Anionic Ring-Opening Polymerizations of *N*-Sulfonylaziridines in Ionic Liquids

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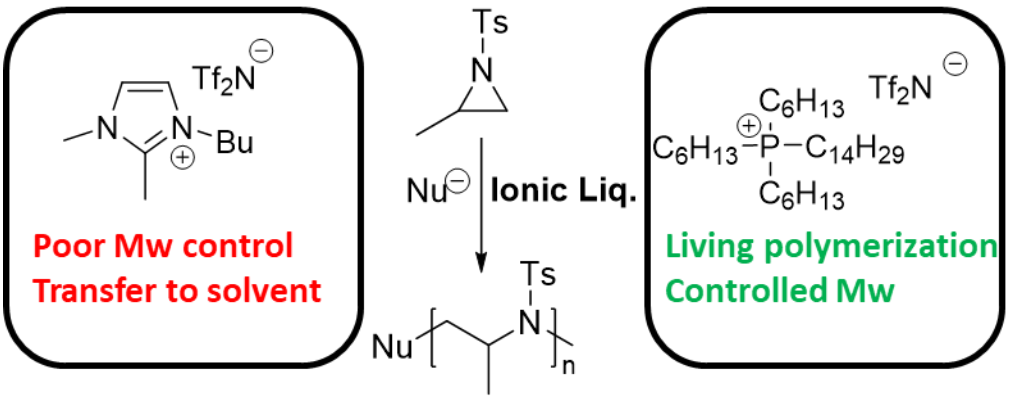


Abstract: The anionic ring-opening polymerization (AROP) of sulfonylaziridines in ionic liquids (ILs) is reported. In imidazolium ILs, the polymerization of 2-methyl-*N*-tosylaziridine (**TsMAz**) is not controlled due to poor solubility at higher degrees of polymerization and apparent solvent-

transfer reactions. In the phosphonium IL [$P_{6,6,6,14}$][Tf_2N], the polymerization of **TsMAz** is controlled and living, and capable of sequential block copolymer synthesis. The polymerization of **TsMAz** is first order with respect to monomer in ILs, with rates slower than observed in traditional aprotic polar solvents (*e.g.,* DMF). Molecular dynamics simulations were used to compare DMF vs IL solutions consisting of **BuN(K)Ts** (as a model for the propagating chain end). The molecular dynamics simulations suggest better monomer/anion organization in DMF and poorer mobilities in the ILs; both are consistent with observed reduction in polymerization rates in the ILs compared to DMF.

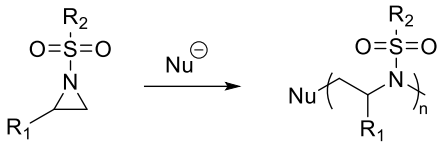
Introduction:

Ionic liquids (ILs) are widely used as green solvents due to their low vapor pressures, unusual solubilizing properties, and extensive electrochemical windows.[1] In the context of polymer synthesis, reports on radical based polymerizations in ILs have shown accelerated polymerization rates, impacts on tacticity, and increased molecular weights compared to non-IL media.[2-5] Cationic polymerizations have also been explored, including examples of polyisobutylenes,[3] poly(*p*-methylstyrene),[6] and polyisoprene.[7]

Although not as tolerant towards functional groups as their radical counterparts,[8] living anionic polymerizations allow for the synthesis of polymer chains of targeted molecular weights, narrow molecular weight distributions, excellent control of polymer end groups, and are ideal for the synthesis of complex polymer architectures.[9-11] However, anionic polymerizations in ILs have been largely unexplored due to the nucleophilic nature of the propagating anions. These strong nucleophiles are sufficiently basic to degrade common ILs through deprotonation pathways such as Hoffman eliminations.[12]

