Supporting Information

Non-metal with Metal Behavior: Metal-free Coordination - Insertion Ring-Opening Polymerization

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Experimental details

Materials

All operations of air- and moisture-sensitive chemicals and materials were carried out inflamed Schlenk-type glassware under an inert atmosphere of argon or in an inert argon-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. Trimethylene carbonate (TMC, > 98%, TCI) was purified by recrystallization from benzene-*n*-hexane three times and dried by the vacuum before use. ε-Caprolactone (ε-CL, > 99%, TCI), δ-valerolactone (δ-VL, technical grade, Aldrich) was distilled over CaH_2 under reduced pressure and stored in argon. γ-Butyrolactone (γ-BL, > 99%, TCI) was dried over CaH_2 overnight, purified by distillation, and stored in the glovebox for further use. L-lactide (98%, Aldrich) was purified by recrystallization from dichloromethane/hexane three times and dried by the vacuum before use. Allyltrimethylsilane (ATMS, > 98%, TCI) and bis(trifluoromethanesulfonyl)imide ($HNTf_2$, > 99.0%, Acros) were both used as received. Dichloromethane (CH_2Cl_2; > 99.5%) was distilled over CaH_2 under an argon atmosphere. Triethylamine (> 99%, TCI) was distilled over NaOH under an argon atmosphere and stored in the glovebox for use. Chloroform D ($CDCl_3$, > 99.5%, J&K) was dried over activated Davison 4 Å molecular sieves. Methanol (> 99.9 %, Superdry, J&k) was stored in the glovebox prior to use. Benzyl alcohol (anhydrous, 99.8%, Aldrich), 2,2-diphenylethanol (99%, Aldrich) were used as received. All the chemicals and reagents, except the ones specified above, such as methanol (AR), were provided by Sinopharm Chemical Reagent Co.

Characterizations

Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) measurements were recorded with a Buker Avance spectrometer with 300 MHz or 400 MHz or 500 MHz at 25 °C. The size exclusion chromatography (SEC) analysis was performed with a Waters Styragel® HR 2 THF, 5 μm, 300 × 7.8 mm column (Waters Corporation, U.S.A.) using a SSI 1500 pump, coupled with successively connected a Wyatt DAWN HELEOS-II multi-angle light scattering (MALS) detector (laser at $\lambda = 658$ 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 25 °C in THF, 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) and molecular weight distributions (M_w/M_n, $Đ$) were determined using the experimentally measured dn/dc value [0.0409 ml g^{-1} in THF at 25 °C] for polytrimethylene carbonate (PTMC) and [0.070 ml g^{-1} in THF at 25 °C] for polycaprolactone (PCL). 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. The polymer sample was dissolved in CH_2Cl_2 (HPLC grade, 5 mg/mL), the matrix 2,5-dihydroxybenzoic acid dissolved in an aqueous solution of trifluoroacetic acid and acetonitrile (volume ratio = 70/30) was prepared (1%, 10 μL). Samples were prepared by mixing the matrix and polymer. Spectra of 500 shots were accumulated for the spectra at an accelerating voltage of 25 kV.

The refractive index increments (dn/dc) of PTMC and PCL were 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 before use. Six THF solutions with different and precisely known polymer concentrations (0.20-2.0 mg mL^{-1}) were prepared and injected into 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.

Kinetic Experiments

In the argon-filled glovebox, $TMSNTf_2$ solution from a stock solution in CH_2Cl_2 was injected sequentially into a series of 6 mL vials loaded with TMC or ε-CL stock solution in CH_2Cl_2. After specified time intervals, each vial was taken out of the glovebox. An aliquot of the reaction mixture was obtained from the vial and quenched with an excess of triethylamine for determining the monomer conversion from ^{1}H NMR measurements. The residual reaction was quenched at the same time by adding an excess amount of triethylamine, and then all the solvent was removed. The precipitates were collected from the mixture dissolved in dichloromethane 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 ring-opening polymerization mediated by TMSNTf$_2$

A typical homopolymerization procedure was as follows: In the argon-filled glovebox, the TMSNTf$_2$ stock solution was first prepared as following: HNTf$_2$ (0.562 g, 2.0 mmol) and allyltrimethylsilane (0.251 g, 2.2 mmol) were dissolved in 2 mL CH_2Cl_2, the mixture was well stirred for another 30 min until no bubbles existed. Then the TMSNTf$_2$ stock solution (60 μL, 60 μmol) was added to TMC (4.3 mL, 3.0 mmol) or ε-CL (3.0 mL, 3.0 mmol) stock solution. After stirred for the designated period under an argon atmosphere at 25 °C, the polymerization was quenched by adding a small amount triethylamine. The whole process was monitored by ^{1}H NMR measurements. When the monomer was consumed, the polymer was purified by reprecipitation in cold methanol and dried under vacuum. PTMC, Conv.: 97 %. M_n (SEC) = 6.1 kg mol^{-1}; $Đ$ = 1.17. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.9 (q, 2H, J = 6.1 Hz, $–CH_2CH_2OH$), 2.0–2.05 (m, 2H × n − 1, $(–OCH_2CH_2–)_{n-1}$), 3.73 (t, 2H, J = 6.0 Hz, $–CH_2OH$), 4.20–4.24 (m, 4H × n − 1, $(–OCH_2CH_2CH_2O–)_{n-1}$; m, 2H, $–OCH_2CH_2CH_2OH$). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.2, 65.5, 155.2. PCL, Conv.: 95 %. M_n (SEC) = 6.5 kg mol^{-1}; $Đ$ = 1.18. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 4.10 (t, 2H × n – 1, $-CH_2CH_2O-$), 3.61 (t, 2H, J = 6.3 Hz, $HOCH_2-$), 2.30 (t, 2H x n, n $-COCH_2-$), 1.65 (m, 4H x n, $-CH_2CH_2CH_2-$), 1.38 (m, 2H x n, $-CH_2CH_2CH_2-$). ^{13}C NMR ($CDCl_3$): δ (ppm) 174.1, 64.8, 34.3, 28.3, 25.4, 24.5.

