SUPPORTING INFORMATION

for

Triethyl Borane-Regulated Selective Production of Polycarbonate and Cyclic Carbonate for the Coupling Reaction of CO_2 with Epoxides

Zheng Chen[1], Jia-Liang Yang[1], Xin-Yu Lu[1], Lan-Fang Hu[1], Xiao-Han Cao[1], Guang-Peng Wu[1], Xing-Hong Zhang*[1,2]

[1]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

[2]Center of Chemistry for Frontier Technologies, Zhejiang University, Hangzhou 310027, China

Contents

1. Methods

Representative Procedure for Copolymerization Reactions.

A 10 mL autoclave with magnetic stirrer was dried in an oven at 110 °C overnight, then immediately placed into the glove box chamber. After keeping under vacuum for 1-2 h, the reaction vessel was put into the glove box under nitrogen atmosphere. The copolymerization of CO_2 with PGE described below is taken from entry 4 in Table 1 as an instance. Bis(triphenylphosphine)iminium chloride (PPNCl, 16.1 mg, 0.028 mmol) was firstly added into the reactor and dissolved in 2 mL of THF. Afterwards, triethyl borane (168 µL, 0.168 mmol), PGE (2.0 ml, 14 mmol) was added into the autoclave respectively. The reactor was sealed and taken out from the glove box and charged with 1.4 g CO_2 (CO_2: epoxide = 1.5:1, molar ratio). The copolymerization was carried out at 60 °C for 8 h. Afterwards, the autoclave was cooled in ice-water bath and the unreacted CO_2 was slowly vented. A spot of crude product was taken for determining PGE conversion and the ratio of the copolymer/cyclic products by the ^{1}H NMR spectrum. The crude product was quenched with HCl in methanol (1 mol/L). Next, the polymer was dissolved with CH_2Cl_2 and then precipitated in methanol. The final product was dried in vacuum at 40 °C until a constant weight.

2. General Information

Characterization.

All ^{1}H NMR and ^{13}C NMR spectra was recorded on a Bruker AVANCE DMX 400 MHz instrument in $CDCl_3$. Chemical shift values were referenced to $CHCl_3$ at 7.26 ppm for ^{1}H NMR. Molecular weights and molecular weight distributions of the resultant copolymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF with 1.0 mL/min at 40 °C. The sample concentration was 0.4wt%, and the injection volume was 50 µL. Calibration was performed using monodisperse polystyrene standards covering the molecular-weight range from 500 to 5000000 Da. The glass transition temperature (T_g) of the polymer was determined by DSC on a TA DSC-Q200 instrument. The sample was heated in two cycles from room temperature to 130

°C at a rate of 5 °C /min under a nitrogen atmosphere. And T_g was determined from the second run. Samples for thermal analyses were all purified. The refractive index was measured by ellipsometer.

Calculation of Copolymer Selectivity and TOF.

Copolymer Selectivity was calculated based on the ^{1}H NMR spectrum of the crude product. Protons with chemical shift of 2.72, 2.86, 3.31, 3.90 and 4.18 ppm belong to the methane, methenyl of PGE respectively, the corresponding peaks in 4.28-4.58, 4.09 and 5.18 ppm belong to the copolymer. The peaks in 4.07, 4.20, 4.46, 4.53 and 4.97 ppm belong to cyclic propylene carbonate. And the peaks in 3.73 ppm belong to polyether. And the area ratio of these parts were taken to determine the copolymer selectivity and the selectivity of polycarbonate. Together with the mass of pure product, we can precisely get the TOF values.

