Macromolecules

pubs.acs.org/Macromolecules

Article

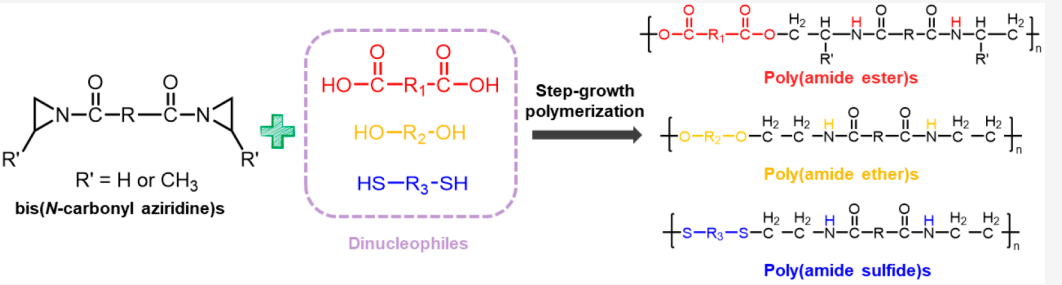
Carbonyl Aziridines: Strained Amides for Rapid Polyamide Synthesis

Taoguang Qu and Paul A. Rupar*

Cite This: *Macromolecules* 2022, 55, 9513–9519

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: The polymerizations of bis(*N*-carbonyl aziridine)s to form polyamide copolymers are reported. Terephthalaziridine (**TP-Az**), derived from postconsumer PETE, reacts with a variety of dinucleophiles, including dicarboxylic acids, diphenols, and disulfides, to form poly(amide ester)s, poly(amide ether)s, or poly(amide sulfide)s, respectively. The step-growth polymerization of the aliphatic adipoyl aziridine (**AD-Az**) and the 2-methyl-substituted **TP-MeAz** mirrors that of **TP-Az**. The polymerizations of **TP-Az, AD-Az**, and **TP-MeAz** are performed under mild conditions and open air, conditions that are compatible with many functional groups. As examples, both itaconic acid (containing a vinylidene group) and D-tartaric acid (containing a diol) copolymerize with **TP-Az** without the need for protecting group chemistry.

INTRODUCTION

Polyamides are among the most important class of polymeric materials[1] and are widely used in the automotive, furniture, textile, and electronics industries.[2−4] There are a limited number of routes to polyamides,[5−7] the most common being step-growth polycondensations of carboxylic acids and amines[8−10] or by the ring-open polymerizations of caprolactam and related cyclic amides.[11,12] Chain-growth polycondensations have also been reported in polyamide synthesis.[13] Unfortunately, existing polyamide syntheses lack flexibility, are functional group intolerant, can require complex monomer synthesis and purification, and often require the removal of byproducts during the polymerization.

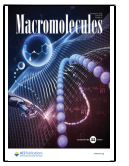
We now report the base-catalyzed copolymerization of bis(*N*-carbonyl aziridine)s and dinucleophiles to form polyamides (Scheme 1a). The polymerization is driven by the nucleophilic ring-opening of *N*-carbonyl aziridines to form amide linkages. Compatible dinucleophiles include dicarboxylic acids, diphenols, and dithiols. Stringent reaction conditions are avoided as the bis(*N*-carbonyl aziridine)s polymerizations are performed in an ambient atmosphere under mild conditions. Furthermore, there are no condensation byproducts to remove during or postpolymerization. Moreover, excellent functional group tolerance allows polymerization with highly functionalized comonomers without the need of protecting group chemistry.

Our work builds on the development of the anionic polymerization of *N*-sulfonyl aziridines (Scheme 1b), which are now recognized as valuable monomers to prepare poly(*N*-sulfonyl aziridine), poly(sulfonamide amine), polyimines, thiacyclic polymers, and poly(*N*-sulfonyl aziridine) containing copolymers and composites.[14−28] We have also recently reported the polymerization of a *tert*-butyloxycarbonyl (BOC)-activated aziridine, demonstrating that non-sulfonyl electron-withdrawing groups can support anionic aziridine polymerizations.[29] The versatility of *N*-sulfonyl aziridines has expanded with reports that bis(*N*-sulfonyl aziridine)s form polysulfonamides, the sulfonyl analogues of amides, upon reaction with dinucleophiles. Specifically, Yoon prepared a bis(*N*-sulfonyl aziridine) monomer derived from bisphenol A that reacts with various dinucleophiles under mild conditions (Scheme 1c), although competing AROP chain growth also occurred.[30] In addition, Zhang developed a bis(*N*-sulfonyl aziridine) that polymerized with nucleophilic comonomers in the presence of organobase catalysts (Scheme 1d).[31]

RESULTS AND DISCUSSION

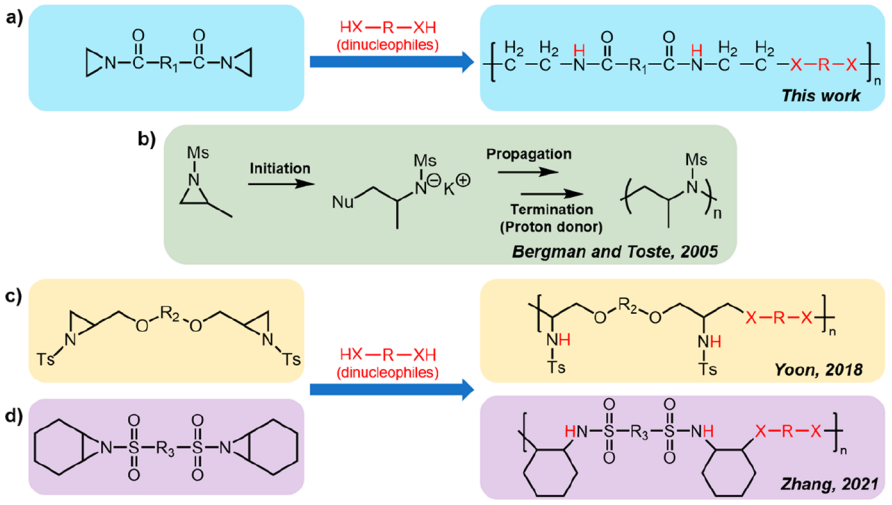
There are only a few examples of polymer synthesis involving bis(aziridine)s.[32−34] Here, we began our investigation into the

