Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Linear and Star Poly(ε-caprolactone) with Controlled and High Molecular Weights via Cyclic Trimeric Phosphazene Base Catalyzed Ring-Opening Polymerization

Huaike Li,† Na Zhao,† Chuanli Ren, Shaofeng Liu,* and Zhibo Li*

Key Laboratory of Biobased Polymer Materials, Shandong Provincial Education Department; School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

E-mail: shaofengliu@qust.edu.cn and zbli@qust.edu.cn

†These authors contributed equally.

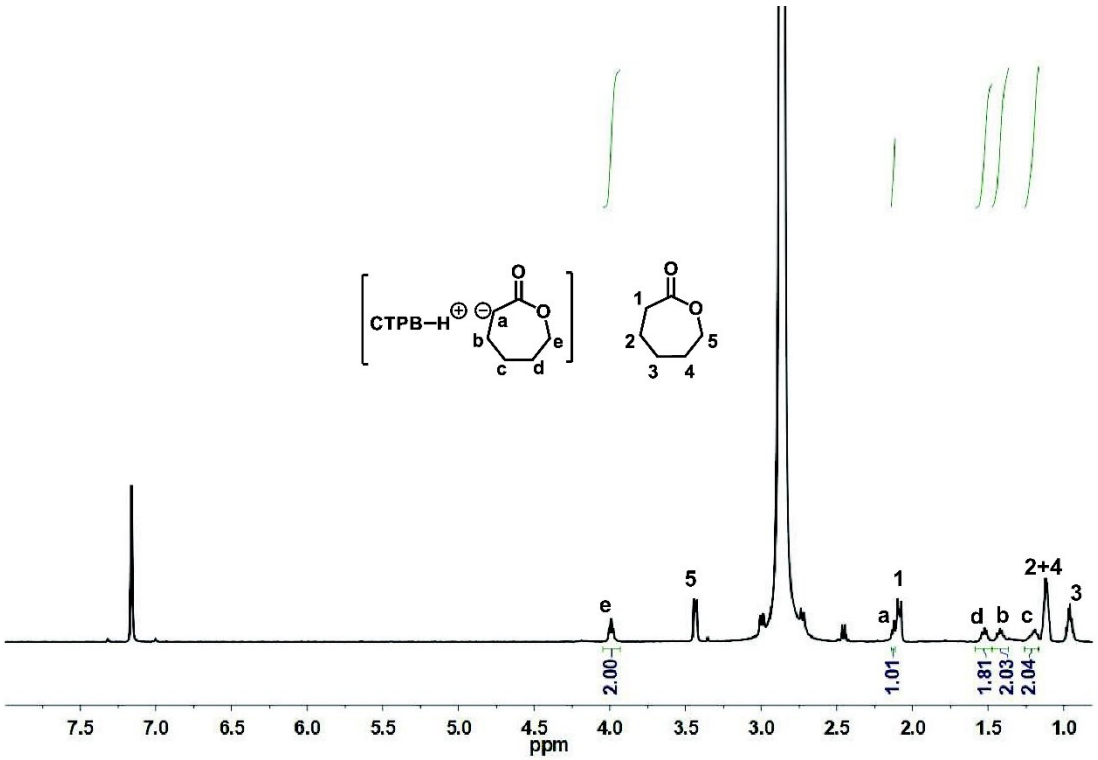

Figure S1. ^{1}H NMR spectrum of **CTPB** + 1 equiv. ε-CL for 2 hours at room temperature in C_6D_6.

