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Activated Monomer Polymerization of an *N*-Sulfonylazetidine

Louis Reisman, Elizabeth A. Rowe, Jennifer A. Jefcoat, and Paul A. Rupar*

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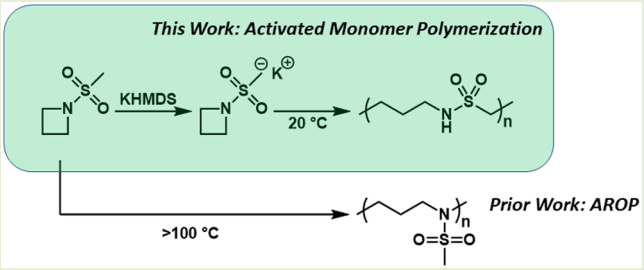
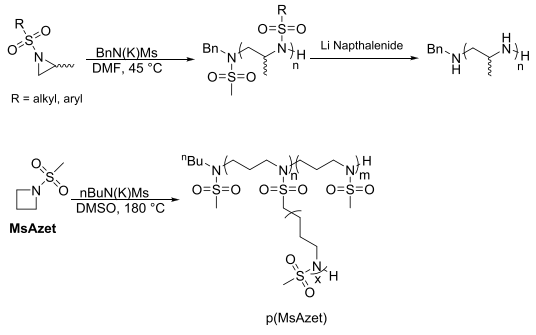
ABSTRACT: Previously, *N*-(methanesulfonyl)azetidine (**MsAzet**) was found to polymerize anionically via ring-opening at temperatures >100 °C to form p(MsAzet) in the presence of an anionic initiator. In the current report, potassium(azetidin-1-ylsulfonyl) methanide (**KMsAzet**), formed from deprotonation of the methanesulfonyl group of **MsAzet** by KHMDS, is shown to undergo spontaneous AROP at room temperature to form p(*N*-K-MsAzet). The structure of p(*N*-K-MsAzet) differs from that of p(MsAzet), as the sulfonyl groups are incorporated into the polymer backbone of p(*N*-K-MsAzet). Reaction of p(*N*-K-MsAzet) with MeOH produces p(*N*-H-MsAzet), a semicrystalline polymer with a structure like that of polyamides, but with sulfonylamides in place of the carboxamides found in polyamides. Reaction of p(*N*-K-MsAzet) with benzyl bromide results in the formation of amorphous p(*N*-Bn-MsAzet). P(*N*-K-MsAzet) is hypothesized to form via an activated monomer anionic polymerization; this is supported by polymerization kinetic data and structural characterization of the resulting polymers.



Despite structural similarities, the polymerization of aziridines and azetidines are distinct from their oxygen analogs oxirane and oxetane.[1] Whereas oxiranes and oxetanes polymerize via a variety of mechanisms, aziridines and azetidines polymerize almost exclusively via a cationic mechanism, and usually form branched polymers.[2,3]

In 2005, Bergman and Toste discovered that 2-substituted-*N*-sulfonylaziridines undergo living anionic ring-opening polymerization (AROP; Scheme 1) to form linear polysulfonylazir-

Scheme 1. Previously Reported AROP of *N*-Sulfonylaziridines[4] and *N*-Sulfonylazetidines[19]



idines.[4] Others have since expanded this approach[2] to include *N*-sulfonylaziridine copolymers,[5−8] functional *N*-sulfonylaziridines,[9−12] unsubstituted *N*-sulfonylaziridines,[7,13] and the organocatalyzed polymerization of *N*-sulfonylaziridines.[14−17] Some of these polysulfonylaziridines can be converted to linear polyimines, which are otherwise difficult to obtain from aziridines.[7,18]

Inspired by *N*-sulfonylaziridine polymerizations, we recently reported on the AROP of *N*-(methanesulfonyl)azetidine (**MsAzet**) to form p(MsAzet) in an effort to access linear poly(trimethylenimine)s (Scheme 1).[19] Due to a high activation energy for anionic ring-opening, the polymerization of **MsAzet** requires temperatures >100 °C (c.f. <50 °C for *N*-sulfonylaziridines). An unexpected consequence of this high temperature was a chain transfer reaction that occurred via deprotonation of the methanesulfonyl group, and therefore, the resulting p(MsAzet) had a branched structure. Steric effects were found to not prevent chain transfer, as *N*-(ethanesulfonyl)azetidine (**EsAzet**) and *N*-(2-propanesulfonyl)azetidine (*i***PsAzet**) also produce branched polymers.[20] However, the related *N*-tolylsulfonylazetidines were found not to undergo chain transfer under similar AROP conditions, as they lack protons alpha to the sulfonyl group.[21]

