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Synthesis and thermal analysis of crosslinked imidazolium-containing polyester networks prepared by Michael addition polymerization

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ABSTRACT

Several new covalently crosslinked imidazolium-containing polyester networks were prepared by Michael addition polymerization to probe how ionic functionality might affect thermal properties such as glass transition temperature (T_g) and thermal decomposition ($T_{d5\%}$). A structure–activity relationship was investigated involving a variation of the methylene spacer and the counteranion of the acetoacetate precursors. Analysis of T_g by differential scanning calorimetry (DSC) indicated that a longer methylene spacer (n = 6 versus 2) resulted in lower T_g values due to increased chain mobility. It was also discovered that the larger the counteranion, the lower the $T_g(Br^- > NO_3^- \approx BF_4^- > CF_3CO_2^- > NTf_2^-)$. Thermogravimetric analysis (TGA) indicated that the thermal stability of the polyesters was inversely related to the basicity of the counteranion used, following the trend: ($NTf_2^- > BF_4^- > NO_3^- \gg Br^-$). The exception was the trifluoroacetate-containing polyester, which exhibited the lowest thermal stability.

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1. Introduction

Ionic liquids have become a major avenue of research over the past decade, resulting in a wide variety of synthetic applications ranging from small molecule organics and solvents to macromolecular architectures. Ionic liquids (ILs) are defined as cation-anion pairs that exhibit melting points less than 100 °C while room temperature ionic liquids (RTILs) are a subclass of ionic liquids that have melting points at or below room temperature (around 25 $^{\circ}$ C) [1]. The attraction of ionic liquids as an area of research can be traced to many factors, including low volatility, high ionic conductivity and large electrochemical windows with the choice of cation-anion pair having a dramatic impact on these properties [2]. Typical cations used in ionic liquids can be divided into four main classes: tetraalkylammonium, tetraalkyphosphonium, N,N'-dialkylimidazolium and N-alkylpyridinium. On the other hand, the variation in anion selection is too numerous to list here but can vary from small inorganic anions such as bromide and chloride to larger organic anions such as trifluoroacetate and bis(trifluoromethylsulfonyl)imide.

The imidazolium group in particular has found a number of synthetic applications due to its relative ease of functionalization. The interest in the preparation of polymerizable ionic liquids containing the imidazolium group has increased significantly over the last decade and several recent reviews have been published [3–5]. Polymers prepared from these imidazolium-containing monomers have been shown, in many cases, to exhibit enhanced thermal stability and enhanced ionic conductivities compared to analogous non-ionic materials [1,2,6]. These properties are partially attributed to a combination of intermolecular ionic hydrogen bonding and π -stacking associated with the aromatic nature of the imidazolium ring [6,7]. The use of imidazolium-containing polymers comprises a wide field of applications of current interest, including electro-active/conducting devices [8,9], gas separation and absorption membranes [10,11] and drug delivery systems for suppressing gene expression [12,13]. As this field continues to grow, the synthetic polymer chemist must begin to decipher the often difficult relationship between structure and desired activity.

The majority of the synthetic applications reported to date involve the free radical polymerization of imidazolium-containing (meth) acrylic or vinyl monomers. Ohno and coworkers, for example, have investigated a variety of synthetic techniques to prepare chain growth polymers which contain a pendant imidazolium group in the hopes of achieving enhanced ionic conductivity [3]. However, it was determined that the ionic conductivity of these initial systems was less than that observed for the monomers themselves, presumably due to decreased segmental motion. Ohno has also reported the use of imidazolium-containing difunctional acrylates in an effort to produce covalently crosslinked networks [14]. The resulting networks exhibited thermal stabilities above 400 °C and improved ionic conductivities.





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Despite many of the recent advances in chain-growth polymers, there remains a need to more clearly elucidate the relationship between changes in polymer structure and the corresponding properties for non-vinyl, step-growth polymers. In a step-growth architecture, the charged imidazolium group can be anchored into the main chain of the polymer rather than remain pendant as is the case with chain-growth polymers. Ohno and coworkers looked into the formation of these types of charged polymers through the hydroboration polymerization of imidazolium-containing dienes with boranes [15] while Long and others have used the Menshutkin reaction, which involves a series of S_N2 reactions, to combine dihalides with tertiary diamines [16,17]. Gibson and coworkers have recently reported the synthesis of a series of linear imidazolium-containing polyesters where imidazolium-containing diols were mixed with diacid chlorides [18]. Many of the semicrystalline polymers that resulted from this work exhibited high conductivity in the soft phase while the crystalline phase provided good mechanical properties.

Our interest is also in the area of imidazolium-containing stepgrowth polyesters in which the charged group is anchored into the backbone of a covalently crosslinked polymer network (Fig. 1). This novel approach will probe how ionic functionality affects the thermal properties of these networks (as opposed to the linear systems reported by Gibson and Long [17,18]). To achieve network formation, the Michael addition reaction will be used as the key polymerization mechanism. The Michael addition involves the reaction of a difunctional Michael donor (imidazolium-containing bisacetoacetate) and a difunctional Michael acceptor (aliphatic diacrylate) in the presence of a base catalyst and remains one of the most versatile and efficient methods of carbon-carbon bond formation in organic chemistry [19]. In addition to its utility in small-molecule organic synthesis, the Michael addition has also been applied to the synthesis of several novel polymeric structures, many of which have been reviewed [20]. The Michael addition is an attractive method for the polymerization of polyester frameworks due to the mild reaction conditions and the synthetic versatility of the starting precursors. It can provide an alternative to traditional polyester synthetic methods since the reactions typically require neither high temperatures nor produce byproducts that must be removed.

