Supporting Information

Organocatalyzed anionic ring-opening polymerizations of N-sulfonyl aziridines with organic superbases

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Contents

Experimental section

Materials

All operations of air- and moisture-sensitive chemicals and materials were carried out in flamed Schlenk-type glassware under an insert atmosphere of argon or in an inert argon-filled glovebox. (1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phos-phoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) *t*-Bu-P_4) (0.8 mol L^{-1} in hexane) and 2,8,9-Triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (TiPP) were available from the Sigma-Aldrich Chemicals Co. 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, GC, >98%, TCI), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, GC, >95%, TCI), *N*,*N*,*N*',*N*'-tetramethylguanidine (TMG, GC, >99%, TCI), and *N*-Benzyl-*p*-toluenesulfonamide (BnN(H)Ts, HPLC, >98%) were purchased commercially and used without further purification. Anhydrous DMF was purchased from J&K and used without further purification. Chloroform D ($CDCl_3$, > 99.5 %, J&K) was dried over activated Davison 4 Å molecular sieves. 2-methyl-*N*-tosylaziridine (TsMAz), 2-methyl-*N*-ethylsulfonyl aziridine (EsMAz), and 2-phenyl-*N*-tosylaziridine (TsPhAz) were prepared according to literature procedures.[1,2] All the chemicals and reagents, except the ones specified above, were purchased from commercial vendors (Sinopharm Chemical Reagent Co).

Characterizations

Nuclear magnetic resonance (^{1}H NMR) measurements were recorded with a Buker Avance AV-300 spectrometer at 300 MHz at 25 °C. The size exclusion chromatography (SEC) analysis was performed with a SDV Lux 1000 Å, 10 μm, 8 × 7300 mm, S/N.: 2122001 column using a SSI 1500 pump, coupled with successively connected a Wyatt DAWN HELEOS-II multi-angle light scattering (MALS) detector (laser at λ = 658 nm) (Wyatt Technology Corporation, U.S.A.) and a Wyatt Optilab rEX differential refractive index (DRI) detector (Wyatt Technology Corporation, U.S.A.). The system was equilibrated at 50 °C in DMF, which served as the polymer solvent and eluent with a flow rate of 0.7 mL min^{-1}. All data were collected and analyzed using the Wyatt Astra V 6.1.1 software (Wyatt Technology Corporation, U.S.A.). The number-average molecular weight (M_n(SEC)) and molecular weight distributions (Đ, M_w/M_n) were determined using the experimentally measured dn/dc value (TsMAz, 0.1099 mL g^{-1}; EsMAz, 0.0728 mL g^{-1}, TsPhMAz, 0.1425 mL g^{-1}) in DMF. Matrix assisted

laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded with an Ultraflextreme mass spectrometer (Bruker) equipped with a Smartbeam/Smartbeam II modified Nd: YAG laser. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in THF at 10 mg/mL. The matrix solution (*trans*-3-indoleacrylic acid, IAA) was prepared by dissolving 10 mg/mL in THF. A MeOH solution of cationization agent (NaI, 10 mg/mL) was also prepared. Solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationization agent. Samples were prepared by mixing the matrix and polymer. The turnover frequency (TOF) for the propagation reaction was evaluated using the following formula.

$$\text{TOF } (h^{-1}) = \frac{[M]_0 \times \text{Conv.}}{[\text{Catalyst}]_0 \times \text{Polymerization (h)}}$$

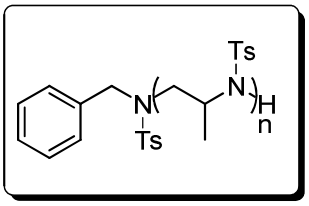
The refractive index increment (dn/dc) of samples was measured using Wyatt Optilab rEX differential refractive index (DRI) detector and Wyatt Astra V 6.1.1 software dn/dc template. The polymers were purified twice prior to use. Six DMF solutions with different and precisely known polymer concentrations (0.80-4.0 mg mL^{-1}) were prepared and injected to the DRI detector. The dn/dc value was obtained from the linear fit to a plot of refractive index versus polymer concentration through the Wyatt Astra software.

