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Alcohol- and Water-Tolerant Living Anionic Polymerization of Aziridines

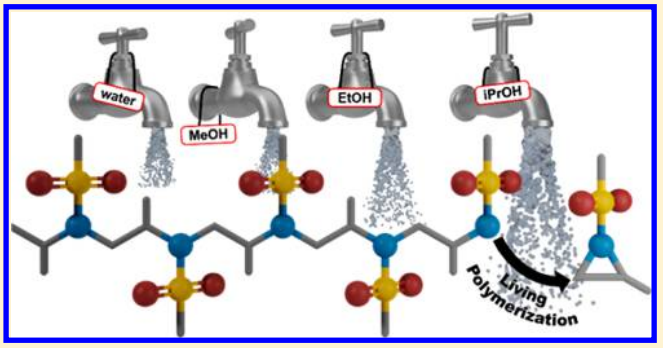
Tassilo Gleede,[§,‡] Elisabeth Rieger,[§,‡] Lei Liu,[§] Camille Bakkali-Hassani,[†] Manfred Wagner,[§] Stéphane Carlotti,[†] Daniel Taton,[†] Denis Andrienko,[§] and Frederik R. Wurm*[,§]

[§]Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

[†]Laboratoire de Chimie des Polymères Organiques (LCPO), Université de Bordeaux, IPB-ENSCBP, 16 av. Pey Berland, 33607 PESSAC Cedex, France

Supporting Information

ABSTRACT: Living anionic polymerization gives access to well-defined polymers, but it demands strict purification of reagents and solvents. This work presents the azaanionic polymerization (AAROP) of aziridines as a robust living polymerization technique, with the ease of controlled radical polymerizations. AAROP does not require inert atmosphere and remains living in the presence of large amounts of water or alcohols. Mesyl-, tosyl-, or brosyl-activated aziridines were polymerized with up to 100-fold excess of a protic impurity with respect to the initiator and still being active for chain extension. This allowed the preparation of polyols by anionic polymerization without protective groups, as only minor initiation occurred from the alcohols. The tolerance toward protic additives lies in the electron-withdrawing effect of the activating groups, decreasing the basicity of the propagating species, while maintaining a strong nucleophilic character. In this way, competing alcohols and water are only slightly involved in the polymerization, making living anionic polymerization an easy-to-conduct technique to well-defined polyamides and -amines.



INTRODUCTION

Living anionic polymerization (LAP) is the best technique to control molar mass, chain-end fidelity, and to achieve well-defined (co)polymers.[1,2] It also provides a precise way for introducing of heteroatoms in the polymer backbone.[3,4] LAP is, however, sensitive to protic impurities and, in many cases, oxygen. Thorough drying of reagents and solvents, high-vacuum, and inert gas purifications make it much more difficult to carry out than, for example, a controlled radical polymerization.[5,6] It would therefore be beneficial to combine the robustness of the controlled radical polymerization with the precision of the living ionic polymerization.

Ionic polymerizations can be terminated by moisture, protic solvents, or CO_2.[7] In the epoxide polymerization, water or alcohols act as initiator, and only low-molecular-weight products are obtained.[8−10] Importantly, protic impurities at concentrations above the initiator concentration inhibit the propagation, which makes protecting groups essential (e.g., for alcohols).

A robust LAP that can tolerate protic solvents, especially water, while maintaining the living character, is not known. To circumvent the demanding conditions of LAP, emulsion polymerization elegantly exploits the hydrophobic nature of monomers and polymers and separates the active chain end from the protic aqueous phase. As a result, the polymerization takes place at the interface or inside of the hydrophobic dispersed phase and is the only strategy for conducting an ionic polymerization in the presence of protic solvents. Unfortunately, it cannot suppress termination or transfer reactions, as reported for the aqueous emulsion polymerization of cyclic siloxanes[11,12] or phenyl glycidyl ether, leading to oligomers.[13] Similar approaches of anionic polymerizations of α-carbonyl acids[14] or glycidol in the presence of water[15] bypass the typical anionic polymerization mechanism (e.g., by monomer-activation). Organocatalyzed polymerization also circumvents typical characteristics of anionic polymerization, and recently, we demonstrated that carbenes allow NH-selective initiation of activated aziridines with 2-methylaminoethanol as initiator to synthesize polysulfonamides with a single terminal hydroxyl group for further modifications.[16]