During our study of the **MsAzet** chain-transfer mechanism, we synthesized potassium(azetidin-1-ylsulfonyl) methanide (**KMsAzet**) through deprotonation of **MsAzet** with KHMDS (Scheme 2), which was isolated as a white powder.[19] **KMsAzet** was found to ring-open **MsAzet**, and thus supported the hypothesis that sulfonylmethanide anions are responsible for the branched structure of p(MsAzet). In this report, we show that **KMsAzet** undergoes spontaneous AROP at room

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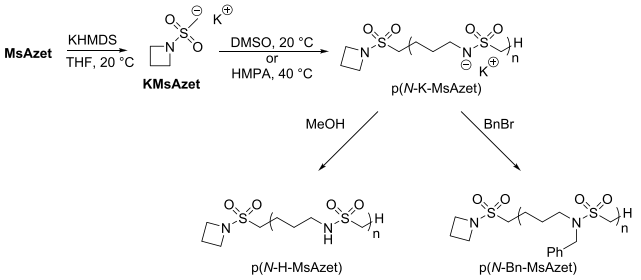
ACS Macro Lett. 2020, 9, 334–338

Scheme 2. Deprotonation of MsAzet by KHMDS in THF, Followed by AROP of KMsAzet in DMSO or HMPA To Form p(*N*-K-MsAzet); Reaction of p(*N*-K-MsAzet) with MeOH and BnBr To Produce p(*N*-H-MsAzet) and p(*N*-Bn-MsAzet), Respectively



temperature to form p(*N*-K-MsAzet), the structure of which is significantly different from that of p(MsAzet).

We were motivated to further study **KMsAzet**, as it is comprised of both a strained azetidine ring and nucleophilic methanide anion, and we suspected that **KMsAzet** may polymerize in the absence of an initiator. The initial indication that **KMsAzet** undergoes spontaneous chemical transformation came from the fact that a white precipitate forms from **KMsAzet** solutions in DMSO after many hours at room temperature (DMSO solutions of **MsAzet** are stable indefinitely at room temperature). Direct analysis of the precipitate was challenging due to its insolubility; however, the addition of a small amount of MeOH to the DMSO suspensions resulted in the dissolution of the precipitate. Subsequent analysis of the homogeneous DMSO solution revealed the formation of p(*N*-H-MsAzet) (Scheme 2). Therefore, we propose that the insoluble precipitate is p(*N*-K-MsAzet) and that the addition of MeOH protonates it to form p(*N*-H-MsAzet) (Scheme 2). The polymerization of **KMsAzet** also proceeds in HMPA, although the rate of the polymerization is qualitatively slower than that in DMSO and requires increased temperature (40 °C). The polymers studied in this work were synthesized in HMPA.

P(*N*-H-MsAzet) is soluble in polar, aprotic solvents such as DMSO, DMF, NMP, and HMPA. The ^{1}H NMR spectra of p(*N*-H-MsAzet) is notably different from p(MsAzet) (Figure 1). The ^{1}H NMR spectra of p(*N*-H-MsAzet) features a broad signal at about 7.00 ppm that undergoes H-D exchange upon addition of D_2O (Figure S3); this signal is assigned to the amide protons of the polymer backbone. A cluster of signals at about 3.00 ppm arise from methylene protons alpha to the nitrogen atom of the sulfonamide and the methylene protons alpha to the sulfonyl functional group. Next, there are a group of signals at about 1.70 ppm that are attributed to backbone methylene protons that are beta to the nitrogen atom of the sulfonamide and the methylene protons beta to the sulfonyl functional group. Finally, there are a pair of weak signals at 3.75 and 2.20 ppm that match that of a sulfonyl azetidine ring, believed to be on one chain end of p(*N*-H-MsAzet). This permits an estimation of the M_n to be 2700 g/mol (ca. 20 repeat units) by ^{1}H NMR end group analysis. The MALDI-TOF MS of p(*N*-H-MsAzet) has a repeat unit mass of 135.04 g/mol, which is identical to that of p(MsAzet) and is expected given the proposed structure of p(*N*-H-MsAzet) (Figure S8).