Kinetics Experiments

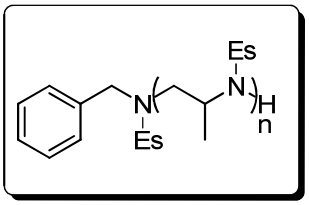
In the argon-filled glovebox, catalyst, initiator and DMF were firstly added sequentially into a series 6 mL vials. Then, the solutions of the monomer in DMF were injected to the vials in turn, and the vial was sealed with a screw cap. The vial was removed from the box and stirred and heated in an oil bath under 50 ^{o}C. After specified time intervals, each vial was taken out from the oil bath. An aliquot of the reaction mixture was obtained from the vial and quenched with an excess of MeOH for determining the monomer conversion from ^{1}H NMR measurements. The residual reaction was quenched at the same time by adding excess amount of MeOH and then all the solvent was removed. The precipitates were collected from the mixture dissolved in THF, and sequentially precipitated in cold methanol. The obtained polymers were further dried in a vacuum oven for SEC analysis. Each reaction was used as one data point.

General procedure for anionic ring-opening polymerizations of *N*-sulfonyl aziridines mediated by organic superbases

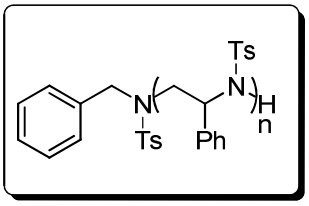
In the argon-filled glovebox, a 10 mL vial was charged with superbase, initiator, DMF, and a stirbar. Then, a solution of the monomer in DMF was added, and the vial was sealed with a screw cap. The vial was removed from the box and stirred and heated in an oil bath under 50 ^{o}C for ~17.5 h. The product polymer was precipitated by slow addition of the reaction solution to excess of methanol. The white precipitate was collected via centrifugation, purified by reprecipitation in methanol, and dried at 50 °C in a vacuum oven for ~3-4 days. Complete consumption of monomer was confirmed by ^{1}H NMR in these cases.



PTsMAz: ^{1}HNMR ($CDCl_3$, 300 MHz) δ 0.9-1.2 (m, 3 H, a), 2.2-2.4 (m, 3 H, b), 3.0-3.7 (m, 2 H, c), 3.8-4.5 (br s, 1 H, d), 7.1-7.4 (m, 2 H, f), 7.6-8.0 (m, 2 H, g) ppm. See Figure 1 (a).



PEsMAz: ^{1}HNMR ($CDCl_3$, 300 MHz) δ 1.1-1.4 (m, 6 H, b and f), 2.4 (m, 3 H, a), 3.0 (s, 2 H, e), 3.2-3.5 (m, 2H, c), 3.7-4.0 (br, 1 H, d) ppm. See Figure S5 (c).



PTsPhMAz: ^{1}HNMR ($CDCl_3$, 300 MHz) δ 2.2-2.5 (m, 3H, a), 3.4-4.0 (m, 2H, b), 4.3-5.1 (br, 1 H, c), 6.3-7.5 (m, 5H, e and f) ppm. See Figure S5 (a)

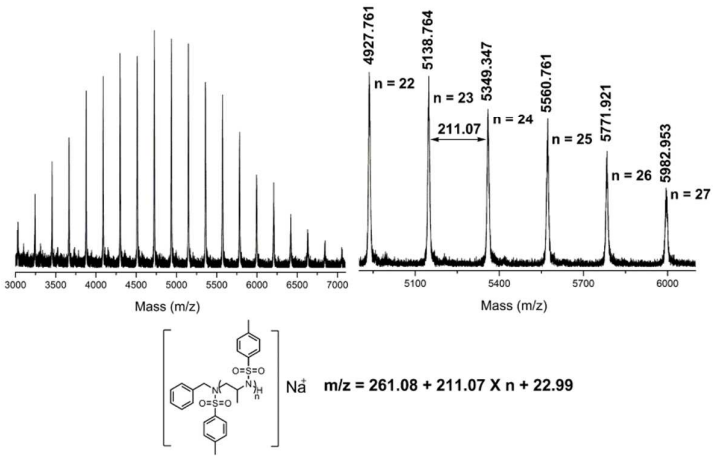


Figure S1. MALDI-TOF MS spectrum of the obtained PTsMAz (entry 7, Table 1) catalyzed by TiPP.

