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Short communication

Enhanced photopolymerization rate & conversion of 1-vinylimidazole in the presence of lithium bistriflimide

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ABSTRACT

The high solubility of lithium bistriflimide ($LiTf_2N$) in 1-vinylimidazole can be utilized to significantly improve overall monomer conversion and photopolymerization rate. We observed that $LiTf_2N$ was miscible with 1-vinylimidazole in stoichiometric equivalence corresponding to a final mixture that is >75% by mass $LiTf_2N$. The rate and conversion of vinyl groups was dynamically monitored using ATR-FTIR. In comparison with the 1-vinylimidazole control, all samples containing $LiTf_2N$ exhibited increased monomer conversion and all except the 1:1 sample displayed a more rapid initial reaction rate. The specific effects of the rate and conversion vary with the molar ratio of 1-vinylimidazole to $LiTf_2N$ and may be a consequence of coordination complexes between 1-vinylimidazole and the Li^+ cation. These results may warrant further investigation into the utility of coordinated, polymerizable ionic liquids that are readily formed from polar organic monomers and $LiTf_2N$.

In response to the difficulties experienced in achieving high monomer conversion in bulk photopolymerizations, several methods have been proposed to decrease mass transport limitations in the reaction mixtures. Among the most prevalent of the techniques developed are those in which intermolecular interactions are utilized to increase the local monomer concentration. Previous studies have demonstrated that both inter- and intramolecular forces affect the rate of polymerization [1–3]. Although many of these studies have examined interactions between conventional monomers and solvents, ionic liquids (ILs) have also been considered as media for radical polymerizations. ILs, generally defined as salts with melting points <100 °C, are a class of materials with distinct properties that have led to their proposed use in a variety of applications [4–8]. Among these characteristics is the ability of ILs to self-organize into polar and non-polar regions [9,10]. This behavior may lead to increased local concentrations of polymerizable functionalities that explain the observed increases in polymerization rates [11,12].

ILs based on coordinated metal cations ions have also been developed around a weakly coordinating anion coupled with a coordinated metal cation. Coordinated ILs have been synthesized containing Zn^{2+}, Cu^+, Cu^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, and Li^+ metal centers and a variety of alkanolamine, ether, nitrile, and ferrocene ligands [13–20], and have been found to display many of the desirable properties associated with conventional ILs while affording synthetic ease.

We are aware of few applications where coordinated ILs have been examined as monomers for radical polymerizations, although these ILs have multiple characteristics which make them suitable for such an application. Coordinated ILs containing polymerizable ligands may have the potential to display the enhanced reaction kinetics characteristic with the advantage that the salt could be extracted

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from the resulting polymer. In addition, previous studies have indicated that salts containing Zn^{2+}, Al^{3+}, Li^{+}, and Mg^{2+} cations can form complexes with monomers that increase both the rate of reaction and monomer conversion in radical polymerization [21–25]. Yet, as the salts used in these studies contained strongly coordinating anions (e.g. Cl^{-}), the reactions were either performed in solution or using a large stoichiometric excess of monomer. However, the results of these experiments suggest that ILs formed from weakly coordinating anions and metal cations coordinated to polymerizable ligands should enhance the reaction kinetics of these monomers.

Recently, there have been two reports on the polymerization kinetics of coordinated ILs containing methacrylate monomers and lithium triflate (LiOTf) [26,27]. However, the primary focus of these studies was on the determination of the reaction rate parameters as opposed to the effect of salt concentration on the monomer conversion and reaction rate profiles [26,27]. In addition, these studies used LiOTf, a salt with a melting point > 300 °C and were performed at monomer:salt stoichiometries greater than 1:1 or with a co-solvent such as ethylene carbonate [26,27].

Here, we report on the behavior of a coordinated IL monomer formed between $LiTf_2N$ and 1-vinylimidazole (Vim), and the chemical structures of these compounds are displayed in Fig. 1a and b, respectively.