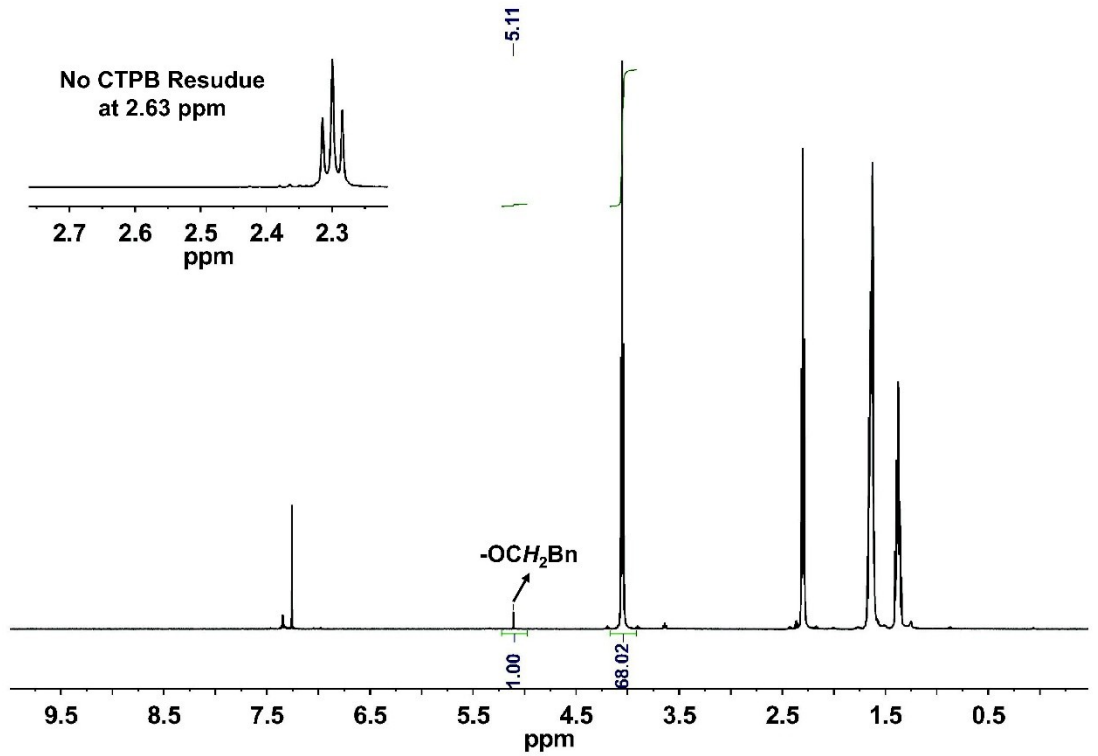

Figure S2. ^{1}H NMR spectrum of PCL obtained in Table 1 entry 11 (ε-CL/**CTPB**/BnOH = 5000/1/50; $M_{n,NMR}$ = 7.8 kDa).