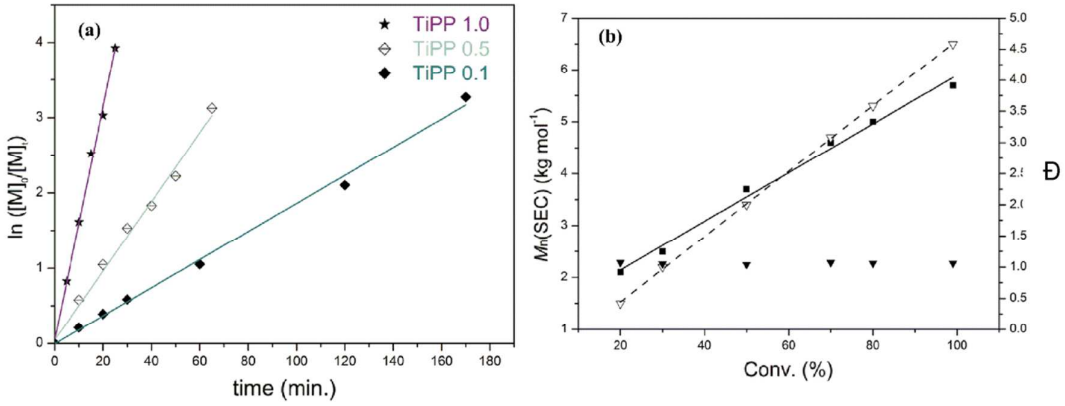


Figure S2. (a) Plots of $\ln([M]_0/[M]_t)$ versus reaction time for the TiPP catalyzed AROPs of TsMAz with BnN(H)Ts as initiator in DMF at various ratios of BnN(H)Ts to TiPP (purple line, $[TsMAz]_0/[BnN(H)Ts]_0/[TiPP]_0$ =30/1/1 (entry 5); pale green line, $[TsMAz]_0/[BnN(H)Ts]_0/[TiPP]_0$ =30/1/0.5 (entry 6); dark green line, $[TsMAz]_0/[BnN(H)Ts]_0/[TiPP]_0$ =30/1/0.1 (entry 7); $[M]_0$ = 1.0 M; 50 °C). (b) Plots of $M_{n,SEC}$ versus monomer conversion for TiPP catalyzed AROP of TsMAz (entry 7): (solid line) M_n (SEC, using the dn/dc [0.1099 mL g^{-1}]); (dashed line) M_n (theory); (▼) Đ (M_w/M_n, from SEC).

