# Supplementary Information

# Synthesis of $CO_2$-based polycarbonate-g-polystyrene copolymers via NMRP

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## Materials and Methods

### Chemicals and materials

zinc oxide, glutaric acid, styrene was purchased from Engry Chemical and used without further purification. Epichlorohydrin was received from Engry Chemical and was stored under Ar atmosphere over pre-dried 3 Å molecular sieves. High purity $CO_2$ gas was obtained from Sinopharm Chemical Reagent Co. Ltd. and used as received. Acetone, toluene, dichloromethane, chloroform, hexane, anhydrous methanol and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. Ltd., in which toluene was stored under Ar atmosphere over pre-dried 3 Å molecular sieves. hydrochloric acid (36-38%) was obtained from Beijing Chemical Works.

### Preparation of Zinc glutarate (ZnGA)

The synthetic procedures of ZnGA catalyst as follows. In a heated 250 mL three-necked flask with reflux condenser and mechanical agitator, 8.139 g (100.0 mmol) of zinc oxide and 12.947 g (98.0 mmol) of glutaric acid were suspended in 150 mL of toluene. The white suspension was refluxed at 55°C with vigorous stirring for 8 h. After cooling the reaction mixture to room temperature, the white precipitate (ZnGA) was filtered and washed with 300 mL of acetone, and the product was dried in under vacuum at 80 °C delivering 20.573 g of ZnGA (97.56 %).

### Preparation of P($CO_2$/ECH)

General procedure for copolymerization of ECH with $CO_2$: ZnGA (0.1 g) and ECH (10 mL, 127mmol) were charged into a pre-dried 100 mL autoclave with a magnetic stirrer under Ar atmosphere at room temperature. The reaction mixture was applied with 5 MPa of $CO_2$. The mixture was stirred at 60 °C for 48 h. After copolymerization, the pressure was slowly released at room temperature. The viscous reaction mixture was dissolved in 5% dilute hydrochloric acid and dichloromethane, and the polymer was washed and precipitated with a large amount of methanol. The obtained polycarbonate was vacuum dried at 60 °C for 15 hours until constant weight.

### Preparation of P($CO_2$/ECH)-TEMPO

P($CO_2$/ECH) (1 g), TEMPO (0.15 g) and ZnGA were placed in a dry Schlenk tube and 5 mL of toluene was added, and the feed ratio of repeat unit and TEMPO of 8 : 1. The mixture was stirred to obtain a homogeneous solution. Then, the mixture was degassed by three freeze-pump-thaw cycles and the polymerization was left to proceed at 100 °C for 15 h under $N_2$ atmosphere. The crude product was purified by repeated precipitated with methanol. The recovered solid was finally dried under vacuum until constant weight and characterized by $^1$H NMR and GPC.

### Preparation of P($CO_2$/ECH)-g-PS

ZnGA (0.1 g), P($CO_2$/ECH)-TEMPO (1 g) and different feed ratio of styrene were placed in a dry Schlenk tube and 5 mL of toluene was added. The mixture was stirred vigorously to obtain a homogeneous solution. Then, the mixture was degassed by three freeze-pump-thaw cycles and the polymerization was left to proceed at 125 °C for 20 h under $N_2$ atmosphere. The crude product was purified by repeated precipitated with methanol. The recovered solid was finally dried under vacuum until constant weight and characterized by $^1$H NMR, GPC, DSC, and TG analysis.

