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Polymerizations of 2-(Trimethylsilyl)ethanesulfonyl-activated aziridines

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ABSTRACT

A novel *N*-sulfonyl aziridine, *N*-((2-(trimethylsilyl)ethyl)sulfonyl)-2-methyl-aziridine (SES-MeAz) was synthesized, and its controlled anionic ring-opening polymerization to form poly(SES-MeAz) studied. The desulfonylation of poly(SES-MeAz)s can be achieved under mild conditions, with tetrabutylammonium fluoride (TBAF) to form polypropylene imine (PPI), although purification of the PPI was not completely successful. The block copolymer p(pTs-MeAz)-*b*-p(SES-MeAz), (pTs-MeAz = *N*-*para*-tosyl-2-methyl-aziridine) was prepared by a sequential polymerization. The desulfonylation of the block copolymer is the first example of the selective removal of a sulfonyl protecting group from a poly(sulfonylazirdine) block copolymer and this is the first formation of a polysufonylaziridine-block-polypropylene imine copolymer. Three-armed star-shaped poly(SES-MeAz)s were also successfully synthesized and exhibited improved solubility compared with linear poly(SES-MeAz)s.

1. Introduction

Linear polyethylenimine (lPEI) is a member of the polyamine family. As a commercially available polymeric material, PEI has been used in applications, including non-viral gene-transfection, [1–3] antimicrobial and anti-viral coatings, [4] and metal chelation in wastewater treatments [5]. These applications are made possible due to the high amino group density in the backbone. However, research on PEI derivatives such as polypropylene imine (PPI) are less studied [6–8]. This is mainly due to the lack of efficient strategies to synthesize PPI.

Anionic ring-opening polymerizations (AROP) are a reliable method to synthesize well-defined polymers with complex architectures and low dispersity [9]. In 2005, Bergman and Toste reported the AROP of *N*-sulfonyl-2-methylaziridines to form poly(sulfonylazirdine), where the sulfonyl group was either toluenesulfonyl (tosyl) or methanesulfonyl (mesyl) [10]. The sulfonyl groups activate the aziridine rings towards nucleophilic ring-opening and further stabilize the propagating anion of the resulting polymer chain. In addition, the sulfonyl groups may be removed to produce linear polypropylene imine (lPPI) using a strong reducing agent (*i.e.,* lithium naphthalenide) (Scheme 1).

After Bergman and Toste's initial report, sulfonyl aziridines have been used in the preparation of more complex polymer architectures. Examples including telechelic polymers initiated by bifunctional initiators, [11] and graft polymers initiated by hyperbranched PEIs [12]. Sulfonylaziridines have also been copolymerized with cyclic anhydrides, [13–15] ethylene oxide, [16] L-type lactide, [17] and carbonyl sulfide [18] among others [19,20]. Poly(sulfonylaziridines) were recently used to modify cellulose paper for application in water purification [21].

Since Bergman and Toste's initial report on the AROP of *N*-tosyl and *N*-mesyl activated aziridines, numerous other sulfonyl groups have been found to activate aziridines towards AROP. These have been studied in the context of introducing new functionalities, to assess the impacts of different sulfonyl groups on polymerization kinetics, and to change polymer properties. Examples of activating sulfonyl aziridines include *N*-(4-cyanobenzolsulfonyl)-2-methyl-aziridine (pCN-MeAz), [22] *N*-((*ortho*-nitrophenyl)sulfonyl)aziridine (oNs-Az), [23] *N*-ferrocenylsulfonyl-2-methyl-aziridine (fc-MeAz) [24], *N*-tosyl-2-decyl-aziridine (TsD-Az), [25] *N*-brosyl-2-methyl-aziridine (Bs-MeAz) [26] amongst others [22] (Chart 1). Various initiating systems have also been established for AROP, including *N*-activated sulfonamides in the presence of potassium hexamethyldisilazide (KHMDS); [27] carboxylic acids, [28] activated/non-activated amines or alcohols with organocatalysts such as *N*-heterocyclic carbene, [29] *N*-heterocyclic olefins, [30] phosphazene base; [31] and ionic pair tetrabutylammonium halide (TBAX, X = F, Cl) [32].

Various approaches to deprotect sulfonyl groups from poly(sulfonylziridine) have been reported. Examples include reducing reagents such as lithium napthalenide, [10] lithium metal with *tert*-butanol in hexamethylphosphoramide (HMPA), [6] and sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) [33]. Reaction of 4-

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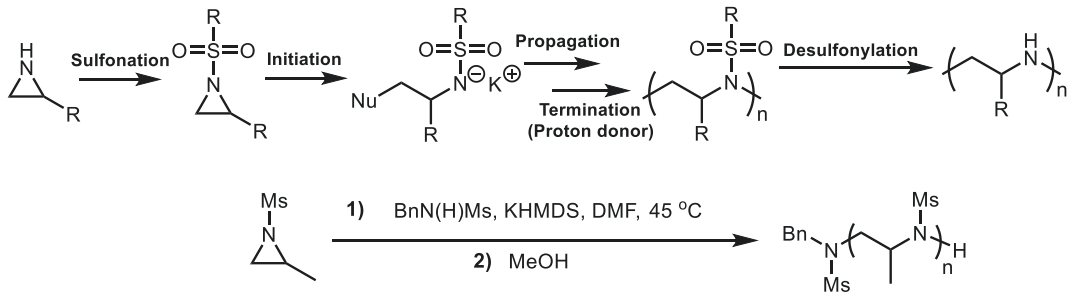


Scheme 1. Top: Anionic ring-opening polymerization of sulfonylaziridines and deprotection. Bottom: The synthetic route of a typical poly(sulfonylazirdine) from an activated 2-methyl-aziridine, as reported by Bergman and Toste [10].