General procedure for diblock copolymerization of *ε*-CL and TMC

In the argon-filled glovebox, the $TMSNTf_2$ stock solution (60 μL, 60 μmol) was added to the *ε*-CL (1.2 mL, 1.2 mmol) stock solution. After stirred for the designated period under an argon atmosphere at 25 °C, when the monomer *ε*-CL was almost consumed (conversion > 95 %), the monomer TMC (0.184 g, 1.8 mmol) was added to start the diblock copolymerization. After stirred for the designated period under an argon atmosphere at 25 °C, the polymerization was quenched by adding a small amount of triethylamine. The whole process was monitored by ^{1}H NMR measurements. When the monomer was consumed, the polymer was purified by reprecipitation in cold methanol and dried under vacuum. Conv.: 96 %/93 %. M_n (SEC) = 5.4 kg mol^{-1}; $Đ$ = 1.19.

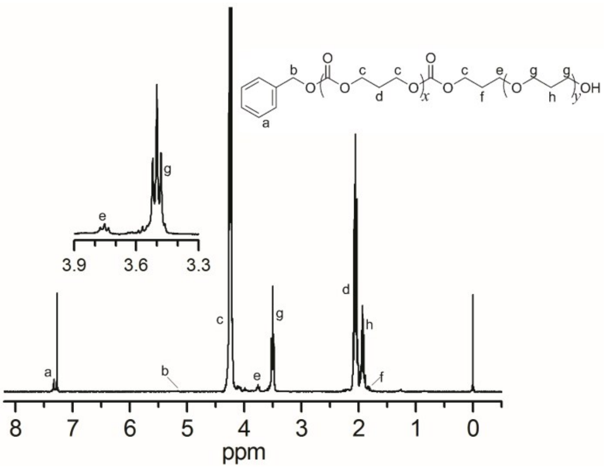

Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) of PTMC containing ether units obtained by $HNTf_2$-catalyzed TMC at 25 °C.

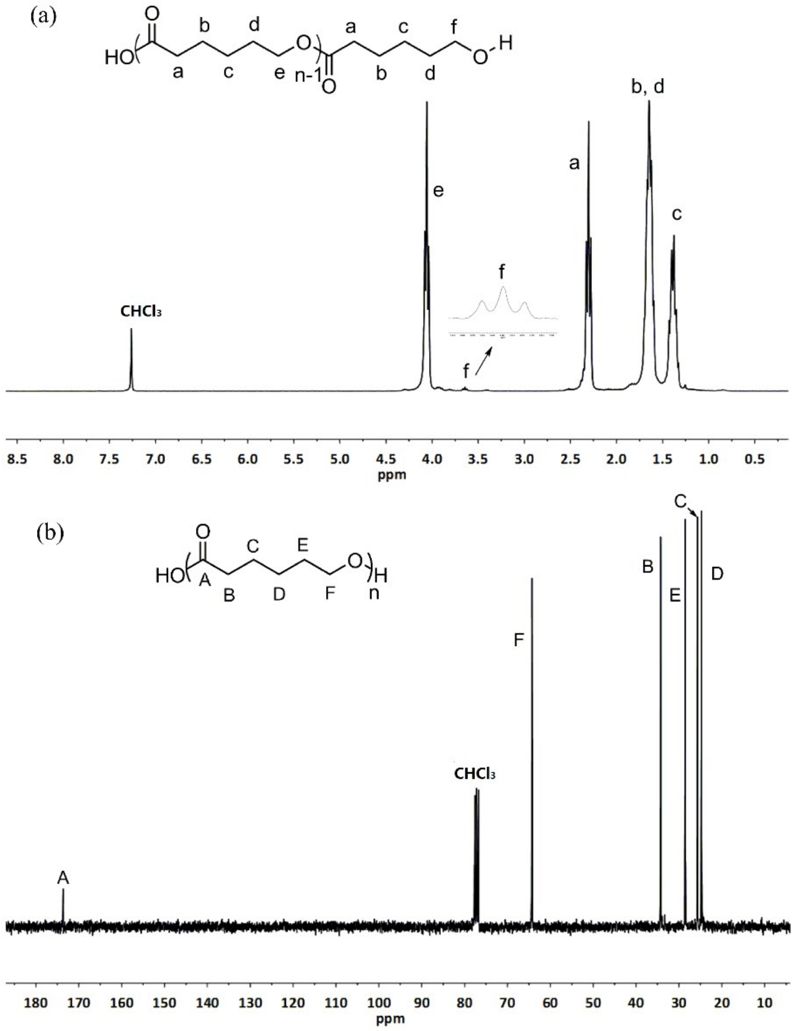

Fig. S2 ^1H NMR (a, 400 MHz, $CDCl_3$, 25 ^oC) and ^{13}C NMR (b, 100 MHz, $CDCl_3$, 25 ^oC) spectra of the obtained PCL ($[M]_0/[I]_0 = 20$, Table1, entry 6) initiated by $TMSNTf_2$ at room temperature.

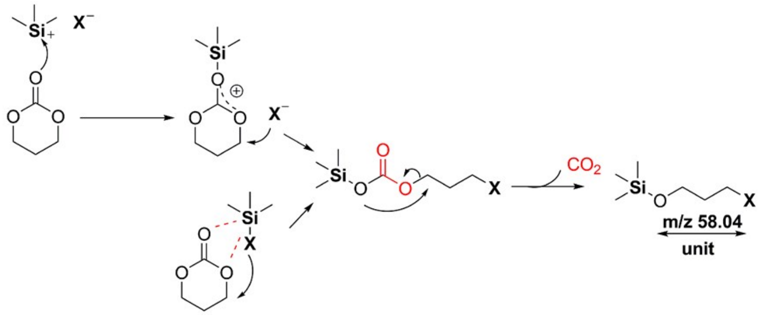

Fig. S3 Reported mechanisms of silicon Lewis acid-initiated ROP of TMC.