3. Typical ^{1}H NMR Spectra

Typical NMR Spectra are presented here to give a comprehensive information.
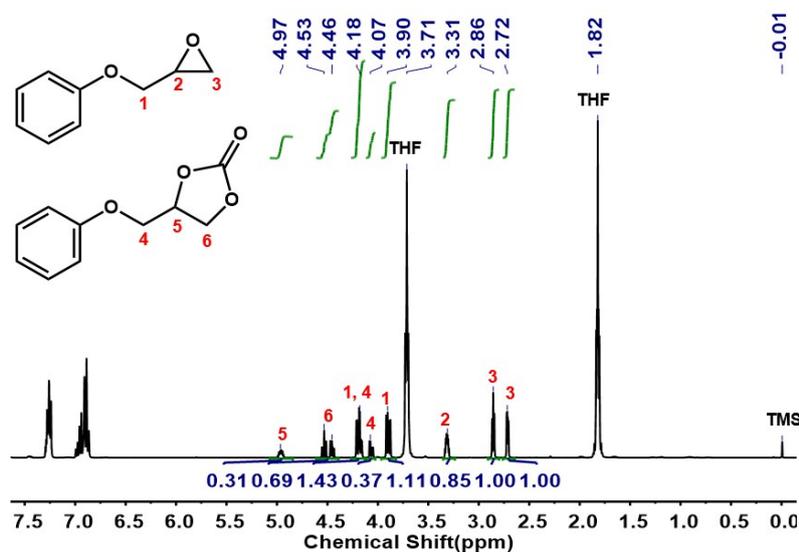
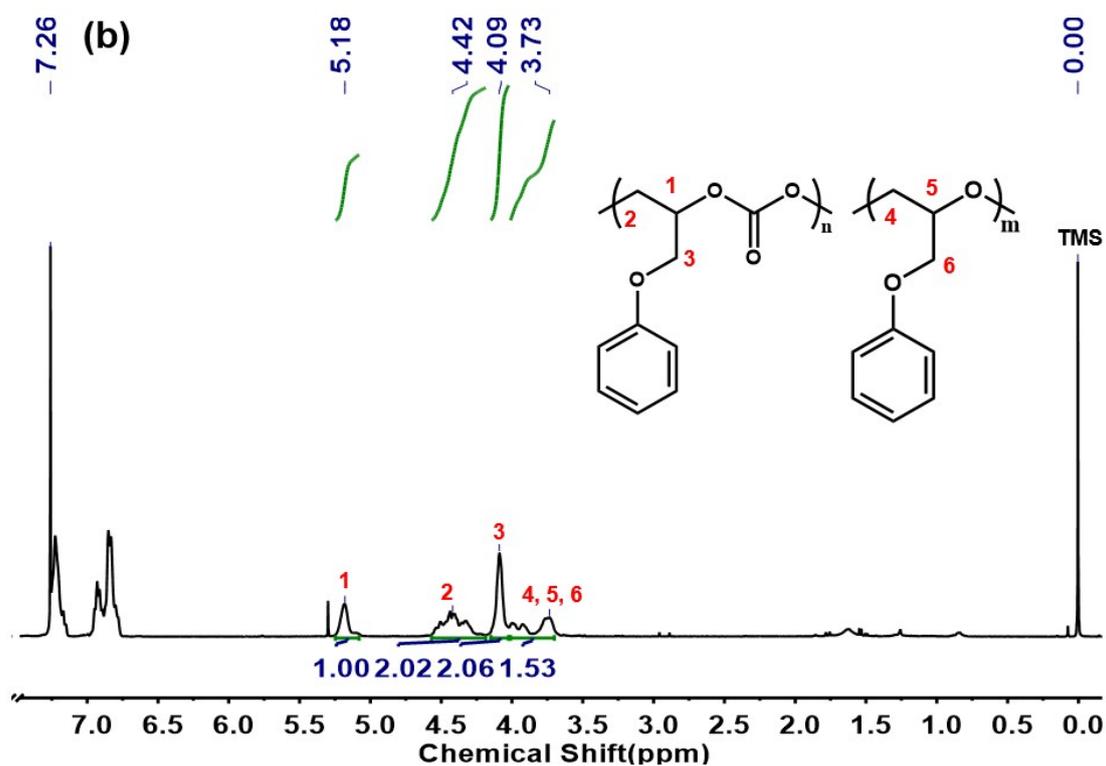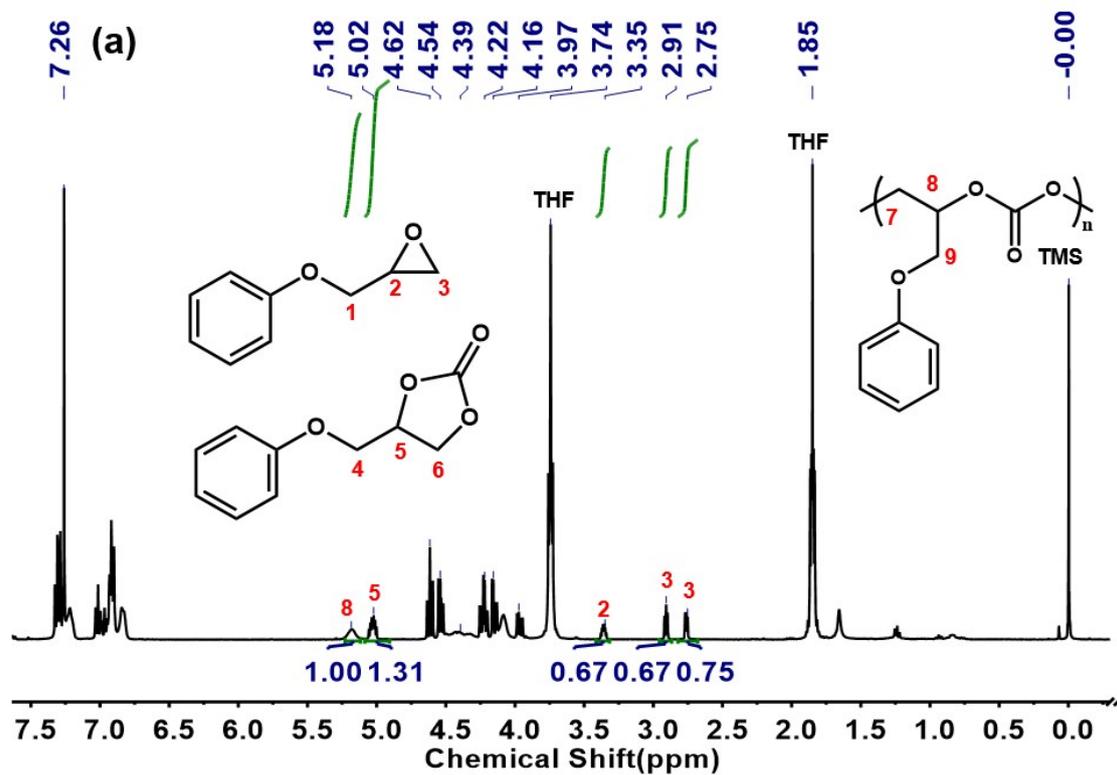**Figure S1.** ^{1}H NMR spectrum of the crude product of entry 1, Table 1.