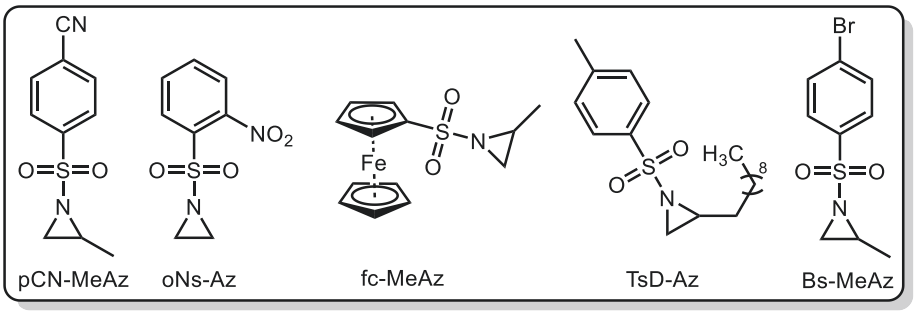
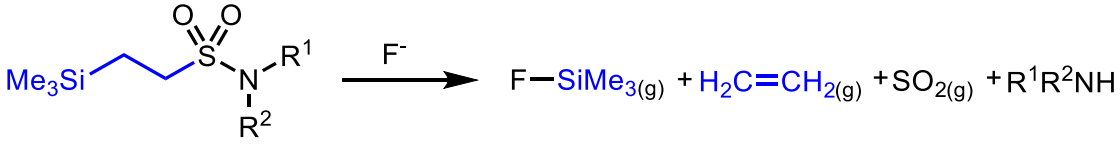


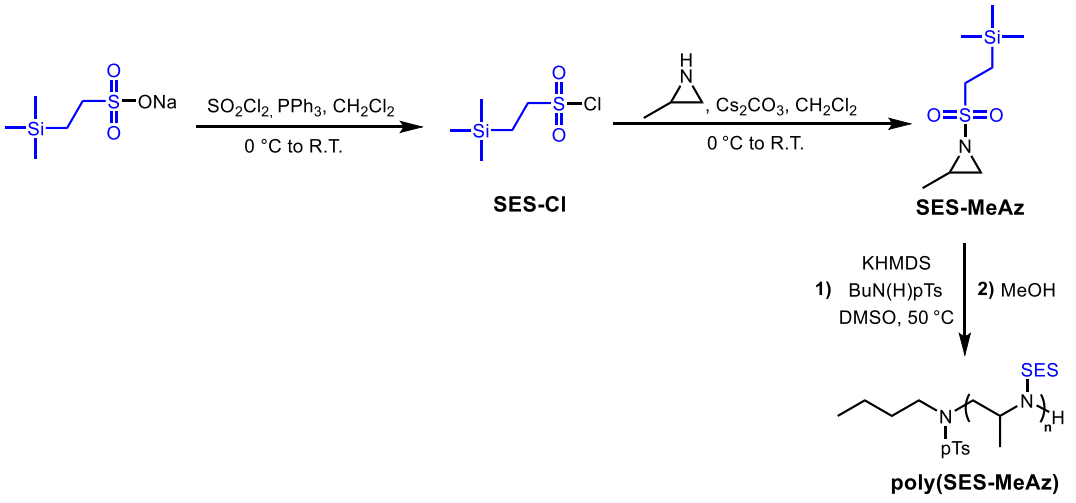
Chart 1. Examples of AROP capable activated aziridines.



Scheme 2. The deprotection of SES-protected amines by fluoride anions.

cyanobenzolsulfonyl groups with dodecanethiol [7] and a microwave-assisted method have also been reported [8]. However, many of these desulfonylation strategies resulted in the low isolated yields and/or incomplete desulfonylation and/or suffer from polymer backbone scission under the harsh reaction conditions [34].

Amine protecting groups play important roles in peptide synthesis, nucleoside preparation, or total synthesis of natural products [35–37]. The 2-(Trimethylsilyl)ethanesulfonyl (SES) group is a classic amine protecting group, which is stable under various reaction conditions, easily accessible and selectively cleavable [38]. The SES group was first developed by Weinreb in 1986 as an alternative to other sulfonyl groups such as tosyl, nosyl, or brosyl groups, which are problematic to deprotect [39]. SES is normally removed under mild conditions using fluoride ions. These conditions are compatible with highly functionalized,



Scheme 3. The preparation of SES-Cl, SES-MeAz, and poly(SES-MeAz).