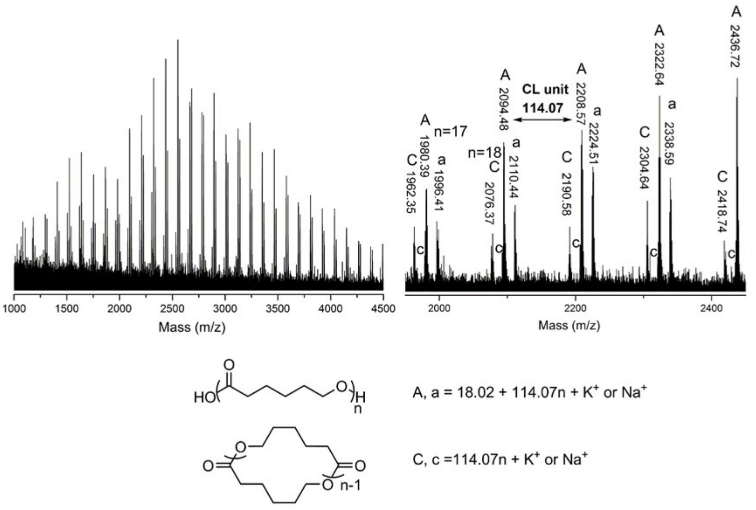

Fig. S4 MALDI-TOF MS spectra of the obtained PCL ($[M]_0/[I]_0 = 20$, Table 1, entry 6) initiated by $TMSNTf_2$.

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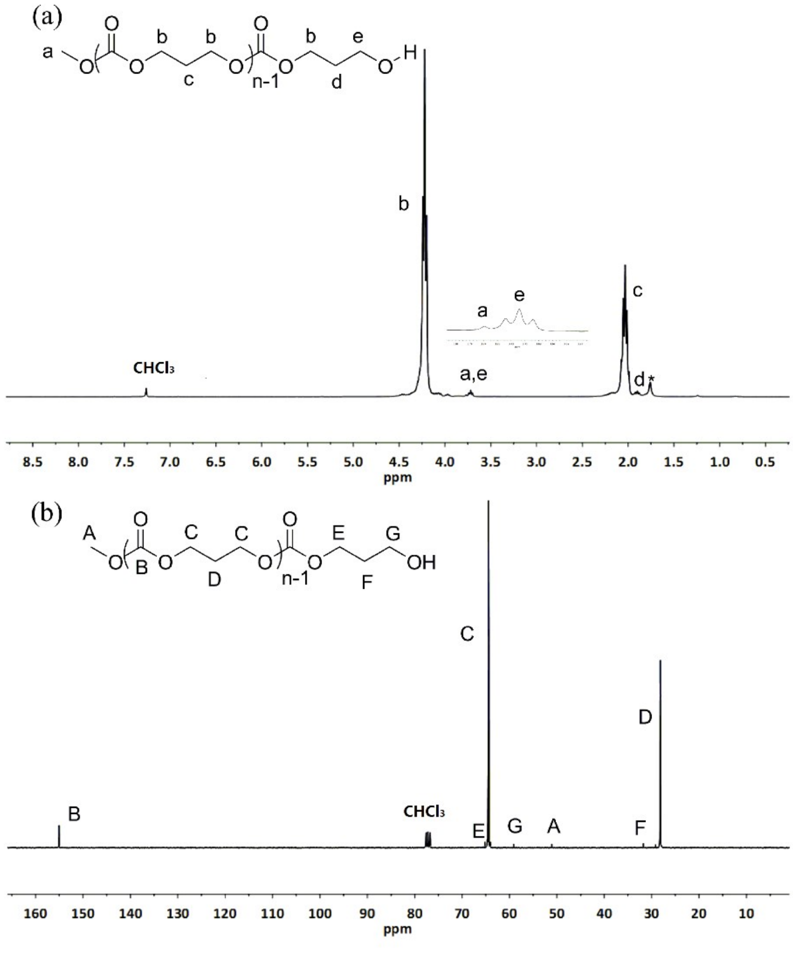


Fig. S5 ^{1}H NMR (a, 400 MHz, $CDCl_3$, 25 °C) and ^{13}C NMR (b, 100 MHz, $CDCl_3$, 25 °C) spectra of PTMC ($[M]_0/[I]_0 = 20$) precipitated by super dry methanol.

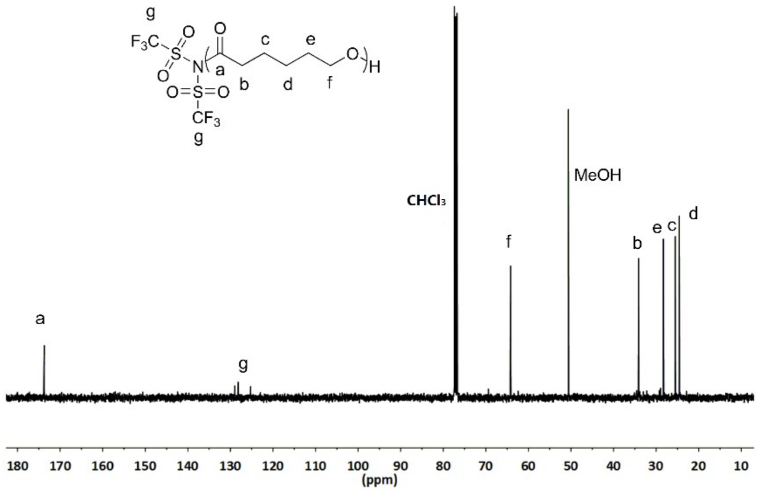


Fig. S6 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of the obtained PCL ($[M]_0/[I]_0 = 20$) initiated by $TMSNTf_2$ as soon as the polymer precipitated from super dry methanol without further exposing in air.