Received: August 22, 2022
Revised: October 10, 2022
Published: October 25, 2022



https://doi.org/10.1021/acs.macromol.2c01748
Macromolecules 2022, 55, 9513−9519

Scheme 1. (a) Alternating Polyamides Prepared by Step-Growth Polyaddition of Bis(*N*-carbonyl aziridine)s (This Work); (b) Anionic Ring-Opening Polymerization of *N*-Sulfonyl Aziridines; (c, d) Examples of Alternating Polymers Prepared by Step-Growth Polyaddition of Bis(*N*-sulfonyl aziridine) Containing Monomers

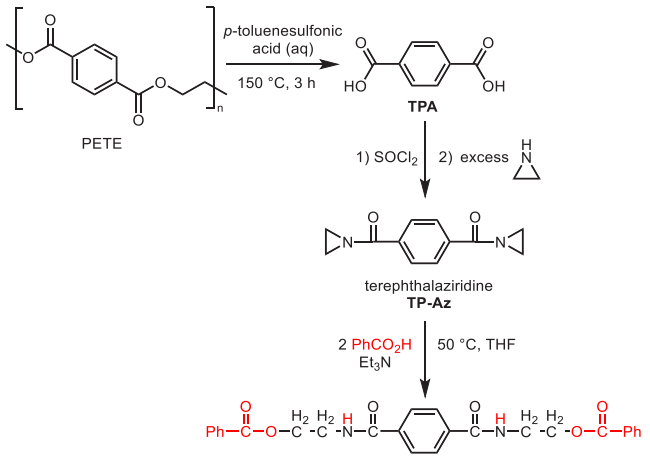


polymerization of bis(*N*-carbonyl aziridine)s using terephthalaziridine (**TP-Az**). In 1967, **TP-Az** was disclosed to copolymerize to form poorly characterized, low molecular weight materials under acidic conditions.[33] However, this initial work on acid-catalyzed **TP-Az** copolymerization predates reports on base-catalyzed polymerizations of *N*-sulfonyl aziridines[35−37] as well as work on nucleophilic carbonyl aziridine ring-opening.[38−43] Therefore, we suspected that **TP-Az** should copolymerize to form polyamides under basic conditions.

N-Carbonyl aziridines are known to undergo ring-opening with a variety of nucleophiles and have been employed as cross-linking agents.[38−44] We decided to investigate the potential for terephthalaziridine (**TP-Az**) as a representative bis(*N*-carbonyl aziridine) for use in step-growth polymerizations. **TP-Az** was synthesized from terephthalic acid, which was generated by hydrolyzing post-consumer poly(ethylene terephthalate) (Scheme 2, Figures S1 and S2).[45]

We observed that in the presence of a base, **TP-Az** reacted rapidly with benzoic acid to quantitatively form an amide ester (Scheme 2 and Figure S3). Encouraged by this result, we next attempted a polymerization between **TP-Az** and terephthalic acid with catalytic P_4-*t*-Bu.[46] P_4-*t*-Bu has been used previously to promote the AROP of *N*-sulfonyl aziridines.[21,37] After 72 h, the polyamide **PA-1** (Table 1, entry 1) was precipitated in methanol and isolated in a moderate yield and molecular weight (54%, $M_{w,GPC}$ = 12.5 kDa, $Đ$ = 1.67, Figure S31). The ^{1}H NMR spectrum of **PA-1** is consistent with the proposed poly(amide ester) copolymer structure (Figure S4) as is the MALDI-ToF MS spectrum (Figure S5).

Scheme 2. Synthesis of TP-Az and Its Reaction with Benzoic Acid



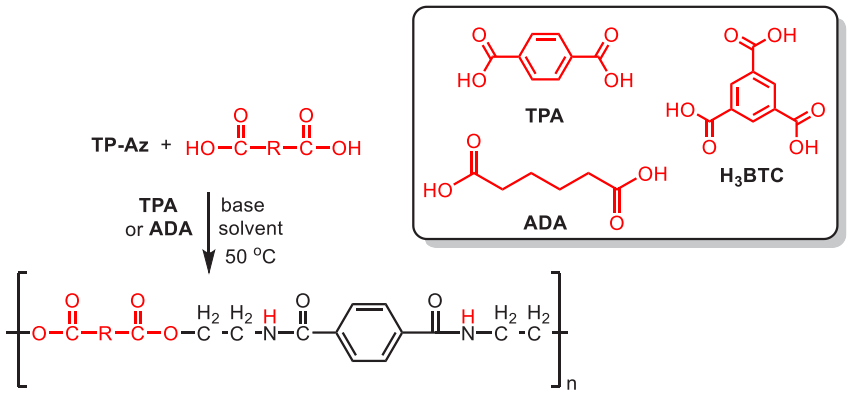
There is no evidence in the ^{1}H NMR spectrum of **PA-1** to suggest that **TP-Az** is homopolymerizing or that branching is occurring.[22] The lack of **TP-Az** homopolymerization or branching contrasts that of bis(*N*-sulfonyl aziridine)s, which can undergo chain-growth propagations concurrently with step-growth copolymerizations.[30] We propose that this is due to the reduced electron-withdrawing capability of carbonyl groups compared to sulfonyl groups. Less electron-withdrawing activating groups on aziridines correlate with reduced rates of aziridine homopolymerizations.[47]

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylamine (Et_3N) were evaluated as catalysts in the copolymerization of **TP-Az** and **TPA** (terephthalic acid). The attempted polymerization using DBU produced a complex reaction by ^{1}H NMR spectroscopy. Although the desired polyamide appeared to be forming, the ^{1}H NMR spectrum of the reaction mixture was much more complicated than what was observed during the P_4-*t*-Bu-catalyzed reaction. Attempts to purify the poly(amide ester) were unsuccessful, and polymerizations with catalytic DBU were not explored further. In contrast, 10 mol % Et_3N promoted polyamide formation (Table 1, entry 3, **PA-2**) in similar yields $M_{w,GPC}$, and $Đ$ to that of **PA-1** (Table 1, entry 1).