Table 1
AROP of SES-MeAz with various molar ratios of monomer to initiator.

entry	$[M]_0/[I]_0/[B]_0$[a]	Target polymer	M_n(theor)[b] (g/mol)	M_n(NMR)[c] (g/mol)	M_n(GPC)[d] (g/mol)	Dispersity (Đ)[d]	Isolated yield (%)
1	20/1/1	poly(SES-MeAz)$_{20}$	4647	4426	1631	1.16	72.8
2	50/1/1	poly(SES-MeAz)$_{50}$	11,277	10,835	3465	1.21	70.3
3	80/1/1	poly(SES-MeAz)$_{80}$	17,907	16,802	6724	1.14	82.5
4	110/1/1	poly(SES-MeAz)$_{110}$	24,537	24,316	10,937	1.24	76.2

[a] **M**: SES-MeAz, **I**: n-BuN(H)pTs, **B**: KHMDS.
[b] Calculated as follows: M_n,theor = ([M]/[I]) × MW_M + MW_I, M: monomer, I: initiator.
[c] degree of polymerization determined by end group analysis from ^{1}H NMR spectroscopy.
[d] Number-average molecular weight (M_n,GPC) and polydispersity (*Đ*) determined by GPC in HFIP at 35 °C (PMMA calibration).

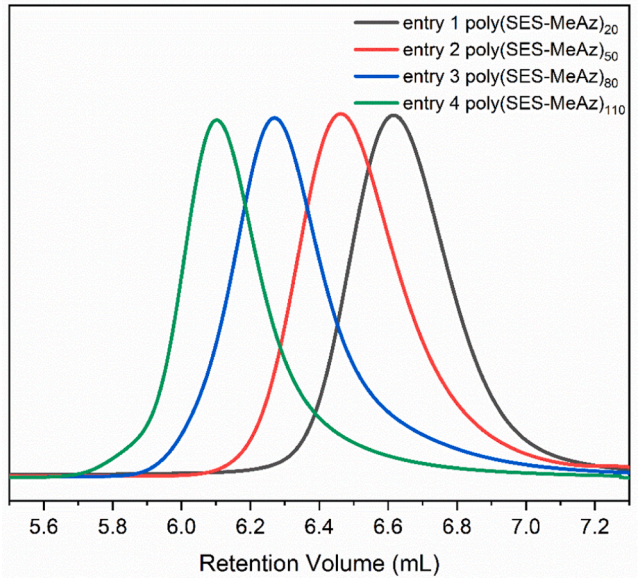


Fig. 1. GPC traces for the polymers listed in Table 1 with HFIP as eluent.

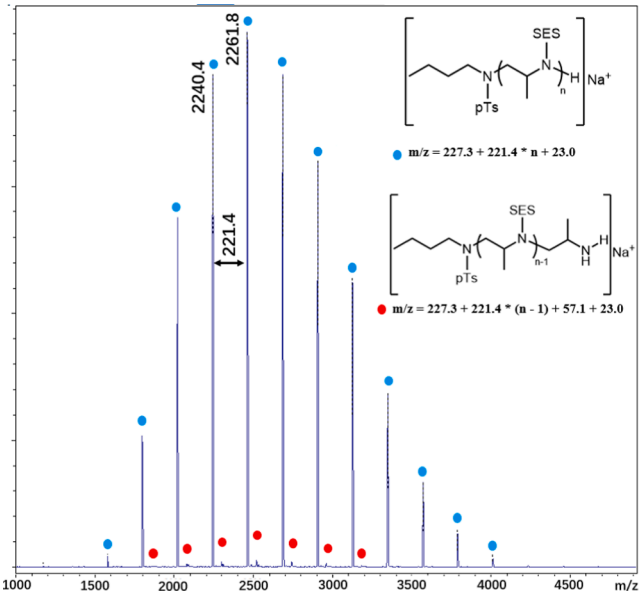


Fig. 2. MALDI-TOF mass spectrum of a n-BuN(H)pTs initiated poly(SES-MeAz) ([M]/[I] = 20).

sensitive substrates. In the deprotection of SES, the fluoride ions attacked the silicon atoms leading to a β-elimination, which release the deprotected amine and volatile fluorotrimethylsilane, ethylene, and sulfur dioxide (Scheme 2). The SES group has been widely applied for amine protection and activation, *e.g.,* with pyrroles, pyrrolidines, or sulfonimidamides [40–42]. However, to the best of our knowledge, SES-protected amines have not been used in functional monomers for polymer preparation and deprotection.

Herein, we report on a novel sulfonyl aziridine monomer, *N*-((2-(trimethylsilyl)ethyl)sulfonyl)-2-methyl-aziridine (SES-MeAz), featuring the SES group. The SES protecting group is relatively easier to remove compared to other sulfonyl groups in aziridine derived polymers. A highly effective strategy for the synthesis of well-defined poly(SES-MeAz) with different molecular weights has been developed. Polymerization kinetics have been studied at 50 °C and a possible polymerization mechanism proposed. Deprotection of as-synthesized poly(SES-MeAz) was investigated under relatively mild conditions. In addition, a poly(pTs-MeAz)-*b*-(SES-MeAz) block copolymer and star-shaped poly(SES-MeAz)s were synthesized.

2. Results and discussion

2-(trimethylsilyl)ethanesulfonic acid sodium salt (SES-ONa) was reacted with $SOCl_2$ to prepare 2-(trimethylsilyl)ethanesulfonyl chloride [43] (SES-Cl) (Scheme 3 and Figure S1). SES-Cl was further reacted with 2-methyl-aziridine (MeAz) to produce *N*-((2-(trimethylsilyl)ethyl)sulfonyl)-2-methyl-aziridine (SES-MeAz, Scheme 3, Figure S2 and S3). Enantiopure SES-MeAz has been reported before and used as a substrate to prepare functionalized piperidines by cycloaddition [44]. However, the racemic SES-MeAz has not been previously reported to the best of our knowledge.