The aza-anions of p(*N*-K-MsAzet) react rapidly with electrophiles allowing for the rapid synthesis of p(*N*-K-MsAzet) derivatives. For example, the addition of BnBr to

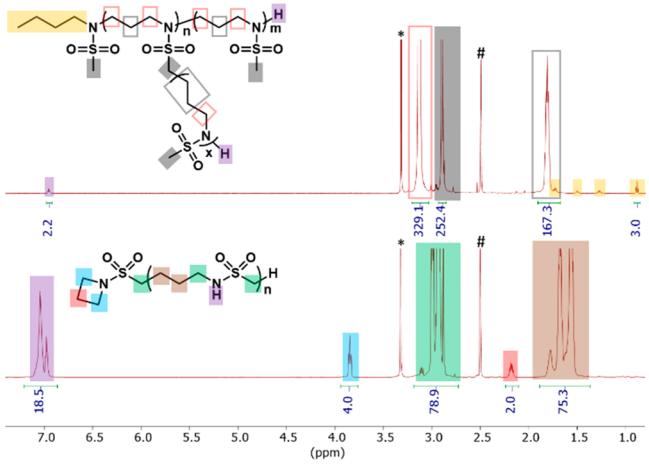


Figure 1. Comparison of the ^{1}H NMR spectra of p(MsAzet) (top) and p(*N*-H-MsAzet) (bottom). The signals labeled "*" and "#" are attributed to H_2O and $DMSO_{d5}$, respectively.

DMSO or HMPA suspensions of p(*N*-K-MsAzet) resulted in the formation of p(*N*-Bn-MsAzet) (Scheme 2), which is soluble in polar, aprotic solvents such as DMSO, DMF, NMP, and HMPA. The ^{1}H NMR spectra of p(*N*-Bn-MsAzet) is like that of p(*N*-H-MsAzet), but also contains signals at about 4.15 ppm and in the aromatic region at about 7.25 ppm corresponding to the benzyl and aryl protons, respectively (Figure S4).[22] As with p(*N*-H-MsAzet), a triplet near 3.8 ppm was observed in the ^{1}H NMR spectra of p(*N*-Bn-MsAzet) and was hypothesized to be an azetidine ring at one terminus of the polymer. MALDI-TOF MS of p(*N*-Bn-MsAzet) were consistent with a polymer structure with an azetidine monomer on one chain end and a proton on the other with a benzylated monomer repeat unit (Figure S10). The maximum M_n obtainable for p(*N*-Bn-MsAzet) was 7500 g/mol versus PS standards (6300 g/mol by ^{1}H NMR end group analysis). The reason for the low molecular weights appears to be due to the precipitation of the parent p(*N*-K-MsAzet) at low degrees of polymerization. The p(*N*-K-MsAzet) dispersions in both DMSO and HMPA were stable over the course of the times examined in this work (1−2 days).

The kinetics of **KMsAzet** polymerizations were studied using real-time ^{1}H NMR spectroscopy in $DMSO_{d6}$. These studies could only be carried out to low conversion as p(*N*-K-MsAzet) begins precipitating from solution. The plot of natural log of [**KMsAzet**] with respect to time is approximately linear (Figure 2), suggesting the polymerization is first order with respect to [**KMsAzet**] with an apparent propagation rate constant, k_{app}, of 5.6×10^{-3} L/mol·h^{-1}. Addition of a small amount of **MsAzet** to **KMsAzet** polymerizations greatly accelerated the rate of polymerization, indicating that **MsAzet** also plays a role in the polymerization process (Figure 2).

We believe that p(*N*-K-MsAzet) is formed via the activated monomer polymerization of **KMsAzet** and that the mechanism has similarities to the anionic polymerizations of cyclic lactams.[23] In contrast to the AROP of lactams, in the polymerization of **KMsAzet**, there is no proton transfer occurring, as all monomers are already deprotonated. Because there is no proton transfer occurring, rather than the monomer being activated, it is instead the polymer chain end being activated. In addition to this, rather than a small amount of base necessary to initiate polymerization, as is the case with