To understand the impact of catalytic base on the rate of the copolymerization of **TP-Az** and **TPA**, the polymerizations listed in Table 1, entries 1 (10 mol % P_4-*t*-Bu), 3 (10 mol %, Et_3N), and 4 (20 mol % Et_3N), were monitored by real-time ^{1}H NMR spectroscopy in DMSO-d_6 (Figure S6). Two features were observed: (I) at identical concentrations, reaction kinetics are independent of catalyst species; (II) increasing the catalyst concentration only shortened the polymerization time. There-

https://doi.org/10.1021/acs.macromol.2c01748
Macromolecules 2022, 55, 9513−9519

Table 1. Step-Growth Polymerizations of TP-Az with Dicarboxylic Acids[a]



entry, polymer	comonomer	solvent, 10 mol % base	M_w/kDa ($Đ$)	yield/%
1, **PA-1**	TPA	DMSO, P_4-*t*-Bu	12.5 (1.67)	54
2, n/a	TPA	DMSO, DBU	n/a	n/a
3, **PA-2**	TPA	DMSO, Et_3N	11.8 (1.79)	58
4, **PA-3**	TPA	DMSO, Et_3N[b]	12.6 (1.86)	61
5, n/a	TPA	NMP, Et_3N	n/a	n/a
6, **PA-4**	TPA	DMF, Et_3N	12.1 (1.82)	50
7, **PA-5**	TPA	THF, Et_3N	23.3 (1.61)	82
8, **PA-6**	ADA	THF, Et_3N	27.8 (1.80)	86
9, **PA-7**	H_3BTC	THF, Et_3N	n/a	82

[a]Weight-average molecular weight (M_w) and dispersity ($Đ$) were determined by GPC in HFIP at 35 °C (PMMA calibration). [b]20 mol % Et_3N.

fore, 10 mol % Et_3N was used throughout the rest of the project.

We then studied the impact of solvent on the polymerization between **TP-Az** and **TPA**, examining the aprotic, polar solvents NMP, DMF, and THF (Table 1, entries 5−7). Because NMP is a high-boiling-point solvent, the polymerizations were conducted at 50, 100, and 150 °C, respectively. Reactions in NMP produced no polymeric materials as GPC analysis showed only low molecular weight compounds (M_n < 1.2 kDa, M_w < 2.5 kDa), and the ^{1}H NMR spectra were complex. The outcome of polymerization in DMF is indistinguishable from that in DMSO (Table 1, entry 6). THF appears to be the best solvent (Table 1, entry 7) because the polymerization resulted in a satisfactory isolated yield (82%) and a high molecular weight (**PA-5**, $M_{w,GPC}$ = 23.3 kDa, $Đ$ = 1.61), and THF is an easier solvent to remove postreaction. The thermal properties of **PA-5** are summarized in Figures S29 and S30 and in Tables 3 and S1.

We next explored the copolymerization of **TP-Az** with two other carboxylic acid containing comonomers, adipic acid (**ADA**) and trimesic acid (**H_3BTC**), under the optimized conditions. In the case of **ADA**, the resulting polymer (**PA-6**) was characterized by ^{1}H NMR spectroscopy, MALDI-ToF MS, and GPC. **PA-6** was isolated in good yield and molecular weight, thus showing that aliphatic dicarboxylic acids react in a similar fashion to their aryl counterparts (Figures S7 and S8). Copolymerization of **TP-Az** and **H_3BTC** produced a colorless, insoluble film, presumably cross-linked, that was characterized by FT-IR spectroscopy (Figure S9).

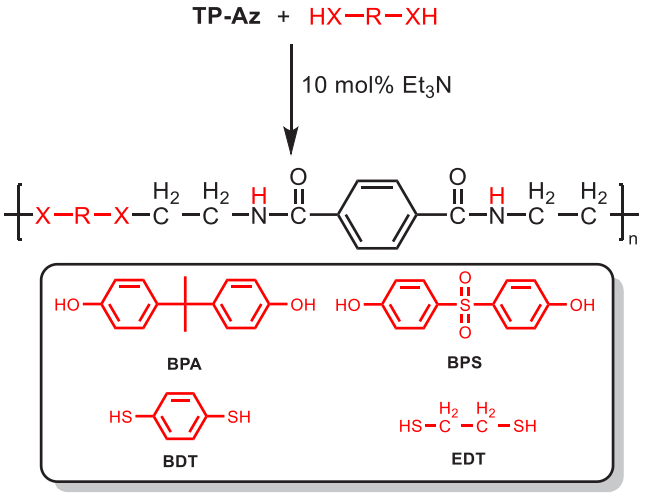
Upon establishing that **TP-Az** readily polymerizes with dicarboxylic acids, we explored the polymerizations of **TP-Az** with other dinucleophilic comonomers, including bisphenols, diols, and dithiols. Both bisphenol A (**BPA**) and bisphenol S (**BPS**) polymerized cleanly with **TP-Az**. The copolymerization of **TP-Az** with **BPA** produced a white powder polyamide with a 74% isolated yield (**PA-8**, M_w = 20.6 kDa, $Đ$ = 1.86). Similarly, bisphenol S (**BPS**) copolymerized readily to form **PA-9** with a M_w of 32.7 kDa and a $Đ$ of 1.81. The ^{1}H NMR spectroscopic and MALDI-ToF mass spectra of **PA-8** and **PA-9** were consistent with their proposed structures (Figures S10−S13). Surprisingly, the aliphatic diols 1,4-butanediol or 1,4-benzenedimethanol did not copolymerize with **TP-Az** under the conditions examined; rather, both produced reaction mixtures with complex ^{1}H NMR spectra.

