

# Crosslinked imidazolium-containing polyester networks containing a pendant imidazolium group: Swelling studies and thermal properties



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## ABSTRACT

A series of covalently crosslinked polyester networks containing a pendant imidazolium group was prepared by Michael addition polymerization in order to probe how structural variations in cation and anion affect thermal properties such as glass transition temperature ( $T_g$ ) and thermal decomposition ( $T_{d5\%}$ ). Analysis of network  $T_g$  values by differential scanning calorimetry (DSC) indicated that, for the aromatic-based series of cations, larger counteranions such as triflate [ $\text{TfO}^-$ ] and bis(trifluoromethylsulfonyl)imide [ $\text{NTf}_2^-$ ] led to the lowest  $T_g$  values. However, it was determined that no correlation between  $T_g$  value and either anion size or basicity was evident for the aliphatic-based series of cations. Thermal stability ( $T_{d5\%}$ ) of the polyester networks, as determined by thermogravimetric analysis (TGA), was inversely related to the basicity of the counteranion used, regardless of cation substructure. Networks that employed the least basic anions, namely hexafluorophosphate [ $\text{PF}_6^-$ ] or bis(trifluoromethylsulfonyl)imide [ $\text{NTf}_2^-$ ], exhibited the highest thermal stabilities ( $>260^\circ\text{C}$ ).

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## 1. Introduction

Ionic liquids (ILs) are a class of poorly-coordinating salts which result from combinations of bulky, organic cations such as imidazolium or tetraalkylphosphonium and anions that range from small, inorganic species such as chloride [ $\text{Cl}^-$ ] and bromide [ $\text{Br}^-$ ] to larger, organic ions such as trifluoromethanesulfonate (triflate) [ $\text{TfO}^-$ ] and bis(trifluoromethylsulfonyl)imide [ $\text{NTf}_2^-$ ] [1–6]. Interest in ionic liquids has grown exponentially over the past two decades due to their numerous prospective applications in the areas of organic reaction solvents [1–4,7–9] and polymer science [10–12]. Due to the vast range of cation and anion structures available, ionic liquid properties can often be fine-tuned for a targeted application. In creating these “designer” ionic liquids, correlating physico-chemical properties with intermolecular interactions between ions as well as solvent–solute interactions is paramount. However, correlations of these interactions with solvent parameters such as polarity, conductivity or viscosity are difficult due to complex cation–anion interactions (dipole, Coulombic, electron pair donor–acceptor and hydrogen bonding). Although structure–property relationships of ionic liquids continue to be an area of focus, it is generally agreed upon that a “good” ionic liquid is one in which the

cations and anions do not act as ion pairs but rather as interpenetrating quasi-lattices [13].

In an attempt to extrapolate the properties of ionic liquids to macromolecular frameworks, a number of novel polymeric architectures have been prepared through the polymerization of ionic liquid-containing monomers [10–12]. Imidazolium-containing polymers in particular have found a great deal of merit in applications such as electroactive devices, transducers and actuators [14–20], gas separation and absorption membranes [21,22] and drug delivery systems for suppressing gene expression [23,24]. In many cases, imidazolium-containing polymers have exhibited enhanced thermal stability and improved ionic conductivities compared to analogous non-ionic materials [10–12,14], the properties of which have been attributed to a combination of intermolecular ionic hydrogen bonding and  $\pi$ – $\pi$  interactions between imidazolium rings [14,25].

The majority of work in the area of imidazolium-containing polymers has focused on the free radical polymerization of the corresponding (meth)acrylic or vinyl monomers. Ohno has been very active in this area and a variety of synthetic architectures which contain a pendant imidazolium group have been produced as a result of the efforts of his research group [19,20,26,27]. Many of these ionomers have been shown to exhibit reasonable ionic conductivities. However, these values were not as high as those observed for the monomers themselves, presumably due to decreased segmental motion from the lack of imidazolium ring

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mobility. Imidazolium-containing difunctional acrylates have also been employed by Ohno and coworkers in an effort to produce covalently crosslinked networks [28]. The resulting networks exhibited thermal stabilities above 400 °C and improved ionic conductivities. Other research groups have attempted to improve the electroactive properties of imidazolium-containing chain-growth polymers by focusing their efforts on correlating cation and anion structural variations with conductivity and dielectric response. For example, Colby and coworkers have used dielectric spectroscopy to study the ionic conduction and dielectric response of homopolymers prepared from imidazolium-containing acrylates [29,30] while Long and coworkers have investigated the role that charge placement plays on the thermal, mechanical and conductive properties of ABA triblock copolymers containing a pendant imidazolium moiety [31].

Imidazolium-containing step-growth architectures have been explored to a much lesser extent despite the attraction of having the charged imidazolium group anchored into the main chain of the polymer (rather than pendant as is the case with the majority of chain-growth polymers). Ohno and coworkers investigated the synthesis of step-growth frameworks through the hydroboration polymerization of imidazolium-containing dienes with boranes [32] while Long and others have used a series of Menshutkin ( $S_N2$ ) reactions by combining dibromoalkanes with 1,1'-(1,4-butanediyl) bis(imidazole) [33,34]. Long and coworkers have also recently prepared a number of imidazolium containing polyurethanes [35]. Dielectric spectroscopy demonstrated that, upon incorporation of ionic liquid electrolytes, a general increase in conductivity of the polyurethane membranes was observed. A series of linear imidazolium-containing polyesters where imidazolium-containing diols were mixed with diacid chlorides was reported by Gibson and coworkers [36]. Many of the semicrystalline polymers that resulted from this work exhibited good mechanical properties in the crystalline phase while the soft phase provided high conductivity.