### Characterization methods

A laser scattering particle size distribution analyzer (Horiba LA-960) was used to measure the particle size of ZnGA. The magnetic test was performed on a Brucher AM 600 M superconducting nuclear magnetic resonance apparatus (VARIAN, USA) using DMSO and $CDCl_3$ as the solvent and TMS as the internal standard. GPC test using the United States Waters GPC2000 high temperature gel permeation chromatography with THF as eluent, which was calibrated by poly(styrene) standard. DSC was carried out by using NETZSCH DSC 200 F3 instrument. Thermal scans were conducted on 3-5 mg samples under nitrogen atmosphere. All samples were heated from -50 °C to 160 °C then cooled to -50 °C and heated again to 160 °C at a cooling/heating rate of 10 °C min$^{-1}$. TGA was carried out by using Seiko EXSTAR 7200 TGA/DTA instrument. Thermal scans were conducted on 3-5 mg samples under nitrogen atmosphere. All samples were heated from 25 °C to 800 °C at a standard rate of 10 °C min$^{-1}$.

**Table S1.** Reaction of P($CO_2$/ECH) and TEMPO[a].

| **Entry** | **Time** [h] | **Yield**[b] [%] | **TEMPO content**[c] [%] |
|---|---|---|---|
| **1** | 5 | 91 | 1.2 |
| **2** | 10 | 91 | 1.4 |
| **3** | 15 | 93 | 2.0 |
| **4** | 20 | 92 | 1.9 |

[a] Reaction conditions: 100 °C, 0.1 g ZnGA. [b] Measured by gravimetric method. [c] Molar content was estimated by $^1$H NMR spectroscopy.

**Table S2.** TGA and DSC results of P($CO_2$/ECH) and P($CO_2$/ECH)-g-PS.

| **Entry** | **St** [mL] | **Time** [h] | $T_{-5\%}$ [℃] | $T_{max}$ [℃] | $T_g$ [℃] |
|---|---|---|---|---|---|
| **P($CO_2$/ECH)** | -- | 48 | 139.6 | 210.6 | 9.4 |
| **P($CO_2$/ECH)-g-PS4** | 5 | 20 | 160.3 | 425.2 | 91.4 |
| **P($CO_2$/ECH) -g-PS5** | 10 | 20 | 173.7 | 422.5 | 94.5 |
| **P($CO_2$/ECH) -g-PS6** | 30 | 20 | 185.4 | 427.4 | 99.2 |
| **P($CO_2$/ECH) -g-PS7** | 50 | 20 | 289.1 | 422.1 | 100.2 |
| **PS** | -- | -- | -- | -- | 106[a] |

[a] H. Zeng, N Maeda, N. Chen, M. Tirrell, J. Israelachvili, *Macromolecules* 2006, *39,* 2350-2363.