Conditions similar to those previously established by the Toste group were used in our attempt to prepare poly(SES-MeAz) by AROP of SES-MeAz [10]. Specifically, initiation by KHMDS activated BuN(H)pTs in anhydrous DMSO (Scheme 3). Polymerizations of SES-MeAz were performed in which the monomer:initiator ratios were 20:1, 50:1, 80:1, and 110:1. In the ^{1}H NMR spectrum of the resulting poly(SES-MeAz), resonances at ~7.69 ppm (protons on the aromatic ring of the initiator) and ~0.05 ppm (protons of TMS groups) were used for end group analysis. The degree of polymerization (D.P.) as determined by ^{1}H NMR spectrometric analysis closely matched theoretical values, suggesting the AROP was controlled (Table 1, Figure S4-S8). GPC traces of the resulting polymers were monomodal with relatively low dispersities (Table 1, Fig. 1, Figure S9, HFIP is used as eluent). Unfortunately, further increasing the monomer to initiator ratio beyond 110:1 led to precipitation of the polymer, low isolated yields, and loss of control over the molecular weights. It appears that high molecular weight poly(SES-MeAz) is not soluble in DMSO. Poly(SES-MeAz) was also insoluble in DMF and various ionic liquids [45].

MALDI TOF mass spectra of poly(SES-MeAz) were as expected as the main series of peaks were consistent with polymer chains initiated by BuN(H)pTs and terminated by a proton (Fig. 2, Figure S10-S11). A smaller series in the mass spectrum is attributed to partly deprotected polymer, in which one of the repeating units has lost the SES protecting group. We believe that this loss of an SES group occurs during MALDI-

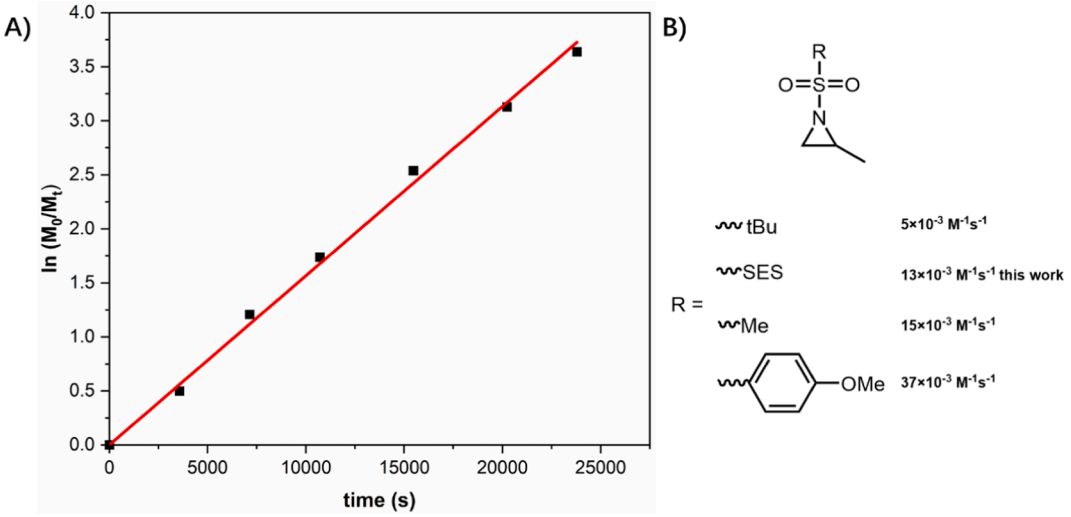
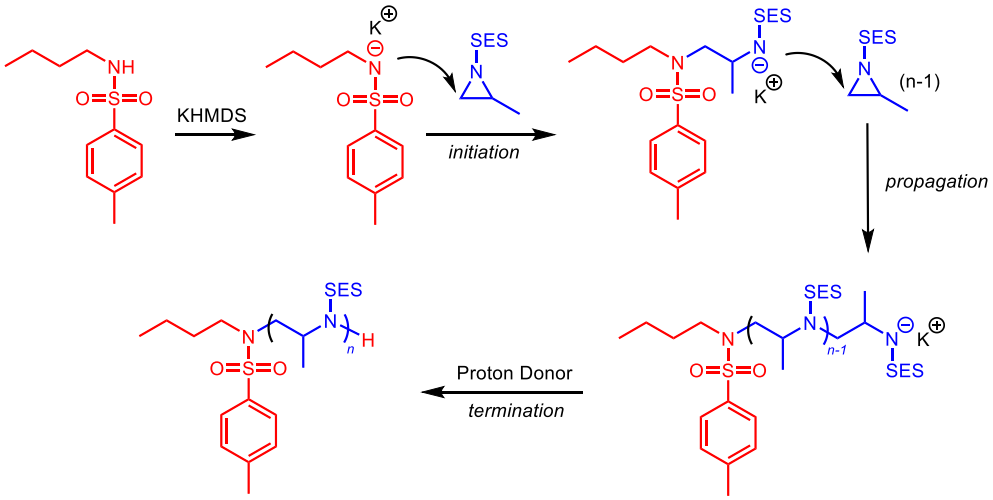


Fig. 3. A) Kinetic plot for the polymerization of **SES-MeAz** in DMSO-d_6 at 50 °C. The consumption of **SES-MeAz** was monitored by ^{1}H NMR spectroscopy. B) The structures of various sulfonylazirdines and their propagation rate constants (this work measured in DMSO, other reported works measured in DMF) at 50 °C [22].