Synthetic polyamides containing sulfide linkages have attracted attention due to their promising applications in membrane preparation or as an adsorbent of heavy metal ions.[48,49] Reported methods for poly(amide sulfide)s syntheses are performed at high temperatures that require stringent conditions to remove byproducts.[48−50] We found that both the aromatic dithiol, benzene-1,4-dithiol (**BDT**, Table 2, entry 3), and the aliphatic dithiol, 1,2-ethanedithiol (**EDT**, Table 2, entry 4), react rapidly to form the expected poly(amide sulfide)s **PA-10** and **PA-11**, respectively. The polymers were characterized by ^{1}H NMR spectroscopy, MALDI-ToF MS, and GPC (Figures S14−S17 and S31). The low melting point of **BDT** (94−97 °C) also facilitated a solvent-free polymerization of **TP-Az** at 100 °C. The resulting polymer (**PA-12**, Table 2, entry 5) was indistinguishable from that synthesized in THF solution.

We synthesized adipoyl aziridine (**AD-Az**, Figure S18) to examine if aliphatic carbonyl aziridines polymerize similarly to the aryl **TP-Az**.[51] The step-growth polymerization of **AD-Az** with **TPA** or **ADA** was performed under the same conditions as those used in **TP-Az** polymerizations (Scheme 3). Poly(amide ester)s **PA-13** and **PA-14** were precipitated in methanol and analyzed by GPC (Figure S31). The ^{1}H NMR spectra and MALDI-ToF MS of **PA-13** and **PA-14** were consistent with the structures depicted in Scheme 3 (Figures

https://doi.org/10.1021/acs.macromol.2c01748
Macromolecules 2022, 55, 9513−9519

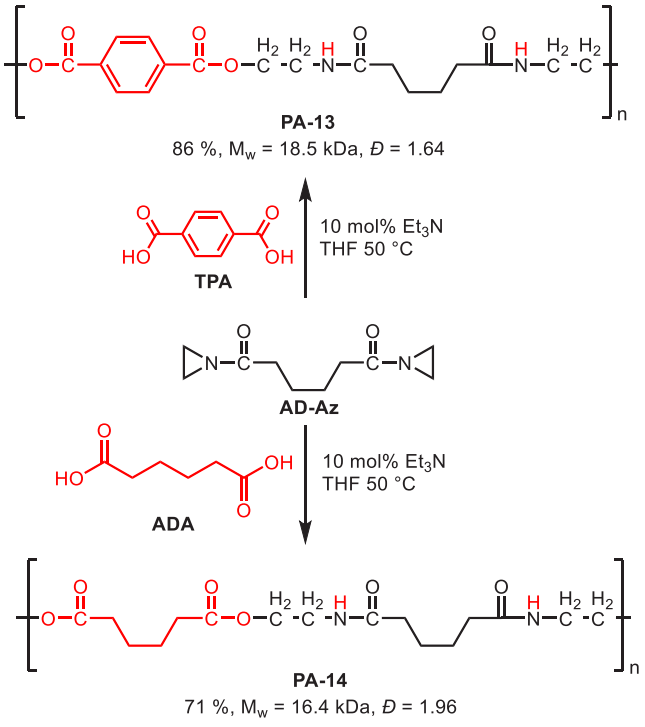
Table 2. Step-Growth Polymerizations of TP-Az with Diphenols or Dithiols[a]



entry, polymer	comonomer	solvent	M_w/kDa ($Đ$)	yield/%
1, **PA-8**	**BPA**	THF	20.6 (1.86)	74
2, **PA-9**	**BPS**	THF	32.7 (1.81)	79
3, **PA-10**	**BDT**	THF	25.6 (1.94)	91
4, **PA-11**	**EDT**	THF	34.1 (1.72)	82
5, **PA-12**	**BDT**	no solvent	3.7 (3.85)	84

[a]Weight-average molecular weight (M_w) and dispersity ($Đ$) were determined by GPC in HFIP at 35 °C (PMMA calibration).

Scheme 3. Step-Growth Polymerization of AD-Az with Dicarboxylic Acids[a]



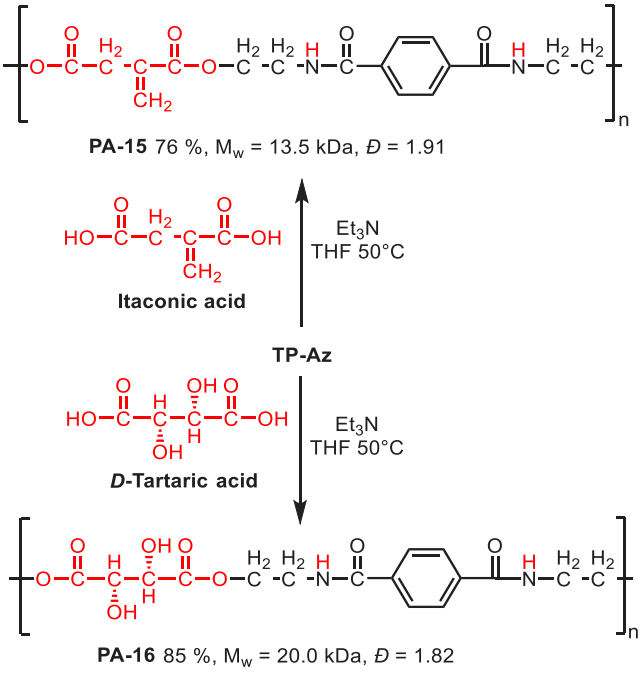
[a]Weight-average molecular weight ($M_{w,GPC}$) and polydispersity ($Đ$) were determined by GPC in HFIP at 35 °C (PMMA calibration).

S19–S22), and there was no indication of **AD-Az** branching or homopolymerization.