Figure S2. (a) ^{1}H NMR spectrum of the crude product of entry 3, Table 1. (b) ^{1}H NMR spectrum of the purified product of entry 3, Table 1.
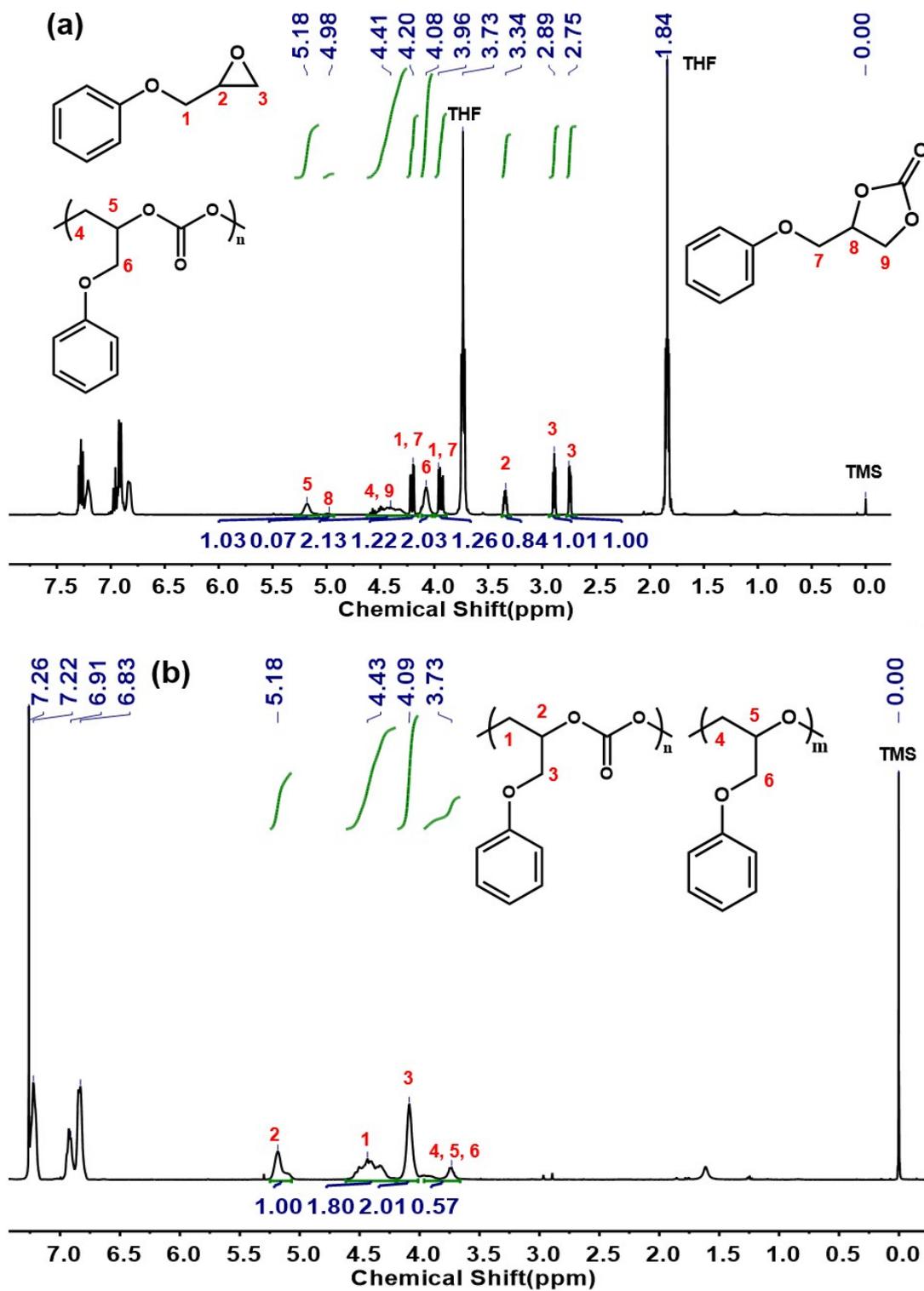
Figure S3. (a) ^{1}H NMR spectrum of the crude product of entry 6, Table 1. (b) ^{1}H NMR spectrum of the purified product of entry 6, Table 1.
