Supporting Information

Organocatalytic Sequential Ring-Opening Polymerization of Cyclic Ester/Epoxide and N-Sulfonyl Aziridine: Metal-Free and Easy Access to Block Copolymers

Huishan Huang, Wenyi Luo, Linlin Zhu, Ying Wang and Zhen Zhang*
**Scheme S1.** (a) Phenylmethanol initiated ROP of TsMAz using succinic anhydride; (b) failed sequential ROP of \(\varepsilon\)-caprolactone and TsMAz using succinic anhydride; (c) failed phenylmethanol initiated ROP of TsMAz using \(n\)-hexyl isocyanate.

**Figure S1.** \(^1\)H NMR (CDCl\(_3\), 400 MHz) spectrum of P(TsMAz\)\(_{27}\) (sample of Scheme S1a).
Figure S2. SEC traces (THF, 35 °C) of samples synthesized in Scheme S1a & c.

Figure S3. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P(TsMAz) (sample of Scheme S1c).
Figure S4. $^1$H NMR (400 MHz, CDCl$_3$) spectra of (a) phenylmethanol (BnOH); (b) a mixture of BnOH (1.0 equiv), and TSI (1.5 equiv) in CDCl$_3$; (c) a mixture of BnOH (1.0 equiv), TSI (1.5 equiv), and $t$-Bu-P$_2$ (0.3 equiv) in CDCl$_3$. The mixtures b & c were prepared and kept for ~5 minutes at room temperature, then measured by $^1$H NMR analysis. Benzyl tosylcarbamate was formed in the mixture b & c. Benzyl tosylcarbamate: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.43 (3H, s), 5.08 (3H, s), 7.23-7.26 (2H, m), 7.29 (2H, d, $J = 8.0$ Hz), 7.32-7.33 (3H, m), 7.69 (1H, bs), 7.88 (2H, d, $J = 8.0$ Hz). This data agrees with that reported previously (Ref. J. Am. Chem. Soc. 2009, 131, 33, 11701–11706).
Figure S5. MALDI-ToF MS of P(TsMAz) (sample of entry 1, Table 1).

Figure S6. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of P(TsMAz) (sample of entry 1, Table 1). The molar mass determined by end-group analysis was calculated as follows: $M_{n,NMR} = MW_{BuOH} + MW_{TSI} + MW_{TsMAz} \times (I_c/I_a \times 2)$, $I_c$: the integral of signal c, $I_a$: the integral of signal a.
The molar mass determined by end-group analysis was calculated as follows:

\[ M_{n,NMR} = \text{MW}_{\text{BnOH}} + \text{MW}_{\text{TSI}} + \text{MW}_{\text{MsMAz}} \times (I_c/I_a \times 2), \]

where \( I_c \) is the integral of signal c, and \( I_a \) is the integral of signal a.

**Figure S7.** \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum of P(MsMAz) (sample of entry 2, Table 1).

**Figure S8.** SEC traces (THF, 35 °C) of P(TsMAz)\(_{49}\) (sample of entry 3, Table 1).
Figure S9. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of P(TsMAz) (sample of entry 4, Table 1). $M_{n,NMR}$ was not determined due to the overlap of signals h and b.

Figure S10. SEC traces (THF, 35 °C) of PEG and PEG-$b$-P(TsMAz) (sample of entry 4, Table 1).
Figure S11. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of ω-NHTs PCL.

Figure S12. SEC traces (THF, 35 °C) of ω-NHTs PCL.
Figure S13. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of PCL$_{12}$-b-P(MsMAz)$_{38}$ (sample of entry 3, Table 2). The molar mass determined by end-group analysis was calculated as follows: $M_{n,NMR} = MW_{BnOH} + MW_{TSI} + MW_{CL} \times (I_d/I_a \times 2)/4 + MW_{MsMAz} \times (I_f/I_a \times 2)/2$, $I$: the integral of the related signal.

Figure S14. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of PPO$_{56}$-b-P(MsMAz)$_{41}$ (sample of entry 6, Table 2). The molar mass determined by end-group analysis was calculated as follows: $M_{n,NMR} = MW_{BnOH} + MW_{TSI} + MW_{PO} \times (I_d/I_a \times 2)/3 + MW_{MsMAz} \times (I_f/I_a \times 2)/3$, $I$: the integral of the related signal.
Figure S15. $^1$H NMR (400 MHz, CDCl₃) spectrum of P(TsMAz)$_{50}$-b-PPO$_{42}$-b-P(TsMAz)$_{50}$ (sample of entry 7, Table 2). The molar mass determined by end-group analysis was calculated as follows: $M_{n,NMR} = MW_{\text{initiator}} + MW_{\text{TSI}} \times 2 + MW_{\text{PO}} \times [(I_d + I_g - I_h)/I_a \times 4]/3 + MW_{\text{TsMAz}} \times (I_h/I_a \times 4)/3$, $I$: the integral of the related signal.

Figure S16. $^1$H NMR (400 MHz, CDCl₃) spectrum of P(TsMAz)$_{16}$-b-PCL$_{50}$-b-P(TsMAz)$_{16}$ (sample of entry 8, Table 2). The molar mass determined by end-group analysis was calculated as follows: $M_{n,NMR} = MW_{\text{initiator}} + MW_{\text{TSI}} \times 2 + MW_{\text{CL}} \times [(I_e/I_a \times 4)/2] + MW_{\text{TsMAz}} \times [(I_h/I_a \times 4)/3]$, $I$: the integral of the related signal.
Figure S17. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of [PCL$_{26}$-$b$-P(TsMAz)$_{16}$]$_3$ (sample of entry 9, Table 2). The molar mass determined by end-group analysis was calculated as follows: $M_{n,NMR} = MW_{initiator} + MW_{TSI} \times 3 + MW_{CL} \times [(I_e/I_a \times 6)/2] + MW_{TsMAz} \times [(I_f/I_a \times 6)/3]$, $I$: the integral of the related signal.

Figure S18. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of [PPO$_7$-$b$-P(TsMAz)$_{11}$]$_3$ (sample of entry 10, Table 2). The molar mass determined by end-group analysis was calculated as follows: $M_{n,NMR} = MW_{initiator} + MW_{TSI} \times 3 + MW_{PO} \times [(I_d + I_g - I_h)/I_a \times 6]/3 + MW_{TsMAz} \times [(I_f/I_a \times 6)/3]$, $I$: the integral of the related signal.
Figure S19. Kinetic plots of $\ln([M]_0/[M]_t)$ versus time for the ROP of TsMAz in their sequential ROP for the synthesis of PCL-$b$-P(TsMAz) and PPO-$b$-P(TsMAz).

Figure S20. Plots of $M_{n,SEC}$ and $D$ versus monomer conversion.
Figure S21. DSC curves (1\textsuperscript{st} (cooling) and 2\textsuperscript{nd} run (heating), 10 °C/min) of P(TsMAz)\textsubscript{49} (sample of entry 3, Table 1).

Figure S22. DSC curves (2\textsuperscript{nd} run (heating), 10 °C/min) of representative copolymers.
Figure S23. DSC curves (2nd run (heating), 10 °C/min) of representative 3-arm star copolymers.