Research in our group has focused primarily on the preparation of imidazolium-containing step-growth polyester networks that combine covalent and ionic crosslinking (Fig. 1). From these networks, we can attempt to correlate variations in cation and anion structure with core thermal properties such as  $T_g$  (glass transition temperature) and  $T_{d5\%}$  (thermal decomposition temperature). To achieve network formation, we utilize the Michael addition as the key polymerization step. The Michael addition has been an attractive approach for polyester network synthesis due to the mild reaction conditions, synthetic versatility of the starting precursors and the lack of appreciable byproducts [37]. In a typical polymerization, a diacetoacetate (Michael donor) and diacrylate (Michael acceptor) are employed, however there exists the possibility for disubstitution when excess acrylate is added due to the two acidic protons present on each acetoacetate group, thus resulting in covalent crosslinking between polymer chains. While the  $pK_a$  difference between the two protons is sufficiently different enough ( $pK_{a1} \sim 12$ ,  $pK_{a2} \sim 13$ ) to minimize bis-adduct formation (given equimolar amounts of acrylate and acetoacetate) [38], the use of

amine bases often results in higher bis-adduct content due to increased basicity [39]. Based upon previously reported work completed in collaboration with Long, we 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 while avoiding over-crosslinking, which might overshadow any changes in thermal properties that result from subtle changes in cation or anion structure [38].

We recently reported the synthesis and thermal features of a series of covalently crosslinked, imidazolium-containing polyester networks where the imidazolium group was anchored directly into the backbone of the polyester chain [40]. As part of this structure-activity study, changes in the structure of the cation and anion were made in order to correlate thermal properties such as glass transition temperature ( $T_g$ ) and thermal stability ( $T_{d5\%}$ ). It was determined that longer methylene spacers within the polyester chain as well as larger counteranions such as trifluoroacetate [ $CF_3CO_2^-$ ] and bis(trifluoromethylsulfonyl)imide [ $Ntf_2^-$ ] led to depressed  $T_g$  values. Thermal stability, however, was directly dependent upon the basicity of the counteranion, with stronger anions such as bromide [ $Br^-$ ] resulting in poor  $T_{d5\%}$  values.

We have now turned our attention to networks in which the imidazolium group is *pendant* to the main polymer chain of the network, thus (theoretically) increasing the degree of freedom in which the ring has to develop ionic interactions. In order to achieve this synthetically, we have employed a trifunctional aromatic or aliphatic core as part of the acetoacetate precursor (Fig. 2). As a part of this study, it was also desirable to investigate how ion pair affinity and/or size of various counteranions would affect thermal properties. As a result, for both the aliphatic and aromatic-based networks, a series of anions ([ $Br^-$ ], [ $MsO^-$ ], [ $NO_3^-$ ], [ $TfO^-$ ], [ $PF_6^-$ ] and [ $Ntf_2^-$ ]) of different basicities and sizes were employed. It was anticipated that trends in thermal measurements would be similar to those observed for the previously reported networks in which the imidazolium ring was anchored into the polymer chain.

## 2. Experimental

### 2.1. Materials

*tert*-Butylacetoacetate (*t*BAA, Aldrich, 98%), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU, Acros, 98%), 1,4-butanediol diacrylate (Alfa Aesar, 99+%), *N*-methylimidazole (Acros Organics, 99%), silver mesylate (Acros Organics, 99%), silver nitrate (Acros Organics, 99.85%), silver triflate (Acros Organics, 99+%), lithium bis(trifluoromethylsulfonyl)imide (Acros Organics, 99%), potassium hexafluorophosphate (Acros Organics, 99%), toluene (Pharmco-AAPER, Reagent Grade ACS), chloroform (Pharmco-AAPER, Reagent Grade ACS) and dichloromethane (Pharmco-AAPER, Reagent Grade ACS) were used without any further purification. Acetonitrile (99+%) 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 $\Omega$ -cm.  $^1H$  and  $^{13}C$  NMR spectra were obtained on a JEOL-ECS 400 MHz spectrometer at ambient temperature. Chemical shift values are reported in parts per million relative to using residual solvent signals as internal standards (acetone- $d_6$ :  $^1H$ , 2.05 ppm;  $^{13}C$ , 29.84 ppm or DMSO- $d_6$ :  $^1H$ , 2.50 ppm;  $^{13}C$ , 39.52 ppm). All ionic liquid monomers were stored in a vacuum oven at 60 °C for 48 h prior to spectroscopic analyses. (5-(Bromomethyl)-1,3-phenylene)dimethanol **1** was prepared following a procedure published by Fréchet et al. [41] while 2-(bromomethyl)-2-methylpropane-1,3-diol **4** was prepared according to a process reported by Bowden [42].

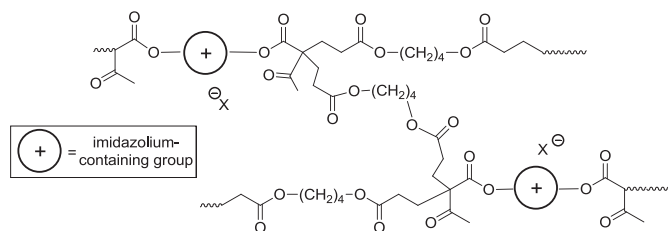


Fig. 1. Imidazolium-containing Michael addition polyester network.

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