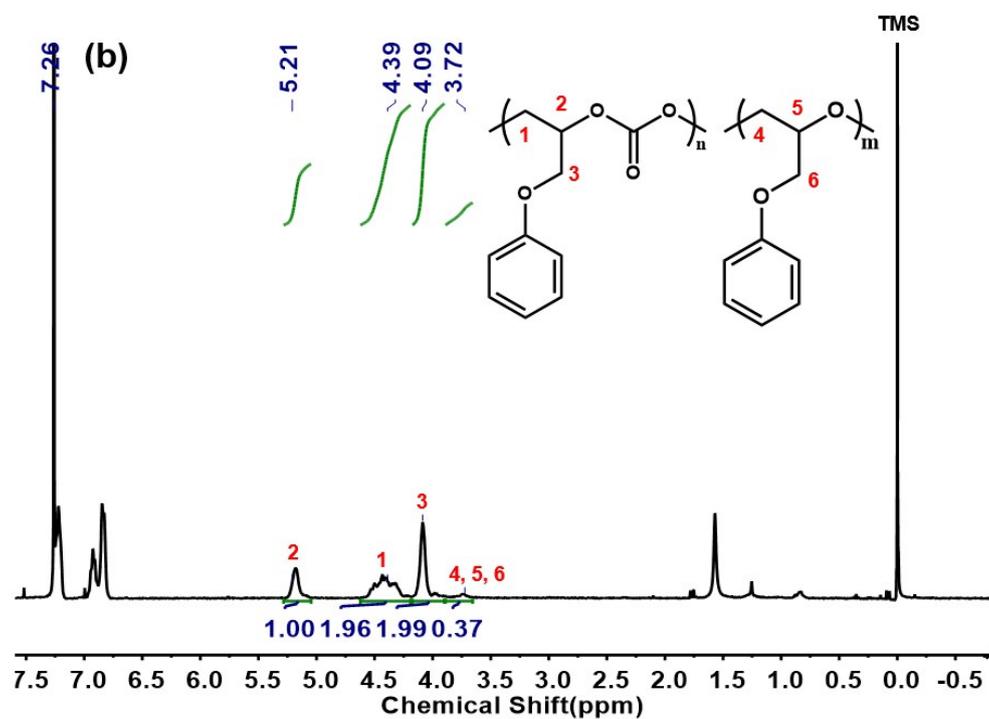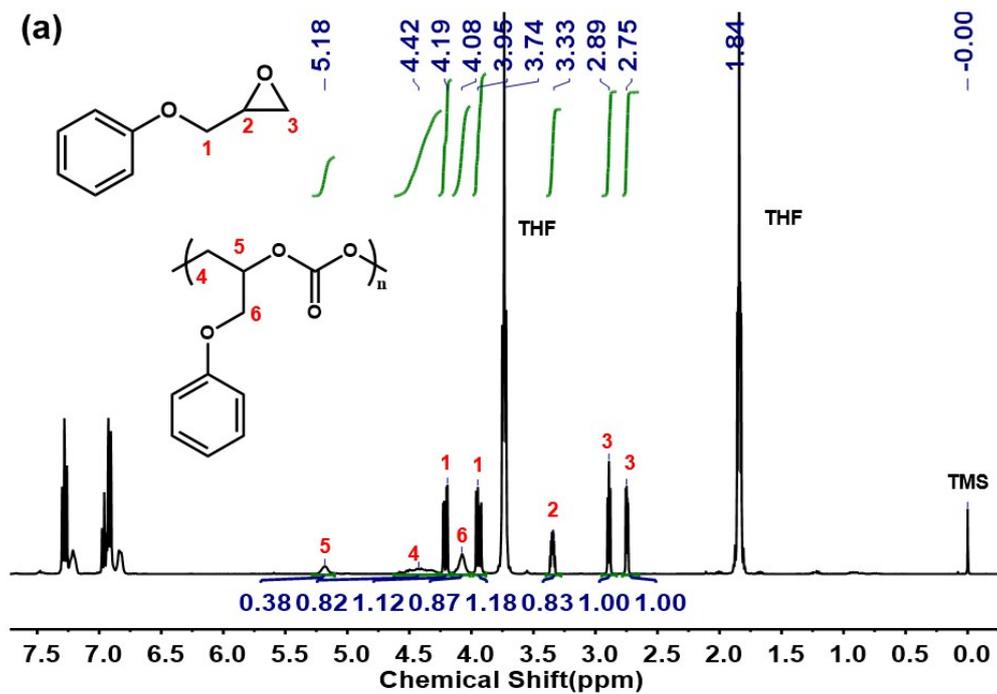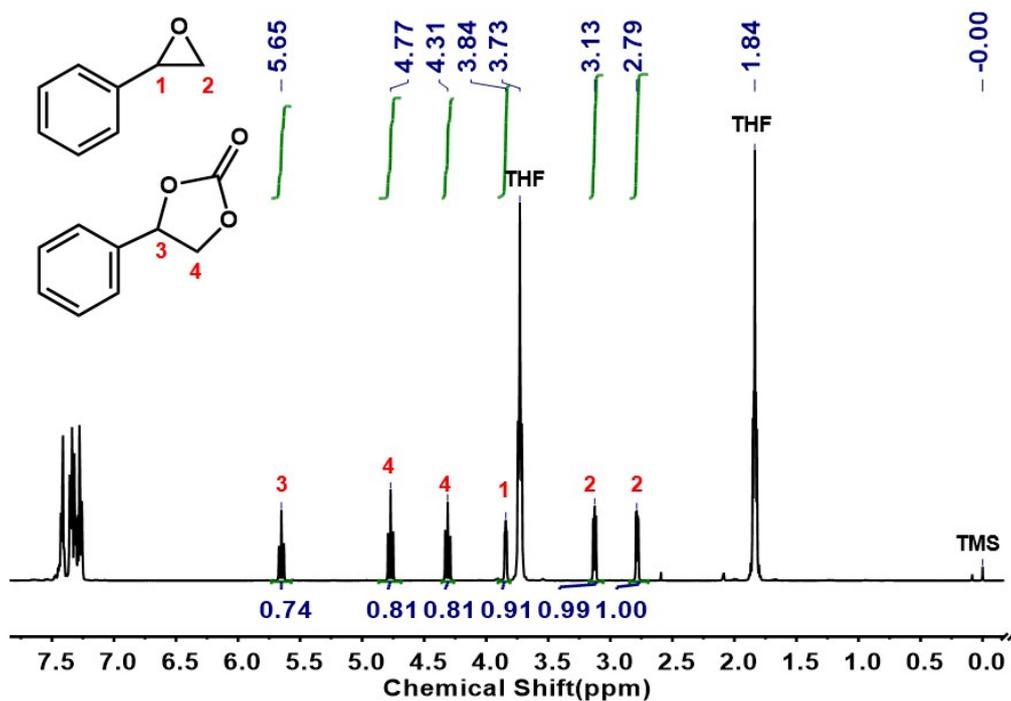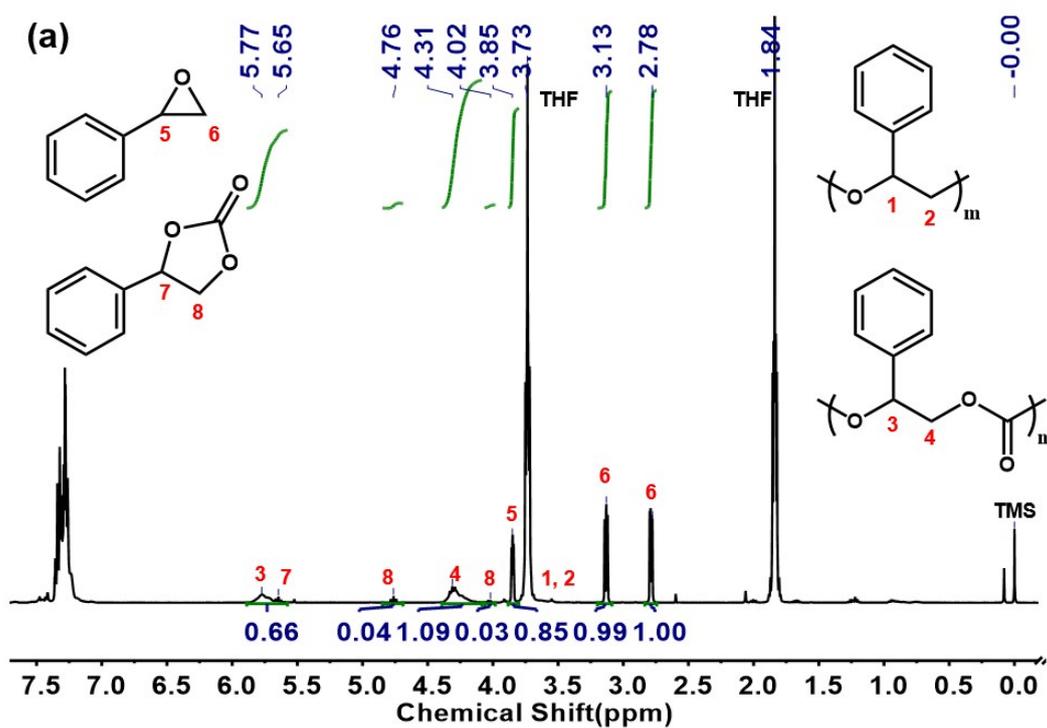
Figure S4. (a) ^{1}H NMR spectrum of the crude product of entry 1, Table 2. (b) ^{1}H NMR spectrum of the purified product of entry 1, Table 2.

