



Thermal, mechanical and conductive properties of imidazolium-containing thiol-ene poly(ionic liquid) networks



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ABSTRACT

A series of imidazolium-based bis(trifluoromethylsulfonyl)imide [NTf₂] poly(ionic liquid)s (PILs) were prepared by conducting the solventless thiol-ene 'click' photopolymerization of bisallylimidazolium [NTf₂] and pentaerythritol tetrakis(3-mercaptopropionate) (PTMP). The thiol:ene molar ratio was varied in order to examine changes in the thermal, mechanical and conductive properties of the resulting polymer networks. The 1.0:2.0 thiol-ene PIL network exhibited the highest glass transition temperature (T_g of -5.0 °C) and storage modulus (E' of 9.24 MPa at 100 °C) values. Temperature-dependent ionic conductivities were found to rely on both the T_g /crosslink density as well as the IL content, with the highest ionic conductivity observed for the 1.0:3.0 thiol-ene PIL network (1.42×10^{-5} S/cm at 25 °C). Application of Vogel-Fulcher-Tammann and Williams-Landel-Ferry theories revealed the impact of both T_g /crosslink density and free ion concentration on temperature-dependent conductivity data, and indicated lower free volumes and fragilities for the thiol-ene networks relative to other non-network PILs.

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1. Introduction

Thiol-ene 'click' photopolymerization represents a robust, solventless, user-friendly, rapidly curing platform for the preparation of homogeneous polymer networks, the mechanism of which involves the step-growth radical reaction between a multi-functional thiol and an ene [1–5]. A high degree of flexibility has been observed with respect to the thermal and mechanical properties of the resulting networks due to the large number of thiol crosslinkers and ene monomers available (commercially and synthetically). As a result, thiol-ene photopolymerization chemistry has been employed in a number of different applications, recent examples of which include nanoprint/soft imprint lithography [6–8], electrospun fibers and nonwovens [9,10], gas barrier and transport membranes [11–14] and lithium ion batteries [15].

One research area where thiol-ene photochemistry has yet to be exploited is in the development of polymerizable ionic liquids or poly(ionic liquid)s (PILs). PILs allow for the cationic or anionic center of an ionic liquid (IL) to be constrained within the repeating unit of a polymer chain through the incorporation of a

polymerizable group(s). PILs are advantageous in that they combine the unique physical, electrochemical and thermal characteristics of ILs with the thermal and mechanical properties of various macromolecular architectures. As a result, research in PILs (especially cationic PILs) and their applications has increased exponentially over the last decade and several recent reviews have highlighted applications in electroactive and energy devices [16–21]. PILs have many advantages over the use of free ILs in electroactive devices, including enhanced stability, reduced leaching issues and improved mechanical stability. Additionally, PILs act as single-ion conductors since only the counteranion (or counter-cation) is mobile. Despite these benefits, a constant observed drawback of PILs is that anchoring the IL group causes a restriction in ion mobility, leading to a decrease in ionic conductivity. New structural variations are constantly being explored in order to improve upon this shortcoming, leading to a better understanding of the relationship between structure, morphology and ion-transport.

PILs that contain the imidazolium cation, in particular those derived from vinyl- or (meth)acryloyl-substituted imidazolium salts, have provided the greatest versatility in terms of synthesis and applications [22–35]. Some of the highest ionic conductivities have been observed when the imidazolium group has been placed pendant at the end of a long chain, coupled with a large, non-

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coordinating anion such as bis(trifluoromethylsulfonyl)imide [NTf₂]. For example, Long et al. reported the morphology and ionic conductivity of a series of alkyl-substituted imidazolium-based PILs and found that larger counteranions led to depressed glass transition temperature (T_g) values and increased conductivities [26,29]. More recently, modifications of the structural architecture of imidazolium-containing chain-growth polymers have been reported, either by employing pendant ethyleneoxy or long alkyl chains to increase flexibility and improve ion mobility [28,32] or by synthesizing block or triblock copolymers, where microphase separation between the PIL block and the non-ionic block(s) creates conductive microchannels [31,35].

Step-growth PIL architectures have been explored to a far lesser extent. In 2012, Gibson et al. reported on a series of linear imidazolium-containing polyesters where imidazolium-containing diols were mixed with diacid chlorides [36]. Several semicrystalline polyesters that resulted from this work exhibited high conductivities (up to 3.0×10^{-5} S/cm at 25 °C) and good mechanical stabilities. Long et al. discussed the use of imidazolium and phosphonium hydroxy-terminated IL monomers in the preparation of segmented polyurethanes for electroactive applications [37,38] while Drockemuller et al. explored CuAAC ‘click’ cyclization as a method to gain access to 1,2,3-triazolium-containing polymers with alkyl and ethyleneoxy spacers (conductivities up to 1.0×10^{-5} S/cm at 25 °C) [39–41].