We present the first living anionic polymerization that proceeds in open air and in the presence of large amounts of protic impurities, such as water and alcohols. The azaanionic ring-opening polymerization (AAROP) is chosen as a unique technique to access well-defined polysulfonamides or -amines (Scheme 1).

The exceptional tolerance toward water and alcohols during the polymerization allows, for the first time, the ability to work

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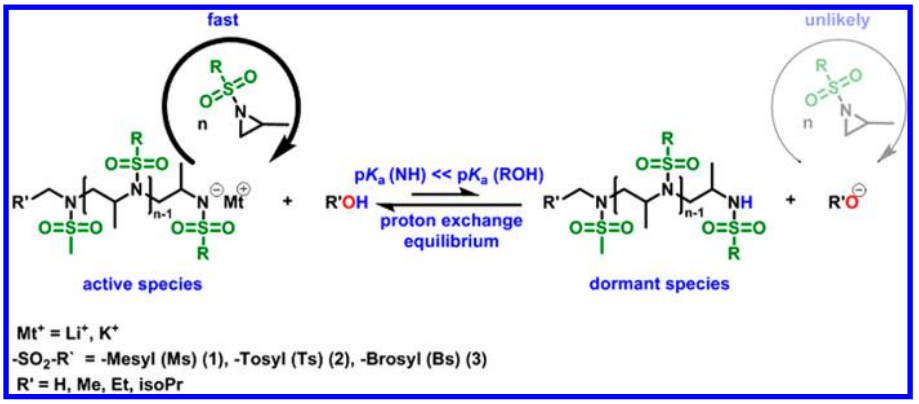
Scheme 1. Schematic Overview of the A-AROP with Protic Additives Showing the Dormant Polymer Species and Active Polymer Species



without strict inert gas conditions and to use solvents without vigorous purification. The tolerance toward alcohol groups further allows polymerizing monomers containing unprotected hydroxyl groups to synthesize polyols without using any protective groups (see below). Such polyols might be interesting for the preparation of polyurethanes or for antifouling surface coatings. In contrast to the robustness of the tosylated and mesylated aziridines in this report, Rupar and co-workers recently showed that when using aziridines with 2-nitrosulfonyl activation group, even small amounts of nucleophilic impurities can cause spontaneous polymerization.[17] This further underlines the chemical versatility of sulfonamide-activated aziridines.

Polysulfonamides, prepared from the AAROP of sulfonyl-activated aziridines, have been first polymerized via living polymerization in 2005.[18] The monomer family has been significantly expanded since then,[19,20] and new methods were developed to polymerize sulfonamides via organocatalytic[21−24] or anionic polymerization in solution[25−27] and in emulsion.[28] After cleavage of the sulfonyl groups, polysulfonamides are an alternative pathway to linear polyethylene imine (LPEI),[26,29] which, together with hyperbranched PEI (*hb*PEI), is a standard synthetic cationic transfection agent.[30−33]

The role of the sulfonamide activating groups is 2-fold: they control the microstructure of copolymers,[27] as well as regulate the nucleophilicity and basicity of the active chain end. The latter allows tuning reaction tolerance to additives, protic solvents, or nucleophilic functionalities in the monomers, which is the focus of this contribution. We believe that the ease of conducting a living anionic polymerization to access well-defined polyamines will contribute to diverse fields, such as gene delivery or the preparation of chelating agents or polyols for polyurethane fabrication.

