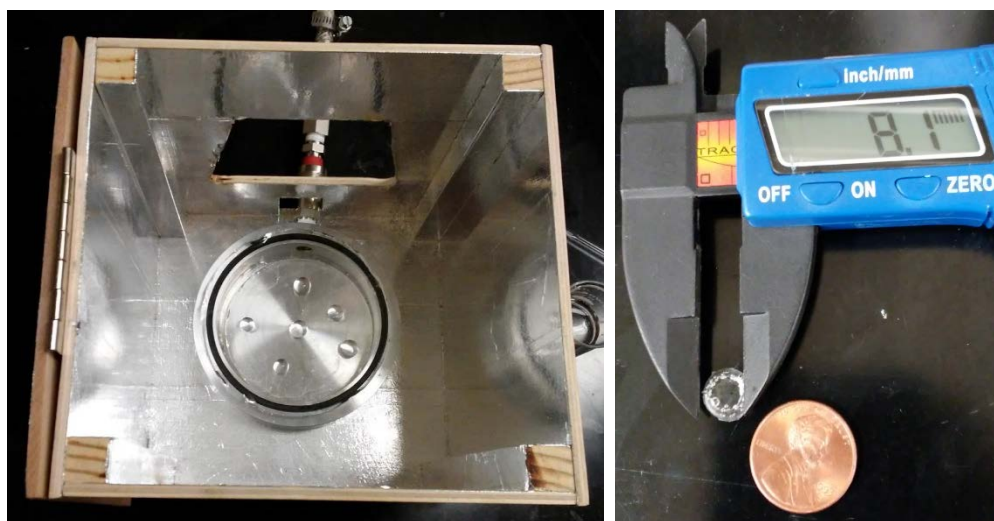


**PRF# 56819-ND7**  
**Investigating Polymer-Metal Bistriflimide Interactions for Functional Materials Design**  
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Coordinated ionic liquids (IL) monomers allow for the possibility of new opportunities to create polymer materials with large inorganic fractions. This approach could allow for a facile means of tailoring mechanical, thermal and electrical properties which may find use in the development of resins for photocuring-based 3-D printing. Our prior work has focused on coordinated IL monomers formed from methyl methacrylate (MMA), 1-vinylimidazole (Vim) and other small organic monomers with lithium bistriflimide ( $\text{LiTf}_2\text{N}$ ). The bistriflimide ( $\text{Tf}_2\text{N}^-$ ) anion is a bulky, non-coordinating species which is highly soluble in many polar organic compounds. Our prior results have shown that the presence of  $\text{LiTf}_2\text{N}$  accelerates photopolymerization rates as along with improving monomer conversion and yielding polymers with larger MW values than were achieved without the salt present. We have recently extended this work to crosslinkable species such as tetraethylene glycol diacrylate (TeEGDA), poly(ethylene glycol) diacrylate (PEGDA) and 1,6-hexanediol diacrylate (HDDA). In TeEGDA and PEGDA, the  $\text{Li}^+$  cation can coordinate to both ethers and carbonyls, while in HDDA, only carbonyls are present, thus distinctly different molecular-level structures may occur. This report focuses on the polymerization behaviors of these crosslinkable species in the presence of  $\text{LiTf}_2\text{N}$  and the properties of the resulting networks, such as swelling behaviors in  $\text{H}_2\text{O}$  and DMSO.

Samples of TeEGDA, PEGDA (MW = 250 and 575 g/mol) and HDDA were combined with  $\text{LiTf}_2\text{N}$  at molar ratios of 1:1, 1:2, 1:3, 2:1, 3:1, and 10:1. The samples were mixed via vortex mixer while heating to ensure that all  $\text{LiTf}_2\text{N}$  had dissolved as was uniformly dispersed. Then, 1 wt% of a suitable photoinitiator was added and the sample further homogenized while mixing and heated. The mixture was then pipetted into PTFE molds which were placed in a vacuum chamber and covered with a quartz plate (Figure 1, left). The chamber was evacuated and a 254 nm UV light source was placed on top of the quartz plate to begin the photocuring process. Samples were exposed to UV light for 24 h. Samples were then liberated from their PTFE molds, an example of which is shown in Figure 1 (right).

