formed, the gels were dried thoroughly and weighed. They were then swollen in tetrahydrofuran (THF) solutions of varying lithium bis(trifluoromethanesulfonyl imide) (LiTFSI) concentrations. After swelling for three days, they were thoroughly dried and weighed again. The difference in weight was used to calculate the molar ratio of ether oxygens in the PEG chains to lithium ions (EO/Li). (For further details on the network preparation and salt loading, see the experimental section in the Supporting Information (SI).)

The ion conductivity of PEG and PEG-PDMS networks obtained from impedance spectroscopy is shown in Figure 2. Loading either network with lithium salt increases the ion conductivity by at least 2 orders of magnitude when compared to the control networks which contain no added salt. The PEG
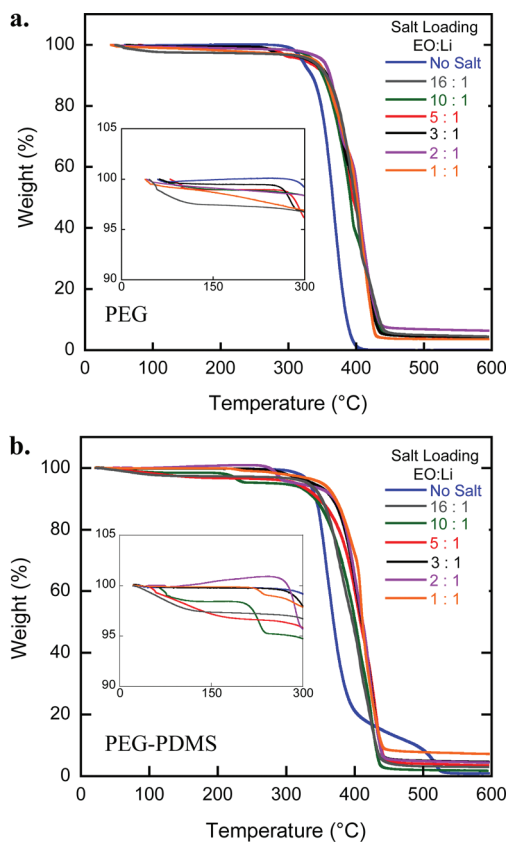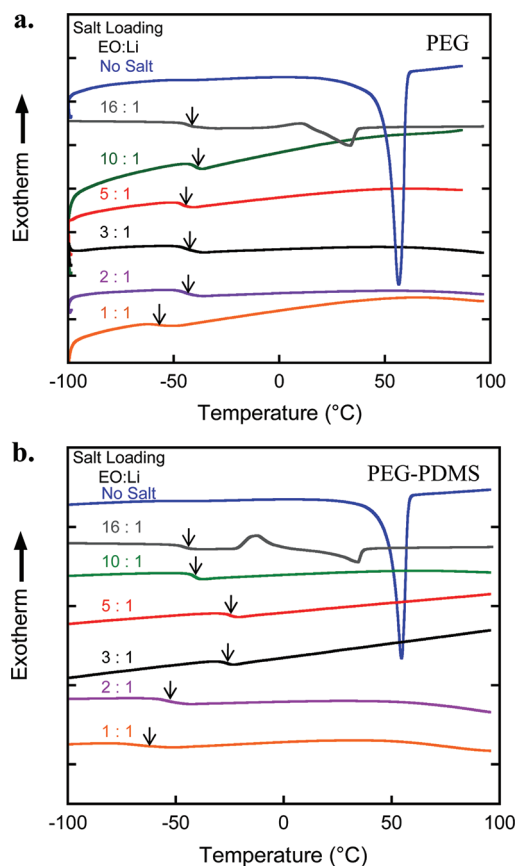
Figure 3. TGA of (a) PEG networks and (b) PEG-PDMS networks with a heating rate of 10 °C/min. Figure insets show only slight weight loss due to solvent or moisture.