To control the polymerization of sulfonyl aziridines, all previously published articles highlighted the necessity to strictly avoid moisture, impurities and the protection of nucleophilic monomer functionalities. Preparation of the experiment was thus conducted in a glovebox or with Schlenk techniques under an inert gas atmosphere.[21,22,25,26] Concerning the water content of solvents, an in situ distillation from elemental sodium or calcium hydride is established for anionic polymerization, but it is known that some solvents are difficult to dry efficiently.[6,9] A method that sustains the presence of protic compounds is necessary. The tolerance of the active chain end in an anionic polymerization toward nucleophilic impurities (such as water or alcohols) strongly depends on the pK_b-value of the growing chain end and the propagation rate constants. For sulfonyl-aziridines, both factors can be tuned by the choice of the activating group that influences the basicity of the azaanionic chain end and at the same time the propagation rates and thus controls the chance of initiation of protic impurities in the reaction mixture. We selected three different monomers, in order of their increasing propagation rates and different nucleophilicity of the chain end: 2-methyl-*N*-mesyl-aziridine (MsMAz, **1**) 2-methyl-*N*-tosylaziridine (TsMAz, **2**), 2-methyl-*N*-brosylaziridine (BsMAz, **3**) (Scheme 1).[27] Monomers **1**−**3** have all been previously shown to undergo AAROP under an inert environment.

RESULTS AND DISCUSSION

Strikingly, we found that polymerizations could be carried out in open vials (SI, Section D) in DMF (without any purification or drying), resulting in narrowly distributed PAz ($Đ \leq 1.11$, M_n = 4400), which remained living and allowed further chain extension, proving the living nature under such wet conditions, without recognizable initiation of water and achieving the targeted degree of polymerization (Figure S31 and SI, Section F), polyaziridines with molar masses of M_n = 4400 to 3600 were obtained by varying the amount of added water from 1 to 100 equiv. Additionally, the AAROP followed living characteristics in reactive solvents, which would inhibit other anionic polymerizations ($P(\mathbf{2})_{50}$ was prepared in acetone ($Đ$ = 1.16, M_n = 6400), ethyl acetate ($Đ$ = 1.18, M_n = 3700) and iPrOH ($Đ$ = 1.23, M_n = 2500). The low dispersity from the polymers prepared in open air or such solvents prove that the AAROP is unaffected by CO_2 and O_2 remains living in "non-conventional" solvents of anionic polymerization (Figure S25, S30, S31).

In order to understand the influence of chain-end and monomer reactivity on the control of the A-AROP, (**1**) and (**2**) were polymerized in the presence of protic additives. Different amounts (1−1000 equiv relative to the initiator) of water (H_2O), methanol (MeOH), ethanol (EtOH), and isopropanol (iPrOH), which usually act as transfer or terminating agents for other anionic polymerizations, were added to the reaction medium. The maximum amount of each additive was limited due to the solubility of the polymers in polar solvent mixtures (see experimental details in SI). However, if the amounts of water were increased to 1170 equiv for (**2**) and 740 equiv for (**1**), a significant reduction in the molar mass from targeted 5500 to 1200 g/mol and from 4000 to 500 g mol^{-1} of the final polymer was detected,

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indicating a non-negligible amount of competitive initiation by the additive (Figure S22, S27). Lower amounts of the additive had no or only little influence on the molar mass as similar elution times by SEC were detected for the polymers (Figure S26, Table S8). In all cases, chain extension experiments with additives were performed (90−360 equiv depending on the solvent), proving that the chain ends remained reactive for further monomer addition with reasonable final dispersities ($Đ \leq 1.25$) and quantitative conversions ≥99% for **1** with all additives tested (see SI Section F, Figures S38−S41).

Taking a closer look at the monomers **1** and **2**, TsMAz (**2**), with its stronger electron-withdrawing group, demonstrated a higher tolerance to the presence of additives, as propagation rates were 5-fold faster compared to MsMAz (compare Figure S22−S25 for (**1**) and Figure S26−S30 for (**2**)). The influence of counterions (K^+, Li^+) was also studied with all additives tested, showing no significant difference; both indeed show full monomer conversion and low molecular weight distributions ($Đ < 1.25$, compare Figure S26−S30, S32, S33).

