Electronic Supplementary Information

$Sn(OTf)_2$-catalyzed continuous flow ring-opening polymerization of ε-caprolactone

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Materials

ε-Caprolactone (J&K, 99%) and benzyl alcohol (Sinopharm chemical Reagent, 99%) were distilled over CaH_2 under reduced pressure prior to use. Toluene and tetrahydrogenfuran (THF) (Sinopharm chemical Reagent, 99.5%) was distilled over sodium. The $Sn(OTf)_2$ (Meryer, 98%) was dried over night in vacuum and stored in argon-purged ampoule.

Characterization

^1H NMR (400 MHz) spectra were recorded on a Bruker 400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference. The size exclusion chromatography (SEC) was performed on a DionexUltiMate-3000 chromatograph in THF (1.0 mL/min) at room temperature using commercial polystyrene standards for calibration. It was composed of a P680 HPLC pump equipped with a MKF-GPC-300 column (7.8 mm, 300 mm, 7 mm) (Nanjing Microspheres Hi-Efficiency Isolation Carrier Co. Ltd., Nanjing, China). Matrix assisted laser desorption ionization time of flight mass spectra (MALDI TOF MS) were recorded at 25 kV on the Bruker mass spectrometer (ultra extreme). The polymer and the matrix 2, 5-dihydroxybenzoic acid (DHB) were dissolved in CH_2Cl_2. 1 μl of the sample solution was piped onto the thin NaI crystal layer and dried in air. All mass spectra were collected by employing 500 individual laser shots.

General procedures for $Sn(OTf)_2$ catalyzed polymerization in the batch reactor

Batchwise polymerizations were carried out in the previously flamed and argon-purged 20 mL ampoules via Schlenk technique. $Sn(OTf)_2$ (0.0243g, 0.0576 mmol) was weighed directly into the ampoule. BnOH (0.10 mL, 0.96 mmol) and 3.75 mL toluene/THF (80/20) was added to the ampoule via syringe and stirred for 30 min at room temperature. The polymerization started at designed temperature after adding CL (3.00 mL, 28.20 mmol). Aliquots were precipitated and immediately taken to ^1H NMR for conversion detection. The polymers were precipitated in the cold methanol, filtrated, and dried in vacuum at room temperature.

General procedures for $Sn(OTf)_2$ catalyzed polymerization in the microreactor

The microreactor platform is consisted of two 50 mL gas tight syringes/plug pumps, 15m 1/8'' PTFE tubing and PEEK T-type mixer. Argon-purged stock solution A ($Sn(OTf)_2$ (0.243g, 0.576 mmol) and BnOH (1.00 mL, 9.60 mmol) in 37.5 mL toluene/THF (80/20)) and stock solution B (CL (30.00 mL, 282.0 mmol)) were prepared in advance *via* Schlenk technique and transferred into two 50 ml gas tight syringes. The assembled tubular microreactor system was flushed with nitrogen and dried toluene to remove the moisture and air. The stock solution A and B were pumped into T-type mixer with predictable flow rate. The reaction mixture passed through the tubular reactor at designed temperature. The fluid was precipitated and immediately taken to ^1H NMR for conversion detection. The products were precipitated in the cold methanol, filtrated, and dried in vacuum at room temperature.

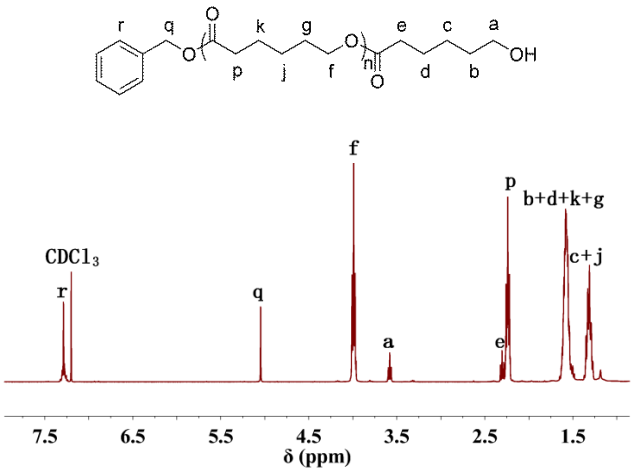
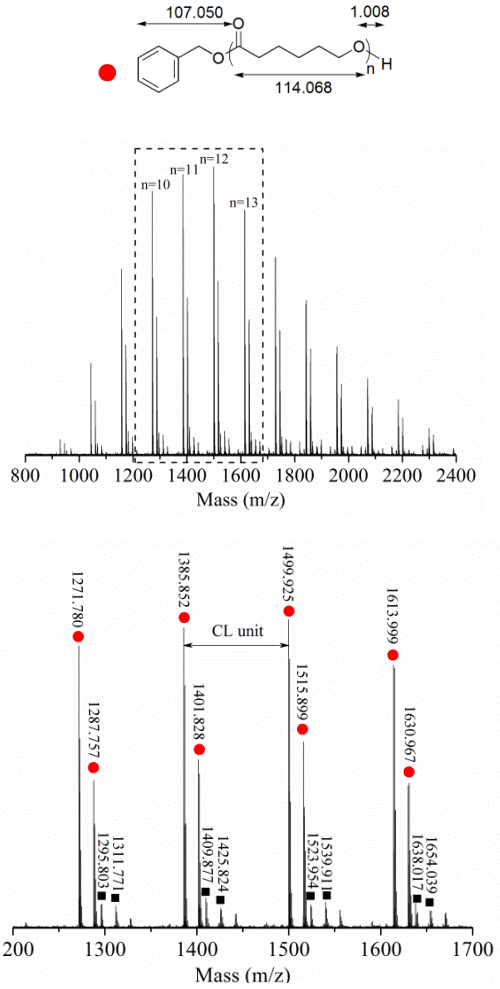


Fig. S1 ^{1}H NMR of PCL ([CL]/[BnOH]/[Sn]=10:1:0.02, 80 ^{o}C, 40 min) prepared in microreactor.



	ion	Theoretical values (Mn,theo)			
		10	11	12	13 (n)
initiated by BnOH	Na^+	1271.755	1385.823	1499.891	1613.959
	K^+	1287.702	1401.770	1515.838	1629.907
initiated by H_2O	Na^+	1181.708	1295.776	1409.844	1523.912
	K^+	1197.655	1311.723	1425.791	1539.859

Fig. S2 MALDI TOF MS of PCL ([CL]/[BnOH]/[Sn]=10:1:0.02, 80 ^{o}C, 40 min) prepared in microreactor.