

## Supporting Information for

### A Direct Comparison Between Ring-Opening Copolymerization and Polycondensation to Produce Polyesters Using Poly(ethylene succinate) as An Example

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## Chemicals

Succinic anhydride (SA), ethylene glycol (EG), succinic acid (SAc), antimony triacetate ( $\text{Sb}(\text{OCOCH}_3)_3$ ), tetrahydrofuran (THF), *n*-hexane, ethanol, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), and chloroform ( $\text{CHCl}_3$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd., Energy Chemical Co., and Shanghai Titan Scientific Co., Ltd. Calcium hydride ( $\text{CaH}_2$ ), *n*-butyllithium (*n*-BuLi) and deuterated solvents were purchased from Meryer Co. Ethylene oxide (EO) was received from Minxing Chemical Co. EO was stirred over  $\text{CaH}_2$  at room temperature for 12 h in a Schlenk flask and vacuum transferred by trap-to-trap distillation into another Schlenk flask. SA was purified by sublimation under high vacuum. EG, SAc, and  $\text{Sb}(\text{OCOCH}_3)_3$  were used without further purification.  $\text{CDCl}_3$  was distilled over  $\text{CaH}_2$  for 12 h and then stored over activated Davison 4 Å molecular sieves.

## Characterizations

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400 spectrometer ( $^1\text{H}$  NMR 400 MHz,  $^{13}\text{C}$  NMR 101 MHz) at 25 °C.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were referenced using the internal standard shifts or the residual solvent signals ( $^1\text{H}$ : TMS in  $\text{CDCl}_3 = 0$  ppm;  $^{13}\text{C}$ :  $\text{CDCl}_3 = 77.16$  ppm). Data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation.

Gel permeation chromatography (GPC) was conducted on a system equipped with a Waters Chromatography, Inc. model 1515 isocratic pump, a model 2414 differential refractometer, and a two-column set of Polymer Laboratories, Inc. Styragel columns (PLgel 5  $\mu\text{m}$ Mixed C, 500 Å, and 104 Å, 300×7.5 mm columns).

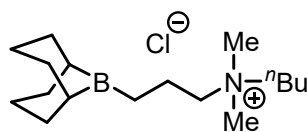
The system was equilibrated at 35 °C in  $\text{CHCl}_3$ , which served as the elute solvent with a 1.00 mL/min flow rate. Calibration was done with a series of narrowly dispersed polystyrene (PS) standards to obtain apparent number average molar mass ( $M_n$ ) and *D* of the polymers. Polymer solutions were prepared at a concentration of 10 mg/mL and an injection volume of 100  $\mu\text{L}$  was used.

MALDI-TOF-MS analyses were performed on a Bruker Daltonics UltrafleXtreme system. Crude polymer samples were dissolved in  $\text{CHCl}_3$  at a concentration of 10  $\text{mg}\cdot\text{mL}^{-1}$ . 2,5-Dihydroxybenzoic acid (DHB) was chosen as matrix and was added with a concentration of 40  $\text{mg}\cdot\text{mL}^{-1}$ . The resulting spectra were analyzed using the Bruker Daltonics flexAnalysis 3.4 software package.

## Procedural Information

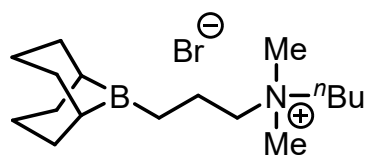
### Synthesis of organoboron catalysts

#### [BBN-C<sub>3</sub>-N<sup>n</sup>BuMe<sub>2</sub>][Cl]



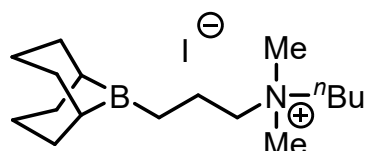
The synthesis procedure and characterization data were consistent with literature reports.<sup>1</sup>

#### [BBN-C<sub>3</sub>-N<sup>n</sup>BuMe<sub>2</sub>][Br]



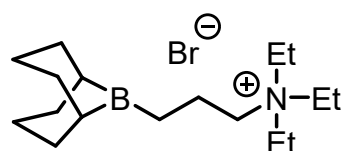
The synthesis procedure and characterization data were consistent with literature reports.<sup>1</sup>