The polymerization kinetics and the amount of the PAz initiated by the additive were determined via real-time ^{1}H NMR spectroscopy of the polymerizations of **1**, **2**, and BsMAz (**3**) in the presence of ^{13}C-labeled alcohols. In Figure 1, the polymerization kinetics of **2** are summarized, proving an influence of the protic additives on the overall reaction rates. Within the presence of 100 equiv of isopropanol (green), almost the same k_p-value was determined as for the polymerization in dry DMF (black) without any additive. However, propagation rates decreased in the presence of ethanol (orange), water (blue), and methanol (red), probably due to an increased concentration of initiating species from the additives and the equilibrium between active and dormant species, since the rate constant depends on the nature of the alcohol. Nevertheless, in all cases, the degrees of polymerization were close to the control (typically above 95%) and had narrow molecular weight distributions ($Đ \leq 1.18$, Figure 1b).

Table 1 summarizes the data from the real-time NMR measurements of TsMAz. The trend observed from the kinetic plots in Figure 1A is reflected in the propagation rates (k_p), that range between $22.9 \pm 1.4 \times 10^{-3}$ L mol^{-1} s^{-1} for methanol and $49.9 \pm 3.6 \times 10^{-3}$ L mol^{-1} s^{-1} for the pure reaction mixture (Figure 2). Also, reaction times from 2.6 h (pure) to 9.4 h (MeOH) for full conversion, indicate the presence of the dormant species, as the protonation of the chain end is reversible (Scheme S1). For the other two monomers (**1** and **3**), similar trends were observed (see SI, Section B). A comparison of their propagation rates (k_p) in Figure 2 (solid line, points) depicts that the general reactivity of the monomers increases from MsMAz (**1**, red) to TsMAz (**2**, green) to BsMAz (**3**, yellow), as reported earlier.[27] The trend of decreasing molar mass (M_n) (Figure 2, dotted line, squares) is in accordance to the decreasing propagation rates, which is due to a certain side initiation by the additives. MALDI-TOF-spectra of P(TsMAz) obtained in the presence of 100 equiv of additives (H_2O, MeOH, EtOH, iPrOH) (see SI, Section E), show a narrowly distributed main population of PAz chains initiated with the sulfonamide initiator. In all cases, a smaller fraction can be identified as TsMAz initiated by the additive. Notably, iPrOH as a secondary alcohol does not influence the k_p-value, with only a minor influence on M_n or $Đ$.

As MALDI is not quantitative, we used ^{13}C NMR to quantify the amount of alcohol-initiated polymers from the integral of the ether signal of ^{13}C-labeled alcohols, used as