The Michael addition typically consists of a base-catalyzed reaction between an enolate anion (Michael donor) and an α , β -unsaturated carbonyl compound such as an acrylate ester (Michael acceptor). The base catalyst varies widely and its selection is strongly dependent upon the acidity of the enolate precursor. Our group and others have found that the use of inorganic bases such as

carbonates or organic bases such as amines is appropriate given that the starting Michael donor contains an acidic acetoacetate ester group ($pK_{a1} \sim 12$) [19,20]. Once deprotonated, the enolate anion undergoes a 1,4-conjugate addition to the acrylate olefin, resulting in a new enolate anion, which is quickly protonated to regenerate the base catalyst (Scheme 1).

The difunctionality of the acetoacetate group allows for network formation when excess acrylate is used. Since there are two acidic protons present on each acetoacetate group, there exists the possibility for disubstitution and thus covalent crosslinking between polymer chains. The pK_a difference between the two protons is sufficiently different enough ($pK_{a1} \sim 12$, $pK_{a2} \sim 13$) that formation of the bis-adduct is limited given equimolar amounts of acrylate and acetoacetate [21]. The use of amine bases as opposed to inorganic bases, however, typically results in higher bis-adduct content due to their increased basicity [19]. Long and co-workers have investigated the effect acrylate concentration has on covalent crosslinking in these systems and its effects on the thermal and mechanical properties of various polyester networks. It was concluded that a 1.4:1.0 acrylate:acetoacetate ratio was appropriate for observing well-defined networks with uniform molecular weights between cross-link points [21]. Additionally, polymers prepared using a 1:1 acrylate:acetoacetate ratio were found to contain low gel content and high sol due to numerous unreacted endgroups. As a result, we targeted a 1.4:1.0 acrylate:acetoacetate ratio to ensure a reasonable degree of gel fraction while avoiding over-crosslinking, which might overshadow any observable effects a change in counteranion might cause.

While the Michael addition has been reported as a polymerization route for step-growth polyesters containing the imidazolium ring, neither thermochemical nor structural analysis was reported [5]. Therefore, it was of interest to us to explore a more detailed structure-activity analysis. In preparing our polyesters, two key structural variations were targeted and the resulting materials analyzed thermally by DSC and TGA (Fig. 1). First, the length of the methylene chain spacer (n = 2 or 6) was changed with the expectation that a longer spacer would result in a more flexible polymer and a lower glass transition temperature (T_g) . Secondly, it was desirable to investigate how the ion pair affinity and/or size of various counteranions could affect thermal properties. Toward this end, a series of anions of different basicities and sizes were chosen: [Br⁻], [CF₃CO₂⁻], [NO₃⁻], [BF₄⁻] and [NTf₂⁻]. While it was anticipated that the incorporation of larger anions would result in a material with inefficient chain packing (thus a lower T_g), the effect (if any) of basicity (and ionic hydrogen bonding capability) could not be hypothesized. Spange [22,23] and Gibson [24]



Fig. 1. Imidazolium-containing Michael addition polyester networks.



Scheme 1. General Michael addition mechanism.

have recently found that the choice of counteranion can have a dramatic effect on ion pair affinity in imidazolium-containing ionic liquids. Based upon their work, counteranions such as bromide [Br⁻] and trifluoroacetate [CF₃CO₂⁻] should exhibit the strongest ion-pairing and the highest affinity to form ionic hydrogen bonds. On the other hand, tetrafluoroborate [BF₄⁻] and bis(trifluoromethylsulfonyl)imide [NTf₂⁻] should display the weakest ion-pairing while the nitrate [NO₃⁻] anion should show an intermediate affinity. While many structure–property relationships in imidazolium-containing ionic liquids have been studied, it remains to be seen if such properties translate over to the macromolecular level.

2. Experimental

2.1. Materials

tert-Butyl acetoacetate (Aldrich, 98%), 1,8-diazabicyclo[5,4,0] undec-7-ene (DBU, Acros, 98%), 1,4-butanediol diacrylate (Alfa Aesar, 99+%), silver nitrate (Acros Organics, 99.85%), lithium bis(trifluoromethylsulfonyl)imide (Acros Organics, 99%), sodium tetrafluoroborate (Acros, 98%), silver trifluoroacetate (Alfa Aesar, 99%), 1,6-hexanediol (Aldrich, 99%), chloroform (Pharmco-AAPER, Reagent Grade ACS), ethyl ether (BDH Aristar[®], 99.9%), ethyl acetate (Pharmco-AAPER, Reagent Grade ACS) and dichloromethane (Pharmco-AAPER, Reagent Grade ACS) were used without any further purification. Acetonitrile (99+%), tetrahydrofuran (THF) (99.9%), N,N-dimethylformamide (DMF) (99.8%) and dimethylsulfoxide (DMSO) (99.9%) were purchased as anhydrous from Acros Organics and used as received. An ELGA Purelab[®] Ultra filtration device produced ultrapure water having a resistivity of 18 MΩ-cm. ¹H and ¹³C NMR spectra were obtained on a JEOL-ECS 400 MHz spectrometer. High resolution mass spectrometry was conducted on a Bruker Daltonics MALDI-TOFMS in the positive ion mode or on a JEOL JMS-700T MStation (ESI) for acetoacetate monomer 21.