#### [BBN-C<sub>3</sub>-N<sup>n</sup>BuMe<sub>2</sub>][I]



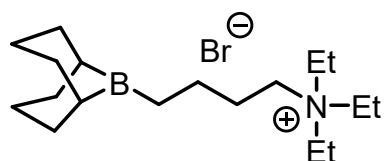
The synthesis procedure and characterization data were consistent with literature reports.<sup>1</sup>

#### [BBN-C<sub>3</sub>-NEt<sub>3</sub>][Br]



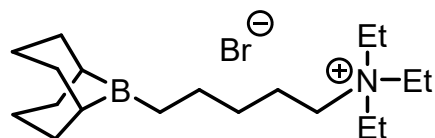
The synthesis procedure and characterization data were consistent with literature reports.<sup>2</sup>

#### BBN-C<sub>4</sub>-NEt<sub>3</sub>][Br]



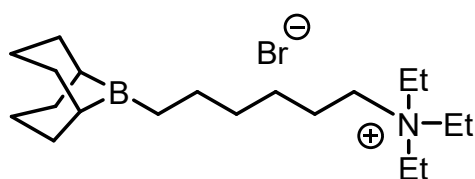
The synthesis procedure and characterization data were consistent with literature reports.<sup>2</sup>

#### [BBN-C<sub>5</sub>-NEt<sub>3</sub>][Br]



The synthesis procedure and characterization data were consistent with literature reports.<sup>2</sup>

### [BBN-C<sub>6</sub>-NEt<sub>3</sub>][Br]



The synthesis procedure and characterization data were consistent with literature reports.<sup>2</sup>

### Representative procedure for the ring-opening copolymerization (ROCOP) of EO and SA.

A typical procedure of entry 2 in Table 1 is as follows. In a glovebox, SA (2.27 g, 22.7 mmol) and catalyst [BBN-C<sub>3</sub>-N<sup>n</sup>BuMe<sub>2</sub>][Cl] (17 mg, 56.7 μmol) were weighed into a 10-mL vial equipped with magnetic stirrer. And then EO (1 g, 22.7 mmol) was vacuum transferred by trap-to-trap distillation into the vial. The vial was sealed and the polymerization was stirred at 80 °C in an aluminum bath for 3 hours. After then, the reaction was quenched by cooling to -10 °C and diluted with 3 mL CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. And then a small part of the solution was taken out for the analysis of the conversion of SA by <sup>1</sup>H NMR spectrum. The resulting poly(ethylene succinate) was obtained by precipitation from ethanol for only once. Then the polymer was dried under vacuum at 50 °C overnight.

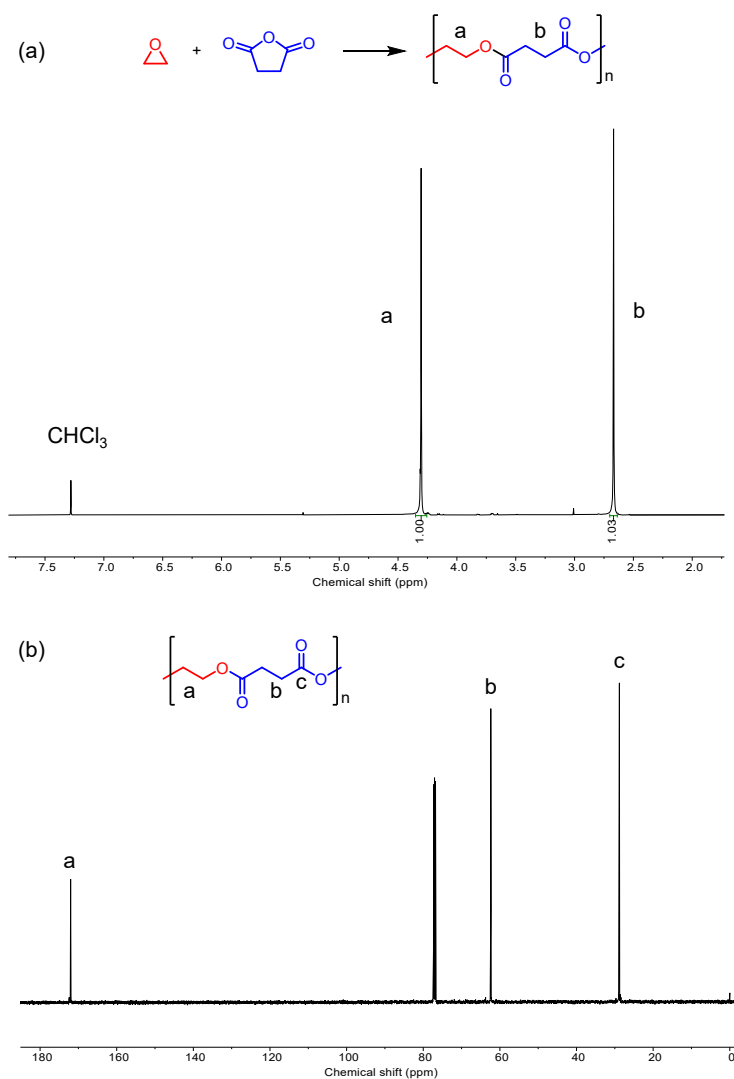
### Representative procedure for polycondensation of EG and SAc.