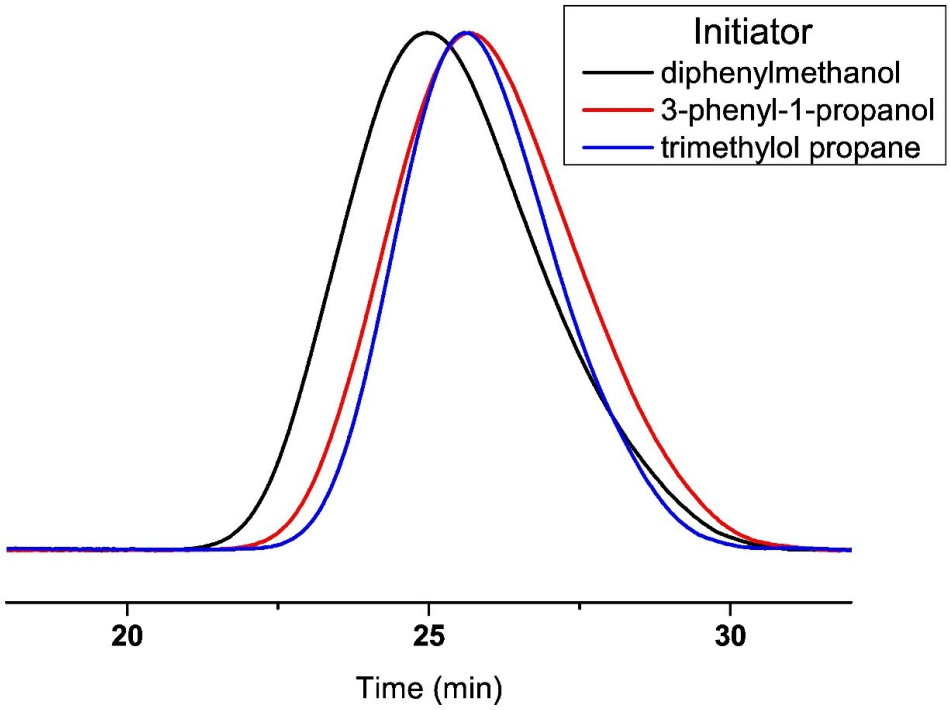

Figure S3. GPC traces with different initiators in Table 1 entries 12-14.

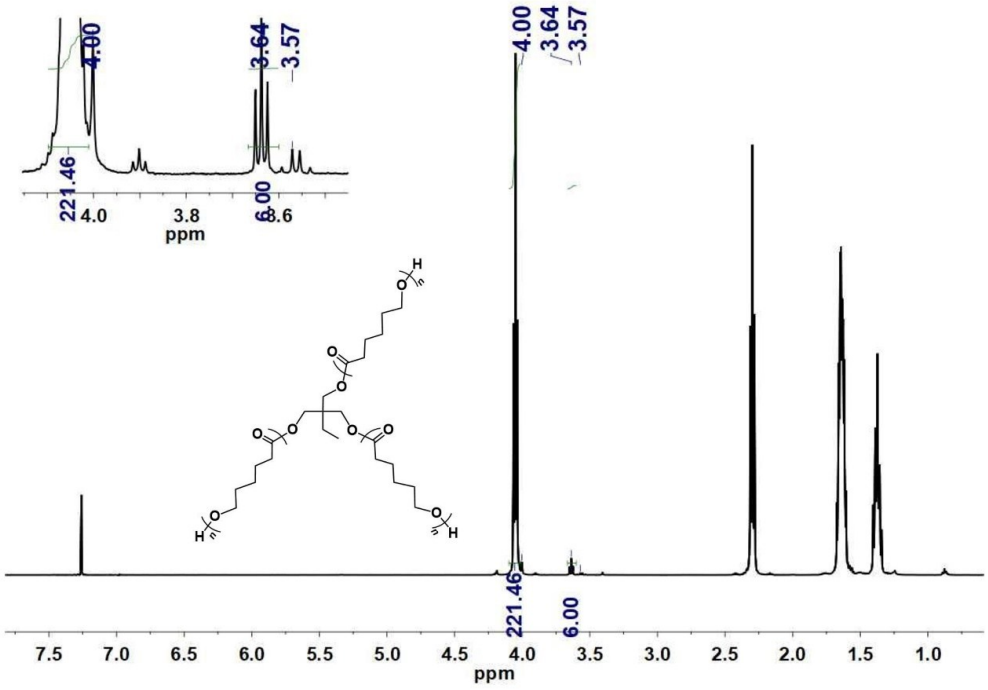

Figure S4. ^{1}H NMR spectrum of PCL obtained in Table 1 entry 14 (ε-CL/**CTPB**/TMP = 300/1/3).