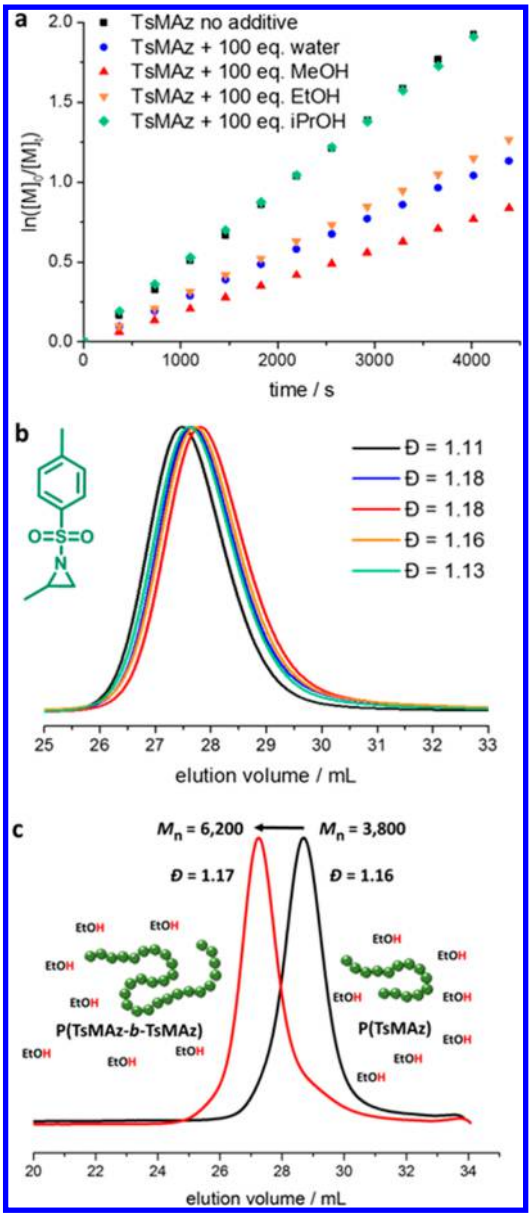

Figure 1. (a) Kinetic plots of $\ln([M]_0/[M]_t)$ vs time of TsMAz (2) and 100 equiv of different additives in DMF-d7 at 50 °C. (b) SEC traces of the polymers corresponding to panel a in DMF (RI signal) (data listed in Table 1). (c) SEC traces (RI signal) of chain extension of P(TsMAz and P(TsMAz-*b*-TsMAz), polymerization was performed with 90 equiv excess of ethanol (compared to 1 equiv initiator).

additives. HSQC-spectra proved the existence of ^{13}C-labeled ethers (see SI, Section C). Distinctive ^{13}C-ether resonances below 10% (except for MsMAz with MeOH as additive) were detected, as depicted in Figure 2 (dashed line, triangles) and summarized in Table S3. TsMAz (**2**) is the most tolerant monomer, as all ^{13}C-ether signals are below the quantification limit of NMR-spectroscopy (≤1%), determined by a high signal/noise ratio (S/N). For all three monomers, the signals of ^{13}C-isopropyl ether are also below the quantification limit of NMR-spectroscopy, showing a negligible amount of initiation for this secondary alcohol. The more acidic and nucleophilic the additive, the higher the amount of secondary initiation.

Because of the much lower pK_a value of the sulfonamide compared with the protic additives, the majority of living

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Table 1. Overview of the Polymerization Kinetics of TsMAz (2) in DMF-d_7 with the Respective Additive, Including SEC-Analyses and Calculated Propagation Rates (k_p)

monomer	TsMAz	TsMAz	TsMAz	TsMAz	TsMAz
additive	pure	H_2O	MeOH	EtOH	iPrOH
k_p / 10^{-3} L mol^{-1} s^{-1}	49.9 ± 3.6	28.1 ± 2.0	22.9 ± 1.4	29.6 ± 2.1	48.6 ± 3.5
M_n[a] / g mol^{-1}[b]	5500	4700	4400	4800	5100
DP/units	56	--	55.8	53.7	55.4
DP/%	100	--	99.6	95.9	98.9
$Đ$[a]	1.11	1.18	1.18	1.16	1.13
reaction time/h	2.6	5.5	9.4	4.7	2.8
conversion/%	>99	>99	>99	>99	>99

[a]Number-average molar mass and molecular weight dispersities determined via SEC in DMF (vs. PEO standards). [b]The molecular weight of polyaziridines determined by SEC vs PEO standards is underestimated on our setup (ca. by the factor of 2 to 3).