2.2. Synthesis of 1,3-bis(2'-acetoacetoxyethyl)imidazolium bromide 5

1,3-Bis(2'-hydroxyethyl)imidazolium bromide **2** was prepared according to a previously published procedure [26]. To a 50-mL round-bottomed flask equipped with a magnetic stir bar and a condenser was charged 1,3-bis(2'-hydroxyethyl)imidazolium bromide **2** (3.70 g, 0.016 mol), *tert*-butyl acetoacetate (24.7 g, 0.16 mol) and acetonitrile (50 mL). The biphasic mixture was vigorously stirred

at reflux for two days. The reaction was then cooled to ambient temperature and the top layer was separated and discarded. The remaining crude product was washed three times with diethyl ether (10 mL each) and then placed in a vacuum oven (<0.1 mm) at 60 °C for 24 h. The reaction yielded 5.76 g of a viscous, orange oil (91%). ¹H NMR (DMSO-d₆): δ 2.15 (s, 6H, CH₃), 3.64 (s, 4H, CH₂), 4.42–4.79 (m, 8H, CH₂), 7.80 (s, 2H, Ar–H^{4,5}), 9.20 (s, 1H, Ar–H²). ¹³C NMR (DMSO-d₆): δ 30.16, 47.96, 49.36, 62.45, 122.74, 137.16, 166.89, 201.66. HR MS (MALDI-TOF, *m/z*): [M–Br]⁺ calculated for C₁₅H₂₁N₂O₆, 325.1400; found, 325.1411.

2.3. Synthesis of 1,3-bis(6'-acetoacetoxyhexyl)imidazolium bromide 6

1,3-Bis(6'-hydroxyhexyl)imidazolium bromide **4** was prepared by following a previously published procedure [18]. To a 250-mL round-bottomed flask equipped with a magnetic stir bar and a condenser was charged 1,3-bis(6'-hydroxyhexyl)imidazolium bromide **4** (10.5 g, 0.03 mol), *tert*-butyl acetoacetate (19.0 g, 0.12 mol) and acetonitrile (100 mL). The stirred solution was brought to reflux and held for 4 h. The solvent, tert-butanol byproduct, and excess tert-butyl acetoacetate were then removed by distillation under reduced pressure, yielding 15.0 g of a viscous, yellow oil (97%). ¹H NMR (DMSO-d₆): δ 1.21–1.35 (m, 8 H, CH₂), 1.55 (m, 4H, CH₂), 1.78 (m, 4H, CH₂), 2.15 (s, 6H, CH₃), 3.58 (s, 4H, CH₂ on AcAc group), 3.32 (t, J = 7 Hz, 4H, AcAcO–CH₂), 4.13 (t, J = 7 Hz, 4H, N-CH₂), 7.79 (s, 2H, Ar-H^{4,5}), 9.21 (s, 1H, Ar-H²). ¹³C NMR (DMSOd₆): δ 24.44, 25.04, 27.80, 29.00, 30.08, 48.70, 49.66, 64.20, 122.48, 135.94, 167.30, 201.66. HR MS (MALDI-TOF, m/z): [M-Br]⁺ calculated for C₂₃H₃₇N₂O₆, 437.2652; found, 437.2663.

2.4. Synthesis of 1,3-bis(2'-acetoacetoxyethyl)imidazolium nitrate 7

To a 25 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1,3-bis(2'-acetoacetoxyethyl)imidazolium bromide **7** (0.50 g, 1.23 mmol) in deionized water (5 mL). To this stirred solution was added a solution of silver nitrate (0.21 g, 1.24 mmol) in deionized water (5 mL). A precipitate formed immediately. Stirring continued overnight at room temperature then the solids were filtered. The solvent was removed under reduced pressure to afford 0.41 g (85%) of the target compound as a viscous, light red oil. ¹H NMR (DMSO-d₆): δ 2.14 (s, 6H, CH₃), 3.63 (s, 4H, CH₂ on AcAc group), 4.44 (m, 8H), 7.78 (s, 2H, Ar–H^{4,5}), 9.18 (s, 1H, Ar–H²). ¹³C NMR (DMSO-d₆): δ 30.10, 48.00, 62.45, 122.78, 137.04, 166.90, 201.67. HR MS (MALDI-TOF, *m/z*): [M–NO₃]⁺ calculated for C₁₅H₂₁N₂O₆, 325.1400; found, 325.1411.

2.5. Synthesis of 1,3-bis(2'-acetoacetoxyethyl)imidazolium bis(trifluoromethylsulfonyl)imide **8**

To a 25 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1,3-bis(2'-acetoacetoxyethyl)imidazolium bromide 7 (0.50 g, 1.23 mmol) in deionized water (5 mL). To this stirred solution was added a solution of lithium bis(trifluoromethylsulfonyl) imide (0.37 g. 1.25 mmol) in deionized water (5 mL). After several minutes, an orange oil was observed at the bottom of the flask. Chloroform (5 mL) was added to the flask and the mixture was stirred vigorously at room temperature overnight. The organic phase was then separated, washed twice with DI water and the solvent removed under reduced pressure to afford 0.68 g (91%) of the target compound as a light yellow oil. ¹H NMR (DMSO-d₆): δ 2.14 (s, 6H, CH₃), 3.64 (s, 4H, CH₂ on AcAc group), 4.45 (m, 8H), 7.79 (s, 2H, Ar-H^{4,5}), 9.15 (s, 1H, Ar–H²). ¹³C NMR (DMSO-d₆): δ 30.03, 48.06, 49.35, 62.49, 119.54 (q, J = 308 Hz, CF₃), 122.76, 137.18, 166.94, 201.71. HR MS (MALDI-TOF, *m*/*z*): [M–NTf₂]⁺ calculated for C₁₅H₂₁N₂O₆, 325.1400; found, 325.1401.