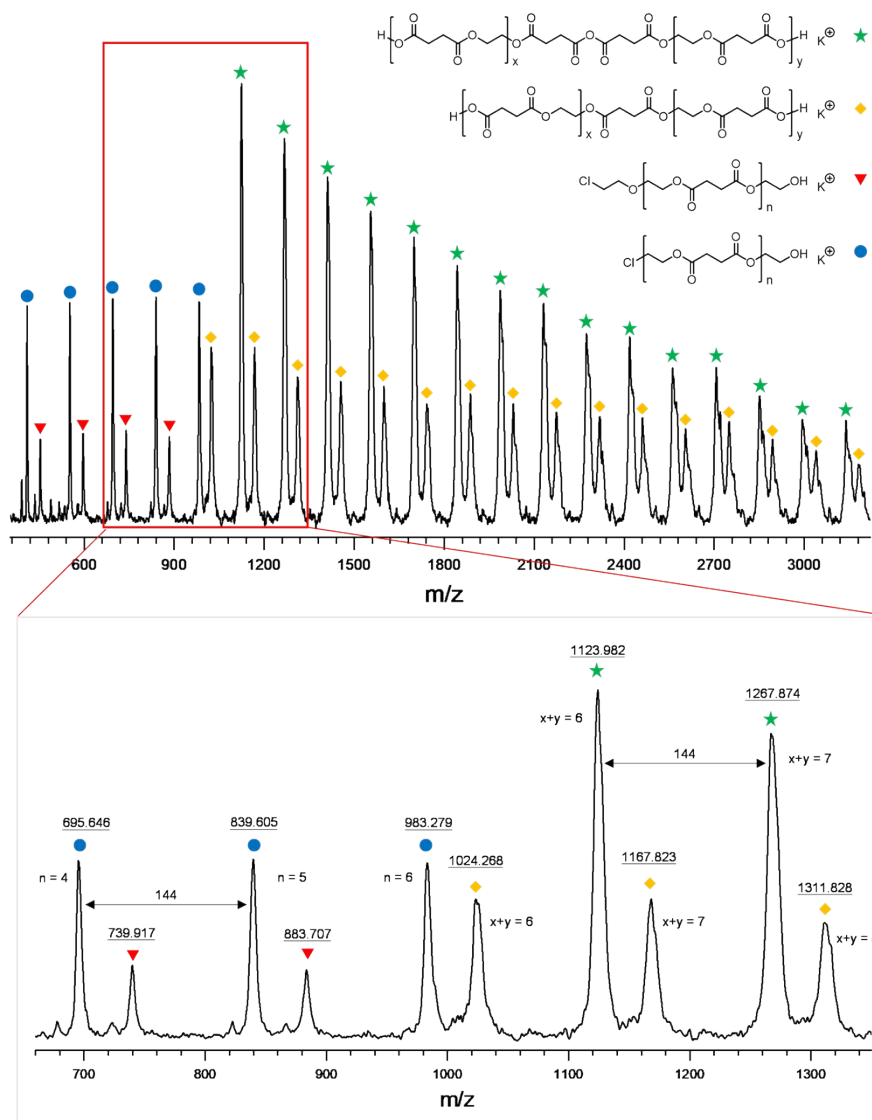
A typical procedure of entry 1 in Table 2 is as follows. EG (2 g, 32.2 mmol) and Sb(OCOCH<sub>3</sub>)<sub>3</sub> (48 mg, 0.161 mmol) were weighed into a 25-mL three-necked, round-bottomed flask equipped with magnetic stirrer. After Sb(OCOCH<sub>3</sub>)<sub>3</sub> was completely dissolved under stirring, SAc (1.9 g, 16.1 mmol) was added. The reactor was heated to 200 °C and stirred in a nitrogen atmosphere for 1 hour. After then, the reactor was evacuated to low pressure (about 0.3-3 mmHg) and heated to 240 °C. After 2 hours, the temperature was further increased to 280 °C and low pressure was kept for 4 hours. Then, the reaction was quenched by cooling to -10 °C and diluted with 15 mL CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. To obtain purified copolymer, 1M HCl/MeOH was added into the mixture and then precipitated from ethanol. This procedure was repeated for three times. Then the polymer was dried under vacuum at 50 °C overnight.