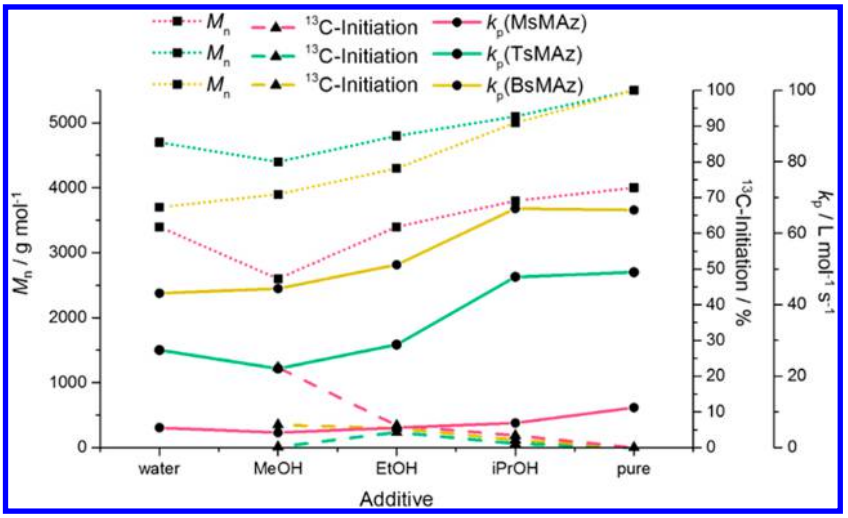

Figure 2. Comparison of the molar masss (M_n) (dotted line, squares, left y-axis), amount of ^{13}C-initiation (dashed line, triangles, first right y-axis) and propagation rates (k_p) (solid line, points, right y-axis) of all online NMR-kinetics of the three monomers MsMAz (**1**, red), TsMAz (**2**, green) and BsMAz (**3**, yellow) with the respective additives (pure, water, MeOH, EtOH, iPrOH).

chains remains on the aza-anion, and only an almost negligible amount of the additive is deprotonated and can initiate the polymerization (Figure 3B and Scheme S1 for a detailed mechanistic explanation).

Such amounts of "undesired" initiation can be circumvented by working under absolute inert conditions as typical for anionic polymerizations. However, compared to controlled radical polymerizations, where up to 10% of all chain ends can be undesirably initiated (in RAFT), even without including "dead" polymers by radical termination,[34−36] we believe the ease of reaction conditions makes the AROP of aziridines an attractive alternative.

In most cases, the secondary initiation was below 10%, (MsMAz with MeOH around 22%), but without "dead" polymers (i.e., the chain end remains always active). The highest percentage of secondary initiation was demonstrated for MsMAz (**1**) because its slow reaction kinetics allows also the slow initiation of alkoxides to occur. Whereas, BsMAz (**3**) (the most reactive monomer) reveals a higher percentage of ^{13}C-signals than TsMAz (**2**), which is most likely due to its stronger electrophilic character and makes the monomer susceptible for nucleophilic attacks. Concluding, TsMAz (**2**) is well-balanced between fast reaction kinetic and susceptibility for nucleophilic attacks, (**2**) is the most robust monomer of the three tested sulfonyl aziridines (Figure 3).

DFT Calculations. To rationalize the effect of initiation of different additives, we performed density functional theory (DFT) calculations for the propagation steps. The results are summarized in Figure 3 and Tables S19−21 (for computational details see SI, Section G). The chain end and monomer reactivity can be elaborated from the comparison of the energies of the frontier orbitals (Figure 3A). The highest occupied molecular orbitals (HOMO) of the active chain ends were calculated from corresponding model compounds of deprotonated *sec*-butyl(-*R*-)amides ((Table S20), R = brosyl (Bs), tosyl (Ts), or mesyl (Ms)). The activating groups proved to have a stronger effect on the monomer reactivity compared to the active chain ends, as the difference (−0.24 to −1.75 eV) in LUMO levels are larger than the HOMO levels (−5.30 to −5.44 eV). In addition, calculations show that the alkoxides (from deprotonation of the added alcohols) exhibit more reactive HOMO levels of ca. −4.7 eV, which are around 0.7 eV higher in energy than the HOMO levels of the chain ends. These findings go along with the expectations that lower LUMO levels are easier to be occupied by nucleophiles with higher HOMO levels; that is, the alkoxides should preferably act as an initiator for the azaanionic polymerization, as soon as they are formed in solution. Moreover, we have computed the electrophilicity index ω^+ and the nucleophilicity index ω^- regarding the homopolymerization of each monomer (Figure 3B and Table S19, S20). The nucleophilicity of additives and sulfonamides varies in the range of 0.13 to 0.27 eV, which show that alkoxides are strong competitors to the active chain ends, especially if the concentration of alcohol exceeds the