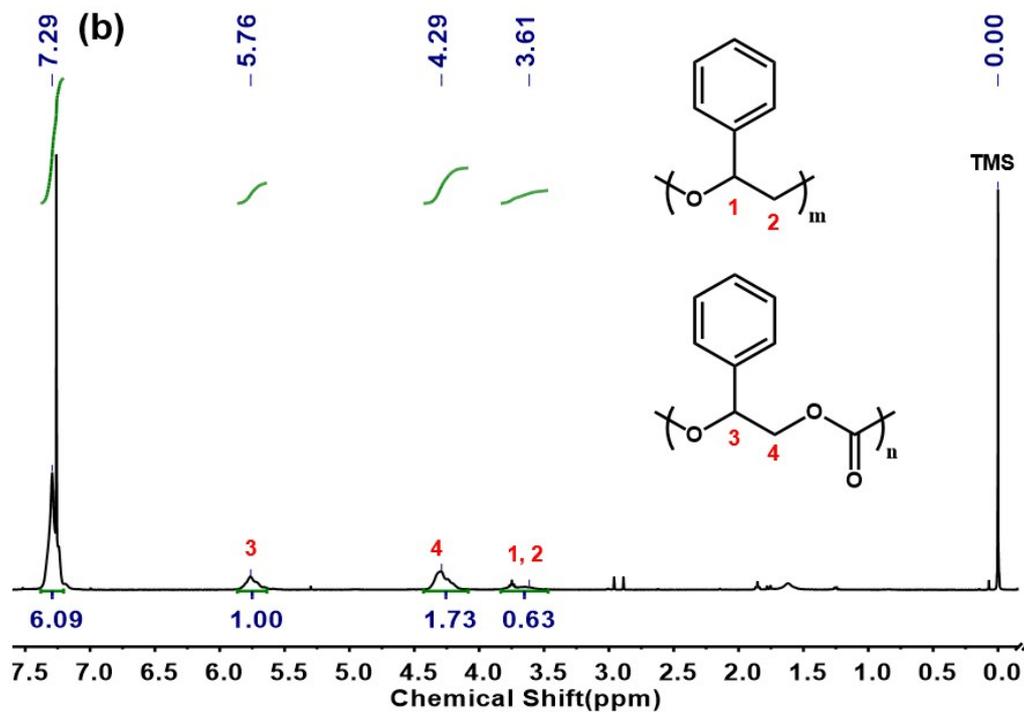**Figure S5.** ^{1}H NMR spectrum of the crude product of entry 1, Table 3.