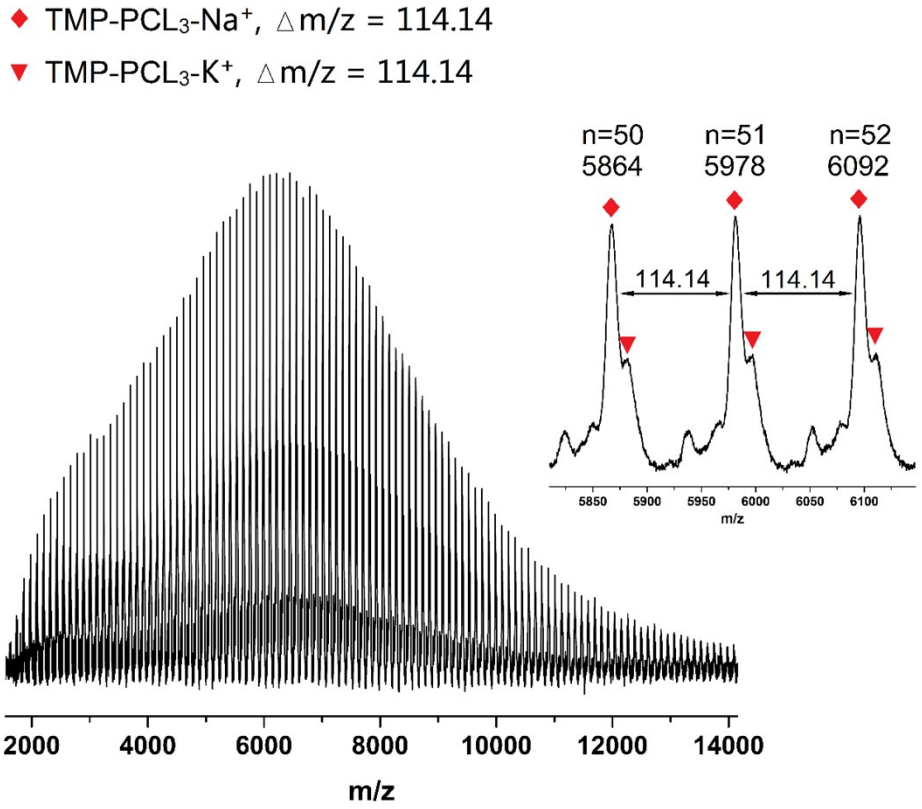

Figure S5. MALDI-TOF mass spectrum of PCL produced by ε-CL /**CTPB**/TMP = 300/1/3 for 2 min (Table 1 run 14, $M_{n,theor}$ = 11.6 kDa, $M_{n,GPC}$ = 12.0 kDa, $M_{n,MALDI}$ = 6.4 kDa).

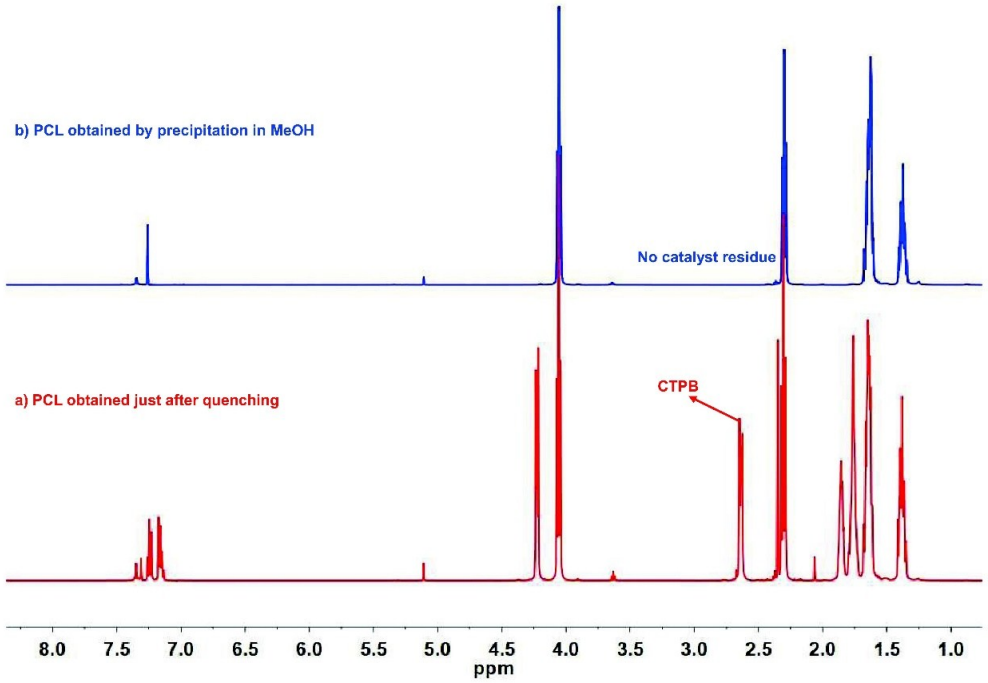

Figure S6. ^{1}H NMR spectra of PCL obtained in Table 1 entry 11 (ε-CL/**CTPB**/BnOH = 5000/1/50); (**a**) PCL obtained just after quenching and (**b**) PCL obtained by precipitation in MeOH.