We note the similarities in the ring-opening chemistries of carbonyl aziridines and 2-oxazolines. 2-Oxazolines are structural isomers of *N*-carbonyl aziridines. Bis(2-oxazoline)s can undergo ring-opening with dinucleophiles to produce polyamides similar to those we have reported.[52,53] Indeed, Luston reported the copolymerization of a bis(2-oxazoline) with **ADA** to produce a poly(amide ester)[54] which has the same structure as **PA-6**. However, the polymerizations of oxazolines require inert atmospheres and high temperatures (170 °C) and yield polyamides with lower molecular weights. The *N*-carbonyl aziridines provide a distinct advantage, as the polyaddition reactions occur under mild conditions that are likely more tolerant of functional groups.

To illustrate the potential of *N*-carbonyl aziridines to undergo copolymerization with highly functional monomers, we examined the copolymerization of **TP-Az** with itaconic acid and D-tartaric acid, both of which are naturally derived diacids.[55,56] Itaconic acid can be derived from citric acid and contains a vinylidene group, while D-tartaric acid is a diol isolated from many fruits. As desired, both itaconic acid and D-tartaric acid copolymerize with **TP-Az** to form the desired polyamides (**PA-15** and **PA-16**, Scheme 4, Figures S23 and

Scheme 4. Step-Growth Polymerization of TP-Az with Bioderived Dicarboxylic Acids[a]



[a]Weight-average molecular weight ($M_{w,GPC}$) and polydispersity ($Đ$) were determined by GPC in HFIP at 35 °C (PMMA calibration).

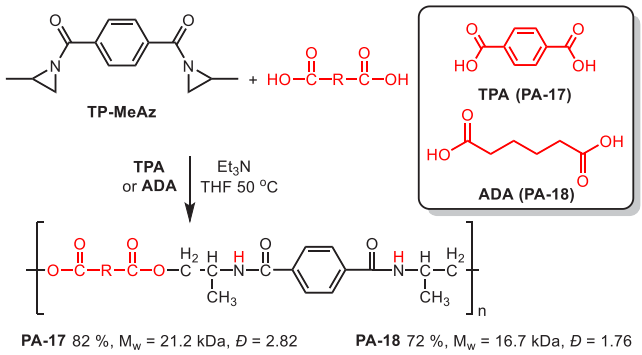
S24). The successful copolymerization of D-tartaric acid with **TP-Az** is especially noteworthy as it exhibits the tolerance of *N*-carbonyl aziridine step-growth polymerizations to unprotected alcohols. We believe that the alcohol groups of D-tartaric acid are not acidic enough to be activated by the Et_3N base and therefore do not react during copolymerization with **TP-Az.**

The presence of substituents at the 2-carbon of the aziridine ring plays a significant role in terms of extending the monomer scope and product property control of aziridine-derived polymers.[16,57] We synthesized a 2,2′-dimethyl terephthalaziridine (**TP-MeAz**, Figures S25 and S26) to evaluate this

https://doi.org/10.1021/acs.macromol.2c01748
Macromolecules 2022, 55, 9513–9519

method. **TP-MeAz** and either **TPA** or **ADA** were copolymerized under the same conditions for the unsubstituted version. Encouragingly, **TP-MeAz** polymerized smoothly with **TPA** and **ADA** to produce two polyamides, **PA-17** and **PA-18** (Scheme 5, Figures S27 and S28). It can be expected that if an enantiopure **TP-MeAz** is employed, optically active polyamides are likely to be obtained.[58,59]

Scheme 5. Step-Growth Polymerization of TP-MeAz with Dicarboxylic Acids[a]



[a]Weight-average molecular weight ($M_{w,GPC}$) and polydispersity ($Đ$) were determined by GPC in HFIP at 35 °C (PMMA calibration).

The thermal properties of these polyamide copolymers were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All the polyamides showed good thermal stability with onsets of mass loss ranging from 284.1 to 374.7 °C (Figure S29 and Table S1). The DSC measured T_g's for **PA-6**, **PA-8**, **PA-9**, **PA-11**, **PA-13** to **PA-16**, and **PA-18** varied between 67.2 and 168.5 °C (Figure S30 and Table 3). The highest glass transition temperatures were

Table 3. Differential Scanning Calorimetry (DSC) of the Synthesized Polyamides[a]

polyamide copolymers	glass transition temp (°C) T_g[b]	polyamide copolymers	glass transition temp (°C) T_g[b]
PA-5	no observed	**PA-13**	86.1
PA-6	69.8	**PA-14**	143.7
PA-8	145.6	**PA-15**	116.5
PA-9	168.5	**PA-16**	114.2
PA-10	not observed	**PA-17**	not observed
PA-11	67.2	**PA-18**	125.7[c]

[a]The data from the third heating cycle are reported. [b]The small change in free volume during glass transition is a plausible reason to explain that T_g signals were not detectable for **PA-5**, **PA-10**, and **PA-17**. This has been observed in other polyamide systems.[60] [c]A T_g-like signal was only observed in the first heating scan of the sample.

observed for the BPA or BPS-containing polyamides **PA-8** and **PA-9**. In addition, the DSC trace of **PA-14** exhibited endothermic and exothermic peaks consistent with melting and crystallizing transitions (T_m = 171.6 and T_c = 127.2 °C) (Figure S30). An endothermic peak for **PA-8** was found in the first heating step, which is likely a melting transition; however, no crystallization exotherms were observed upon cooling.

CONCLUSIONS

In summary, we have reported the base-catalyzed, step-growth polymerizations of bis(*N*-carbonyl aziridine)s with a variety of nucleophilic comonomers including diacids, diphenols, and dithiols. The resulting polyamides were synthesized in good yields and molecular weights. The mild reaction conditions and functional group tolerances enabled bis(*N*-carbonyl aziridine) **TP-Az** to copolymerize with itaconic acid and with D-tartaric acid, bioderived monomers that contain vinylidene and diol functional groups, respectively. These results hint at a larger potential for carbonyl aziridines in the preparation of polyamides from functional group (e.g., alcohol) rich monomers, including those sourced from bioderived feedstocks.

ASSOCIATED CONTENT

Data Availability Statement

Data used to generate the spectra can be found at https://osf.io/7kvd3/?view_only=0ffb616e154b4b938e10e9b0d6ce441d.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c01748.

