



Covalently crosslinked 1,2,4-triazolium-containing polyester networks prepared by Michael addition polymerization



Andrea T. De La Hoz, Kevin M. Miller*

Department of Chemistry, Murray State University, 1201 Jesse D. Jones Hall, Murray, KY, 42071, USA

ARTICLE INFO

Article history:

Received 20 May 2015

Received in revised form

24 June 2015

Accepted 30 June 2015

Available online 9 July 2015

Keywords:

Polymerizable ionic liquid

1,2,4-triazolium

Michael addition

ABSTRACT

Michael addition polymerization was used to generate a series of 1,2,4-triazolium-based covalently crosslinked polyester networks. Within the series, the acetoacetate to acrylate ratio as well as the counteranion were varied in an attempt to correlate structural changes with the thermal and mechanical properties of the corresponding networks. An increase in acrylate concentration, as expected, led to an increase in the apparent crosslink density ρ_x as well as glass transition temperature (T_g), thermal stability ($T_{d5\%}$) and rubbery plateau storage modulus (E'). Use of larger, non-coordinating anions such as triflate [OTf] and bis(trifluoromethylsulfonyl)imide [NTf₂] led to a decrease in T_g and E' but an increase in the thermal stability ($T_{d5\%} > 295$ °C). Overall, the thermal and mechanical properties of the 1,2,4-triazolium-containing network, at an acrylate to acetoacetate ratio of 1.4:1.0, were found to be on par with the analogous imidazolium-based network.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Ionic liquids (ILs) are classically defined as poorly coordinated cation-anion pairs that exhibit a melting point below 100 °C. Research in the field of ILs continues to expand due to the tunable physicochemical properties and wide electrochemical window that stems from the large number of cation–anion combinations available [1–4]. While common IL cations include tetraalkylammonium, tetraalkylphosphonium, *N*-pyridinium and *N,N'*-dialkylimidazolium, anions are much more numerous, ranging from halides ([Cl], [Br], [I]) and fluorinated inorganics ([BF₄], [PF₆]) to bulkier, hydrophobic organics ([OTf], [NTf₂]).

The development of polymerizable ionic liquids (PILs) or poly(ionic liquid)s has opened the door to an even wider range of prospective applications [5,6]. PILs are a specific type of IL that contains a polymerizable group, thus allowing for the cationic or anionic center to be constrained within the repeating unit of a polymer chain. PILs have gained a great deal of momentum in polymer and materials science over the last 15 years due to the potential for combining the unique physical, electrochemical and thermal characteristics of ILs with the thermal and mechanical properties of a variety of macromolecular architectures [7–11]. A

few representative applications that have been targeted from PIL research include electromechanical devices [12–14], gas separation and carbon dioxide absorption membranes [15,16] and even stabilizers for silver, gold and nickel nanoparticles [17].

Of all the PILs that have been researched, those containing the imidazolium cation have provided the greatest utility insofar as their synthetic versatility is concerned. In many cases, imidazolium-containing polymers have been found to exhibit improved electrochemical and thermal properties when compared to non-ionic analogs [7,8,11]. While the imidazolium cation remains a standard for many PILs and their applications, there exists a need to explore other cations in order to provide more flexibility with regards to specific application requirements. For example, 1,2,3- and 1,2,4-triazolium ionic liquids have gained recent interest for potential use in 'energy-rich applications' due to the increased nitrogen content in the ring and the large, positive heats of formation [18,19].

Shreeve has reviewed the physical properties of a number of 'energetic' ionic liquids which employed the 1,2,3- or 1,2,4-triazolium cation in combination with high energy anions such as perchlorate or nitrate [20–23]. In general, the ionic liquids had good thermal stability, high densities (>1.50 g/mL) and high combustion energies. Rogers has also recently highlighted the use of triazolium-containing ionic liquids as hypergolic fuels [24]. Studies in our laboratories have focused on the physicochemical and thermal properties of 1-alkyl-4-methyl-1,2,4-triazolium ionic

* Corresponding author.