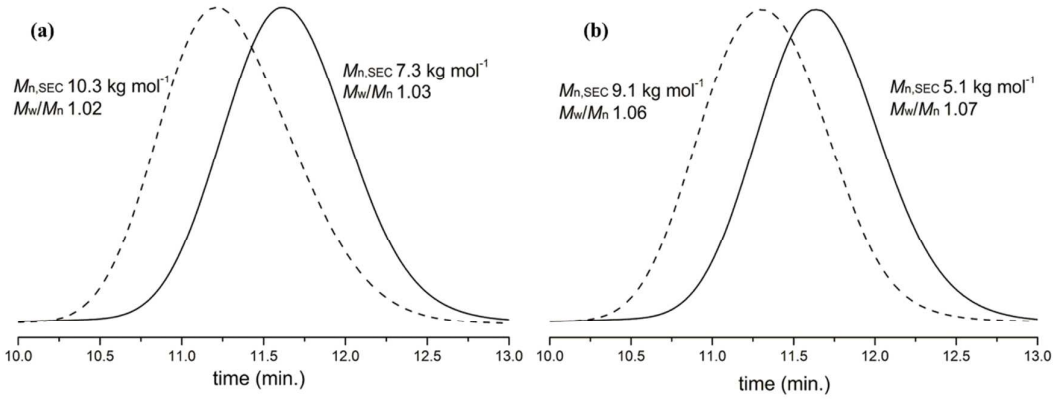


Figure S3. SEC traces of the first PTsMAz sequence from *t*-Bu-P_4 catalyzed AROP of TsMAz (a) (solid line) with M_n(SEC) = 7.3 kg mol^{-1} and M_w/M_n = 1.03 (30 equiv.) and the chain extension polymerization (dashed line) of PTsMAz with M_n(SEC) = 10.3 kg mol^{-1} and M_w/M_n = 1.02 (anther 20 equiv.); from TiPP catalyzed AROP of TsMAz (b) (solid line) with M_n(SEC) = 5.1 kg mol^{-1} and M_w/M_n = 1.07 (30 equiv.) and the chain extension polymerization (dashed line) of PTsMAz with M_n(SEC) = 9.1 kg mol^{-1} and M_w/M_n = 1.06 (anther 20 equiv.) (Details see Experimental Sections) (eluent, DMT; flow rate, 0.7 mL min^{-1}; 50 ^{o}C).

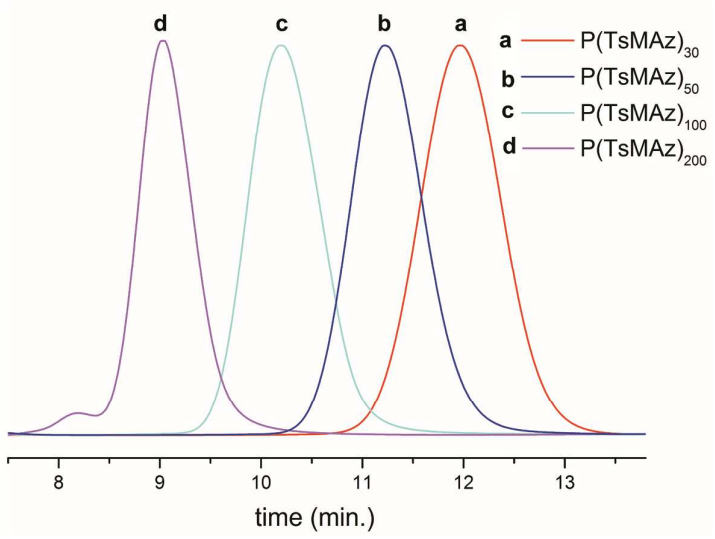


Figure S4. SEC traces of the obtained PTsMAz with various molar ratios of TsMAz/BnN(H)Ts/*t*-Bu-P_4 of 30/1/0.1 (a, red line), 50/1/0.1 (b, dark bule line), 100/1/0.1 (c, pale bule line) and 200/1/0.1 (d, purple line) (See all data in Table S1) (eluent, DMF; flow rate, 0.7 mL min^{-1}; 50 ^{o}C).

Table S1. AROPs of different aziridine monomers with various ratios of monomer/initiator/t-Bu-P4 using BnN(H)Ts as initiator[a]

entry	monomer	$[M]_0/[BnN(H)Ts]_0/[t\text{-}Bu\text{-}P_4]_0$	time /h	conv.[b] /%)	M_n(theor)[c] /kg mol^{-1}	M_n(SEC)[d] /kg mol^{-1}	Đ[d] (M_w/M_n)
11	TsMAz	50/1/0.1	3	96	10.4	10.9	1.03
12		100/1/0.1	5	96	20.5	24.4	1.04
13		200/1/0.1	10	96	40.8	33.3	1.10
14		200/1/0.5	3.5	98	41.5	38.1	1.05
15	EsMAz	30/1/0.1	10	32	2.3	n.d.	n.d.
16		30/1/0.5	3	97	4.6	4.8	1.03
17		30/1/1	1.7	99	4.7	7.1	1.10
18		50/1/0.5	6.5	95	7.4	8.0	1.05
19		100/1/0.5	12	95	14.4	13.6	1.09
20	TsPhAz	30/1/0.1	10	7	n.d.	n.d.	n.d.
21		30/1/1	5	96	8.1	5.9	1.05
22		50/1/1	8	94	13.1	10.2	1.03
23		100/1/1	17.5	95	26.2	13.9	1.08