Scheme 4. Proposed mechanism of amine initiated AROP of SES-MeAz.

TOF MS analysis, as we are unable to observe partial deprotection by NMR spectroscopy.

Thermal analysis of poly(SES-MeAz) showed that it has a T_g of 105 °C and is thermally stable up to 300 °C (Figure S12-S13). Its thermal stability is similar to that of other reported poly(sulfonylaziridine)s [23,46].

2.1. Polymerization kinetics

The kinetics of SES-MeAz polymerization in DMSO-d_6 were measured by monitoring the reaction via real-time ^{1}H NMR spectroscopy. The polymerizations were performed at 50 °C, with a [M]:[I] of ~20:1. The plot of ln([M_0]/[Mt]) vs time for the polymerization of SES-MeAz is linear (Fig. 3), and exhibits classic first-order kinetics with respect to monomer concentration. Assuming the polymerization is first order with respect to original initiator concentration, the propagation rate constant (k_p) for the SES-MeAz polymerization in DMSO is 12.96 × 10^{-3} $M^{-1}s^{-1}$ at 50 °C. Prior work by Wurm has measured the propagation rate constants of various sulfonyl-activated aziridines in DMF [22]. The k_p of SES-MeAz in DMSO is comparable to 2-methyl-*N*-mesyl-aziridine in DMF, and in-between 2-decyl-*N*-busyl-aziridine and 2-methyl-*N*-(4-methoxyphenyl)sulfonylaziridine (Fig. 3) in DMF (all at 50 °C). These measured rates are consistent with prior observations that the rate of sulfonzylaziridine polymerization increases with more electron withdrawing sulfonyl groups [9].

2.2. Possible mechanism

The above experimental data demonstrated that the polymerization of SES-MeAz has typical characteristics of a controlled, living anionic polymerization. Based on the reported research of sulfonyl-activated aziridine polymerization and mechanism, [9] a plausible mechanism including initiation, propagation, and termination is depicted in Scheme 4. The amino group of the initiator is deprotonated by KHMDS, which allows a nucleophilic attack in the 3-position of the aziridine ring to occur. The anion at the growing chain end is further stabilized by the electron withdrawing effect of the (trimethylsilyl)ethanesulfonyl (SES) group. The ‘‘living’’ polymer chain continues to extend until all monomers are consumed or quenched by a proton source, such as methanol.

2.3. Deprotection of Poly(SES-MeAz)

SES amides are commonly transformed to the corresponding amines by removal of the SES group using fluoride [38]. In an effort to convert

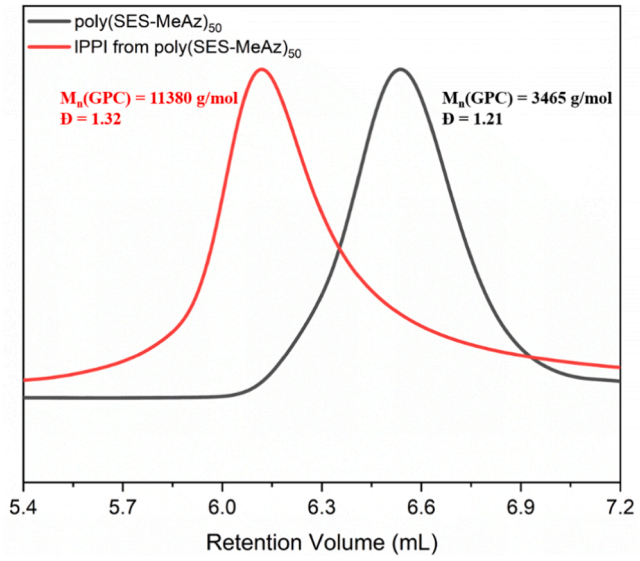


Fig. 4. GPC traces for poly(SES-MeAz)$_{50}$ and lPPI with HFIP as eluent. M_n(GPC) is the relative molecular weight based on PMMA standards. The decrease in retention volume of lPPI (and increase in apparent molecular weight) after deprotection of the sulfonyl group is consistent with prior observations [7].

poly(SES-MeAz) to lPPI, we screened many fluoride reagents, including hydrofluoric acid, [47] cesium fluoride, [48] and tetrabutylammonium fluoride (TBAF) [49]. The most promising results came from TBAF by using poly(SES-MeAz)$_{50}$ as a model substrate. We first dissolved poly (SES-MeAz)$_{50}$ in THF, added TBAF, and allowed the reaction to proceed for two days at room temperature. The deprotection was carried under homogeneous conditions during this process. However, ^{1}H NMR and MALDI (Figure S14, Figure S15) of the polymer isolated from the reaction mixture indicated that only partially deprotected product was obtained (approximate deprotection rate of 80% by ^{1}H NMR integration).

We increased the reaction temperature to 50 °C and continued to use TBAF and THF. After completion of the reaction and subsequent purification, an off-white residue was isolated. The ^{1}H NMR spectrum of the residue (Figure S16) showed almost complete removal of the SES groups from poly(SES-MeAz)$_{50}$, as demonstrated by the loss of the signal of TMS groups at ~0.05 ppm in the ^{1}H NMR spectrum of the polymer. Furthermore, there is a new broad peak appeared between 2.80 and 3.80 ppm, attributed to the polymer backbone of lPPI, and a relatively sharp peak at ~1.30 ppm attributed to main chain methyl groups. The peaks belonging to the initiator was also retained in the aromatic region of the ^{1}H NMR spectrum. However, the NMR spectrum also showed unidentified signals that could not be attributed to lPPI, or poly(SES-MeAz)$_{50}$. We assumed that the purification of the as-prepared PPI was not completely successful. The GPC trace of lPPI (Fig. 4, Figure S17 and Table S1) was monomodal with a relatively low dispersity (1.32). The low dispersity is consistent with an absences of chain scission or cross-linking during the deprotection procedure. The elution volume for the lPPI shifted to lower elution volumes compared to the parent polymer; this was also observed in the literature [7].