E-mail address: kmiller38@murraystate.edu (K.M. Miller).

liquids where the *N*-1 alkyl side chain and/or anion was varied [25–27]. All of the ILs were found to exhibit temperature-dependent properties (viscosity, conductivity, density) similar to their imidazolium analogs, however they were less thermally stable.

Despite the promising properties of triazolium-containing ionic liquids, reports concerning PILs containing these cations have been sparse. Polymers containing the 1,2,3-triazole group have become significantly easier to access due to the versatility of the copper-catalyzed azide-alkyne (CuAAC) ‘click’ reaction [28–31]. From this cyclization concept, 1,2,3-triazolium-based polymers have been prepared using either a post-quaternization approach or through direct polymerization of 1-vinyl-1,2,3-triazolium PILs [32,33]. Step-growth architectures containing 1,2,3-triazolium ionic liquids have also been explored by Drockemuller [34–36]. In these cases, an α -azido- ω -alkyne monomer was subjected to CuAAC polyaddition followed by quaternization and anion exchange to gain access to a wide variety of 1,2,3-triazolium-containing polymers. Of these 1,2,3-triazolium-based polymers, one was found to exhibit ionic conductivity and thermal stability comparable to analogous side-chain PILs [35].

Polymers containing the 1,2,4-triazolium ring have been far less studied. In 2008, Shreeve reported the preparation of chain growth polymers based upon PILs containing the 1,2,4-triazolium ring [37]. Polymers were prepared either by post-quaternization and anion exchange of poly(1-vinyl-1,2,4-triazole)s or direct free radical polymerization of the corresponding 1,2,4-triazolium monomer. These novel ‘energetic’ polymers were found to exhibit higher densities and improved thermal stabilities than the corresponding monomers.

The present study attempts to explore the structure-activity relationships of a series of covalently crosslinked polyester networks containing a polymerizable 1,2,4-triazolium-containing ionic liquid. In order to achieve the desired covalently crosslinked network, Michael addition polymerization was employed [38–40]. In short, the Michael addition, as a polymerization technique, typically consists of a base-catalyzed reaction between a Michael donor such as an diacetoacetate and an α,β -unsaturated carbonyl compound such as an diacrylate ester (Michael acceptor). Once the acetoacetate is deprotonated, the resulting enolate anion undergoes a 1,4-conjugate addition to the activated olefin, resulting in a new enolate anion, which is quickly protonated to regenerate the base catalyst (Scheme 1). Each acetoacetate still contains an acidic proton however ($pK_a \sim 13$) and thus, in the presence of excess diacrylate, a second Michael addition will occur, resulting in covalent crosslinking between polyester chains. Michael addition polymerization is an attractive alternative to conventional polyester synthesis due to the relatively mild reaction conditions and the lack of removable byproducts. Additionally, the degree of crosslinking can be easily controlled and uniform molecular weights between crosslink points can be achieved through manipulation of the acrylate to acetoacetate ratio [39].

Our laboratories have recently shown the utility of the Michael addition in the preparation of imidazolium-containing covalently crosslinked networks where the polymerizable IL moiety was incorporated either in sequence or pendant to the polymer backbone [41,42]. In these studies, a number of structural variations (backbone alkyl chain length, counteranion) were investigated and correlations with thermal properties such as glass transition temperature (T_g) and thermal stability ($T_{d5\%}$) were discussed. In short, the T_g of the polymer networks could be easily controlled through manipulation of the imidazolium-containing acetoacetate monomer, the nature of the counteranion and/or the acrylate concentration. The highest thermal stabilities ($T_{d5\%}$) were observed when bulky, non-coordinating counteranions such as

trifluoromethylsulfonate [OTf] or bis(trifluoromethylsulfonyl)imide [NTf₂] were employed.