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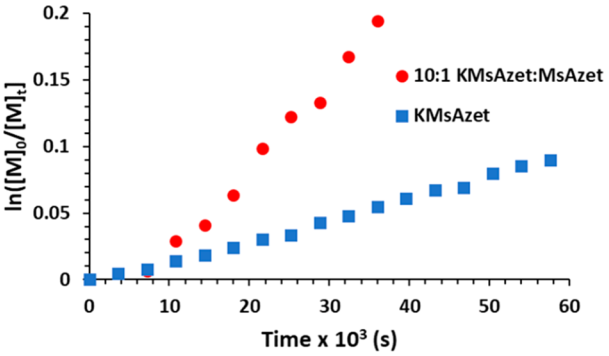
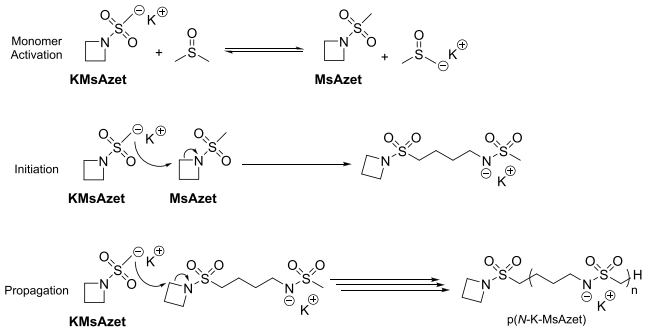


Figure 2. Kinetic data of the polymerizations of **KMsAzet** (blue square) and 10:1 **KMsAzet**:**MsAzet** (red circle) in $DMSO_{d6}$.

lactams, in the AROP of **KMsAzet** a small amount of a protic source is required.

In the proposed mechanism, **KMsAzet** is activated by protonation by DMSO to form **MsAzet** and the dimsyl anion (Scheme 3). When the polymerization is performed in HMPA, protonation likely occurs by trace protic impurities. Chain initiation occurs when **KMsAzet** adds by nucleophilic addition to the formed **MsAzet**, resulting in ring-opening. The polymerization of **KMsAzet** is driven by both the release of the azetidine ring strain and the transfer of the anion from the carbon atom in **KMsAzet** to the more electronegative nitrogen atom in p(*N*-K-MsAzet). Subsequent chain propagation consists of nucleophilic attack of **KMsAzet** monomers at the azetidine of the propagating chain end. Polymerization ceases with precipitation of the polymer from solution due to poor solubility, or when a protic source, such as MeOH, or an electrophile, such as BnBr is added.

Scheme 3. Proposed Mechanism of the Spontaneous Polymerization of KMsAzet in DMSO at Room Temperature[a]



[a]We hypothesize that protonation of **KMsAzet** to form **MsAzet** occurs by trace protic impurities in HMPA.

There are several pieces of evidence that support the activated monomer polymerization mechanism hypothesis. The **KMsAzet**/**MsAzet** equilibrium in DMSO has been established previously through the observation that KMsAzet undergoes rapid H−D exchange in $DMSO_{d6}$ at room temperature.[19] ^{1}H NMR spectra of **KMsAzet** polymerizations have a triplet at 3.8 ppm, attributed to the azetidine at the propagating chain end; this triplet is also present in ^{1}H NMR spectra of p(*N*-H-MsAzet) and p(*N*-Bn-MsAzet) (Figures 1, S1, S3, and S4). MALDI-TOF MS spectra of p(*N*-Bn-MsAzet) are consistent with an azetidine capped chain end and excludes cyclic structures as well as a p(*N*-Bn-MsAzet) structure that would form if p(*N*-K-MsAzet) had a terminal methanide anion. Finally, the activated monomer polymerization hypothesis is supported by the fact that adding a small amount of **MsAzet** to $DMSO_{d6}$ solutions of **KMsAzet** significantly accelerates the rate of **KMsAzet** polymerization due to an increase in the concentration of the species at the active chain end. We suspect that **KMsAzet** itself is not susceptible to nucleophilic ring-opening due to the reduced electrophilicity of the **KMsAzet** azetidine ring.

In the mechanism depicted in Scheme 3, the presence of the very basic **KMsAzet** and dimsyl potassium raises concerns for transfer reactions.[24] In prior work, we showed that the dimsyl anion can initiate AROP of **MsAzet** at temperatures >100 °C.[19] However, at the lower temperatures used in this work, the dimsyl anion does not ring open **MsAzet** (and presumably **KMsAzet**; see Supporting Information). Another potential transfer reaction could arise from an anion shift from **KMsAzet** to methylene carbons alpha to the sulfonyl groups in the polymer chain; this in turn could lead to branching. However, we were unable to detect signals in the ^{1}H or ^{13}C NMR spectra to support polymer chains with a branched structure. Additionally, the crystalline nature of p(*N*-H-MsAzet) also suggests the presence of mostly linear chains. We hypothesize that transfer of the anion from **KMsAzet** to the polymer chain is prevented by the neighboring negative charges on the sulfonamide nitrogen atoms of the polymer.