2.6. Synthesis of 1,3-bis(6'-acetoacetoxyhexyl)imidazolium trifluoroacetate **9**

To a 25 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1,3-bis(6'-acetoacetoxyhexyl)imidazolium bromide 8 (1.50 g, 2.9 mmol) in DI water (8 mL). To this stirred solution was added silver trifluoroacetate (0.70 g, 3.2 mmol), dissolved in DI water (2 mL). The resulting mixture (a precipitate formed immediately) was vigorously stirred overnight at room temperature. The mixture was then filtered and extracted with ethyl acetate. The organic phase was separated, washed twice with DI water and the solvent was removed under reduced pressure to afford 1.35 g (84%) of a yellow oil. ¹H NMR (DMSO-d₆): δ 1.20–1.40 (m, 8H, CH₂), 1.56 (m, 4H, CH₂), 1.78 (m, 4H, CH₂), 2.17 (s, 6H, CH₃), 3.59 (s, 4H, CH₂ on AcAc group), 4.03 (t, *J* = 7 Hz, 4H, AcAcO–CH₂), 4.15 (t, J = 7 Hz, 4H, N–CH₂), 7.80 (s, 2H, Ar–H^{4,5}), 9.20 (s, 1H, Ar– H²). ¹³C NMR (DMSO-d₆): δ 24.56, 25.06, 27.77, 29.14, 48.76, 49.58, 64.22, 117.23 (q, J = 300 Hz, CF₃), 122.46, 135.93, 167.27, 201.63. HR MS (MALDI-TOF, m/z): $[M-CF_3CO_2]^+$ calculated for $C_{23}H_{37}N_2O_6$, 437.2652; found, 437.2647.

2.7. Synthesis of 1,3-bis(6'-acetoacetoxyhexyl)imidazolium nitrate 10

To a 15 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1,3-bis(6'-acetoacetoxyhexyl)imidazolium bromide **8** (0.50 g, 0.97 mmol) in chloroform (5 mL). To this stirred solution was added a solution of silver nitrate (0.17 g, 1.00 mmol) in deionized water (2 mL). A precipitate formed immediately. The mixture was allowed to stir overnight at room temperature. The solids were then filtered and the solvent was removed under reduced pressure to afford 0.47 g (94%) of the nitrate **10** as a light yellow oil. ¹H NMR (DMSO-d₆): δ 1.19–1.38 (m, 8 H, CH₂), 1.56 (m, 4H, CH₂), 1.78 (m, 4H, CH₂), 2.17 (s, 6H, CH₃), 3.58 (s, 4H, CH₂ on AcAc group), 4.04 (t, *J* = 7 Hz, 4H, AcAcO-CH₂), 4.16 (t, *J* = 7 Hz, 4H, N-CH₂), 7.80 (s, 2H, Ar-H^{4,5}), 9.19 (s, 1H, Ar-H²). ¹³C NMR (DMSO-d₆): δ 24.61, 25.04, 27.80, 29.13, 48.75, 49.58, 64.23, 122.43, 135.94, 167.26, 201.66. HR MS (MALDI-TOF, m/z): $[M-NO_3]^+$ calculated for $C_{23}H_{37}N_2O_6$, 437.2652; found, 437.2655.

2.8. Synthesis of 1,3-bis(6'-acetoacetoxyhexyl)imidazolium bis(trifluoromethylsulfonyl)imide **11**

To a 50 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1,3-bis(6'-acetoacetoxyhexyl)imidazolium bromide **8** (2.50 g, 4.83 mmol) in chloroform (20 mL). To this stirred solution was added a solution of lithium bis(trifluoromethylsulfonyl)imide (1.46 g, 5.07 mmol) in deionized water (5 mL). The mixture was vigorously stirred overnight at room temperature. The organic phase was separated, washed twice with DI water and then the solvent was removed under reduced pressure to afford 3.23 g (93%) of a light yellow oil. ¹H NMR (DMSO-d₆): δ 1.21–1.40 (m, 8 H, CH₂), 1.57 (m, 4H, CH₂), 1.79 (m, 4H, CH₂), 2.17 (s, 6H, CH₃), 3.59 (s, 4H, CH₂ on AcAc group), 4.04 (t, *J* = 7 Hz, 4H, AcAcO–CH₂), 4.15 (t, *J* = 7 Hz, 4H, N–CH₂), 7.79 (s, 2H, Ar–H^{4.5}), 9.17 (s, 1H, Ar–H²). ¹³C NMR (DMSO-d₆): δ 25.05, 27.75, 29.14, 30.09, 48.76, 49.57, 64.21, 119.49 (q, *J* = 322 Hz, CF₃), 122.43, 135.92, 167.30, 201.61. HR MS (MALDI-TOF, *m/z*): [M–NTf₂]⁺ calculated for C₂₃H₃₇N₂O₆, 437.2652; found, 437.2661.

2.9. Synthesis of 1,3-bis(6'-acetoacetoxyhexyl)imidazolium tetrafluoroborate **12**

To a 50 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1,3-bis(6'-acetoacetoxyhexyl)imidazolium bromide 8 (3.00 g, 5.79 mmol) in acetone (30 mL). To this stirred solution was added sodium tetrafluoroborate (0.67 g, 6.09 mmol). Precipitate formation was observed within 30 min of stirring at room temperature. The mixture was allowed to continue to stir overnight. The solids were then filtered and solvent removed under reduced pressure. The residue was dissolved in chloroform, washed twice with DI water and solvent removed under reduced pressure, resulting in 2.59 g (85%) of a light yellow oil. ¹H NMR (DMSO-d₆): δ 1.21–1.39 (m, 8 H, CH₂), 1.57 (m, 4H, CH₂), 1.79 (m, 4H, CH₂), 2.17 (s, 6H, CH₃), 3.58 (s, 4H, CH₂ on AcAc group), 4.03 (t, *J* = 7 Hz, 4H, AcAcO-CH₂), 4.14 (t, I = 7 Hz, 4H, N-CH₂), 7.79 (s, 2H, Ar-H^{4,5}), 9.17 (s, 1H, Ar-H²). ¹³C NMR (DMSO-d₆): δ 25.01, 27.70, 29.05, 29.99, 48.73, 49.54, 64.10, 122.48, 135.83, 167.37, 201.62. HR MS (MALDI-TOF, m/z): $[M-BF_4]^+$ calculated for C₂₃H₃₇N₂O₆, 437.2652; found, 437.2653.

