



Enhancing the pre-polymerization coordination of 1-vinylimidazole

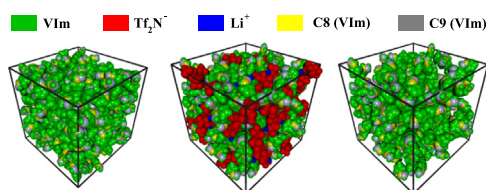
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HIGHLIGHTS

- The polymerization of 1-vinylimidazole is found to be enhanced with LiTf_2N addition.
- Molecular dynamic simulations are used to analyze the structure of these mixtures.
- The local coordination of key reaction sites is found to be enriched by the LiTf_2N .
- The experimental reaction enhancement is attributed to local coordination effects.

GRAPHICAL ABSTRACT



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ABSTRACT

Recent experimental investigations have found that the rate and conversion of the photopolymerization of 1-vinylimidazole (VIm) can be significantly accelerated with the addition of lithium bistriflimide (LiTf_2N). However, the underlying molecular-level interactions responsible for this phenomenon are unclear. The two components, VIm and LiTf_2N , are miscible over a wide range of concentrations and form liquid phases at ambient temperature, and if the fundamental behavior of this mixture can be clearly quantified, there are significant opportunities for tuning the polymerization dynamics, polymer structure, and properties. In this work, molecular dynamics (MD) simulations are used to model the underlying pre-polymerization structure of VIm+ LiTf_2N mixtures at several different concentrations. It is found that the Li^+ enhances the site-site interactions of key functional groups involved in the polymerization, and this is suggested to play a major role in the experimentally-observed enhancement of the polymerization behavior.

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1. Introduction

Poly(vinylimidazole) (poly(VIm)) is a polymer with an imidazole pendant that can be produced via radical polymerization methods as a homopolymer from 1-vinylimidazole (VIm) or as a copolymer with co-monomers, such as vinyl acetate, acrylonitrile and divinylbenzene. Poly(VIm) is hydrophilic and features pendant imidazole groups that can act as bases, nucleophiles and/or

chelating agents and thus has been investigated for a broad range of applications, such as coating electrodes (Yildiz et al., 2014), fuel cell membranes (MacAodha et al., 2013), and separations applications including CO_2 adsorption (Farjaminezhad et al., 2014; Corazza et al., 2014) and the adsorption of metal ions (Wang et al., 2012).

Recently, we explored the photopolymerization of bulk (i.e. solvent-free) VIm as a means of producing poly(VIm). One of the challenges encountered during the bulk photopolymerization of 1-vinylimidazole is that the polymerization is relatively slow, with an ultimate monomer conversion $\sim 80\%$, which results in 20%

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unreacted residual VIm within the poly(VIm) (Whitley et al., 2014). Such behavior in bulk photopolymerization is not unexpected, as it is well known that such limitations are the consequence of mass transport limitations due to increasing viscosity as the polymer chains grow, and the unreacted monomer diffuses ever more slowly to the propagating radical (Whitley et al., 2014).

This auto-deceleration effect is the result of poor reactant diffusion, so various methods of monomer organization have been introduced to reduce the effects of mass transfer on polymerization kinetics (Tajima and Aida, 2000; O'Brien et al., 1998; Gin et al., 2001). In addition to several solid state polymerization methods, multiple liquid crystal phases have been used as media for structured polymerizations (Tajima and Aida, 2000; O'Brien et al., 1998; Gin et al., 2001; Matsumoto and Yokoi, 1998; Matsumoto et al., 1998). These polymerizations, which have been completed in both thermotropic and lyotropic liquid crystals, display improved rates of polymerization, with the specific kinetic behavior dependent on the degree of order in the liquid crystal phase (Guymon and Bowman, 1997; Lester and Guymon, 2002; 2000; Lester et al., 2001).

Recently, ionic liquids (ILs) have also received attention as media for radical polymerizations. ILs are typically considered to be salts with melting temperatures below 100 °C and have many unique and tunable properties that have motivated a great deal of research (Han and Armstrong, 2007; Bara et al., 2010; Earle et al., 2006). In addition, both theoretical and experimental studies have demonstrated the ability of these substances to aggregate into polar and non-polar domains at the nanometer scale (Canongia and Padua, 2006; Russina and Triolo, 2012). As well as their potential applications in organic synthesis, ILs are also attractive as solvents in radical polymerizations due to their ability to increase the rate of propagation and termination of these reactions while also increasing the molecular weight of the resulting polymers (Hallett and Welton, 2011; Kubisa 2009; Hong et al., 2002; Harrisson et al., 2002; Schmidt-Naake et al., 2007; Woecht et al., 2008).