Experimental procedures, NMR spectra, mass spectra, IR spectra, TGA traces, DSC traces, GPC traces (PDF)

AUTHOR INFORMATION

Corresponding Author

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

Author

Taoguang Qu − *Department of Chemistry & Biochemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, United States;* orcid.org/0000-0001-8176-6283

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.2c01748

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Science Foundation (EFMA-2132133) and the University of Alabama for financial support as well as the NSF MRI program (CHE1919906) for the purchase of an NMR spectrometer. We also thank Prof. Kevin N. West from the University of South Alabama for help with TGA data collection and Meng Zheng and Prof. Donghui Zhang from Louisiana State University for help with GPC data collection.

REFERENCES

(1) Marchildon, K. Polyamides - Still Strong After Seventy Years. *Macromol. React. Eng.* **2011**, *5* (1), 22−54.

(2) Stockmann, P. N.; Van Opdenbosch, D.; Poethig, A.; Pastoetter, D. L.; Hoehenberger, M.; Lessig, S.; Raab, J.; Woelbing, M.; Falcke, C.; Winnacker, M.; Zollfrank, C.; Strittmatter, H.; Sieber, V. Biobased chiral semi-crystalline or amorphous high-performance polyamides and their scalable stereoselective synthesis. *Nat. Commun.* **2020**, *11* (1), 509.

(3) Radzik, P.; Leszczyńska, A.; Pielichowski, K. Modern biopolyamide-based materials: synthesis and modification. *Polym. Bull.* **2020**, *77* (1), 501−528.

(4) Nirmala, R.; Navamathavan, R.; Park, S.-J.; Kim, H. Y. Recent Progress on the Fabrication of Ultrafine Polyamide-6 Based