[a] Temperature, 50 °C; solvent, DMF; $[M]_0$ = 1.0 mol L^{-1}. [b] Determined by ^{1}H NMR in $CDCl_3$ using integrals of the characteristic signals. [c] Calculated as follows: ($[TsMAz]_0/[BnN(H)Ts]_0$) × Conv. × (M.W. of TsMAz) + (M.W. of BnN(H)Ts). [d] Determined by a tandem SEC-MALS-DRI system using the dn/dc [0.1099 mL g^{-1}] (TsMAz), dn/dc [0.0728 mL g^{-1}] (EsMAz), dn/dc [0.1425 mL g^{-1}] (TsPhAz),in DMF at 50 °C (flow rate, 0.7 mL min^{-1}).

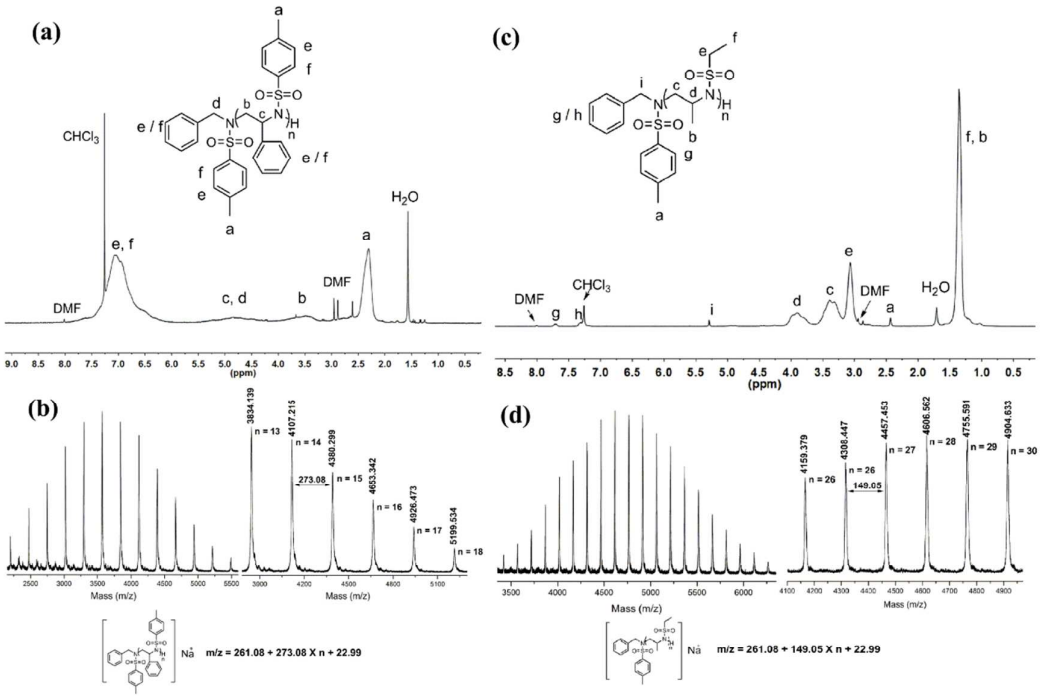


Figure S5. (a) ^{1}H NMR spectrum and (b) MALDI-ToF MS of the obtained PTsPhAz (entry 21, Table S1); (c) ^{1}H NMR spectrum and (d) MALDI-ToF MS of the obtained PEsMAz (entry 16, Table S1).