However, few studies have examined the use of ILs containing coordinated ions in polymerization reactions. Past studies have explored the polymerization of methyl methacrylate (MMA), acrylonitrile, and VIm with the addition of Lewis acids with different metal cations (Matsumoto and Nakamura, 1999; Bamford et al., 1957; Tazuke and Okamura, 1969). These experimental studies have suggested that certain metals are likely to form a ligand complex with monomers and smaller polymer chains in solution, and these specific interactions can enhance the coordination of specific molecules, leading to increased polymerization rates. Lithium bistriflimide (LiTf₂N) is a bulky salt that exhibits significant solubility in organic solvents, and it has been shown to facilitate the polymerization of MMA (Noble et al., 2014) at relatively low concentrations as well as 1-vinylimidazole at higher monomer:salt ratios (Whitley et al., 2014). Both studies indicate an

increase in reaction rate and monomer conversion when LiTf₂N is added.

In this work, we use molecular dynamics (MD) simulations to explore the underlying molecular interactions responsible for the reaction enhancement in mixtures of 1-vinylimidazole (VIm) coordinated to the LiTf₂N solvent. In computational studies, the thermophysical properties of ILs have been an important topic for quite some time, and LiTf₂N has been modeled many times in solution within ILs (Li et al., 2012; Haskins et al., 2014; Hayamizu et al., 2010).

In this study, eight different mixtures of VIm and LiTf₂N solutions were simulated using MD, with molar ratios of VIm to LiTf₂N ranging from 1:1 to 10:1. These ratios were chosen based on the availability of experimental data (Whitley et al., 2014), which were used as initial simulation benchmarks. By comparing experimental properties to those calculated from the simulations of VIm in solution with LiTf₂N, refined molecular models are generated and used to identify the key interactions in these mixtures, in order to understand the polymerization enhancement (Figs. 1 and 2).

Using our MD simulations, we find that the Li⁺ cation enhances the local coordination of the VIm monomers, leading to pre-polymerization structures that are likely to favor enhanced polymerization rates and overall monomer conversion due to the proximity of the vinyl groups. In addition, similar simulations were performed by replacing the Tf₂N[−] group with two other anions, tetrafluoroborate (BF₄[−]) and hexafluorophosphate (PF₆[−]), in order to compare how VIm and Li⁺ coordinate with different anions. Also Li⁺ was replaced with Na⁺ to compare how the coordination of VIm behaves when exposed to different cations. The comparisons show that higher coordination can occur around the larger cation, but LiTf₂N addition still yielded the highest local concentration of VIm molecules in favorable pre-polymerization configurations.

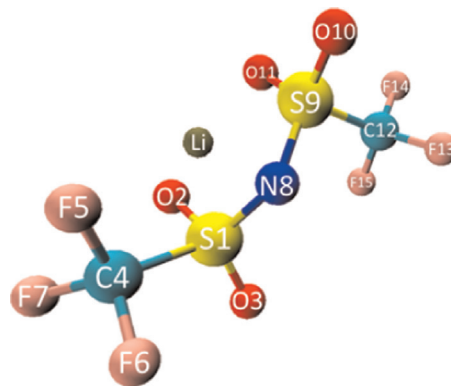


Fig. 2. Illustration of the LiTf₂N model, including labels of the individual sites.

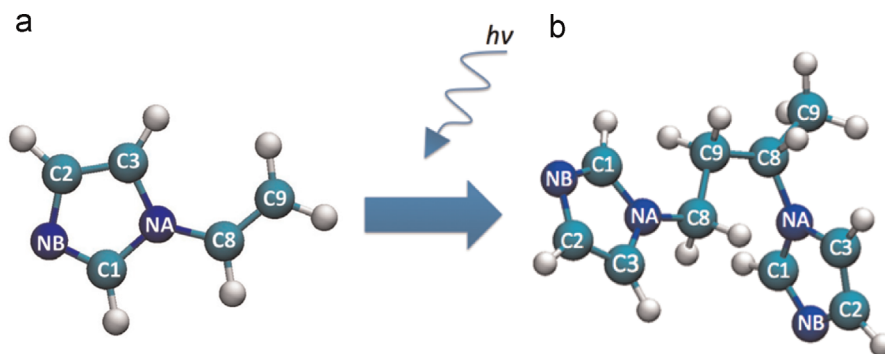


Fig. 1. Illustration of the photopolymerization of (a) VIm to (b) a VIm dimer, including the labels of individual sites. The reaction primarily occurs through the C8–C9 sites.

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