2.4. Block copolymer p(pTs-MeAz)-b-p(SES-MeAz) preparation and deprotection

We conducted a sequential polymerization with pTs-MeAz in a solvent mixture (DMF + DMSO) to synthesize a novel block copolymer. The use of a cosolvent system was necessary to maintain solubility of the resulting block copolymer. First, the polymerization of pTs-MeAz was initiated using BuN(K)Ts in DMF. After 12 h, SES-MeAz in DMSO was added and continued to react for another 12 h. The resulting p(pTs-MeAz)-*b*-p(SES-MeAz) block copolymer was precipitated in methanol and analyzed after dying overnight. ^{1}H NMR analysis indicated a copolymer consisting of both pTs-MeAz and SES-MeAz regions (Figure S18). The ratio of the two monomers in the polymer backbone is 20:15, which is very close to the feed ratio (I:M_{pTs}:M_{SES} = 1:20:20). MALDI TOF mass spectrometry of the copolymer also underlined the success of the sequential polymerization, as all the main peaks in the spectrum were attributed to the mass of the initiator, with various amount of pTs-MeAz and SES-MeAz repeat units (Fig. 5). GPC analysis of

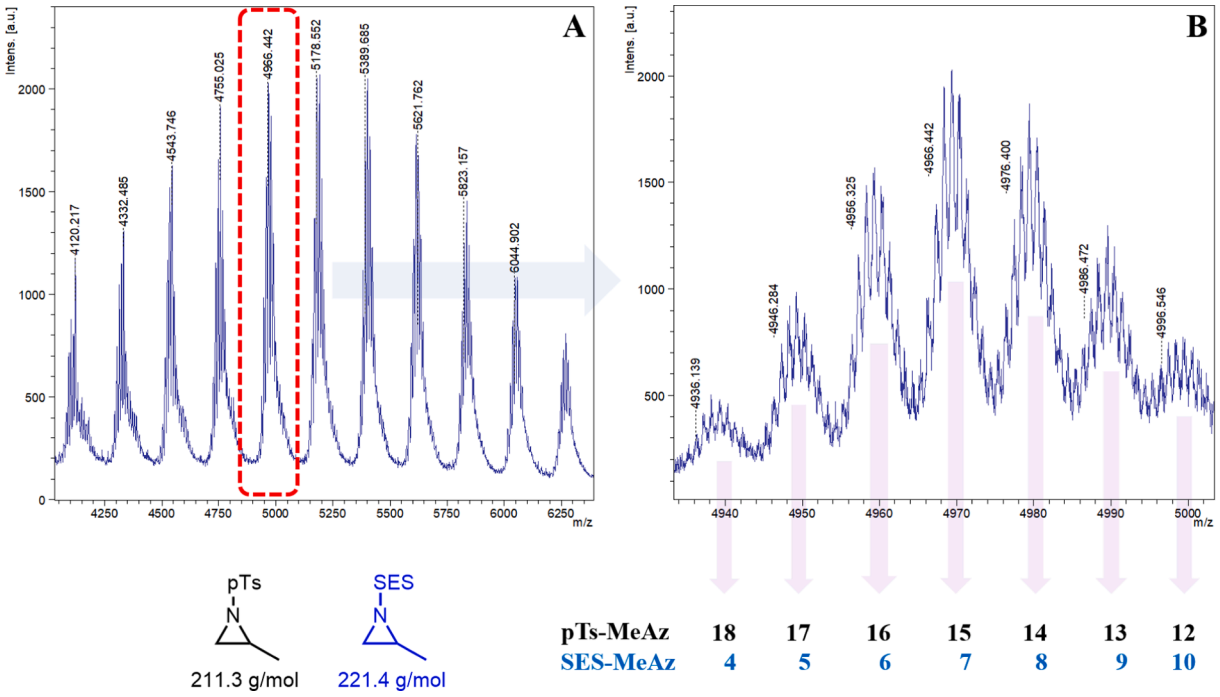
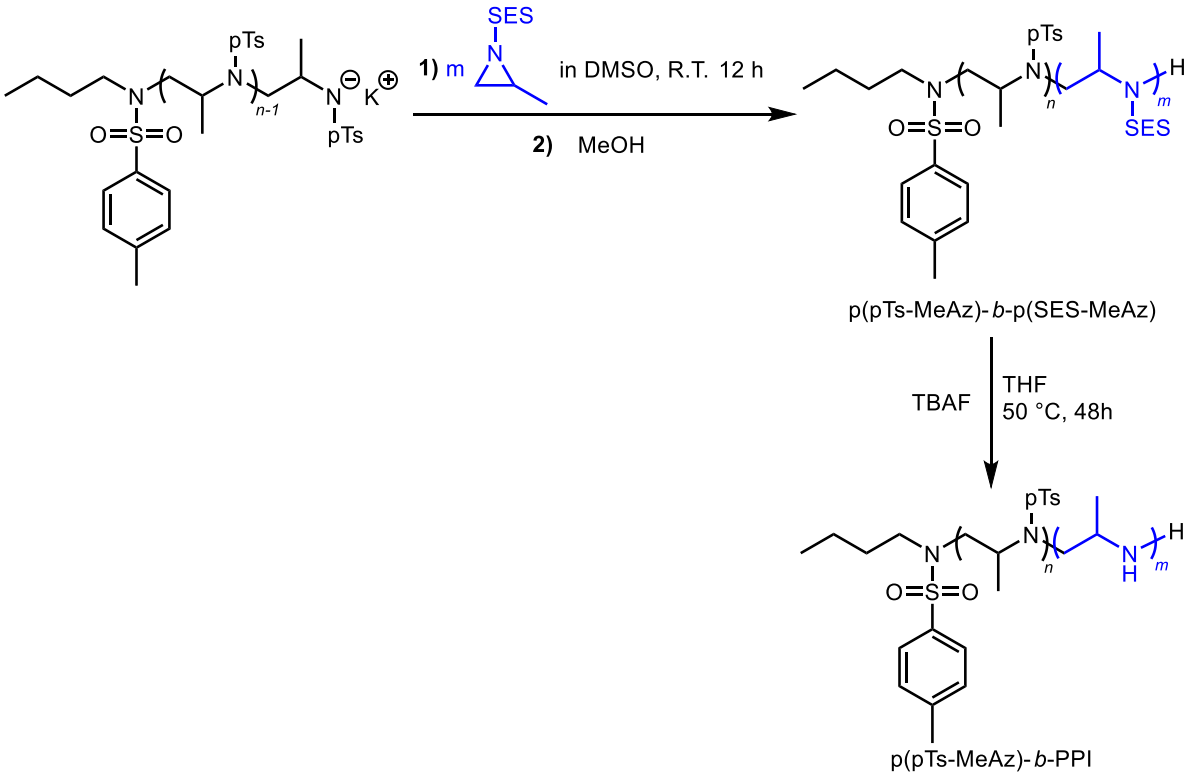
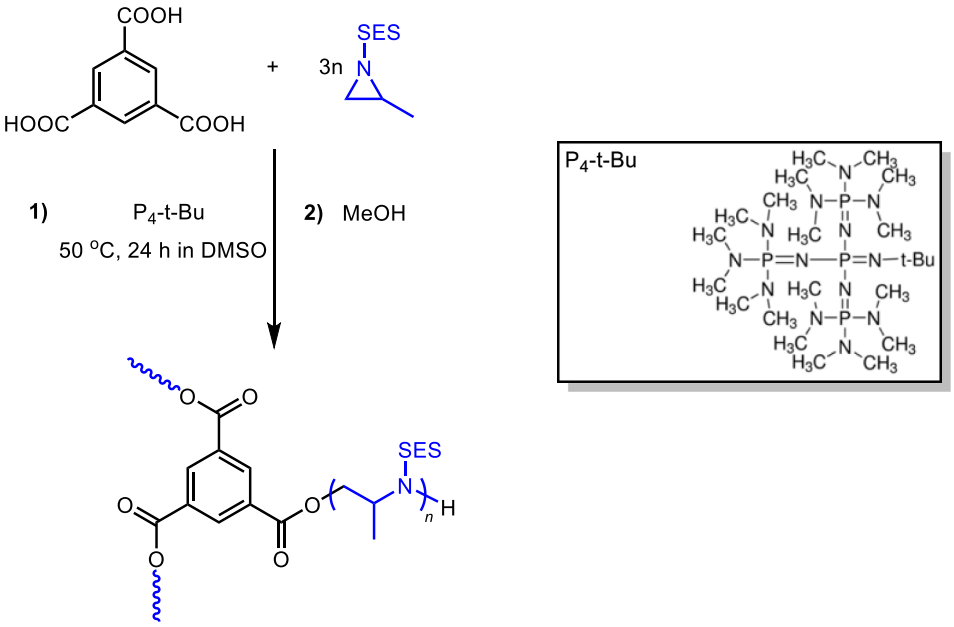


Fig. 5. (A) MALDI-TOF mass spectrum of a n-BuN(H)pTs initiated p(pTs-MeAz)-*b*-p(SES-MeAz) (I:M_{pTs}:M_{SES} = 1:20:20); (B) Zoom-in of the highlighted region. Each set of signals is attributed to pTs-MeAz block SES-MeAz.



Scheme 5. Synthesis of p(pTs-MeAz)-*b*-p(SES-MeAz) via sequential polymerization in a solvent mixture (DMF + DMSO) and its subsequent deprotection.



Scheme 6. Synthesis of star-shaped poly(SES-MeAz).

polymer samples before and after addition of SES-MeAz show chain extension (Scheme 5, Figure S20 and Table S2).