As part of the present study, two structural variations of the covalently crosslinked, 1,2,4-triazolium-containing polyester networks were investigated: the acrylate to acetoacetate ratio (apparent crosslink density) and counteranion (ionic coordination). The thermal and mechanical properties of the corresponding networks as they relate to these structural deviations are discussed. To the best of our knowledge, this study represents the first report of a step-growth polymer prepared from a 1,2,4-triazolium PIL.

2. Experimental

2.1. Materials

Ethyl-6-bromohexanoate (Acros, 98%), 1,2,4-triazole (Acros, 99%), sodium methoxide (5.4 M solution in methanol, Acros), lithium aluminum hydride (Alfa Aesar, 95%), *tert*-butylacetoacetate (Aldrich, 98%), silver trifluoromethanesulfonate (Acros Organics, 99+ %), lithium bis(trifluoromethylsulfonyl)imide (Acros Organics, 99%), 1,4-butanediol diacrylate (Alfa Aesar, 99+%, stabilized with 50–105 ppm hydroquinone), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Acros, 98%), ethyl ether (BDH Aristar[®], 99.9%), toluene (Pharmco-AAPER, Reagent Grade ACS), and chloroform (Pharmco-AAPER, Reagent Grade ACS) were used without any further purification. Tetrahydrofuran (THF) (99.9%) was purchased as anhydrous from Acros Organics and used as received. An ELGA Purelab[®] Ultra filtration device produced ultrapure water having a resistivity of 18 M Ω -cm. 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; DMSO-*d*₆: ¹H, 2.50 ppm; ¹³C, 39.52 ppm). Elemental analyses were completed by Atlantic Microlab, Inc.

2.2. Synthesis of methyl ester 1

To a 50-mL round-bottomed flask was dissolved 1,2,4-triazole (2.00 g, 29.0 mmol) in anhydrous methanol (25 mL). Sodium methoxide solution (5.4 M in methanol, 5.4 mL, 29.2 mmol) was added and the resulting solution was allowed to stir at room temperature for 60 min. Ethyl-6-bromohexanoate (6.40 g, 28.7 mmol) was then added and the resulting stirred solution was warmed to 60 °C and held for 24 h. The reaction was then concentrated under reduced pressure to afford a mixture, which was taken up into ethyl ether (40 mL) and filtered. The solvent was removed under reduced pressure to afford a light yellow oil. The crude oil was purified using high vacuum distillation (142–145 °C, 1.0 mm Hg) to afford 5.21 g of a clear, colorless oil (92%). ¹H NMR (CDCl₃): δ 1.24 (m, 3H), 1.58 (m, 2H), 1.82 (m, 2H), 2.24 (t, 2H), 3.57 (s, 3H), 4.10 (t, 2H), 7.85 (s, 1H), 8.00 (s, 1H). ¹³C NMR (CDCl₃): δ 23.99, 25.68, 29.24, 33.45, 49.18, 51.39, 142.72, 151.66, 173.61. Anal. calculated for C₉H₁₅N₃O₂, C 54.81, H 7.67, N 21.30; found, C 54.08, H 7.60, N 21.13.

2.3. Synthesis of 1-(6'-hydroxyhexyl)-1,2,4-triazole 2

To a 1-L round-bottomed flask equipped with a magnetic stir bar and a nitrogen inlet was charged lithium aluminum hydride (2.12 g, 55.8 mmol) and anhydrous THF (50 mL). The stirred suspension was cooled to 0 °C and a solution of methyl ester 1 (13.75 g, 69.7 mmol) in anhydrous THF (200 mL) was added dropwise over a 60 min period. After the addition was completed, the mixture was allowed to warm to room temperature and stir for 90 min, followed by careful quenching with 1.0 M HCl. The mixture was then filtered and the solvent was removed under reduced pressure to afford a

Download English Version:

<https://daneshyari.com/en/article/5179803>

Download Persian Version:

<https://daneshyari.com/article/5179803>

[Daneshyari.com](https://daneshyari.com)