2.10. Synthesis of 1,6-bis(acetoacetoxy)hexane 21

1,6-Hexanediol (10.0 g, 0.085 mol), *tert*-butyl acetoacetate (53.5 g, 0.34 mmol) and toluene (100 mL) were charged to a twonecked 250 mL flask, equipped with a short-path distillation head, receiving flask, and magnetic stir bar. The stirred solution was warmed to 150 °C and held for 4 h while the *tert*-butanol/toluene azeotrope distilled. The remaining volatiles were then removed under vacuum to achieve 23.2 g of a clear, colorless oil (95%). ¹H NMR (CHCl₃): δ 1.30–1.38 (m, 4 H, CH₂), 1.57–1.63 (m, 4H, CH₂), 2.22 (s, 6H, CH₃ on AcAc group), 3.41 (s, 4H, CH₂ on AcAc group), 4.08 (t, *J* = 7 Hz, 4H, AcAcO–CH₂). ¹³C NMR (CHCl₃): δ 25.43, 28.33, 30.20, 50.09, 65.24, 167.21, 200.69. HR MS (ESI, *m/z*): [M]⁺ calculated for C₁₄H₂₂O₆, 286.1416; found, 286.1428.



Scheme 2. Synthesis of 1,3-bis(2-hydroxyethyl)imidazolium bromide 2.



Scheme 3. Synthesis of 1,3-bis(6-hydroxyhexyl)imidazolium bromide 4.

2.11. Synthesis of 1,3-bis(2'-acetoacetoxyethyl)benzene 22

Synthesis of 1,3-bis(2'-hydroxylethyl)benzene followed a previously reported procedure [25].

2.12. Michael addition polymerization procedure

Due to the incompatibility of acetoacetate monomers **5**, **7** and **8** with the diacrylate monomer, polymerizations were completed in solvent. In a typical procedure, 1,3-bis(2'-acetoacetoxyethyl)imidazolium bromide **5** (0.80 g, 1.97 mmol) and 1,4-butanediol diacrylate (0.55 g, 2.76 mmol, 1.4 M equiv.) were dissolved in dichloromethane (2.5 mL). DBU catalyst (27 mg, 2 wt%) was then added and the resulting solution was mixed vigorously for 2 min by hand. The solution was then transferred to a TeflonTM mold and cured at ambient temperature for 48 h, followed by curing in an oven at 60 °C for an additional 48 h. To ensure complete solvent removal, the sample was further placed in a vacuum oven (<0.1 mm Hg) for 24 h at 50 °C.

All other acetoacetate monomers were prepared as solventless reactions. In a typical procedure, 1,3-bis(6'-acetoacetoxyhexyl) imidazolium bromide **6** (1.50 g, 2.90 mmol) and 1,4-butanediol diacrylate (0.80 g, 4.06 mmol, 1.4 \bowtie equiv.) were mixed by hand in a vial. To this solution was added the DBU catalyst (46 mg, 2 wt%). The resulting solution was vigorously mixed by hand for an additional 1–2 min then quickly transferred to a TeflonTM mold and cured at ambient temperature for 24 h, followed by oven curing at 60 °C for an additional 48 h. A dramatic increase in viscosity indicated that gelation occurred within approximately 3–4 min. All polymer samples appeared as clear films with varying degrees of yellow color.

2.13. Evaluation of residual bromide by ion chromatography

The quantity of residual bromide in the synthesized acetoacetate ionic liquids was determined by ion chromatography (ICS-110, Dionex) under the following conditions: $4.5 \text{ mm} \text{CO}_3^{-7}/1.4 \text{ mm} \text{HCO}_3^{-7}$ eluent concentration, 1.2 mL/min flow rate, 31 mA suppressor current. After chromatographic calibration via aqueous standards prepared by serial dilution of 1000 ppm Br⁻ stock (from sodium bromide, Aldrich, >99.5%), 10–15 mg of each ionic liquid was dissolved in 1 mL of methanol and injected [27]. The amounts of residual bromide in each ionic liquid were determined to be less than 0.01% *w/w*.

2.14. Thermal characterization of acetoacetate monomers

All acetoacetate monomers were stored in a vacuum oven at 50 °C prior to thermal testing. Differential scanning calorimetry (DSC), with a heating rate of 10 °C/min on 5–10 mg samples, was performed using a TA Instrument Q2000 differential scanning calorimeter. Glass transition temperatures (T_g) were determined by the inflection point of the curve observed from the second heating cycle. Thermal stabilities were studied under a constant nitrogen flow using a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min. Onset of thermal decomposition ($T_{d5\%}$) was determined at the temperature at which 5% weight loss was observed.

2.15. Thermal characterization of polymer films

Differential scanning calorimetry (DSC), with a heating rate of 3 °C/min on 5–10 mg samples, was performed using a TA Instrument Q2000 differential scanning calorimeter. Glass transition temperatures (T_g) were determined by the inflection point of the curve observed from the second heating cycle. Thermal stabilities were studied under a constant nitrogen flow using a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min. Onset of thermal decomposition ($T_{d5\%}$) was determined at the temperature at which 5% weight loss was observed.



Scheme 4. Synthesis of acetoacetate ionic liquid monomers.