The structure of p(*N*-H-MsAzet) is notable in that it is can be viewed as a sulfonyl amide analog of nylon-5. Similar to the carboxamides of nylons, sulfonamides are capable of hydrogen bonding.[25,26] We believe that hydrogen bonding does influence the properties of p(*N*-H-MsAzet) and could explain some of the physical differences between p(*N*-H-MsAzet) and p(*N*-Bn-MsAzet). By WAXS, p(*N*-H-MsAzet) is semicrystalline while p(*N*-Bn-MsAzet) is amorphous (Figure S12); this is consistent with their visual appearance as p(*N*-H-MsAzet) is a white powder and p(*N*-Bn-MsAzet) is glassy at room temperature. Both p(*N*-H-MsAzet) and p(*N*-Bn-MsAzet) have similar decomposition temperatures near 300 °C (Figures S13 and S14); however, differential scanning calorimetry (DSC) of p(*N*-H-MsAzet) shows a T_g of 40 °C and a T_m of 170 °C, while p(*N*-Bn-MsAzet) shows a T_g of 50 °C and no T_m is apparent (Figures 3, S15, and S16). By comparison, nylon-5 has been reported to have a T_g around 5 °C and melt at about 290 °C.[27] Since the molecular weights of p(*N*-H-MsAzet) and p(*N*-Bn-MsAzet) are modest, it is likely that T_g and T_m values

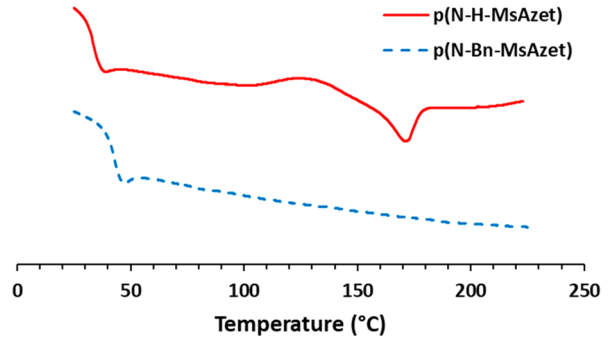


Figure 3. DSC heating traces of p(*N*-H-MsAzet) and p(*N*-Bn-MsAzet) at a heating rate of 10 °C/min. Both traces shown are of the second heating cycle.

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ACS Macro Lett. 2020, 9, 334−338

will be increased in higher molecular weight samples of p(*N*-H-MsAzet) and p(*N*-Bn-MsAzet); this is being further pursued in our lab.

In conclusion, we have discovered a new, anionic monomer, **KMsAzet**, which undergoes polymerization by an activated monomer mechanism. The structure of the resulting p(*N*-K-MsAzet) is different than that of p(MsAzet) (formed from the standard AROP of **MsAzet**), in that the sulfonyl groups are incorporated into the backbone of p(*N*-K-MsAzet). Protonation of p(*N*-K-MsAzet) gives p(*N*-H-MsAzet), while reaction of p(*N*-K-MsAzet) with BnBr produced p(*N*-Bn-MsAzet). The structure of p(*N*-H-MsAzet) is noteworthy in that it can be considered a sulfonyl analog of nylon-5. Given that few aliphatic poly(sulfonylamides) and their properties are known,[28−30] p(*N*-K-MsAzet) may allow for the synthesis of numerous materials with various important applications. Further studies pertaining to these applications are currently being explored in our lab.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00019.

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

■ AUTHOR INFORMATION

Corresponding Author

Paul A. Rupar − *Department of Chemistry and Biochemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, United States;* orcid.org/0000-0002-9532-116X; Email: parupar@ua.edu

Authors

Louis Reisman − *Department of Chemistry and Biochemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, United States;* orcid.org/0000-0003-2330-9804

Elizabeth A. Rowe − *Department of Chemistry and Biochemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, United States*

Jennifer A. Jefcoat − *U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, Mississippi 39180, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmacrolett.0c00019

Notes

The authors declare no competing financial interest.

Unprocessed, experimental data can be found online via Open Science Framework at: DOI: 10.17605/OSF.IO/DP6MQ.

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