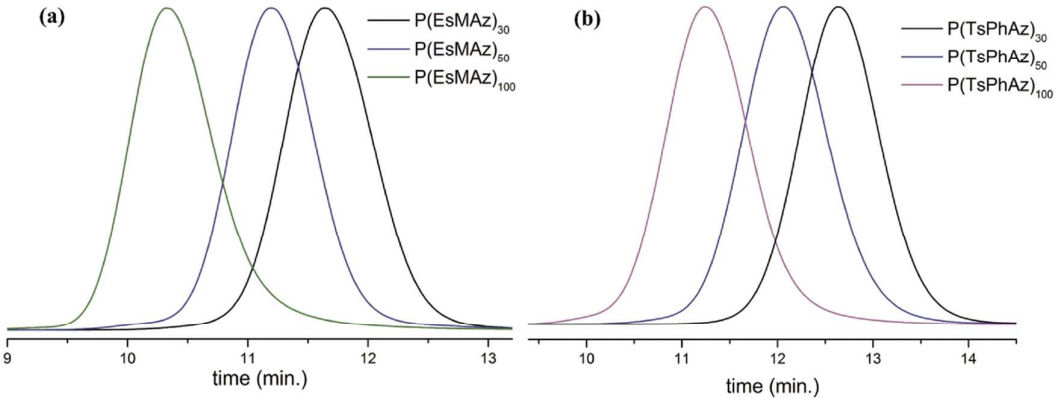


Figure S6. SEC traces of the obtained PEsMAz (a) with various molar ratios of EsMAz/BnN(H)Ts/*t*-Bu-P_4 of 30/1/0.5 (black line), 50/1/0.5 (bule line), 100/1/0.5 (green line) and the obtained PTsPhAz (b) with various molar ratios of TsPhAz/BnN(H)Ts/*t*-Bu-P_4 of 30/1/1 (black line), 50/1/1 (bule line), 100/1/1 (purple line) (See all data in Table S1) (eluent, DMF; flow rate, 0.7 mL min^{-1}; 50 ^{o}C

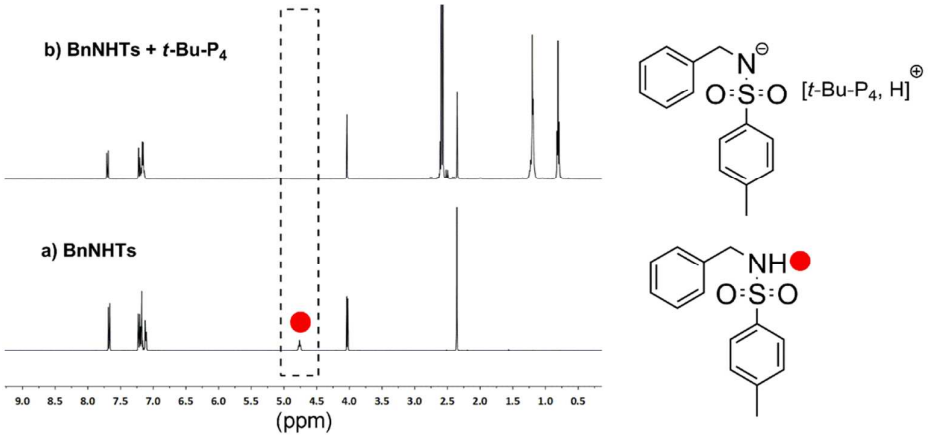


Figure S7. ^{1}H NMR spectra of (a) BnNHTs, (b) *t*-Bu-P_4 and BnNHTs 1:1 mixture in $CDCl_3$

Table S2. The TOF values of *t*-Bu-P_4 in our manuscript and ^{Me}5-Ipr NHC in *Chem. Commun.* **2016,** *52*, 9719-9722

Catalyst	TOF	Conditions
t-Bu-P_4	192 h^{-1}	Table S1, entry 12, $[TsMAz]_0/[BnN(H)Ts]_0/[t\text{-Bu-}P_4]_0$ = 100/1/0.1, in our manuscript
^{Me}5-Ipr NHC	42 h^{-1}	Table 1, run 4, $[TsMAz]_0/[3]_0/[^{Me}5\text{-Ipr NHC}]_0$ = 100/1/0.1, *Chem. Commun.* **2016,** *52*, 9719-9722.

References

(1) Kim, B. M.; So, S. M.; Choi, H. J. *Org. Lett.* **2002**, *4*, 949.

(2) Minakata, S.; Morino, Y.; Oderaotoshi, Y.; Komatsu, M. *Chem. Commun.* **2006**, 3337.