3. Results and discussion

3.1. Synthesis of imidazolium-containing acetoacetate monomers

Dihydroxylated imidazolium ionic liquids **2** and **4** were targeted for functionalization into the corresponding acetoacetate monomers. 1,3-Bis(2'-hydroxyethyl)imidazolium bromide **2** was prepared by first reacting imidazole with sodium hydride followed by addition of ethyl chloroacetate (Scheme 2) [26]. The resulting ester **1** was then reduced with lithium aluminum hydride followed by reaction with 2-bromoethanol to afford diol **2**.

1,3-Bis(6-hydroxyhexyl)imidazolium bromide **4** was prepared following a procedure reported by Gibson [18]. Reaction of imidazole with 6-bromo-1-hexanol in the presence of sodium hydroxide in refluxing tetrahydrofuran afforded 6-hydroxyhexylimidazole **3** (Scheme 3). Further reaction with another equivalent of 6-bromo-1-hexanol provided the desired diol **4**.

Transesterification with *tert*-butylacetoacetate was next performed with diols **2** and **4** in acetonitrile to afford the corresponding bisacetoacetates **5** and **6** (Scheme 4). The use of acetonitrile allowed for an easy removal of the *tert*-butanol byproduct via short-path azeotropic distillation. The functionalization of the diols via transesterification with tBAA provides a more facile and safer route than previous techniques involving diketene or 2,2,6-trimethyl-4H-1,3-dioxin-4-one [29]. Bisacetoacetates **5** and **6** were then subjected to the appropriate anion exchange reactions (AgNO₃, LiNTF₂, NaBF₄ or AgCO₂CF₃) to afford ionic liquids **7–12** [18,26]. All acetoacetate monomers were checked for purity by ¹H and ¹³C NMR as well as HR MS. Ionic liquids **7–12** were checked for residual bromide by ion chromatography, the results of which indicated <0.01% *w/w* present in each sample.

Table 1

Thermal properties of imidazolium-containing acetoacetate monomers.

Entry	Monomer	Anion	п	$T_{g}(^{\circ}C)$	$T_{d5\%}$ (°C)
1	5	Br^{-}	2	-26.7	162
2	7	NO_3^-	2	-32.6	183
3	8	NTf_2^-	2	-37.2	225
4	6	Br-	6	-49.2	159
5	9	$CF_3CO_2^-$	6	-61.8	163
6	10	NO ₃	6	-59.2	182
7	11	NTf_2^-	6	-65.8	235
8	12	BF_4^-	6	-61.1	210

3.2. ¹H NMR and thermal analyses of the imidazolium-containing acetoacetate monomers

¹H NMR studies were completed on the series of acetoacetate monomers where n = 6 in order to determine the effect of counteranion choice on the chemical shift of the imidazolium ring protons. As has been recently described by Gibson and others, the chemical shift values of these protons can be directly correlated to the ion affinity of the counteranion [23,24,28]. In general, the stronger the ion affinity (basicity) of the counteranion, the further downfield the chemical shifts of the imidazolium ring protons will appear. This dependence is especially evident for the proton between the nitrogens of the ring (labeled as H²), which is the most acidic (Fig. 2). ¹H NMR can thus be used as a tool to determine the ion affinity between the counteranion and the imidazoliumcontaining cation.

The solvent used in the ¹H NMR studies also effects the extent of the chemical shift of the imidazolium ring protons [24,28]. In solvents such as D_2O or DMSO- d_6 , the cations and anions are moderately to highly solvated and thus the hydrogen bonding



Fig. 2. ¹H NMR comparison of acetoacetate ionic liquid monomers (n = 6) in acetone-d₆.



Scheme 5. Michael addition polymerization.

associated with the H^2 proton will be decreased, resulting in a signal at higher field. The opposite effect is observed for acetoned₆, which has a lower solvating power, resulting in tighter ion pairs and a further downfield chemical shift.

A comparison of ¹H NMR chemical shift values for the imidazolium ring protons in acetone-d₆ is provided in Fig. 2. As expected, the choice of counteranion has a large effect on the chemical shift values, in particular those corresponding to the acidic H^2 proton. The bromide [Br⁻] 6 and trifluoroacetate [CF₃CO₂⁻] 9 ionic liquids showed the largest downfield shifts at 10.45 and 10.14 ppm, respectively, due to their apparent strong affinity to forma hydrogen bond with the H^2 proton. The bis(trifluoromethanesulfonyl)imide $[NTf_2^-]$ **11** and tetrafluoroborate $[BF_4^-]$ 12 ionic liquids provided the smallest downfield shifts at 9.14 and 9.12, respectively, due to weaker ion affinities. The nitrate $[NO_3^-]$ **10** ionic liquid was observed to have an intermediate effect, with a chemical shift of 9.79 ppm. Overall, the chemical shift of the H² proton increased with increasing basicity and ion affinity of the anion selected: $Br^->CF_3CO_2^->NO_3^->BF_4^-\approx NTF_2^-$ [23]. The effect of counteranion selection on the chemical shift of other two protons on the imidazolium ring (H⁴ and H⁵) is observable and shows a similar trend, but to a lesser degree.

All imidazolium-containing acetoacetate monomers were roomtemperature ionic liquids with low T_g values, as determined by DSC (Table 1). In general, use of the longer alkyl chain length (n = 6 as opposed to n = 2) resulted in monomers that exhibited lower T_g



values. A possible correlation was observed between counteranion size and T_{g} . Use of the larger bis(trifluoromethanesulfonyl)imide [NTf₂⁻] counteranion led to the lowest thermal transitions while the highest T_{g} values were observed when the smaller bromide [Br⁻] anion was employed. The remaining anions (n = 6) displayed T_{g} values that were within experimental error of one another ($\pm 2 \degree C$), thus preventing further clarification of this possible trend.