We recently reported several series of covalently crosslinked imidazolium- and 1,2,4-triazolium-containing polyester networks prepared by Michael addition step-growth polymerization [42–44]. Incorporation of flexible chains and/or bulky, non-coordinating counteranions such as [NTf₂] led to a decrease in the T_g and the rubbery plateau modulus (E') and an increase in thermal stability. Despite the development of these interesting PIL networks, the synthesis and purification of the IL-containing acetoacetate monomers was found to be extremely tedious. Additionally, the polymerizations required the use of solvent due to the incompatibility of the acetoacetate and acrylate monomers, leading to long curing cycles (up to one week). As a result, thiol-ene “click” photopolymerization was targeted as a more robust, rapidly-curing, alternative method for the formation of covalently crosslinked, PIL networks. To date, only one report has utilized this chemistry as a way to incorporate a 1,4-di(vinylimidazolium)butane dibromide monomer into a polymer network for the purposes of studying the material’s anti-corrosion properties [45]. In this manuscript, the preparation of a series of imidazolium-containing polymer networks using thiol-ene photochemistry is discussed. In all of these PILs, the [NTf₂] counteranion was chosen due to its hydrophobic nature and tendency to provide enhanced ionic conductivities [18–21,46]. The thermal, mechanical and conductive properties of the resulting PILs were measured as a function of the thiol:ene molar ratio.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma-Aldrich or Acros Organics and were used as received without further purification. Chemicals used in this study included allyl imidazole (97%), allyl bromide (99%), acetonitrile (ACS grade), lithium bis(trifluoromethylsulfonyl)imide (LiNTf₂, 99%), 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, 99%), and pentaerythritol tetrakis(3-mercaptopropionate) (PTMP, > 95%). 1,3-Diallylimidazolium bromide **1** was prepared following a published procedure [47]. An ELGA Purelab® Ultra filtration device produced ultrapure water having a resistivity of 18 M Ω -cm.

2.2. Monomer characterization

¹H and ¹³C NMR spectra were obtained on a JEOL-ECS 400 MHz spectrometer and chemical shift values reported below were referenced to residual solvent signals (CDCl₃: ¹H, 7.26 ppm; ¹³C, 77.16 ppm). NMR spectra for monomer **2** are included in the Supporting Information. Elemental analyses were completed by Atlantic Microlab, Inc.

2.3. Preparation of 1,3-diallylimidazolium bis(trifluoromethylsulfonyl)imide [NTf₂] **2**

1,3-Diallylimidazolium bromide **1** (5.00 g, 21.8 mmol) was dissolved in DI water (50 mL). To this stirred solution at RT was added a solution of lithium bis(trifluoromethylsulfonyl)imide (6.58 g, 22.9 mmol) in DI water (50 mL). The resulting mixture was stirred at RT overnight, and then chloroform (50 mL) was added. The organic phase was separated, washed with DI water (3 \times 25 mL), and the volatiles were removed under reduced pressure, affording a light yellow oil (8.91 g, 95%). ¹H NMR (CDCl₃): δ 8.74 (s, 1 H), 7.29 (s, 2 H), 5.95 (m, 2 H), 5.47 (m, 4 H), 4.77 (d, 4 H, $J = 6.4$ Hz); ¹³C NMR (CDCl₃): δ 135.7, 129.2, 123.4, 122.4, 119.9 (q, $J = 321$ Hz, –CF₃), 52.4. Anal. calculated for C₁₁H₁₃F₆N₃O₄S₂, C 30.77, H 3.05, N 9.79; found, C 30.80, H 2.92, N 9.81.

2.4. Preparation of thiol-ene networks

The UV curing of thiol-ene networks was conducted at various thiol:ene molar ratios (1.0:1.0, 1.0:1.5, 1.0:2.0, 1.0:2.5, 1.0:3.0) following previously published procedures [6,48,49]. As an example, the polymer network employing the 1.0:2.0 thiol:ene molar ratio was prepared by mixing bisallylimidazolium [NTf₂] **2** (0.88 g, 2.05 mmol) with PTMP (0.50 g, 1.02 mmol) and 1 wt % of the photoinitiator DMPA (13 mg). The mixture was shaken by hand until a homogenous solution was obtained. The solution was then placed into a Teflon™ mold so as to achieve a film thickness of ~0.7 mm. The sample was exposed for 10 min to broadband ultraviolet radiation from a 100 W (8500 lumen) E17 metal halide high-intensity discharge lamp (Osram Sylvania, Wilmington MA) whose glass outer envelope had been removed. This was followed by thermal treatment in a vacuum oven (60 °C, < 0.01 mm Hg) for 48 h prior to any polymer analysis to remove residual moisture. Duplicate specimens at each thiol:ene molar ratio were produced.

2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on a PerkinElmer Spectrum Two™ FT-IR in transmission mode. The Perkin Elmer Spectrum 10™ software was used to follow the desired peaks at 1 cm⁻¹ resolution using 32 scans. Thiol (2570 cm⁻¹) and double bond (1630 cm⁻¹) signals were monitored from multiple FTIR spectra taken for each thiol-ene network specimen: (a) before UV curing (i.e. monomer mixture), (b) after UV curing and (c) after thermal treatment in the vacuum oven (48 h, 60 °C, < 0.01 mm Hg). Functional group conversions were determined from the peak areas (normalized to another peak area unaffected by photopolymerization) using the following equation: degree of conversion = $(A_0 - A_t)/A_0$ where A_0 and A_t refer to the normalized peak area before polymerization occurred (A_0) and at a given time t (A_t), respectively. The error in peak area measurements was determined to be less than $\pm 3\%$.

2.6. Thermal analysis

The glass transition temperature (T_g) for each thermally treated thiol-ene network specimen was determined using a TA

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