Nanofibers Via Electrospinning: A Topical Review. *Nano-Micro Lett.* **2014**, *6* (2), 89−107.
(5) Bolton, E. K. Chemical Industry Medal. Development of Nylon. *Ind. Eng. Chem.* **1942**, *34* (1), 53−58.
(6) Dachs, K.; Schwartz, E. Pyrrolidone, Capryllactam and Laurolactam as new Monomers for Polyamide Fibers. *Angew. Chem., Int. Ed.* **1962**, *1* (8), 430−435.
(7) Deopura, B. L. 2-Polyamide fibers. In *Polyesters and Polyamides*; Deopura, B. L., Alagirusamy, R., Joshi, M., Gupta, B., Eds.; Woodhead Publishing: 2008; pp 41−61.
(8) Yu, Y.; Rong, M. Z.; Zhang, M. Q. Grafting of hyperbranched aromatic polyamide onto silica nanoparticles. *Polymer* **2010**, *51* (2), 492−499.
(9) Rafiee, Z.; Mallakpour, S. Synthesis and properties of novel brominated chiral polyamides derived from 5-[4-(2-tetrabromophthalimidylpropanoylamino)benzoylamino]isophthalic acid and aromatic diamines. *Polym. Bull.* **2016**, *73* (7), 1951−1964.
(10) Ke, J.; Zhang, Y.; Zhang, X.; Liu, Y.; Ji, Y.; Chen, J. Novel chiral composite membrane prepared via the interfacial polymerization of diethylamino-beta-cyclodextrin for the enantioseparation of chiral drugs. *J. Membr. Sci.* **2020**, *597*, 117635.
(11) Carey, M.; Hinton, Z.; Sokol, M.; Alvarez, N. J.; Barsoum, M. W. Nylon-6/Ti3C2Tz MXene Nanocomposites Synthesized by in Situ Ring Opening Polymerization of ε-Caprolactam and Their Water Transport Properties. *ACS Appl. Mater. Interfaces* **2019**, *11* (22), 20425−20436.
(12) Winnacker, M.; Sag, J.; Tischner, A.; Rieger, B. Sustainable, Stereoregular, and Optically Active Polyamides via Cationic Polymerization of ε-Lactams Derived from the Terpene β-Pinene. *Macromol. Rapid Commun.* **2017**, *38* (9), 1600787.
(13) Tanatani, A.; Yokoyama, A.; Azumaya, I.; Takakura, Y.; Mitsui, C.; Shiro, M.; Uchiyama, M.; Muranaka, A.; Kobayashi, N.; Yokozawa, T. Helical Structures of N-Alkylated Poly(p-benzamide)s. *J. Am. Chem. Soc.* **2005**, *127* (23), 8553−8561.
(14) Stewart, I. C.; Lee, C. C.; Bergman, R. G.; Toste, F. D. Living Ring-Opening Polymerization of N-Sulfonylaziridines: Synthesis of High Molecular Weight Linear Polyamines. *J. Am. Chem. Soc.* **2005**, *127* (50), 17616−17617.
(15) Jung, S.; Kang, S.; Kuwabara, J.; Yoon, H. J. Aziridine-based polyaddition, post-modification, and crosslinking: can aziridine rival epoxide in polymer chemistry? *Polym. Chem.* **2019**, *10* (33), 4506−4512.
(16) Gleede, T.; Reisman, L.; Rieger, E.; Mbarushimana, P. C.; Rupar, P. A.; Wurm, F. R. Aziridines and azetidines: building blocks for polyamines by anionic and cationic ring-opening polymerization. *Polym. Chem.* **2019**, *10* (24), 3257−3283.
(17) Gleede, T.; Markwart, J. C.; Huber, N.; Rieger, E.; Wurm, F. R. Competitive Copolymerization: Access to Aziridine Copolymers with Adjustable Gradient Strengths. *Macromolecules* **2019**, *52* (24), 9703−9714.
(18) Mbarushimana, P. C.; Liang, Q.; Allred, J. M.; Rupar, P. A. Polymerizations of Nitrophenylsulfonyl-Activated Aziridines. *Macromolecules* **2018**, *51* (3), 977−983.
(19) Homann-Müller, T.; Rieger, E.; Alkan, A.; Wurm, F. R. N-Ferrocenylsulfonyl-2-methylaziridine: the first ferrocene monomer for the anionic (co)polymerization of aziridines. *Polym. Chem.* **2016**, *7* (35), 5501−5506.
(20) Reisman, L.; Mbarushimana, C. P.; Cassidy, S. J.; Rupar, P. A. Living Anionic Copolymerization of 1-(Alkylsulfonyl)aziridines to Form Poly(sulfonylaziridine) and Linear Poly(ethylenimine). *ACS Macro Lett.* **2016**, *5* (10), 1137−1140.
(21) Xu, J.; Hadjichristidis, N. Well-Defined Poly(Ester Amide)-Based Homo- and Block Copolymers by One-Pot Organocatalytic Anionic Ring-Opening Copolymerization of N-Sulfonyl Aziridines and Cyclic Anhydrides. *Angew. Chem., Int. Ed.* **2021**, *60* (13), 6949−6954.
(22) Xu, J.; Wang, X.; Hadjichristidis, N. Diblock dialternating terpolymers by one-step/one-pot highly selective organocatalytic multimonomer polymerization. *Nat. Commun.* **2021**, *12* (1), 7124.
(23) Gleede, T.; Rieger, E.; Blankenburg, J.; Klein, K.; Wurm, F. R. Fast Access to Amphiphilic Multiblock Architectures by the Anionic Copolymerization of Aziridines and Ethylene Oxide. *J. Am. Chem. Soc.* **2018**, *140* (41), 13407−13412.
(24) Wu, S.; Luo, M.; Darensbourg, D. J.; Zeng, D.; Yao, Y.; Zuo, X.; Hu, X.; Tan, D. Non-Isocyanate and Catalyst-Free Synthesis of a Recyclable Polythiourethane with Cyclic Structure. *ACS Sustainable Chem. Eng.* **2020**, *8* (14), 5693−5703.
(25) Giri, C.; Sisk, S. E.; Reisman, L.; Kammakakam, I.; Bara, J. E.; West, K. N.; Rabideau, B. D.; Rupar, P. A. Anionic Ring-Opening Polymerizations of N-Sulfonylaziridines in Ionic Liquids. *Macromolecules* **2022**, *55* (2), 623−629.
(26) Chen, S.; Zhu, L.; Zhang, Z. Catalyst-free aziridine-based step-growth polymerization: a facile approach to optically active poly(sulfonamide amine)s and poly(sulfonamide dithiocarbamate)s. *Polym. Chem.* **2022**, *13* (29), 4324−4332.
(27) Zhou, Z.; Wang, Y.; Zhu, L.; Dang, D.; Zhang, Z. Tributylphosphine-catalyzed aziridine-based cycloaddition polymerization toward thiacyclic polymers. *Polym. Chem.* **2022**, *13* (33), 4809−4816.
(28) Song, P.-D.; Xia, L.; Nie, X.; Chen, G.; Wang, F.; Zhang, Z.; Hong, C.-Y.; You, Y.-Z. Synthesis of Poly(thioester sulfonamide)s via the Ring-Opening Copolymerization of Cyclic Thioanhydride with N-Sulfonyl Aziridine Using Mild Phosphazene Base. *Macromol. Rapid Commun.* **2022**, *43* (17), 2200140.
(29) Giri, C.; Chang, J.-Y.; Mbarushimana, P. C.; Rupar, P. A. The Anionic Polymerization of a tert-Butyl-Carboxylate-Activated Aziridine. *Polymers* **2022**, *14* (16), 3253.
(30) Kang, S.; Moon, H. K.; Yoon, H. J. Diaziridyl Ether of Bisphenol A. *Macromolecules* **2018**, *51* (11), 4068−4076.
(31) Zhu, L.; Huang, H.; Wang, Y.; Zhang, Z.; Hadjichristidis, N. Organocatalytic Synthesis of Polysulfonamides with Well-Defined Linear and Brush Architectures from a Designed/Synthesized Bis(N-sulfonyl aziridine). *Macromolecules* **2021**, *54* (17), 8164−8172.
(32) Iwakura, Y.; Sakamoto, M.; Yoneyama, M. Polyaddition reactions of bisethyleneureas and 1,1,3,3-diethyleneurea with polymethylene dimercaptans in LiCl-dimethylformamide. *J. Polym. Sci., Part A-1: Polym. Chem.* **1966**, *4* (1), 159−166.
(33) Del Franco, G. J.; Guagliardo, M.; Loewrigkeit, P.; Georgalas, N. Polyaddition reactions of N,N′-bis-1,2-alkylenamides with dicarboxylic acids. *J. Polym. Sci., Part B: Polym. Lett.* **1967**, *5* (6), 487−492.
(34) Nishimoto, S.; Izukawa, T.; Haruta, Y.; Kagiya, T. Photo-induced polyaddition of 1,1′-(2,6-naphthalenedicarbonyl)diaziridine and 1,5-dihydroxynaphthalene. *Journal of Polymer Science: Polymer Letters Edition* **1984**, *22* (4), 199−202.
(35) Bakkali-Hassani, C.; Rieger, E.; Vignolle, J.; Wurm, F. R.; Carlotti, S.; Taton, D. The organocatalytic ring-opening polymerization of N-tosyl aziridines by an N-heterocyclic carbene. *Chem. Commun.* **2016**, *52* (62), 9719−9722.
(36) Bakkali-Hassani, C.; Rieger, E.; Vignolle, J.; Wurm, F. R.; Carlotti, S.; Taton, D. Expanding the scope of N-heterocyclic carbene-organocatalyzed ring-opening polymerization of N-tosyl aziridines using functional and non-activated amine initiators. *Eur. Polym. J.* **2017**, *95*, 746−755.
(37) Wang, X.; Liu, Y.; Li, Z.; Wang, H.; Gebru, H.; Chen, S.; Zhu, H.; Wei, F.; Guo, K. Organocatalyzed Anionic Ring-Opening Polymerizations of N-Sulfonyl Aziridines with Organic Superbases. *ACS Macro Lett.* **2017**, *6* (12), 1331−1336.
(38) Nishimoto, S.-i.; Izukawa, T.; Kagiya, T. Photo-induced Ring-opening Reactions of 1-(2-Naphthoyl)aziridine in Various Solvents. *Bull. Chem. Soc. Jpn.* **1982**, *55* (5), 1484−1488.
(39) Monaco, M. R.; Poladura, B.; Diaz de Los Bernardos, M.; Leutzsch, M.; Goddard, R.; List, B. Activation of Carboxylic Acids in Asymmetric Organocatalysis. *Angew. Chem., Int. Ed.* **2014**, *53* (27), 7063−7067.
(40) Ottesen, L. K.; Jaroszewski, J. W.; Franzyk, H. Ring Opening of a Resin-Bound Chiral Aziridine with Phenol Nucleophiles. *J. Org. Chem.* **2010**, *75* (15), 4983−4991.