Figure 4. DSC traces of (a) PEG and (b) PEG-PDMS networks. All traces are taken from the second heating scan, with a scanning rate of 10 °C/min. Data are offset on the Y-axis for clarity. T_g of PEG is marked with arrows.

and PEG-PDMS networks show an ion conductivity (8.6×10^{-5} to 6.7×10^{-4} and 1.3×10^{-5} to 4.2×10^{-4} S cm^{-1}, at 30 °C, respectively) similar to other materials in the field, (1×10^{-5} to 6×10^{-4} S cm^{-1}).[13−19] The conductivity as a function of temperature shows non-Arrhenius behavior with a decreasing slope at lower temperatures. The control networks show a different behavior, which includes a sharp decrease in conductivity at approximately 55 °C due to the crystallization of the PEG chains. In both networks, the highest salt loadings, EO/Li = 1:1 and 2:1, show a slight increase in conduction over conventional salt loadings, EO/Li = 10:1 and 16:1. As expected, ion conductivity in the PEG-PDMS networks is slightly lower than that of the PEG networks due to the reduced volume fraction of PEG.

The values reported in Figure 2 are taken from a cooling curve after holding the samples at 120 °C under vacuum for several hours. It is well-known that PEG and LiTFSI are hygroscopic. This "baking" process allows for the removal of any residual solvents or moisture from the salt loaded networks. The ion conductivity during this baking process shows that all networks reach a stable state before the samples are cooled, as seen in Figure S2 of the SI where the ion conductivity is plotted against time. It has been demonstrated that the effect of moisture on conductivity is largely reversible once the water is removed with heat.[25] It is logical that the effects of any other plasticizing solvents are also largely reversible. Based on this assumption, THF was chosen as the solvent for salt loading because it is easy to remove on heating.

To corroborate the effectiveness of the baking process, thermogravimetric analysis (TGA) measurements were per-

formed. As shown in Figure S3 of the SI, the pure salt, LiTFSI, contains 20% weight moisture which is removed upon heating to 90 °C, and very little change is observed (<5 wt %) between 90 °C and the decomposition temperature of 400 °C. Plots of weight loss as a function of temperature for the salt-loaded networks (Figure 3) show that the samples are quite stable up to 320 °C which allows for a wide range of operating temperatures. This data also confirms that the "baking" process eliminates the majority of the moisture observed in the TGA curve for the pure salt with less than 5 wt % loss for any sample up to 320 °C (Figure 3 insets). The sample with the greatest weight loss (5%) below 320 °C, PEG-PDMS EO/Li = 10:1, shows a conductivity similar to all of the other samples indicating that the weight loss, possibly related to moisture, above 180 °C does not enhance conductivity compared to the other networks.

LiTFSI is known for its ability to disrupt crystallinity due to the irregular shape of the TFSI anion, making this salt a popular choice for PEG-based ion conducting materials.[26] Differential scanning calorimetry (DSC) measurements (Figure 4) indicate that any salt loading greater than EO/Li = 10:1 completely disrupts the crystallinity of the PEG chains for both sets of networks. The crystallinity in both the PEG and the PEG-PDMS networks for EO/Li = 16:1 is much less than the crystallinity in the control networks that do not contain salt. However, none of the salt-containing samples show a crystallization-related decrease in conductivity in the temperature range investigated.
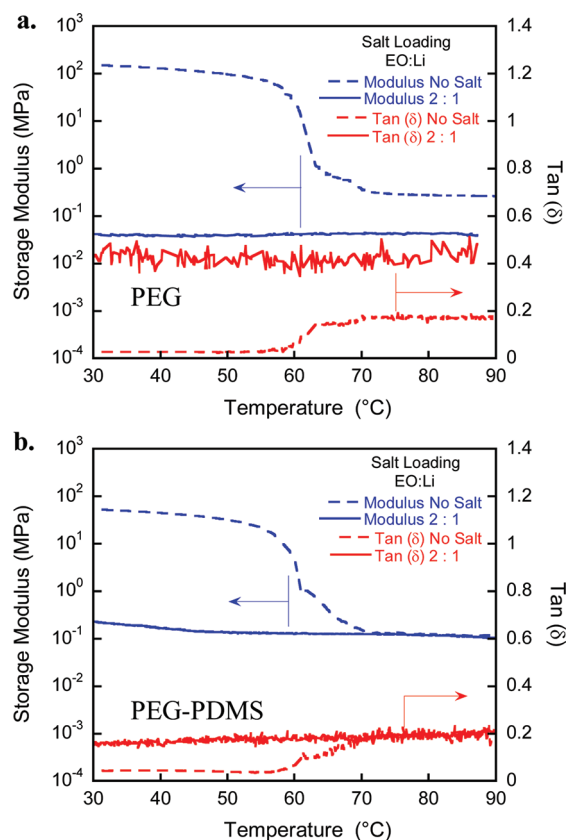
Figure 5. Storage modulus and tan (δ) of (a) PEG networks and (b) PEG-PDMS networks measured at 1 Hz as a function of temperature. The data for the control sample in both network are given by dashed lines while the EO/Li = 2 are solid. The modulus values are shown in blue, while the tan(δ) values are shown in red.