Comparison of the TGA data indicated that monomers with the shorter alkyl chain length (n = 2) resulted in greater thermal stability ($T_{d5\%}$), given the same counteranion, presumably due to restriction of chain mobility. A trend between anion affinity (basicity) and thermal stability, given the same alkyl chain length, was observed. Stronger bases such as bromide [Br⁻] and trifluoroacetate [CO₂CF₃⁻] exhibited poorer thermal stabilities while the use of the weakest counteranion bis(trifluoromethanesulfonyl) imide [NTf₂⁻] resulted in the greatest thermal resistivity.

3.3. Michael addition polymerization and gel fraction analysis

The imidazolium-containing acetoacetate monomers were polymerized by allowing them to react with 1,4-butanediol diacrylate in the presence of 2 wt% DBU (Scheme 5). Acetoacetate monomers **5**, **7** and **8** were found to be insoluble with the diacrylate and thus the polymerizations were completed in dichloromethane. All other acetoacetate monomers were polymerized neat.



Scheme 6. Non-ionic acetoacetoacetate monomers.

The samples were allowed to cure at ambient temperature for 48 h then placed in an oven for 48 h at 60 °C. Polymerizations completed in solvent were further subjected to curing in a vacuum oven at 60 °C for an additional 48 h. All polymerizations resulted in clear, flexible films. A rapid build in viscosity for the solventless systems indicated that gelation occurred within approximately 3–4 min of catalyst addition.

In addition to the imidazolium-containing systems, two nonionic Michael addition networks (aliphatic- and aromatic-based) were prepared and analyzed for reference (Scheme 6). The aliphatic, non-ionic bisacetoacetate precursor 21 was prepared through the transesterification of commercially available 1,6hexanediol with tert-butyl acetoacetate (tBAA) following standard transesterification conditions [21] while the aromatic, non-ionic bisacetoacetate monomer 22 was prepared following a published procedure [25]. Once the monomers were isolated and analyzed for purity, they were reacted with 1,4-butanediol diacrylate in a 1.4:1.0 acrylate: acetoacetate ratio in the presence of catalytic DBU (2 wt%). Polymer networks were prepared without solvent and were allowed to cure at room temperature for 24 h followed by 48 h at 60 °C to ensure complete reaction. As with the imidazoliumcontaining polyester networks, gelation occurred within approximately 3–4 min as evident from a rapid rise in viscosity.

The cured network films were subjected to Soxhlet extraction using dichloromethane and gel fraction and % swelling analyses were completed. A high gel fraction (>95%) was achieved for all polymer samples, regardless of charge, methylene spacer length or counteranion selection (Table 2). Analysis of the swelling data indicated that inclusion of larger anions such as bis(trifluoromethanesulfonyl)imide $[NTf_2^-]$ or trifluoroacetate $[CF_3CO_2^-]$ into the polymer network led to higher swelling than either the non-ionic networks or the ionic networks containing smaller anions (bromide $[Br^-]$, nitrate $[NO_3^-]$ and tetrafluoroborate $[BF_4^-]$). This finding could be attributed to poorer chain packing when larger counteranions are employed. An additional finding was that ionic polymer samples utilizing the monomers with the longer methylene spacers (n = 6 versus n = 2, given the same counteranion) swelled more, which could be attributed to increased chain mobility and flexibility.

3.4. Thermal analysis of imidazolium-containing Michael addition polyester networks

The extracted polymer films were kept in a vacuum oven for 24 h at 50 °C, then analyzed by DSC to determine glass transition temperature (T_g) and TGA to establish thermal stability $(T_{d5\%})$. The results of these analyses are presented in Table 3. In general, the $T_{\rm g}$ values for the polyester networks were higher than those of the corresponding acetoacetate monomers. The T_g values of the networks appeared to correlate with the size of the counteranion in a similar fashion to what was observed for the acetoacetate monomers, although the trend is more well-defined with the polymer networks. Polymers with the smaller bromide [Br⁻] anion provided the highest T_g values while the use of larger anions such as trifluoroacetate $[CF_3CO_2^-]$ or bis(trifluoromethylsulfonyl)imide $[NTf_2^-]$ resulted in the lowest T_g values. It is theorized that the larger anions may prevent effective chain packing and perhaps act more as a plasticizer, resulting to a lower thermal transition. This hypothesis is supported in part by the work Gibson reported on linear imidazolium-containing polyesters [18].

It was also observed that an increase in the size of the methylene spacer from n = 2 to n = 6 lead to a decrease in the T_g (given the same counteranion), presumably due to an increase in chain mobility and flexibility. In comparing the thermal transitions of the imidazolium-containing polyester networks with the non-ionic analogs **21** and **22**,

Table 2

Gel	fraction	and %	swelling	data f	or i	midazoliu	im-conta	aining	polv	meric	networl	ks ^a .
									F J			

Entry	Polymer	Anion	n	Gel fraction	% Swelling
1	21	_	_	$97.2\pm0.6\%$	$160 \pm 7\%$
2	22	_	_	$96.5\pm0.2\%$	$173\pm9\%$
3	13	Br^{-}	2	$97.8\pm0.2\%$	$158\pm7\%$
4	14	NO_3^-	2	$96.8\pm0.5\%$	$169\pm5\%$
5	15	NTf_2^-	2	$97.0\pm0.3\%$	$195\pm4\%$
6	16	Br^{-}	6	$95.8\pm0.5\%$	$175\pm4\%$
7	17	$CF_3CO_2^-$	6	$97.7\pm0.7\%$	$218\pm3\%$
8	18	NO ₃	6	$97.5\pm0.2\%$	$186\pm8\%$
9	19	NTf_2^-	6	$95.5\pm0.5\%$	$239\pm2\%$
10	20	BF_4^-	6	$98.5\pm0.5\%$	$195\pm3\%$

^a Average of duplicate runs in CH₂Cl₂.

a clear trend was not observed. While networks in which the shorter alkyl chain (n = 2) exhibited enhanced T_g values when compared with either of the non-ionic systems, those which used the longer alkyl chain (n = 6) exhibited *lower* T_g values than the non-ionic, aromatic system, but comparable to the non-ionic, aliphatic system. It is possible that the use of the longer methylene spacer could lead to networks that are too flexible to observe any effects that ionic bonding may have in these systems.