Of the few examples of anionic polymerizations reported in ILs, none are controlled. Kubisa,[13] Watanabe,[14] and Takahara and Hirai[15] have all reported on the anionic polymerization of methyl methacrylate (MMA) in imidazolium ILs. The groups of Kubisa and Watanabe both reported low yields and poor control for the polymerization of MMA in ILs, attributed to premature termination of the anionic polymerization via reaction with the IL. More recently, Takahara and Hirai noted higher yields of PMMA compared to earlier work on MMA IL polymerizations, which interestingly was isotatic, but the resulting polymer had high dispersity, indicative of a lack of control. Vijayaraghavan reported the polymerization of styrene initiated by s-butyl lithium in wet $[P_{6,6,6,14}][Tf_2N]$[16]; how the styrene anion was able to propagate in the presence of water is unclear.[16] Furthermore, the polymerization of polystyrene in $[P_{6,6,6,14}][Tf_2N]$ exhibited a significant onset delay (many hours), high dispersities, and molecular weights inconsistent with the monomer to initiator ratio. We believe that the possibility of a radical mechanism in the polystyrene IL polymerization was not fully excluded.

Sulfonylaziridines are a relatively new class of anionic ring-opening polymerization (AROP) capable monomers first reported by Bergmen and Toste[17] and later expanded to include a diverse array of functionalities and architectures (Scheme 1).[18-22] The AROP of sulfonylaziridines is facilitated by the electron withdrawing sulfonyl group, which stabilizes the propagating anion. Sulfonylaziridines are typically polymerized in polar, aprotic solvents such as DMSO and DMF. The related sulfonylazetidines have also been reported to polymerize in NMP.[23-26,27-29] Recently, the copolymerization of a sulfonylaziridine with phthalic anhydride to a poly(ester amide) was reported[18] and the grafting of polysulfonamides from cellulose, with applications in oil-water separations, was demonstrated.[30]



Scheme 1. Synthesis of poly(sulfonylaziridines) via AROP of sulfonylaziridines.

Sulfonylaziridines are intriguing as monomers, as they are able to polymerize under less-stringent conditions than are typically associated with anionic polymerizations.[31-33] In 2018, Wurm reported that the anionic ring-opening polymerization of methylsulfonylaziridines proceeds in wet DMF.[34] The presence of water in the AROP of sulfonylaziridine is possible because the pKa of the sulfonylamides is comparable to that of water and hydroxide is a poor nucleophile for the sulfonylaziridine ring-opening. Therefore, chain transfer to water occurs only minimally during the AROP of sulfonylaziridines in the presence of water. The relatively low basicity of the initiator and the propagating anions of these sulfonylaziridines makes them ideal candidates for polymerizations in ionic liquids. We now report that the polymerizations of sulfonylaziridines proceed in ILs and that in some cases, the polymerizations are living and controlled. This study is motivated by a desire to better understand the impact of ILs on anionic polymerizations. Furthermore, polysulfonylaziridines[17,35,36] (and the related polysulfonylazetidines)[27], often have poor solubility during the polymerization process, and the use of IL solvents may improve the solubility of these polymers.

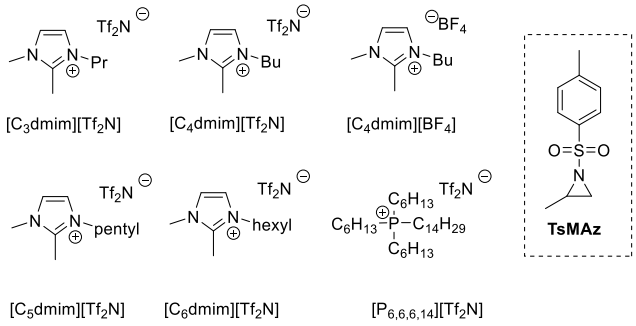
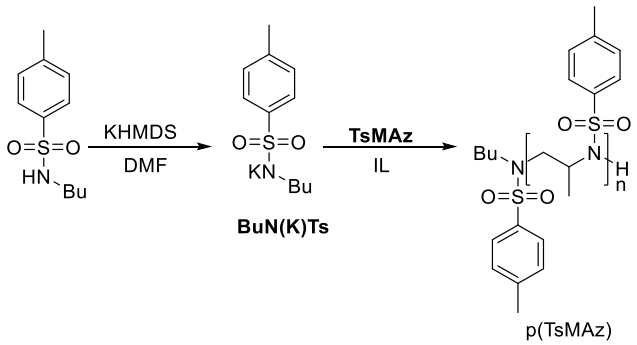


Chart 1. The ionic liquids found to facilitate the AROP of **TsMAz**.