https://doi.org/10.1021/acs.macromol.2c01748
Macromolecules 2022, 55, 9513−9519

(41) Forbeck, E. M.; Evans, C. D.; Gilleran, J. A.; Li, P.; Joullié, M. M. A Regio- and Stereoselective Approach to Quaternary Centers from Chiral Trisubstituted Aziridines. *J. Am. Chem. Soc.* **2007**, *129* (46), 14463−14469.
(42) Galonić, D. P.; van der Donk, W. A.; Gin, D. Y. Site-Selective Conjugation of Thiols with Aziridine-2-Carboxylic Acid-Containing Peptides. *J. Am. Chem. Soc.* **2004**, *126* (40), 12712−12713.
(43) Hu, X. E. Nucleophilic ring opening of aziridines. *Tetrahedron* **2004**, *60* (12), 2701−2743.
(44) Suzuki, T.; Kusakabe, J.-i.; Ishizone, T. Living Anionic Polymerization of N-Methacryloyl-2-methylaziridine: Polymerizable N,N-Dialkylmethacrylamide. *Macromolecules* **2008**, *41* (6), 1929−1936.
(45) Yang, W.; Wang, J.; Jiao, L.; Song, Y.; Li, C.; Hu, C. Easily recoverable and reusable p-toluenesulfonic acid for faster hydrolysis of waste polyethylene terephthalate. *Green Chem.* **2022**, *24* (3), 1362−1372.
(46) Boileau, S.; Illy, N. Activation in anionic polymerization: Why phosphazene bases are very exciting promoters. *Prog. Polym. Sci.* **2011**, *36* (9), 1132−1151.
(47) Rieger, E.; Alkan, A.; Manhart, A.; Wagner, M.; Wurm, F. R. Sequence-Controlled Polymers via Simultaneous Living Anionic Copolymerization of Competing Monomers. *Macromol. Rapid Commun.* **2016**, *37* (10), 833−839.
(48) Jalali, A.; Shockravi, A.; Vatanpour, V.; Hajibeygi, M. Preparation and characterization of novel microporous ultrafiltration PES membranes using synthesized hydrophilic polysulfide-amide copolymer as an additive in the casting solution. *Microporous Mesoporous Mater.* **2016**, *228*, 1−13.
(49) Rezania, H.; Vatanpour, V.; Salehi, E.; Gavari, N.; Shockravi, A.; Ehsani, M. Wholly Heterocycles-Based Polyamide-Sulfide Containing Pyridine and Thiazole Rings: A Super-Adsorbent Polymer for Lead Removal. *J. Polym. Environ.* **2019**, *27* (8), 1790−1800.
(50) Shockravi, A.; Mehdipour-Ataei, S.; Abouzari-Lotf, E.; Yousefi, A. Sulfide and sulfoxide based poly(ether-amide)s: Synthesis and characterization. *Eur. Polym. J.* **2006**, *42* (1), 133−139.
(51) Lai, J.-Z.; Chang, Y.-C.; Yeh, J.-T.; Chen, K.-N. Single component self-curable aqueous-based PU system with new aziridinyl curing agent. *J. Appl. Polym. Sci.* **2004**, *91* (3), 1997−2007.
(52) Frump, J. A. Oxazolines. Their preparation, reactions, and applications. *Chem. Rev.* **1971**, *71* (5), 483−505.
(53) Aoi, K.; Okada, M. Polymerization of oxazolines. *Prog. Polym. Sci.* **1996**, *21* (1), 151−208.
(54) Lustoň, J.; Kronek, J.; Markus, O.; Janigová, I.; Böhme, F. Synthesis and polymerization reactions of cyclic imino ethers. 3. Poly(ester amide)s of the AA + BB type on the basis of 2-oxazolines. *Polym. Adv. Technol.* **2007**, *18* (2), 165−172.
(55) Robert, T.; Friebel, S. Itaconic acid - a versatile building block for renewable polyesters with enhanced functionality. *Green Chem.* **2016**, *18* (10), 2922−2934.
(56) Dhamaniya, S.; Jacob, J. Synthesis and characterization of polyesters based on tartaric acid derivatives. *Polymer* **2010**, *51* (23), 5392−5399.
(57) Rieger, E.; Manhart, A.; Wurm, F. R. Multihydroxy Polyamines by Living Anionic Polymerization of Aziridines. *ACS Macro Lett.* **2016**, *5* (2), 195−198.
(58) García, J. M.; García, F. C.; Serna, F.; de la Peña, J. L. High-performance aromatic polyamides. *Prog. Polym. Sci.* **2010**, *35* (5), 623−686.
(59) Zhong, H.; Deng, J. Preparation and Chiral Applications of Optically Active Polyamides. *Macromol. Rapid Commun.* **2021**, *42* (19), 2100341.
(60) Cywar, R. M.; Rorrer, N. A.; Mayes, H. B.; Maurya, A. K.; Tassone, C. J.; Beckham, G. T.; Chen, E. Y. X. Redesigned Hybrid Nylons with Optical Clarity and Chemical Recyclability. *J. Am. Chem. Soc.* **2022**, *144* (12), 5366−5376.

https://doi.org/10.1021/acs.macromol.2c01748
Macromolecules 2022, 55, 9513−9519