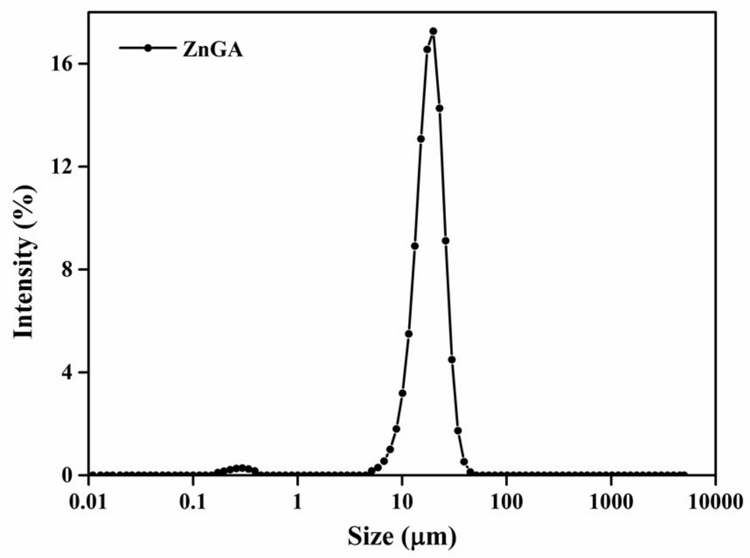

**Fig.S1.** The particle size distribution of ZnGA

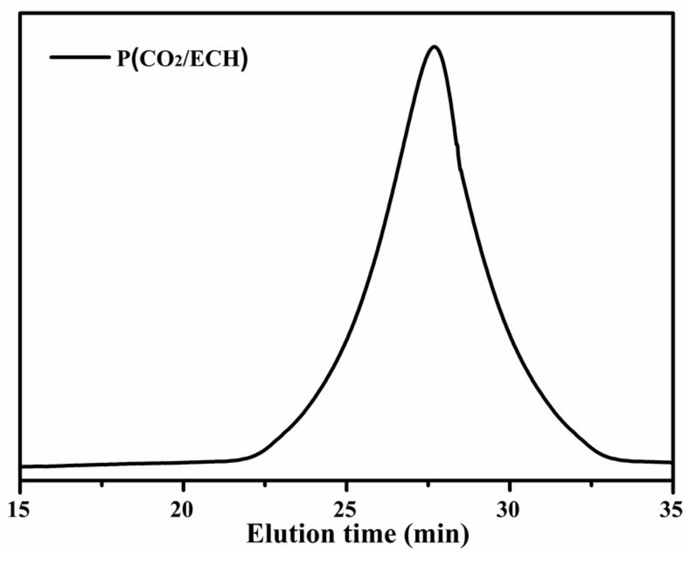

**Fig. S2.** GPC trace of P($CO_2$/ECH).

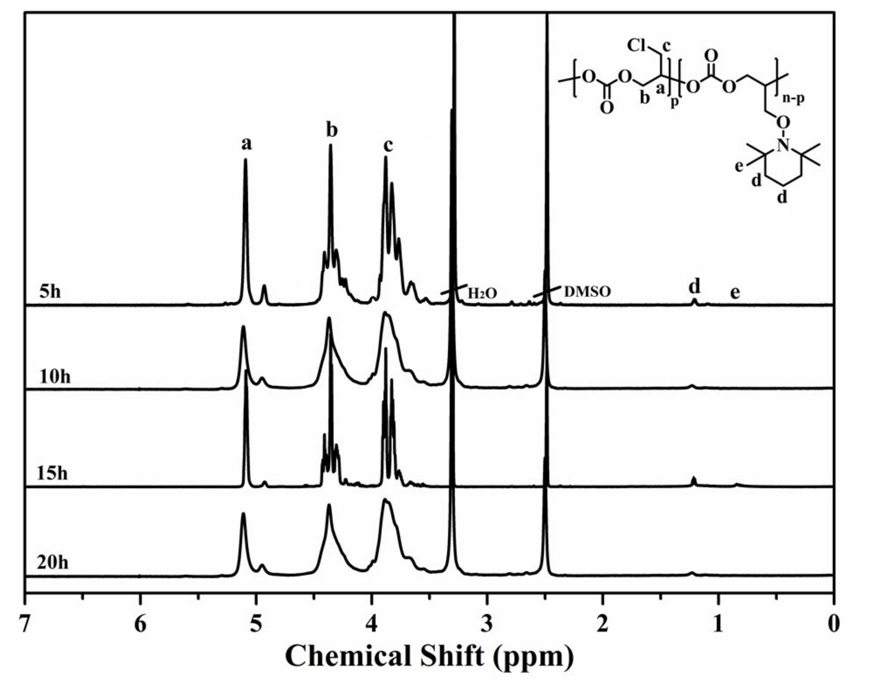

**Fig. S3.** $^1$H NMR spectra of P($CO_2$/ECH)-TEMPO.

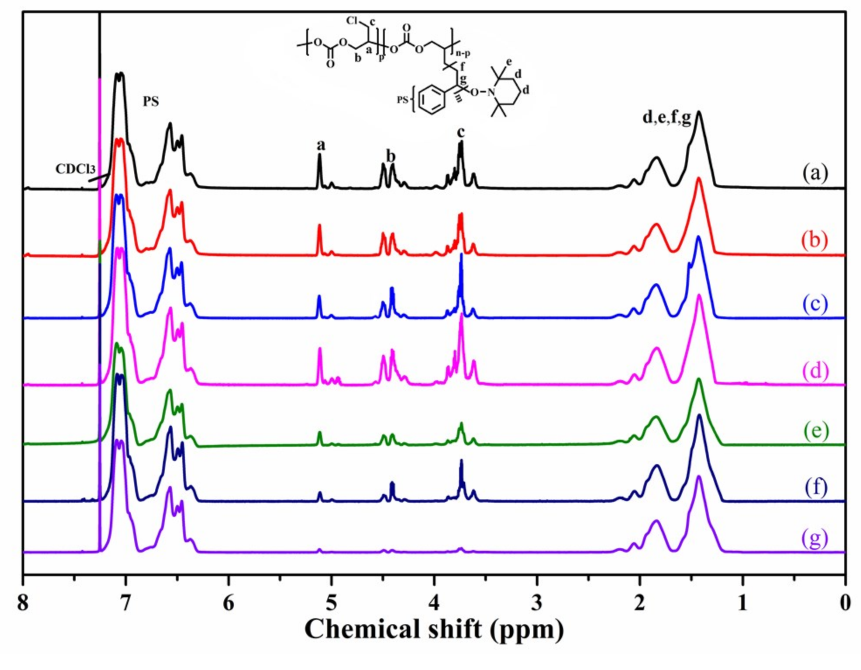