Results and Discussion

The AROP of **TsMAz** (2-methyl-*N*-tosylaziridine) were attempted in a selection of imidazolium and phosphonium ILs using **BuN(K)Ts** as initiator (Chart 1 and Scheme 2). **TsMAz** was chosen as a representative sulfonylaziridine as it is the most studied sulfonylaziridine[19] monomer. Recent work by K. Guo and co-workers showed that halides are capable of initiating sulfonylaziridine AROP and therefore we mostly focused on ILs with bistriflimide anions so as to avoid halide containing ILs.[24] Solutions of the initiators were prepared in DMF using KHMDS and **BuN(K)Ts**, respectively. The initiators were separately prepared in DMF to avoid reactions between KHMDS (which deprotonated the initiator) and the ILs before being added to the IL solutions of **TsMAz**. After polymerizations were complete, they were terminated and the polymer precipitated, by adding the reaction mixtures to methanol.



Scheme 2. Polymerization of **TsMAz** in ILs.

We observed that **TsMAz** undergoes AROP in all the ILs listed in Chart 1. The ^{1}H and ^{13}C NMR spectra of p(TsMAz) synthesized in [C_4dmim][Tf_2N] is identical to that of p(TsMAz) formed under the conditions originally reported by Bergman and Toste (DMF, 50 °C)[17] and indicates that the IL does not impact tacticity (Figures S1, S2). Attempts at controlling the molecular weight of p(TsMAz) synthesized in [C_4dmim][Tf_2N] by varying the monomer to initiator ratio had some

success. The M_n (vs. a PS standard) of p(TsMAz) increased with increasing [**TsMAz**]:**[BuN(K)Ts]** at low ratios, but at monomer:initiator ratios beyond 60, loss of molecular control is observed. We propose that the loss of molecular weight control is in part due to the poor solubility of p(TsMAz) as the polymer begins to precipitate at higher [**TsMAz**]:**[BuN(K)Ts]** ratios. SEC traces of p(TsMAz) formed in [C_4dmim][Tf_2N] showed relatively narrow dispersities at lower [**TsMAz**]:[**BuN(K)Ts**], but shoulders become visible in the SEC traces at higher monomer to initiator ratios (and in some cases, the traces were multimodal) (Figure S15).

MALDI-TOF mass spectra of p(TsMAz) in [C_4dmim][Tf_2N] provide evidence of chain transfer reactions as two distinct polymer series with repeat unit masses of 211 amu were observed (Figure 1). One of these series is attributed to the anticipated **BuN(K)Ts** initiated and proton terminated chains. The masses of the second series are consistent with p(TsMAz) chains that are initiated by 1,2-dimethylimidazole moieties and terminated with protons. The relative intensity of series attributed to 1,2-dimethylimidazole initiated polymer chains increases at higher [**TsMAz**]:**[BuN(K)Ts]** ratios (Figure 1). For example, a MALDI-TOF mass spectrum of p(TsMAz) synthesized with a [**TsMAz**]:**[BuN(K)Ts]** ratio of 25:1 consist almost exclusively of signals initiated by **BuN(K)Ts** (Figure 1A). In contrast, the MALDI-TOF mass spectrum of p(TsMAz) synthesize with a [**TsMAz**]:**[BuN(K)Ts]** ratio of 60:1 is dominated by 1,2-dimethylimidazole initiated polymer chains (Figure 1B). Attempts to further reduce the presence of 1,2-dimethylimidazole initiated chains by changing the reaction conditions were not successful.