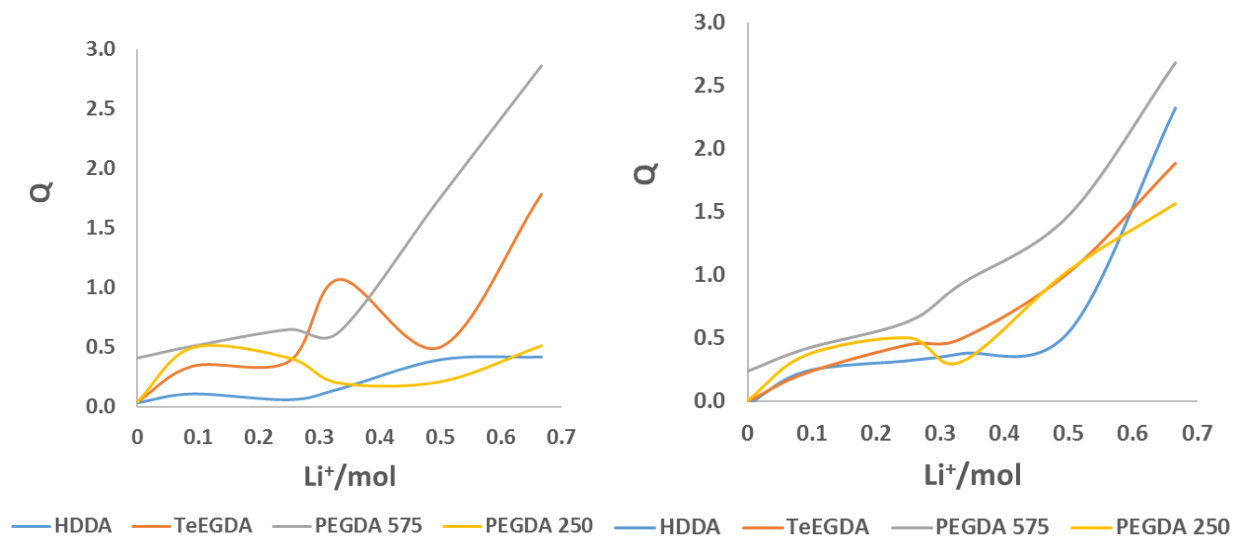


**Figure 1:** Left: photopolymerization chamber. Right: example of photocrosslinked sample containing  $\text{LiTf}_2\text{N}$ .

6 samples of the same composition were produced and their initial masses ( $M_0$ ) were recorded. These samples were then placed in individual vials with either  $\text{H}_2\text{O}$  or DMSO in a large excess and soaked for least 48 h. FT-IR analysis indicated that at least 97% of  $\text{LiTf}_2\text{N}$  had been extracted from the polymer network into the solvent. The samples were then removed and patted dry. Their final masses ( $M_f$ ) were then recorded. Eqn. 1 was used to calculate the swelling ratio ( $Q$ ) of the samples.

$$Q = \frac{M_f - M_0}{M_0} \quad (1)$$

The results of the swelling tests are presented in Figure 2.



**Figure 2:** Swelling of samples in water (left) and DMSO (right) relative to amount of  $\text{Li}^+$  initially present.

Figure 2 shows that  $Q$  generally increases as the amount of  $\text{Li}^+$  initially present, indicating that very different crosslinked networks are formed when  $\text{LiTf}_2\text{N}$  is present.

We are currently in the process of performing thermal and mechanical testing on these materials in order to understand how the presence of  $\text{LiTf}_2\text{N}$  influences macroscopic properties.

This project has benefitted a PhD student, Grayson Dennis and an undergraduate student, Valerie Levine. Grayson is entering his 3<sup>rd</sup> year in graduate school and has learned many aspects of polymerization and polymer processing. Valerie has decided to pursue graduate studies in nanomaterials at a European university. An undergraduate student, Kelsey Bailey, also participated in the project and has gained new skills in FT-IR spectroscopy.

The PI has also greatly benefitted from this research as it opened new applications and intellectual opportunities for him in the areas of polymer-inorganic composites, photopolymerization and materials characterization. This ACS-PRF New Directions has enabled the PI to demonstrate a facile, yet unprecedented, approach to rapidly generating a virtually infinite number of new materials using commercially available substances. This research will undoubtedly continue after the ACS PRF grant ends and the PI will continue to publish results and pursue funding opportunities to further advance this area.