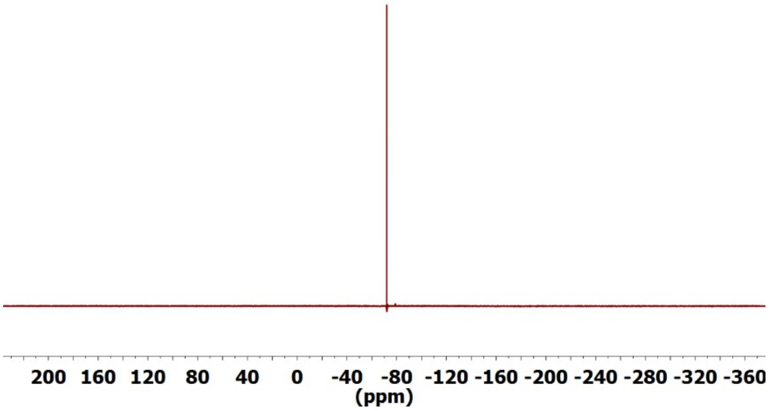


Fig. S7 ^{19}F NMR spectrum (470 MHz, $CDCl_3$, 25 °C) of the obtained PCL ($[M]_0/[I]_0 = 20$) initiated by $TMSNTf_2$ as soon as the polymer precipitated from super dry methanol without further exposing in air.

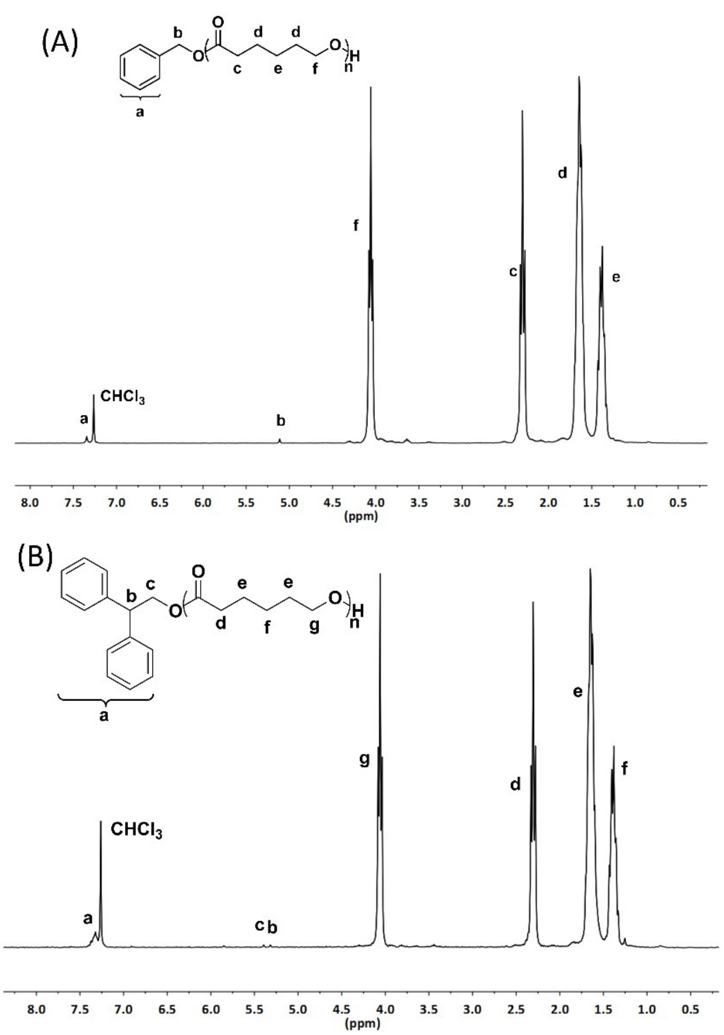


Fig. S8 ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^oC) spectra of PCL ($[M]_0/[I]_0 = 20$) with post-modification by benzyl alcohol (A) and 2,2-diphenylethanol (B).

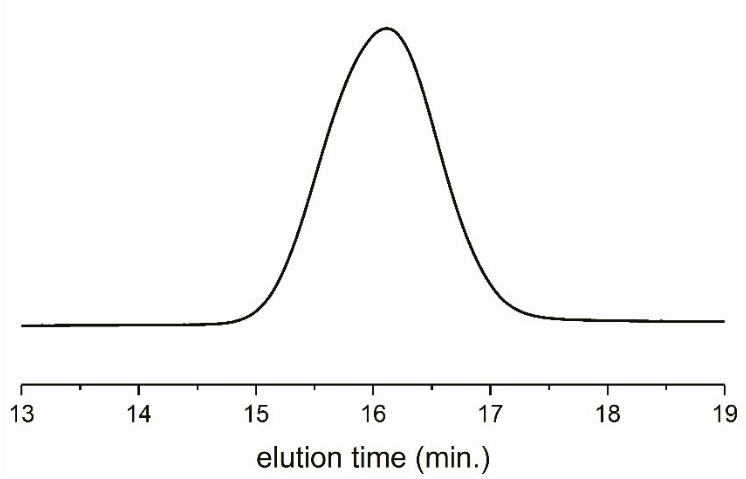


Fig. S9 SEC traces of the obtained PVL ($[\delta\text{-VL}]_0/[TMSNTf_2]_0 = 50/1$) (See all data in Table 1)(eluent, THF; flow rate, 1.0 mL min^{-1}, performed on a VISCOTEK VE2001 system equipped with PSS columns (Styragel HR 2 and 4)).