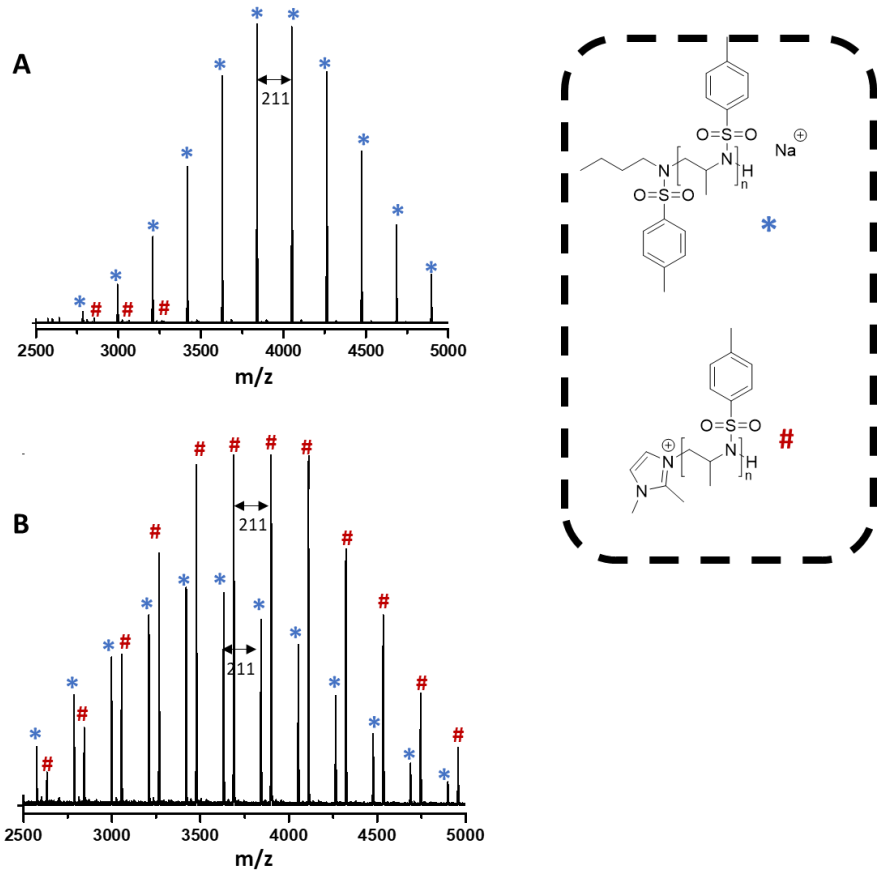


Figure 1. **A)** MALDI-TOF mass spectrum of p(TsMAz) synthesized in [C_4dmim][Tf_2N] IL with [**TsMAz**]:**[BuN(K)Ts]** = 25:1. The spectrum is dominated by signals assignable to **BuN(K)Ts** initiated polymer chains (labeled with *). **B)** MALDI-TOF mass spectrum of p(TsMAz) synthesized in [C_4dmim][Tf_2N] IL with [**TsMAz**]:**[BuN(K)Ts]** = 60: 1. The major series is attributed to polymer chains initiated by 1,2-dimethylimidazole (labeled with #). The minor series is attributed to polymer chains initiated by BuN(K)Ts (labeled with *). Identical spectra with m/z labelled signals can be found in the Supporting Information (Figures S19, S20)

We have found that 1,2-dimethylimidazole does indeed promote the polymerization of **TsMAz** in DMF and that the MALDI-TOF spectrum of this polymer is the same as the 1,2-dimethylimidazole containing signals found in p(TsMAz) samples formed in [C_4dmim][Tf_2N] (Figure S22). We propose that 1,2-dimethylimidazole forms in [C_4dmim][Tf_2N] by Hofmann elimination during the p(TsMAz) polymerization.[12] We also observed that **TsMAz** does not polymerize in [C_4dmim][Tf_2N] in the absence of an anionic initiator. There is precedence for neutral nucleophiles initiating (and catalyzing) the polymerization of sulfonylaziridines.[22]