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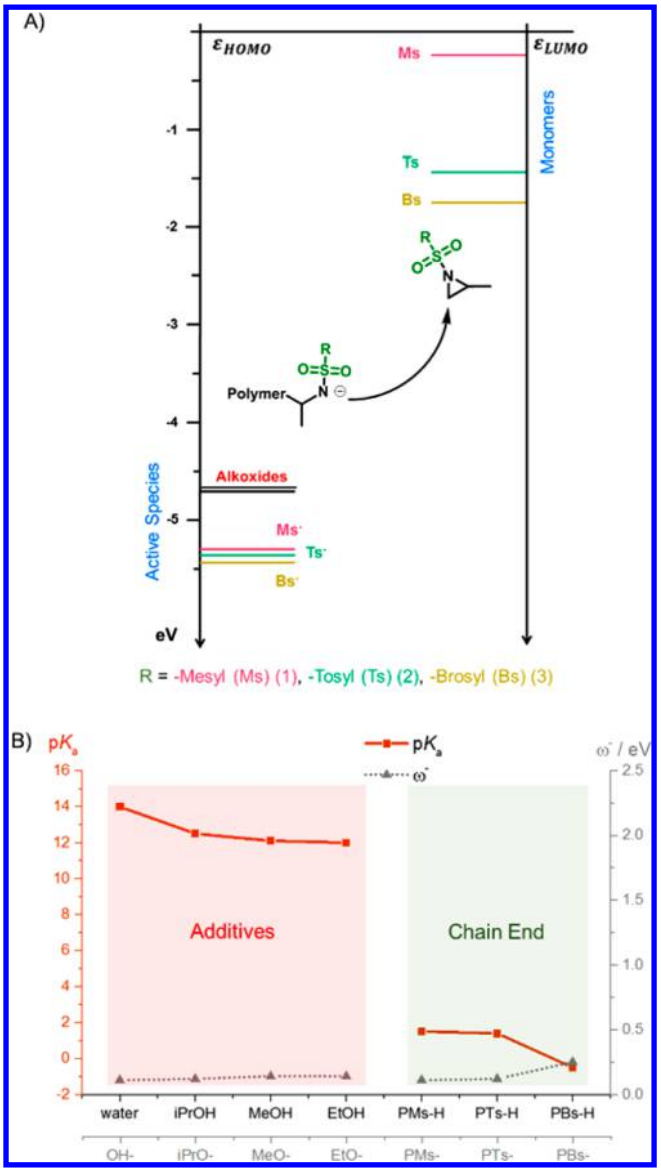

Figure 3. DFT (B3LYP/6-311++G**(SCRF, DMF)//B3LYP/6-31+G*) calculations of the following: (A) HOMO levels of the active species: chain ends and alkoxides (left), and LUMO levels of the monomers (right). (B) pK_a-values (DMF, calculated) (dark red solid line, squares, left *y*-axis) and the nucleophilicity index (ω^-) (gray dotted line, triangles, right *y*-axis and gray *x*-axis on the bottom) for the additives, highlighted in red (left), and the chain ends, highlighted in green (right).

initiator concentration. However, due to the enormous difference in the pK_a-values of a sulfonamide (pK_a = −0.5 to 1.5 in DMF) and the additives (pK_a = 12.0 to 14.0 in DMF) propagation via the azaanion is clearly favored over the deprotonation and initiation by additives (Figure 3B and Table S21, pK_a values were calculated using eq 5 in the SI, section G). DFT calculations therefore help to rationalize the fact that additives such as alcohols or water can be tolerated by the azaanionic ring-opening polymerization.