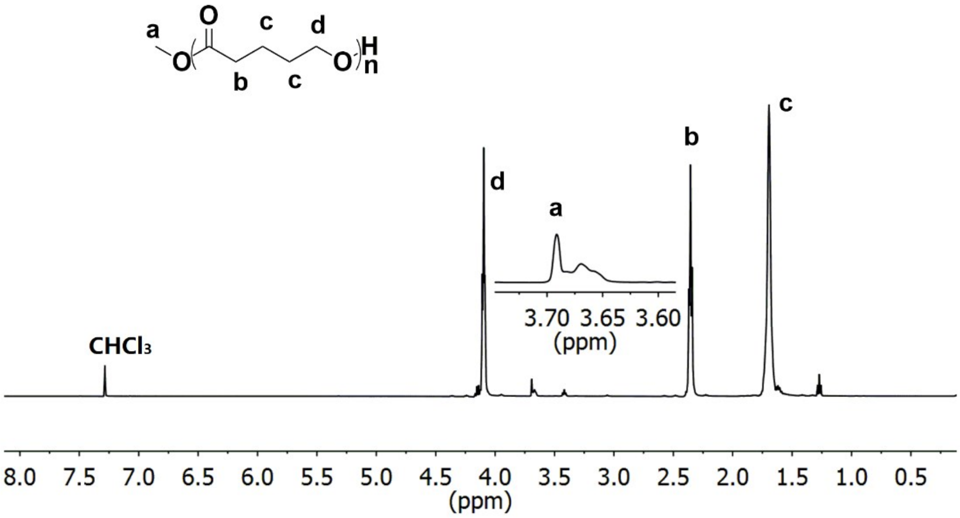
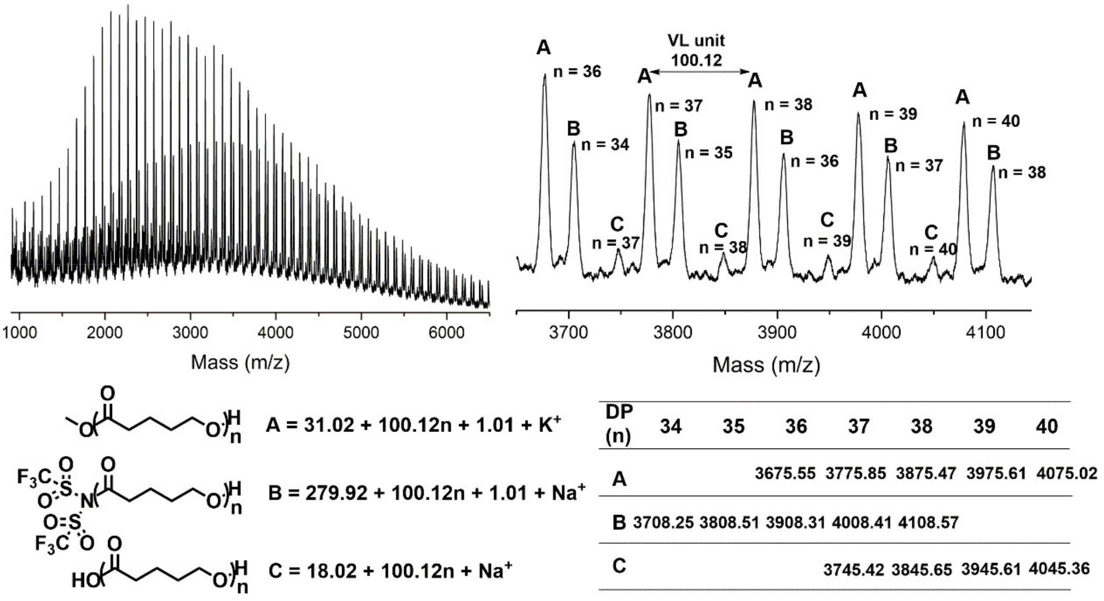


Fig. S10 ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) spectra of PVL ([δ-VL]$_0$/[$TMSNTf_2$]$_0$ = 50/1).



A = 31.02 + 100.12n + 1.01 + K^+

B = 279.92 + 100.12n + 1.01 + Na^+

C = 18.02 + 100.12n + Na^+

DP (n)	34	35	36	37	38	39	40
A			3675.55	3775.85	3875.47	3975.61	4075.02
B	3708.25	3808.51	3908.31	4008.41	4108.57		
C				3745.42	3845.65	3945.61	4045.36

Fig. S11 MALDI-TOF MS spectra of PVL ([δ-VL]$_0$/[$TMSNTf_2$]$_0$ = 50/1) precipitated from super dry methanol initiated by $TMSNTf_2$.

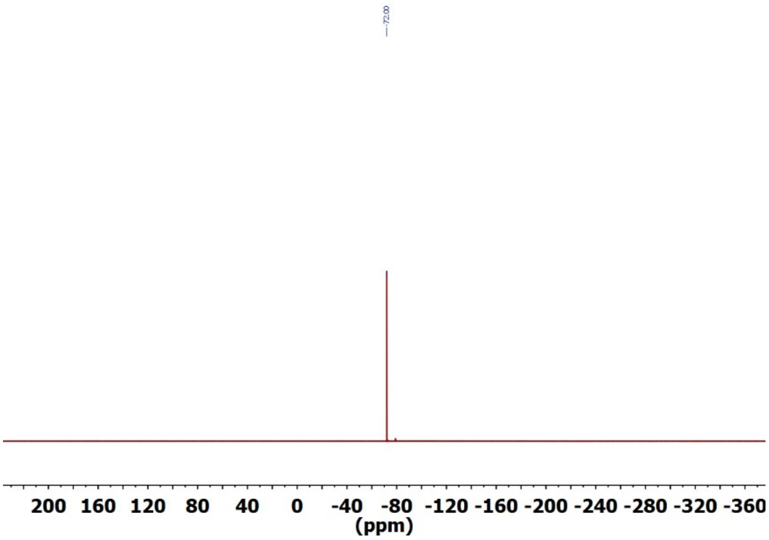


Fig. S12 ^{19}F NMR spectrum (470 MHz, $CDCl_3$, 25 ^{o}C) of the obtained PVL ([δ-VL]$_0$/[$TMSNTf_2$]$_0$ = 50/1) initiated by $TMSNTf_2$.