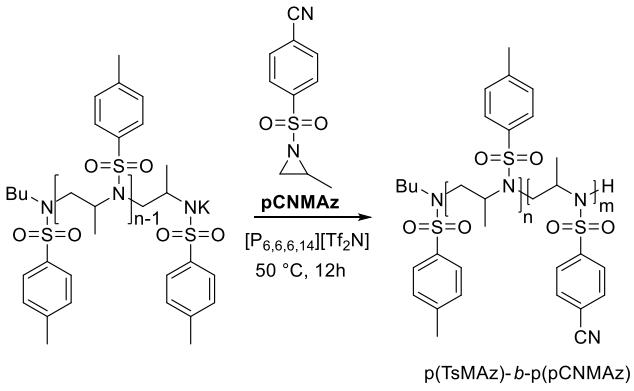
The polymerizations of **TsMAz** in several other [$C_x$dmim][Tf_2N] ILs (Chart 1) with different alkyl chain lengths, gave results that are largely the same as those observed with [C_4dmim][Tf_2N]. Specifically, SEC traces at lower [**TsMAz**]:**[BuN(K)Ts]** ratios were narrow but become multimodal at higher monomer to initiator ratios. MALDI-TOF mass spectra also followed the same trends, with 1,2-dimethylimidazole containing signals becoming prominent at higher [**TsMAz**]:**[BuN(K)Ts]** ratios. Results of **TsMAz** polymerizations performed in the borate IL [C_4dmim][BF_4] were largely identical to that of [C_4dmim][Tf_2N].

In contrast to the complications of polymerizing in imidazolium ILs, the polymerization of **TsMAz** in [$P_{6,6,6,14}$][Tf_2N], appears to be living and controllable. MALDI-TOF mass spectrum of p(TsMAz) polymerized in [$P_{6,6,6,14}$][NTf_2] was consistent with all polymer chains being initiated by the sulfonylamide initiator and terminated by protons (Figure S21). There was no evidence in the MALDI-TOF mass spectra to indicate solvent chain transfer or the presence of non-H terminated chains. The ^{1}H NMR spectrum of purified p(TsMAz) (Figure S3) polymerized in [$P_{6,6,6,14}$][Tf_2N] looks identical to p(TsMAz) polymerized in DMF (Figure S6), indicating that polymerization in the IL does not impact the microstructure of the polymer. The lack of change in microstructure is also supported by the fact that the DSC trace of the IL polymerized p(TsMAz) was comparable to p(TsMAz) synthesized from DMF (Figure S24). The ^{31}P NMR spectra of the [$P_{6,6,6,14}$][Tf_2N] reaction mixture before and after polymerization showed no change, suggesting that the IL is not impacted by the polymerization (Figure S7, S8, S9,S10). Therefore, we conclude that the polymerization of **TsMAz** in [$P_{6,6,6,14}$][Tf_2N] is proceeding without undesirable side reactions with the IL. We note that the purity of the [$P_{6,6,6,14}$][Tf_2N] IL is important for the successful polymerization of **TsMAz**. Some commercially available [$P_{6,6,6,14}$][Tf_2N] samples did

not support polymerization of **TsMAz**, perhaps due to an electrophilic impurity that quenches the propagating anion (see Supporting Information).

Next, we assessed whether the polymerization of **TsMAz** is controlled.[37,38] Polymerizations of **TsMAz** were performed where the ratio of **[TsMAz]:[BuN(K)Ts]** was varied, with the results depicted in Figure S17. We observed that the molecular weights of the resulting p(TsMAz) as measured by SEC (vs. a PS standard) increased with increasing [**TsMAz**]:**[BuN(K)Ts]**. The dispersities of the resulting p(TsMAz) remained low, with a maximum Đ of 1.18 being observed (Figure S17). However, the SEC of trace of p(TsMAz) at higher [**TsMAz**]:**[BuN(K)Ts**] did exhibit a slight higher molecular weight shoulder (Figure S17). We hypothesize that the higher molecular weight fractions may occur due to poor mixing resulting from the high viscosity of the IL-polymer mixture in the NMR tube in which the polymerizations were performed. As the MALDI-TOF MS spectra indicate only a single series of **[BuN(K)Ts]** initiated polymer chains terminated by protons and the protonation of a living sulfonylaziridine is reversible,[34] early termination by protonation is likely not responsible for the SEC trace broadening.

We also performed a sequential polymerization with **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ to synthesize a block copolymer and to demonstrate that the polymerization is living (Scheme 2). First, the polymerization of **TsMAz** was initiated using **BuN(K)Ts**. After 12 h, the sulfonylaziridine monomer **pCNMAz** was added. After another 12 h passed, the resulting p(TsMAz)-*b*-p(pCNMAz) was collected and analyzed. ^{1}H NMR analysis revealed a copolymer consisting of both **TsMAz** and **pCNMAz** regions (Figure S11). SEC analysis of polymer samples before and after addition of **pCNMAz**, show chain extension (Figure S18), and is consistent with the polymerization of **TsMAz** being living (Scheme 3).