**Table S1.** ROCOP of EO and SA catalyzed by various mononuclear organoboron catalysts.

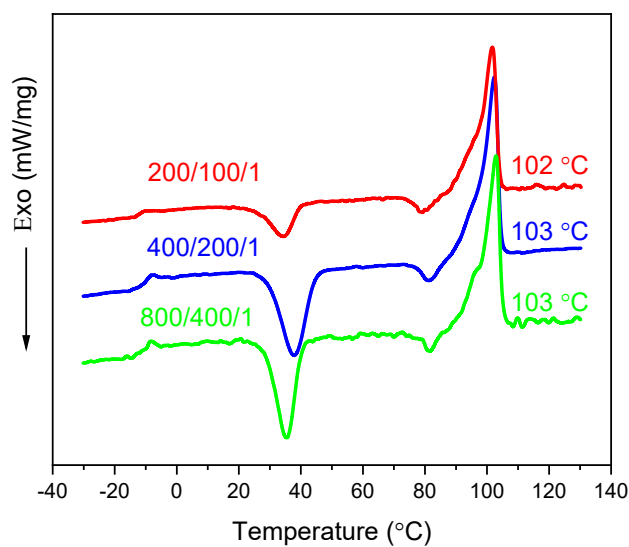
entry	Cat.	EO/SA/Cat.	T (°C)	t (h)	conv. (%) <sup>a</sup>	Ester (%) <sup>a</sup>	TOF (h <sup>-1</sup> )
1	[BBN-C <sub>3</sub> -N <sup>n</sup> BuMe <sub>2</sub> ][Cl]	400/400/1	80	3	58	>99	77
2	[BBN-C <sub>3</sub> -N <sup>n</sup> BuMe <sub>2</sub> ][Br]	400/400/1	80	3	38	>99	51
3	[BBN-C <sub>3</sub> -N <sup>n</sup> BuMe <sub>2</sub> ][I]	400/400/1	80	3	31	>99	41
4	[BBN-C <sub>3</sub> -NEt <sub>3</sub> ][Br]	400/400/1	80	3	41	>99	55
5	[BBN-C <sub>4</sub> -NEt <sub>3</sub> ][Br]	400/400/1	80	3	39	>99	52
6	[BBN-C <sub>5</sub> -NEt <sub>3</sub> ][Br]	400/400/1	80	3	43	>99	57
7	[BBN-C <sub>6</sub> -NEt <sub>3</sub> ][Br]	400/400/1	80	3	40	>99	54
8	[Bora-C <sub>5</sub> -N <sup>n</sup> Bu <sub>3</sub> ][Br]	400/400/1	80	3	59	>99	78

<sup>a</sup>Conv. (%) is the conversion of the SA and ester (%) is the percentage of ester linkage in the polymer, which were both determined by <sup>1</sup>H NMR spectroscopy.





**Figure S2.** The MALDI-TOF MS spectrum of obtained PES from ROCOP of EO and SA using [BBN-C<sub>3</sub>-N<sup>n</sup>BuMe<sub>2</sub>][Cl] catalyst. (Table 1, entry 2).



**Figure S3.** DSC curves for the PES obtained from polycondensation of EG and SAc (red : Table 2, entry 1; blue : Table 2, entry 2; green : Table 2, entry 3).

## References

1. Zhang, Y. Y.; Yang, G. W.; Xie, R.; Yang, L.; Li, B.; Wu, G. P. Scalable, Durable, and Recyclable Metal-Free Catalysts for Highly Efficient Conversion of CO<sub>2</sub> to Cyclic Carbonates. *Angew Chem Int Ed Engl* **2020**, *59*, 23291-23298.
2. Yang, G. W.; Zhang, Y. Y.; Xie, R.; Wu, G. P. Scalable Bifunctional Organoboron Catalysts for Copolymerization of CO<sub>2</sub> and Epoxides with Unprecedented Efficiency. *J. Am. Chem. Soc.* **2020**, *142*, 12245-12255.