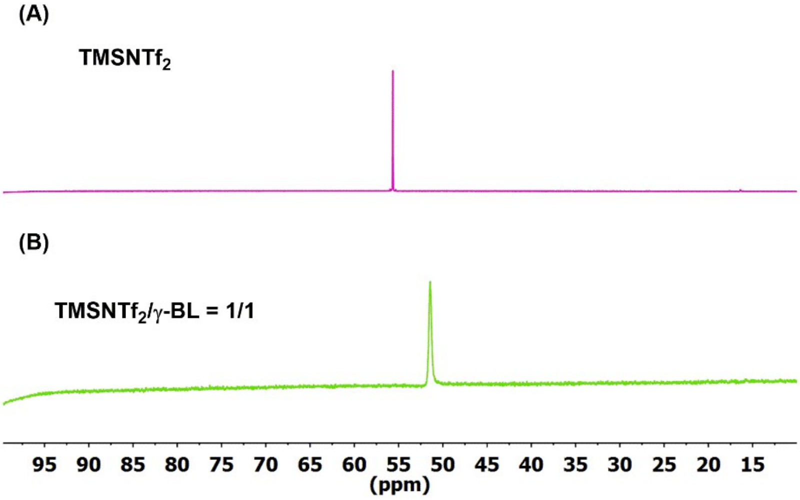


Fig. S13 ^{29}Si NMR spectrum (99 MHz, $CDCl_3$, 25 ^{o}C) of the mixture of $TMSNTf_2$ (1.0 equiv) and γ-BL (1.0 equiv).

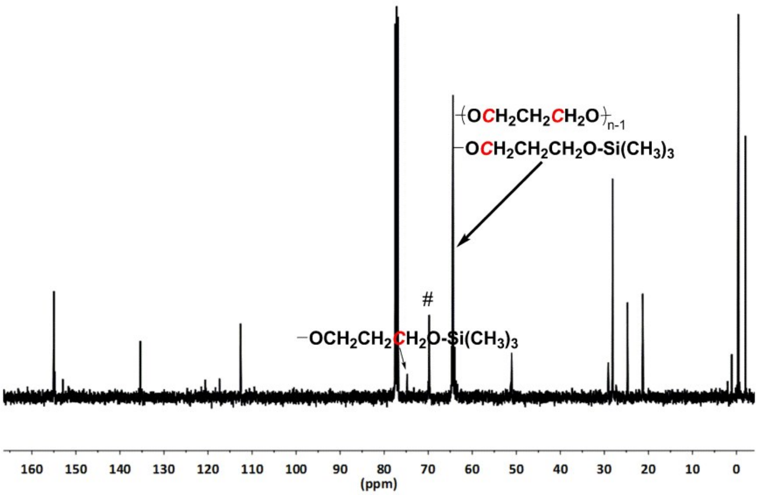


Fig. S14 ^{13}C NMR (100 MHz, CDCl$_3$, 25 ^{o}C) of ROP process of TMC produced by TMC/TMSNTf$_2$ in a ratio of 10:1 before quenching conducted in Teflon-valve-sealed J. Young-type NMR tubes at room temperature in CDCl$_3$ (The peak marked with “#” is attributed to the residual TMC monomer).

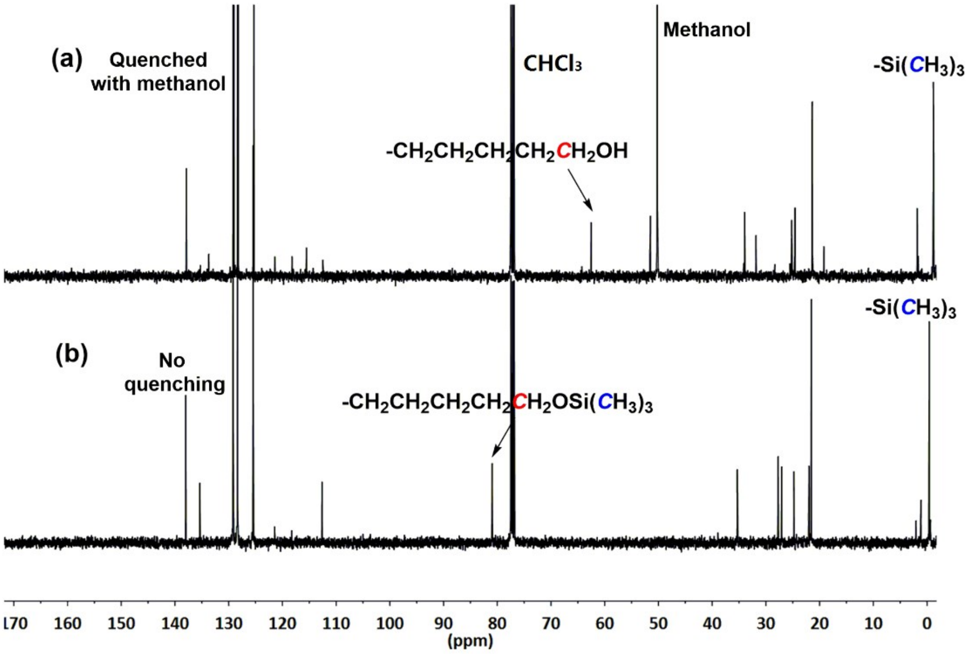


Fig. S15 The ^{13}C NMR (100 MHz, CDCl$_3$, 25 ^{o}C) of ROP process of ε-CL produced by ε-CL/TMSNTf$_2$ in a ratio of 1:1 (a) quenched by methanol; (b) without quenching, using Teflon-valve-sealed J. Young-type NMR tubes at room temperature in CDCl$_3$.