Scheme 3. Synthesis of p(TsMAz)-*b*-p(pCNMAz) via sequential polymerization in $[P_{6,6,6,14}][Tf_2N]$.

One of the advantages of ILs as solvents is that they can be reused[39] for subsequent reactions. After polymerization of **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ IL, we were able to precipitate the resulting p(TsMAz) in methanol and collect the filtrate. Placing the ensuing $[P_{6,6,6,14}][Tf_2N]$/methanol mixture under high vacuum evaporated the methanol, leaving $[P_{6,6,6,14}][Tf_2N]$. This resulting $[P_{6,6,6,14}][Tf_2N]$ supported subsequent polymerizations of **TsMAz** (Figure S12) (see Supporting Information).

Polymerization Kinetics

The rates of the polymerization of **TsMAz** in ILs were determined by monitoring the reactions via ^{1}H NMR spectroscopy. Prior work by Wurm has shown that the rates of the polymerizations of sulfonylaziridines increase with more polar solvents[8] and therefore, we anticipated that the rates of polymerization of **TsMAz** in IL solvents should be rapid. At 50 °C, the polymerization of **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ exhibited a delayed onset (Table 1 and Figure 2). We believe this to be a consequence of the very high viscosity of the solution at 50 °C and the fact that the polymerization is being performed in an NMR tube without stirring. However, at 60 °C and higher temperatures, no onset was observed and polymerization of **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ exhibits traditional first-order kinetics with respect to [**TsMAz**] (Figure 2). At 50 °C in $[P_{6,6,6,14}][Tf_2N]$, the

k_p is 16.3×10^{-3} L $mol^{-1}s^{-1}$. This rate is notably slower than the rate of polymerization of **TsMAz** in DMF, which was reported 39.79×10^{-3} L mol^{-1} s^{-1} at 50 °C. The rate of polymerization of **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ at 50 °C remains faster than the rates in THF (0.76×10^{-3} L mol^{-1} s^{-1}, 50 °C) and benzene (0.56×10^{-3} L mol^{-1} s^{-1}, 50 °C).[8]

$[M]_o/[I]_o$	Temp (°C)	Time (h)	Conversion (%)	M_n (kDa)	Đ	k_p (L mol^{-1} s^{-1})
60	50	18h	>95	8.4	1.15	16.3×10^{-3}
60	60	12h	>95	8.22	1.11	25.4×10^{-3}
60	80	4h	>95	7.71	1.16	84.3×10^{-3}

Table 1. Comparison of the rates of polymerization of **TsMAz** at different temperatures in $[P_{6,6,6,14}][Tf_2N]$.

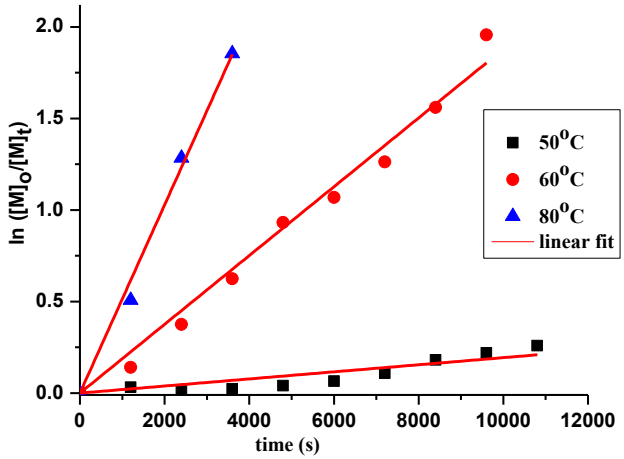


Figure 2. Kinetic plot for the polymerization of **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ at different temperatures. The consumption of **TsMAz** was monitored by ^{1}H NMR spectroscopy.