Synthesis of Polyols without Protective Groups. Since hydroxyl groups are relatively inert during the anionic ROP of sulfonyl aziridines (**1**−**3**), there is no need to protect protic functionalities in the monomers. This allows a direct access to polyols via living AROP.[29] Indeed, the unprotected 2-ω-propanol-*N*-tosylaziridine (**6**) was polymerized with full monomer conversion, and reasonable molecular weight distributions of ($Đ$ = 1.26−1.37) were obtained under standard conditions of A-AROP (compare SI, Section H). A small amount of branching cannot be ruled out, but neither ^{1}H, ^{13}C NMR spectra (Figures S44, S45) nor SEC-data (Figure 4) can provide this information because the monomer is not ^{13}C-labeled and from the experiments in the presence of alcohols, only a small amount of branching can be assumed.

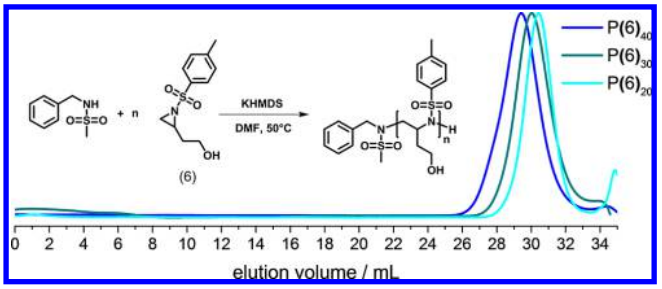

Figure 4. Anionic polymerization of **6**, including SEC traces of three different polymers of **6** with theoretical repeating units (20, 30, 40) in DMF (RI signal) (data listed in Table S22).

CONCLUSIONS

To conclude, the AROP of aziridines eliminates the tedious purification steps and high-vacuum techniques, which make an anionic polymerization unattractive compared to controlled radical polymerizations. Herein, we systematically investigated the influence of protic additives that are water and different alcohols (methanol, ethanol, isopropanol) on the AROP of different sulfonyl aziridines. Even at large excess of the protic impurity (more than 100 equiv compared with the initiator), the AROP of sulfonyl aziridines leads to quantitative monomer conversion and retains excellent control over molar mass and dispersity. The combination of different analyses (real-time ^{1}H NMR spectroscopy, MALDI-TOF, SEC, and ^{13}C NMR) and additional DFT-calculations confirmed a second slow initiation of protic solvents, of up to 10% with 100 equiv of additives (except for MsMAz with MeOH as additive). In spite of the high nucleophilicity of additives, but their high pK_a-values, the propagation of the aza-anions (with much lower pK_a-values) remained almost unaffected by the presence of additives (especially for TsMAz), and the polymerization keeps its living character. Because high control over molar mass, chain fidelity, size distribution, and quantitative monomer conversion remains, the access to well-defined polyamides (and polyamines after hydrolysis) is still guaranteed. With this robust AROP polyols are accessible without the need of protection groups, which are interesting materials for future applications. The AROP of sulfonyl aziridines offers the simplicity of a controlled radical polymerization, where less than 10% of initiator-initiated polymers are accepted, and any termination is avoided.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01320.

Additional spectra and characterization data (PDF)

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AUTHOR INFORMATION

Corresponding Author

*(F.R.W.). E-mail wurm@mpip-mainz.mpg.de. Tel.: 049 6131 379 581. Fax: 0049 6131 370 330.

ORCID

Stéphane Carlotti: 0000-0002-0086-4955
Daniel Taton: 0000-0002-8539-4963
Denis Andrienko: 0000-0002-1541-1377
Frederik R. Wurm: 0000-0002-6955-8489

Author Contributions

‡(T.G., E.R.) These authors contributed equally

Notes

The authors declare no competing financial interest.

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