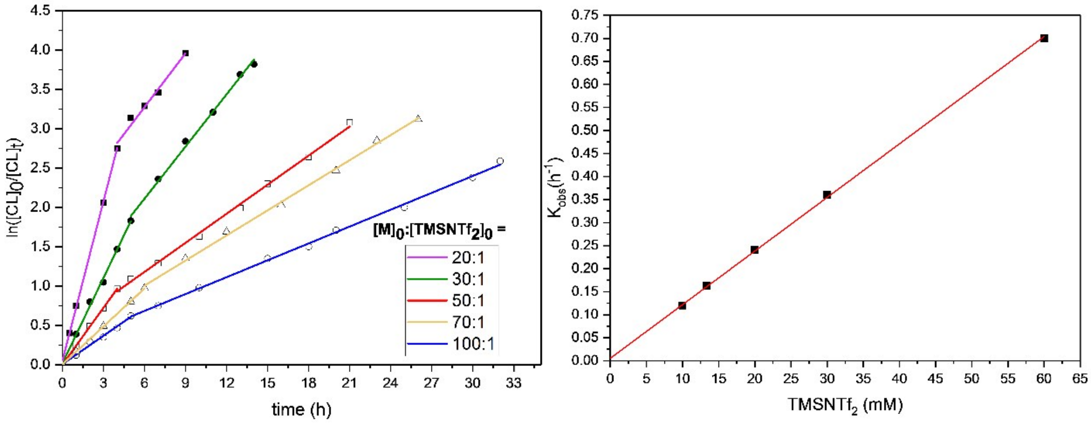


Fig. S16 (A) Plots of ln($[CL]_0/[CL]_t$) *versus* reaction time for the ROP of ε-CL initiated by $TMSNTf_2$ in CH_2Cl_2 at a ratio of ε-CL to $TMSNTf_2$ ($[M]_0$:$[TMSNTf_2]_0$ = 20:1-100:1, $[M]_0$ = 1.0 M, 25 °C). (B) Plot of the observed rate constant (K_{obs}) versus the initial $TMSNTf_2$ concentration for the ROP of ε-CL in the first linearly fitted curve stage.

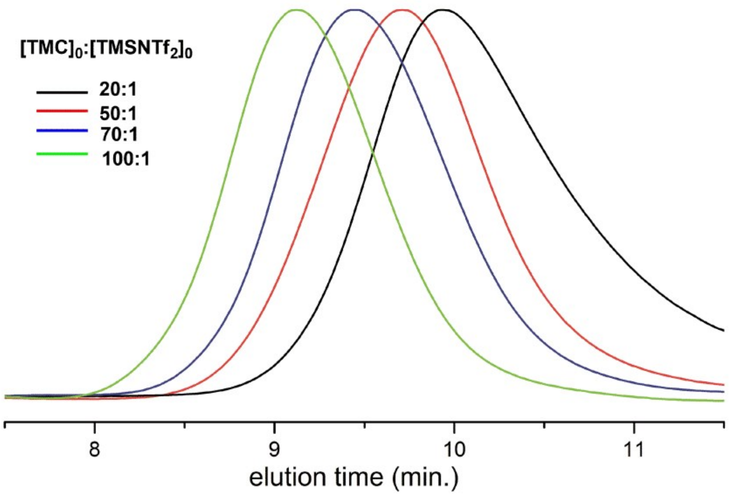


Fig. S17 SEC traces of the obtained PTMC with various molar ratios of TMC to $TMSNTf_2$ ($[TMC]_0/[TMSNTf_2]_0$) of 20 (black line), 50 (red line), 70 (blue line) and 100 (green line) (See all data in Table 1)(eluent, THF; flow rate, 0.7 mL min^{-1}).

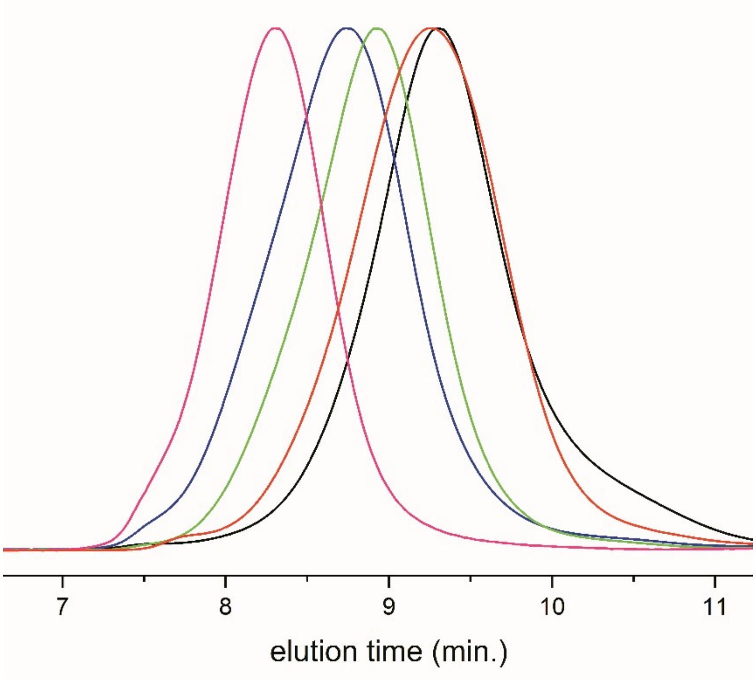


Fig. S18 SEC traces of the obtained PCL with various molar ratios of ε-CL to TMSNTf$_2$ ($[CL]_0/[TMSNTf_2]_0$) of 20 (black line), 30 (red line), 50 (green line), 70 (blue line) and 100 (pink line) (See all data in Table 1)(eluent, THF; flow rate, 0.7 mL min^{-1}).