At 60 °C and higher temperatures, the polymerization of **TsMAz** in $[C_4dmim][Tf_2N]$ IL exhibits kinetics that are approximately first order with respect to [**TsMAz**] (Figure S13), although there appears to be a onset period. We have noticed that the k_p is 8×10^{-3} L$mol^{-1}s^{-1}$ in $[C_4dmim][Tf_2N]$

IL is slower than $[P_{6,6,6,14}][Tf_2N]$ IL, although the evidence of chain transfer in $[C_4dmim][Tf_2N]$ (see above) complicates the interpretation of this result.

Molecular Dynamics Simulations

AROPs of sulfonylaziridines are faster in more polar solvents (*e.g.* DMSO or DMF) and slower in less polar solvents (*e.g.*, THF).[8] The fact that the polymerization of **TsMAz** appears slower in ILs (Figure 3) compared to DMF was surprising. Therefore, molecular dynamics simulations using LAMMPS[40] were performed to study the impact of the ILs on the solvation of sulfonamide anions and perhaps gain insight into the lower polymerization rates in the ILs. Three simulations were constructed with different solvents: one with DMF, one with $[C_2dmim][Tf_2N]$, and one with $[P_{6,6,6,14}][Tf_2N]$. Each simulation was populated with **BuN(K)Ts**, which serves as a model of the propagating chain end, and the monomer **TsMAz**.

To gauge the relative dissociation of K^+ from the initiator, radial distribution functions (rdfs) were constructed between K^+ and the negatively charged nitrogen within the initiator **BuN(K)Ts**, as well as between K^+ with the nitrogen atom within the monomer **TsMAz** (Figure 3a). The rdfs show a very strong localization of K^+ around both the initiator and the monomer units. This localization is stronger for the initiators, with significant differences among the solvents. It is highest for DMF and lowest for $[C_2dmim][Tf_2N]$. Interestingly, the localization of K^+ around the monomers is highest for $[P_{6,6,6,14}][Tf_2N]$ and lowest for DMF.

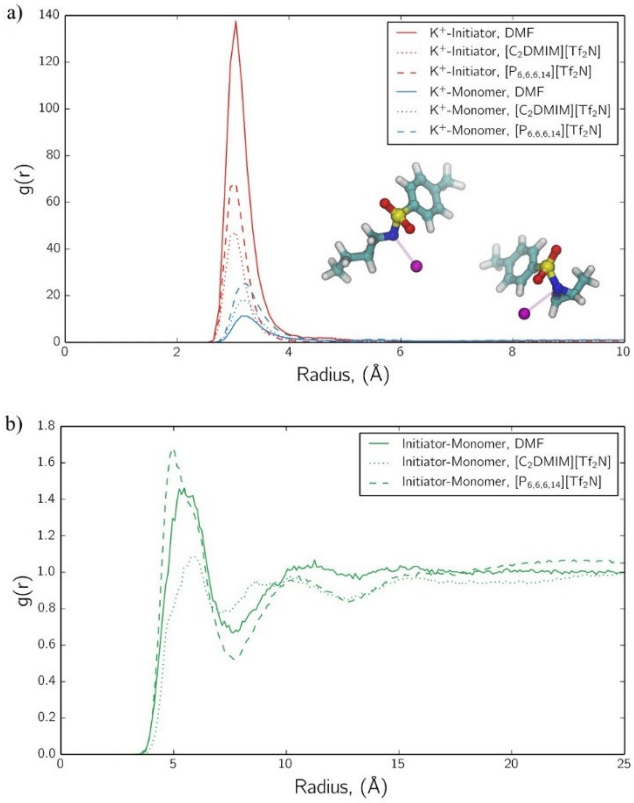


Figure 3. **a**) Radial distribution functions between the K^+ and either the initiator **BuN(K)Ts** or monomer **TsMAz** for each of the solvent systems. **b**) Radial distribution functions between the negatively charged nitrogen of the initiator **BuN(K)Ts** and the nitrogen of the monomer **TsMAz**.