Analysis of the non-ionic and imidazolium-containing polyester networks by TGA to determine thermal stability ($T_{d5\%}$) was performed, the results of which are also included in Table 3. In general, the non-ionic polyester networks exhibited greater thermal stability than the imidazolium-containing analogs. The overall decrease in thermal resistance for the ionic systems is thought to be due to the basicity of the counteranion, which could catalyze decomposition, however a comprehensive analysis of decomposition products and mechanism was not completed as part of this work. Within the imidazolium-containing networks, polymers with the longer methylene spacer (n = 6) provided greater thermal stability than those with the shorter spacer (n = 2), given the same anion ($[X^-] = [Br^-], [NO_3^-]$ or $[NTf_2^-]$).

Unlike the glass transition temperature values, the magnitude of $T_{d5\%}$ does not seem to correlate to the size of the counteranion. Instead, it appears that ion affinity (basicity) dictates thermal stability. Networks where bromide [Br⁻] was employed (a counteranion with a strong ion affinity) proved to be more sensitive to thermal decomposition, resulting in low $T_{d5\%}$ values. However, polymers in which the bis(trifluoromethylsulfonyl)imide [NTf₂⁻] anion was used exhibited the highest resistance to thermal decomposition, presumably due to having the lowest ion affinity. The exception to this trend appears to be the trifluoroacetate-containing polyester, which had the lowest thermal stability of the series when n = 6, despite an ion affinity comparable to the nitrate [NO₃⁻] anion [23]. The $T_{d5\%}$ values observed as part of this study are generally lower than those recently reported for other mono- and bisimidazolium-containing step-growth polymers

Table 3	
DSC and TGA data for imidazolium-containing Michael addition networks ^a .	

Entry	Polymer	Anion	n	$T_{\rm g}(^{\circ}{\rm C})$	$T_{ m d5\%}(^{\circ} m C)$
1	21	_	_	-13.9	265
2	22	-	-	6.3	295
3	13	Br	2	22.4	196
4	14	NO_3^-	2	18.6	208
5	15	NTf_2^-	2	11.8	262
6	16	Br ⁻	6	3.2	202
7	17	$CF_3CO_2^-$	6	-12.9	191
8	18	NO_3^-	6	-4.1	224
9	19	NTf_2^-	6	-18.5	248
10	20	BF_4^-	6	-2.6	240

^a Average of duplicate runs. Error \pm 2 °C.

[17,18] and significantly lower than Ohno's imidazolium-containing acrylate copolymer networks, which achieved thermal stabilities over 400 $^{\circ}$ C [14].

4. Conclusions

This paper reports on the synthesis of several imidazoliumcontaining acetoacetate monomers and their corresponding polyester networks, prepared as a result of using Michael addition polymerization. As part of this structure-activity study, two variables were considered: the length of the methylene spacer and the choice of the counteranion.¹H NMR analysis of the imidazoliumcontaining acetoacetate monomers indicated that the chemical shift of the H² proton of the imidazolium ring increased with increasing basicity and hydrogen bonding capability of the anion selected: $Br^- > CF_3CO_2^- > NO_3^- > BF_4^- \approx NTf_2^-$. Thermal analysis of the acetoacetate monomers by DSC indicated a possible trend between counteranion size and T_g values, with the largest [NTf₂] anion resulting in the lowest thermal transitions. However, many of the T_{g} values were found to be within experimental error. The ion affinity (basicity) of the counteranion had a profound effect on thermal decomposition as determined by TGA while use of the weakest counteranion $[NTf_2^-]$ resulting in the best thermal stability

The resulting polyester networks were then analyzed thermally by DSC and TGA. Analysis of the glass transition temperatures by DSC indicated that the imidazolium-containing polyesters with the longer methylene spacer (n = 6) exhibited lower T_g values, presumably due to an increase in chain mobility. A decrease in T_g was observed (NTf_2 < CF_3CO_2 < BF_4 < NO_3 < Br^-) with an increase in the size of the counteranion (given the same cation). There does not appear to be any correlation between T_g and the ion affinity (basicity) of the counteranion. Comparison with two nonionic Michael addition networks gave mixed results, with systems in which the longer methylene spacer and/or larger counteranion was employed led to T_g values lower or similar to the aliphatic, nonionic system. Networks in which the shorter methylene spacer (n = 2) was used in combination with a smaller counteranion (Br⁻ and NO₃⁻) led to higher T_g values.

With regards to thermal stability by TGA, all imidazoliumcontaining polyester networks demonstrated an onset of thermal decomposition of >190 °C, with the polymers containing the bromide or trifluoroacetate anion exhibiting the lowest thermal stability while those containing the bis(trifluoromethylsulfonyl) imide anion showing the highest thermal stability. It appears that the thermal stability of these polyesters, with the exception of the trifluoroacetate-containing network, inversely correlates with the basicity of the counteranion used. In general, the ionic networks exhibited lower thermal stability than either the aliphatic- or aromatic-based non-ionic polyester network.

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