The block copolymer p(pTs-MeAz)-*b*-p(SES-MeAz) is noteworthy in that it should be possible to selectively deprotect the SES groups of the SES-MeAz block while leaving the pTs-MeAz polymer block unchanged. The desulfonylation of the synthesized p(pTs-MeAz)-*b*-p(SES-MeAz) was investigated by treating the polymer with TBAF in THF at 50 °C for 48 h. The ^{1}H NMR spectrum was consistent with the successful removal of over 95% of the SES groups. The characteristic ^{1}H NMR spectroscopic signal of the pTs group appear unchanged after SES removal (Figure S19). To our best knowledge, this is the first report on the selective removal of different sulfonyl protecting groups from poly(sulfonylazirdine) block copolymers. The GPC analysis is also consistent with our expectation, as the molecular weight of the copolymer

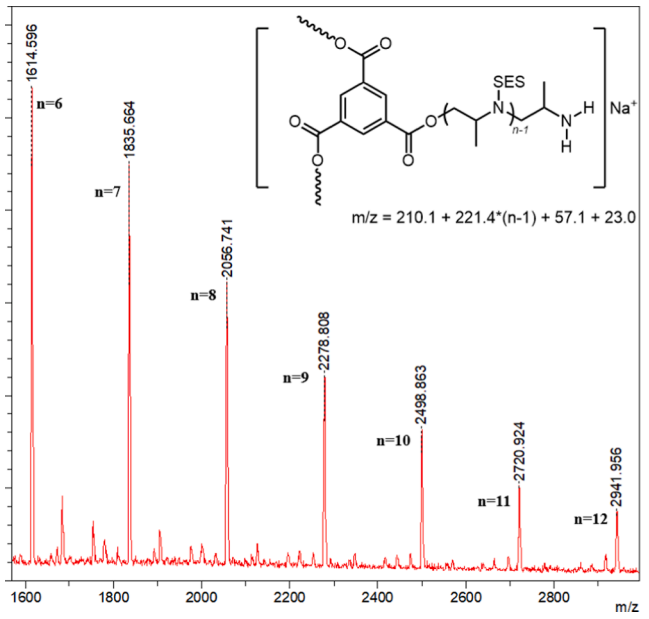


Fig. 6. MALDI-TOF mass spectrum of trimesic acid initiated star-shaped poly (SES-MeAz) (M:I = 60:1).

decreases after the deprotection reaction (Figure S20 and Table S2). The narrow molecular weight distribution in the GPC after deprotection is consistent with polymer backbone be unaffected by the deprotection. Because the two blocks have different hydrophilicities, the as-obtained p (pTs-MeAz)-*b*-PPI is likely to self-assemble under some conditions.

2.5. Star-shaped Poly(SES-MeAz) preparation

Although the polymerization of SES-MeAz appears to be living and controlled, poor solubility of higher molecular weight poly(SES-MeAz) limited the degree of polymerization to about 110 repeat units. Attempts at synthesizing poly(SES-MeAz) with higher degrees of polymerization resulted in precipitation of the polymer during the reaction.

The solubility of branched and star-shaped polymers is generally better than that of linear counterparts [50]. Therefore, to access higher molecular weight poly(SES-MeAz), we attempted to synthesize a poly (SES-MeAz) with a star-shaped architecture using trimesic acid as an initiator [28] (Scheme 6). First, a polymerization was carried out in which the monomer:initiator ratio was 60:1, which should result in arm lengths of *ca.* 20 repeating units. P_4-t-Bu, instead of KHMDS, was used to activate the initiator and to avoid precipitation of deprotonated trimesic acid [31]. In the ^{1}H NMR spectrum, resonances from ~ 8.87 ppm (protons of aromatic ring) and ~0.07 ppm (protons of TMS group) were employed for end group analysis (Figure S21). The D.P., as determined by ^{1}H NMR spectroscopic analysis closely matched the theoretical value, and the GPC trace was monomodal with a dispersity value of 1.26 (Figure S23 and Table S3). The aromatic region of the ^{1}H NMR spectrum had a single signal, which is consistent with the symmetrically substituted trimesate core of a three-arm star polymer. The MALDI TOF mass spectrum consisted of a series of equidistant peaks separated by 221.4 mass units, which corresponds to the molecular mass of SES-MeAz (Fig. 6). Each signal matches the mass of sodium adducts of a star-shaped polymer, with the loss of one SES group (presumably occurring during MALDI-TOF analysis).

Next, we performed a second polymerization in which the monomer: initiator ratio was 600:1, while keeping other conditions unchanged. The ^{1}H NMR spectrum and GPC trace of the resulting polymer (Figure S22, Figure S23 and Table S3) were consistent with a star-shaped poly(SES-MeAz), with arm lengths of 200 repeat units. Gratifyingly, this polymer remained soluble throughout the polymerization, thus illustrating the effectiveness of using a star-shaped architecture to improve solubility of the high molecular weight poly(SES-MeAz).

3. Conclusions

A novel N-activated aziridine monomer, *N*-((2-(trimethylsilyl)ethyl) sulfonyl)-2-methyl-aziridine (SES-MeAz), was synthesized and found to undergo AROP to form poly(SES-MeAz). The polymerization was living and controlled, which allowing the success synthesis of polymers of targeted molecular weights with narrow molecular weight distributions. The deprotection of this homopolymer shows that the SES group can be effectively removed from the polymer backbone, even though the purification of the obtained lPPI needs further investigation. A block copolymer p(pTs-MAz)-*b*-p(SES-MeAz) was prepared and the SES group was removed selectively. Star-shaped poly(SES-MeAz) was also successfully synthesized and was found to have improved solubility compared to the linear version.

Data Availability

Research data required to reproduce these findings can be found from open science framework (OSF) at https://doi.org/10.17605/OSF.IO/HCSZ3

CRediT authorship contribution statement

Taoguang Qu: Experiment, Test, Data Analysis, Writing-original draft and Editing. **Paul A. Rupar:** Supervision, Writing-review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2022.111135.

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