On further inspection of the trajectories, there appeared to be noticeable clustering events wherein the initiator would be connected to one or several other monomers through a bridging K^+. A snapshot of this from the DMF simulation is shown in Figure 4. To further quantify this effect, rdfs were constructed between the negatively charged nitrogen of the initiator and the nitrogen atom of the monomer (Figure 3b). This roughly corresponds to the locations that would be bridged in such an event. These rdfs quantifying the mutual proximity of the initiator to monomer are shown in Figure 3b. In this case, there is a first peak around 5 Angstroms, indicating near contact. The peak is stronger for DMF and $[P_{6,6,6,14}][Tf_2N]$, though slightly weaker for $[C_2dmim][Tf_2N]$. A higher mutual proximity might suggest a higher reaction rate at these elevated concentrations in DMF compared to ILs. Since it was shown earlier that K^+ remains largely connected with the

initiator, it could indicate that the primary role of K^+ is to attract monomer units for propagation and may contribute to the faster polymerization rate in DMF. Furthermore, the simulations also showed notable differences in the mobilities of the monomer units, with the mobility in DMF being over two orders of magnitude higher than the ionic liquids (Figure S25). The mobility in $[C_2dmim][Tf_2N]$ and $[P_{6,6,6,14}][Tf_2N]$ were comparable, with the former being about 25% higher. This is consistent with the higher viscosity of ILs,[41,42] and likely also contributes to the slower reaction rate in the ILs compared to DMF.

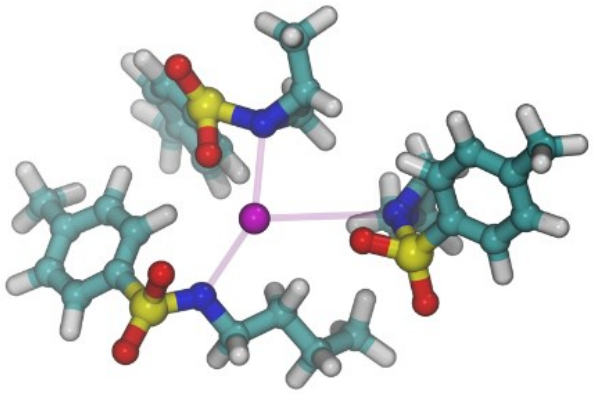


Figure 4. Snapshot showing the clustering of an initiator with several monomer **TsMAz** molecules through a bridging K^+. Transparent purple lines indicate proximity.

Conclusions

In summary, we have reported the anionic polymerization of sulfonylaziridines in ionic liquids (ILs). In $[C_xdmim]$ based imidazolium ILs, the polymerization of **TsMAz** induces Hofmann elimination of the imidazolium cations to form 1,2-dimethylimidazole. 1,2-Dimethylimidazole then acts as an initiator for the formation of new polymer chains. As such, p(TsMAz) samples synthesized in imidazolium ILs have lower molecular weights than anticipated given the [M]/[I] ratio.

In $[P_{6,6,6,14}][Tf_2N]$, the polymerization of **TsMAz** is controlled and living and allows for the synthesis of a block copolymer using **TsMAz** and **pCNMAz** as the comonomers. The rate of polymerization (k_p) of **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ at 50 °C is slower than that in DMF at 50 °C. The slower rate of polymerization of **TsMAz** in $[P_{6,6,6,14}][Tf_2N]$ compared to DMF was surprising, as **TsMAz** tends to polymerize faster in more polar solvents. However, molecular dynamics simulations suggest that the faster kinetics in DMF are a consequence of better anion/monomer ordering compared to the ILs. Slower transport in the ILs is also thought to contribute to the slower rate of polymerization in $[P_{6,6,6,14}][Tf_2N]$.

With the establishment that ILs can support the anionic polymerization of sulfonylaziridines, we are currently exploring ILs as solvents for polymerizing other sulfonylaziridines, many of which produce polymers that are insoluble in traditional solvents[17,35,36] (*e.g.,* DMF, DMSO, THF, etc.). We are also exploring 1,2-dimethylimidazole as initiators for the synthesis of cationic-chain end containing poly(sulfonylaziridines).

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXXX.

Experimental procedures, NMR spectra, MALDI-TOF mass spectra, SEC, kinetic data, and thermal analysis plots (PDF).

Conflict of Interest

The authors declare no conflicts of interest.

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