Figure S6. (a) ¹H NMR spectrum of the crude product of entry 3, Table 3. (b) ¹H NMR spectrum of the purified product of entry 3, Table 3.

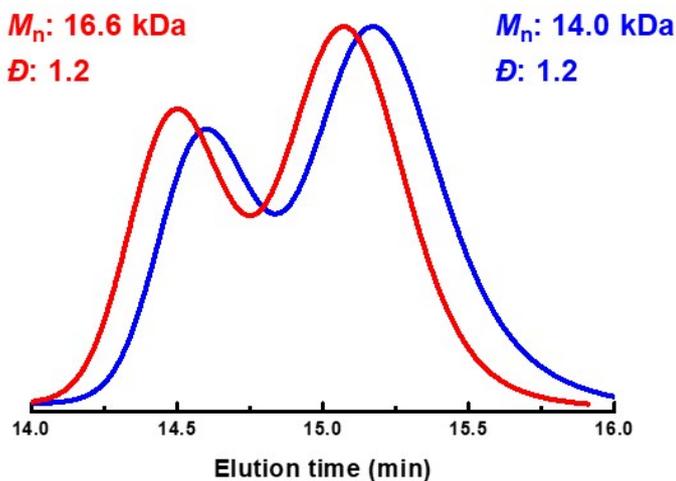## 4. Representative GPC Traces of the Copolymers.

Figure S7. The GPC traces of the representative copolymers (entry 4 (in blue) and entry 6 (in red), Table 1).
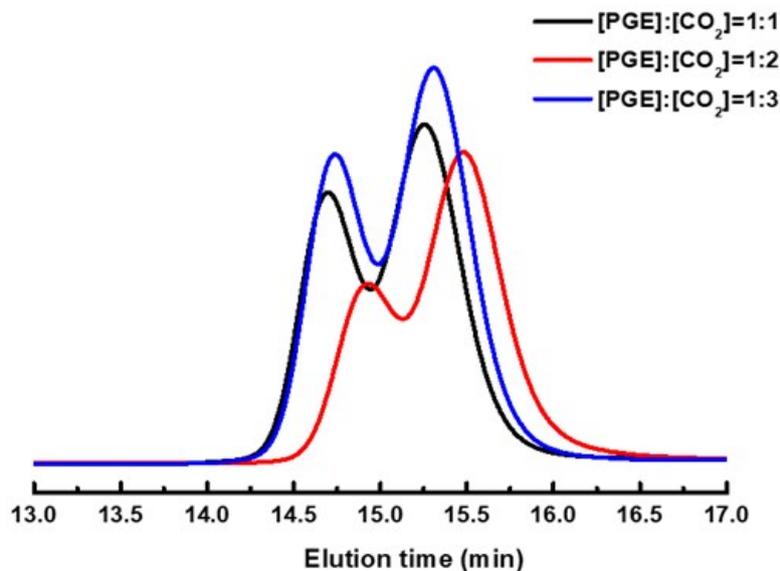
Figure S8. The GPC traces of the representative copolymers (entries 5-7, Table 1).
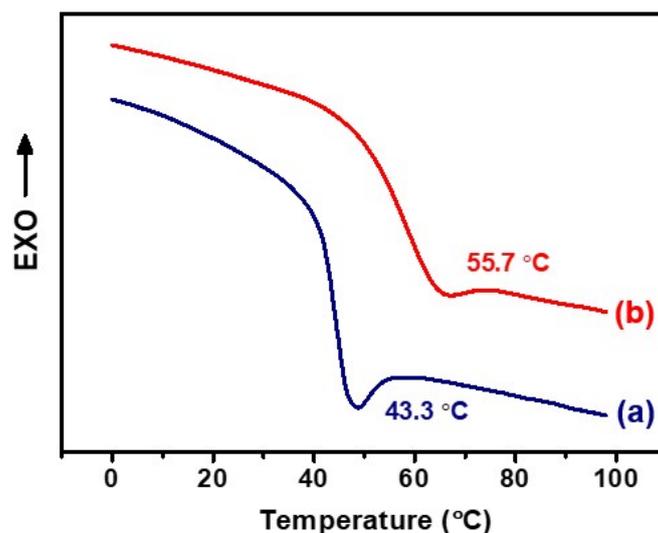
5. DSC Curve of Copolymers.