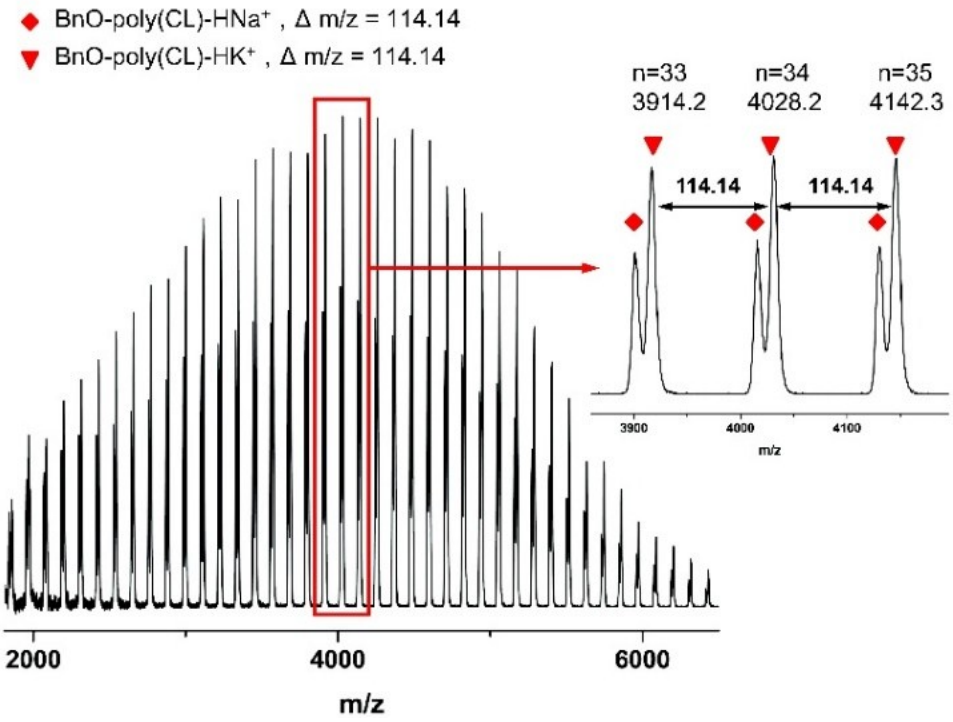

Figure S7. MALDI-TOF mass spectrum of PCL produced by ε-CL /**CTPB**/BnOH = 5000/1/50 (Table 1 run 11, $M_{n,theor}$ = 7.0 kDa, $M_{n,GPC}$ = 7.5 kDa, $M_{n,MALDI}$ = 3.8 kDa).

Table S1. ROP of ε-CL initiated by CTPB/alcohol system.[a]

Entry	$[M]_0/[C]_0/[I]_0$	Initiator	Time [min]	T [°C]	Conv.[b] [%]	$M_{n,theor}$ [kDa]	$M_{n,GPC}$[c] [kDa]	$Đ$[c]
1	100/1/3	BnOH	2	20	67	2.6	2.9	1.31
2	2000/1/1	BnOH	60	20	50	114.1	119.9	2.05
3	5000/1/50	BnOH	30	60	72	8.3	9.1	1.66
4	5000/1/50	BnOH	30	90	88	10.1	11.0	1.65

[a]Conditions: **CTPB** 0.05 mmol; [**CTPB**] was from 0.001 to 0.003 mol/L; base and initiator were mixed firstly in toluene, followed by ε-CL. [b]Determined by ^{1}H NMR. [c]Determined by GPC at 40 °C in THF relative to PS standards.