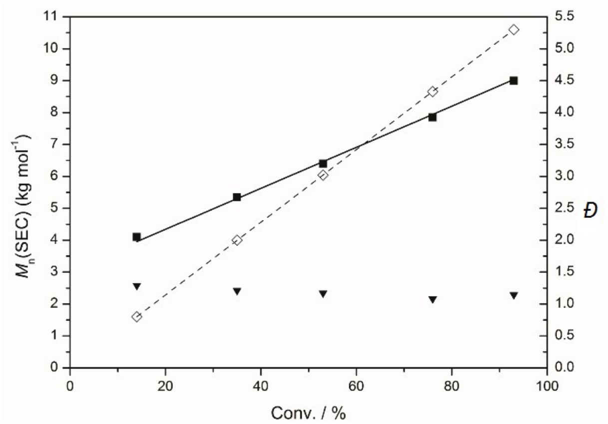


Fig. S19 Plots of $M_{n,SEC}$ versus monomer conversion for the ROP of ε-CL initiated by TMSNTf$_2$ (Table 1, entry 5): (■) M_n (SEC, using the dn/dc [0.070 mL g^{-1}]); (□) M_n (theory); (▼) $Đ$ (M_w/M_n, from SEC).

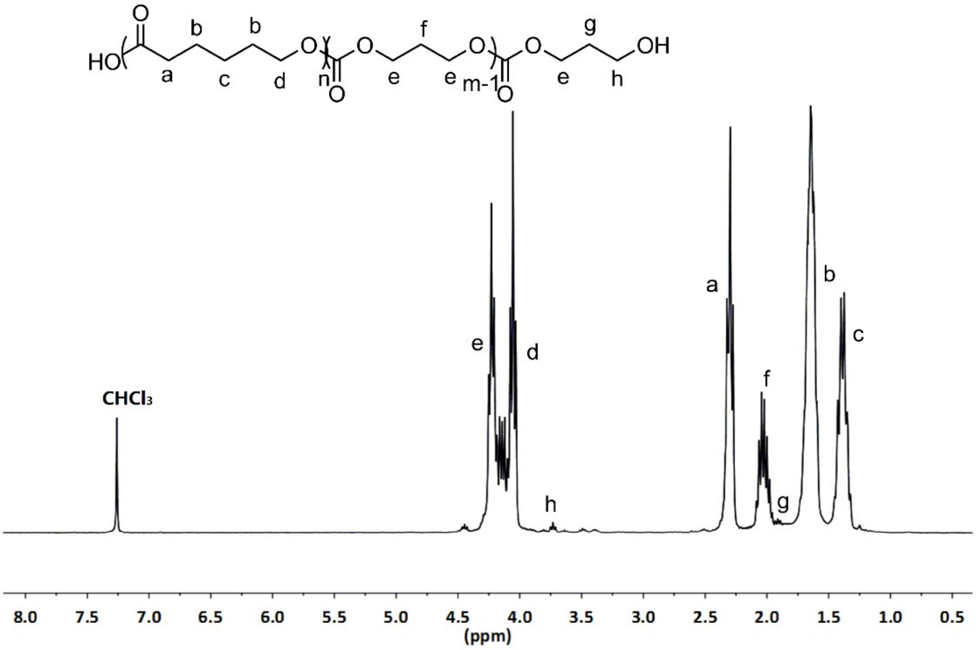


Fig. S20 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 ^oC) of the obtained PCL-*b*-PTMC ([*ε*-CL]$_0$/[TMC]$_0$/[$TMSNTf_2$]$_0$ = 20/30/1) initiated by $TMSNTf_2$ and precipitating in cold methanol at room temperature.

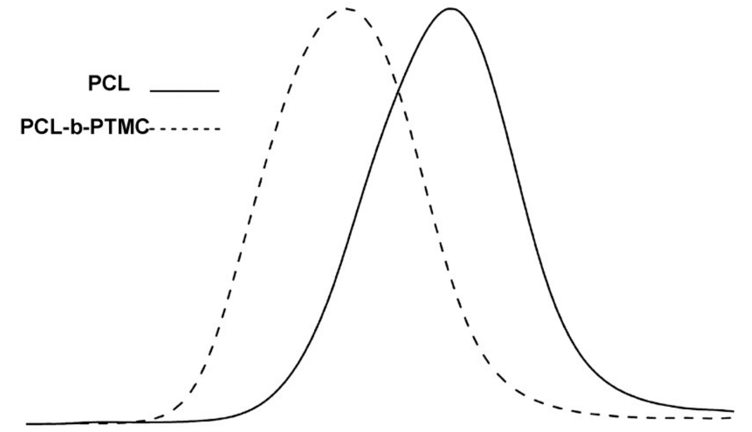


Fig. S21 SEC traces of the first sequence polymer (PCL, black line), and the diblock copolymer (PCL-*b*-PTMC, dashed line) with the initial ratio of [*ε*-CL]$_0$/[TMC]$_0$/[$TMSNTf_2$]$_0$ = 20/30/1 (eluent, THF; flow rate, 0.7 mL min^{-1}).