Figure S9. The DSC curve of the alternating (a) CO_2/PGE copolymer (M_n: 14.0 kg/mol) and (b) CO_2/StO copolymer (M_n:

3.1 kg/mol).

These copolymers are amorphous (Fig. S8), demonstrating by a single glass transition peak in the curves of differential

scanning calorimetry (DSC) at 55.7 °C for CO_2/StO copolymer and 43.4 °C for CO_2/PGE copolymer. The lower T_g than the

previous report, mainly due to imperfect alternating degree, low heating rate and Mns.

6. Typical ^{13}C NMR Spectra

Table S1 Copolymerization catalyzed by TEB and LB at 60 °C, 8 h[a].

Entry	Epoxide	LA/PPNCl/Epoxide	T-H linkages (%)
1	PGE	4:1:500	74
2	PGE	6:1:500	92
3	PGE	8:1:500	92
4	PGE	12:1:500	96
5	PO	1:1:500	72
6	PO	2:1:500	75
7	StO	4:1:500	68
8	StO	8:1:500	82

[a] All polymerizations were carried out with equal volume of THF and epoxide ([CO_2]: [PGE] = 1.5:1, molar ratio) or under conditions otherwise mentioned.

Increasing the molar ratios of [TEB]/[PPNCl] more content of head-to-tail linkages were obtained.

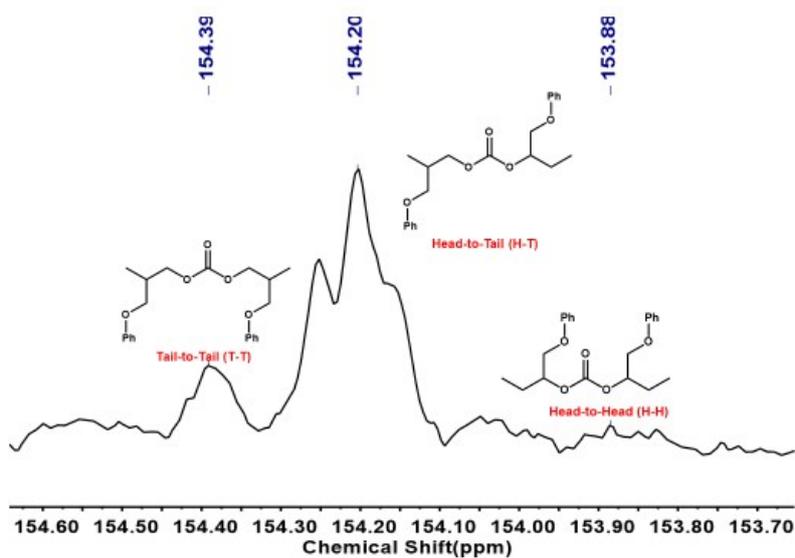**Figure S10.** ^{13}C NMR spectrum of entry 1, Table S1.

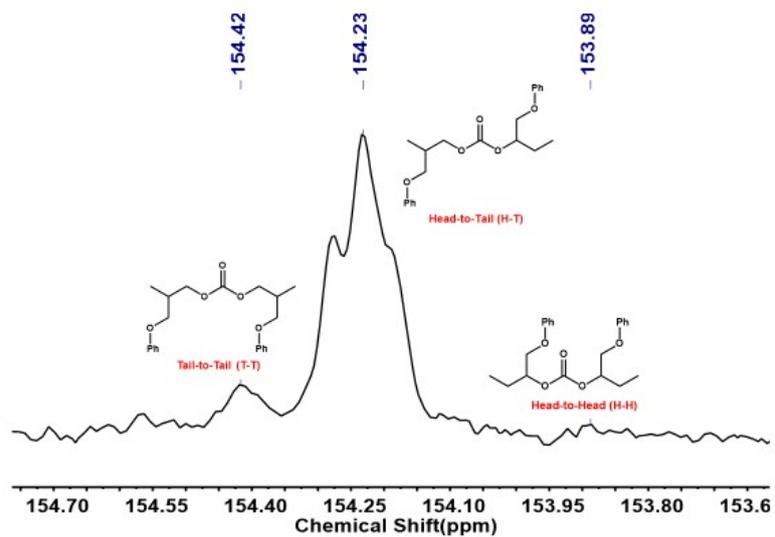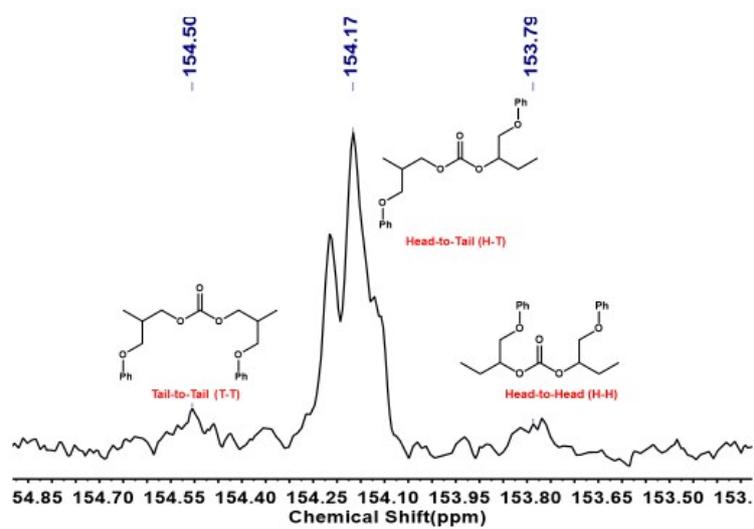**Figure S11.** ^{13}C NMR spectrum of entry 3, Table S1.