Poly(vinylimidazole) (poly(Vim)) has multiple applications including: photolithography, adhesive development, and in fuel cell membranes [28]. In addition, multiple authors have noted potential biomedical applications polymers containing imidazole functionalities [28,29]. These applications, in addition to its logical connection to imidazolium-based ILs, make Vim a rational basis to begin the study of coordinated ILs in radical polymerization. To examine the photopolymerization kinetics and polymer-salt separation performance in this system, a series of coordinated ILs were synthesized by solubilizing 1:1, 2:1, 3:1, and 4:1 mol/mol ratios of Vim:$LiTf_2N$ using only heat (no co-solvent). 1 wt% of a photoinitiator was then added and small amounts of the ILs were photopolymerized using an Omnicure UV lamp attached to a Perkin–Elmer Spectrum Two ATR-FTIR spectrometer (see Supporting Information). FTIR spectra were collected at set time intervals for 180 min and the conversions of the reaction mixtures were determined through integration of the areas of the absorption peaks corresponding to the vinyl group in the monomer (see Supporting Information). The reaction rate of the monomers was estimated using density measurements obtained for mixtures of $LiTf_2N$ and the structurally similar compound, 1-ethylimidazole (see Supporting Information).

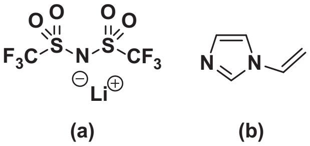

Fig. 1. Chemical structures of (a) $LiTf_2N$ and (b) 1-vinylimidazole.

The coordinated IL composition had a substantial effect on the reaction kinetics of the monomer. As displayed in Fig. 2, the addition of $LiTf_2N$ to the reaction mixture resulted in an increase in the overall vinyl group conversion relative to neat Vim. Generally, bulk radical polymerization reactions proceed through a series of three stages, the last of which occurs as mass transfer limitations cause the reaction rate to decrease until the monomer conversion changes little with time. As displayed in Fig. 1, all reaction mixtures examined in the study entered this phase of the reaction by ~60 min, indicating that the value of the conversion at 180 min is essentially that of the maximum conversion. Although vinyl group conversion in the coordinated ILs was greater at all compositions than neat 1-vinylimidazole (~75% conversion), the greatest final conversion was found for the 1:1 mixture for which 100% reaction of the vinyl groups was achieved. The 2:1 and 3:1 monomer to salt mixtures were found to display similar kinetics, both attaining a final conversion of ~95%. However, a larger Vim:$LiTf_2N$ ratio of 4:1 resulted in a further 5% decrease in conversion to ~90%.

In addition to the effect of this polymerization method on the final monomer conversion, the photopolymerization kinetics were also affected by the presence of $LiTf_2N$. Using a numerical method, the reaction rates for the polymerization of the ILs were calculated for the first 5 min and compared to that of neat Vim. The results are displayed in Fig. 3.

With the exception of the 1:1 mixture, the initial reaction rates of the coordinated ILs were at least 15% greater than the starting reaction rate of Vim. However, following the first minute, the reaction rates of these solutions decreased drastically, and, after the third minute, the reaction rates of these mixtures were ~75% less than that of Vim. In contrast to the kinetic behavior displayed by the 2:1, 3:1, and 4:1 ILs (and to a lesser extent, neat Vim), the reaction rate of 1:1 monomer-salt sample decreased gradually over the examined time interval. Despite its initial reaction rate of 0.55 M min^{-1} (~80% less than the initial rate of the polymerization of Vim), the relatively low decrease in the reaction rate with time resulted in a reaction rate greater than that of the other solutions after 4 min and ~95% conversion after 14 min. A summary of these calculations is presented in Tables 1a and 1b.

Macroscopically, we noted that the polymer produced from neat Vim maintained the strong odor associated with the monomer and was far more fragile than the polymers produced in the presence of $LiTF_2N$. Taken alone, these results do not necessarily indicate the presence of coordinated IL monomers. However, conductivity measurements made using a similar imidazole compound, 1-ethylimidazole, confirm the mixtures are conductive (i.e. cation/anion separation) (see Supporting Information).

The conversion and reaction rate profiles of all coordinated IL compositions examined were found to differ from those of the bulk monomer with all but the 1:1 Vim:$LiTf_2N$ system displaying a greater initial reaction rate and final conversion than the Vim control. The unique reaction kinetics displayed by the coordinated ILs may be explained by the self-organizing effects of the substances on the reaction. Both spectroscopic and computational studies