All of the salt-loaded networks show a T_g for the PEG component between −65 °C and −20 °C. In the PEG-PDMS networks, T_g goes through a maximum at EO/Li = 5:1 and then decreases as the salt loading continues to increase. This sample also had the lowest conductivity values. Although it is less pronounced, the T_g drops at the highest salt loading in the PEG networks. To illustrate this trend more clearly, T_g versus salt loading is plotted in Figure S4 of the SI. This trend indicates that the range of salt loading includes both the salt-in-polymer and the polymer-in-salt regimes. At low salt loadings, the T_g increases as salt loading increases possibly because the lithium cations serve as additional physical cross-links between chains, decreasing the molecular mobility of the polymer chains.[21] However, once the salt is the major component in the system, the T_g decreases similar to previous observations.[20,22] This regime change occurs when the PEG chains are saturated and cannot complex any additional cations.[22]

Dynamic mechanical analysis (Figure 5) shows that both PEG and PEG-PDMS salt-loaded networks have stable mechanical properties in the temperature range probed. As expected, both salt-free control samples show a large drop in storage modulus and a slight increase in tan(δ) as the PEG crystals melt at approximately 60 °C. Even with PEG in the crystalline state, the effect of the soft PDMS chains can be seen as the storage modulus of the control PEG-PDMS network (50 MPa) is lower than that of the PEG control network (150 MPa). The salt-loaded networks do not show this transition because they are predominately amorphous, corroborating the

DSC results. Instead, they maintain a relatively constant modulus over the temperature range investigated, 40 kPa for PEG and 200 kPa for PEG-PDMS. As with conductivity, these materials have comparable mechanical properties (approximately 1 MPa) to other materials in this field.[13−16,27] Even at high salt loadings, both the PEG and the PEG-PDMS networks remain elastic, maintaining a rubbery-like modulus and tan(δ) values much less than unity.

Here, we presented a chemical platform by which the mechanical properties and ion conductivity can be tuned to produce more effective materials. The mechanical properties can be modified by the incorporation of a nonion conducting component without greatly reducing the ion conductivity. As previously demonstrated in block−copolymer systems,[9] the ion conductivity of the material is dependent on the volume fraction of PEG. We envisage that, using the same chemical platform, the mechanical properties can be further improved by substituting PDMS with a stiffer nonion conducting component, while maintaining the same ion conducting properties demonstrated in the PEG-PDMS networks. The ion conduction and mechanical properties could also be tuned by changing the molecular weight of the precursor polymers or the volume fraction of the network components.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental, conductivity versus time, and TGA of LiTFSI. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Fax: +1-413-545-0082; e-mail: tew@mail.pse.umass.edu.

Notes
The authors declare no competing financial interest.

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