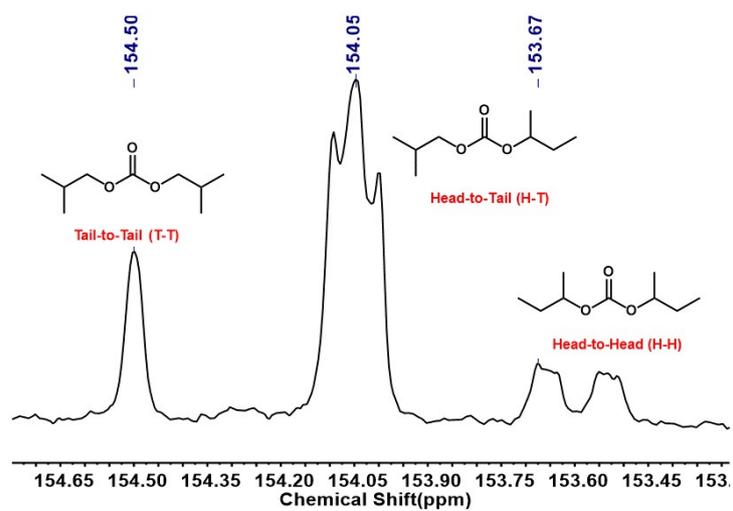**Figure S12.** ^{13}C NMR spectrum of entry 4, Table S1.

Figure S13. ^{13}C NMR spectrum of entry 5, Table S1.

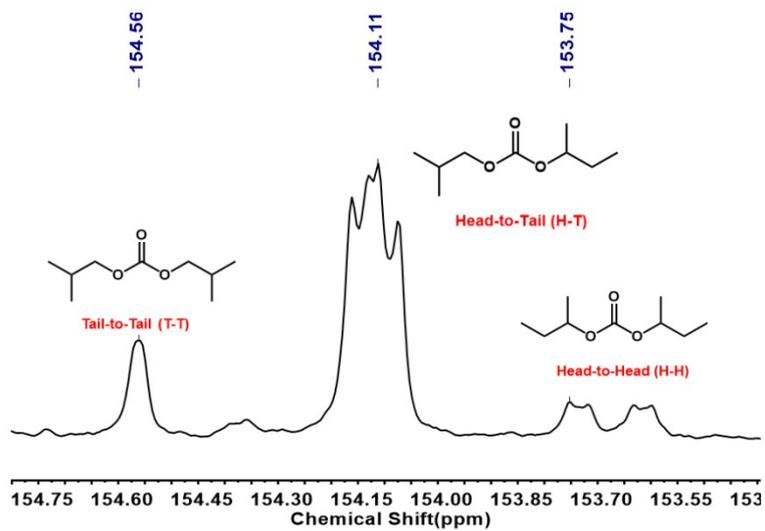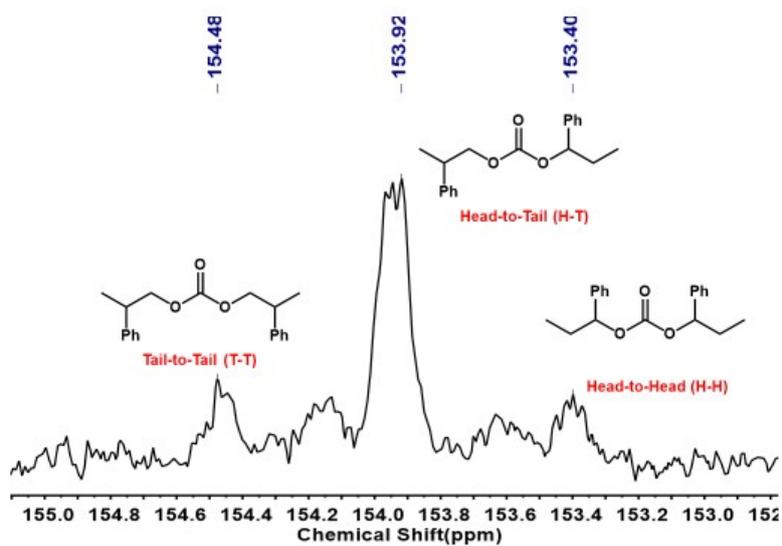**Figure S14.** ^{13}C NMR spectrum of entry 6, Table S1.

Figure S15. ^{13}C NMR spectrum of entry 8, Table S1.