**Fig. S4.** $^1$H NMR spectra of P($CO_2$/ECH)-g-PS, (a) P($CO_2$/ECH)-g-PS1, (b) P($CO_2$/ECH)-g-PS2, (c) P($CO_2$/ECH)-g-PS3, (d) P($CO_2$/ECH)-g-PS4, (e) P($CO_2$/ECH)-g-PS5, (f) P($CO_2$/ECH)-g-PS6, (g) P($CO_2$/ECH)-g-PS7.

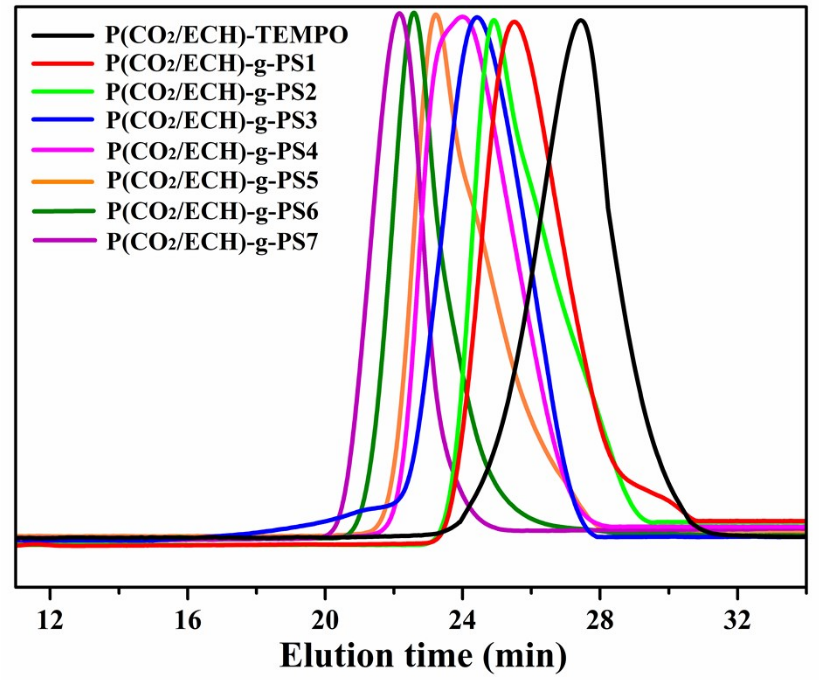

**Fig. S5.** GPC traces of P($CO_2$/ECH)-TEMPO and P($CO_2$/ECH)-g-PS.

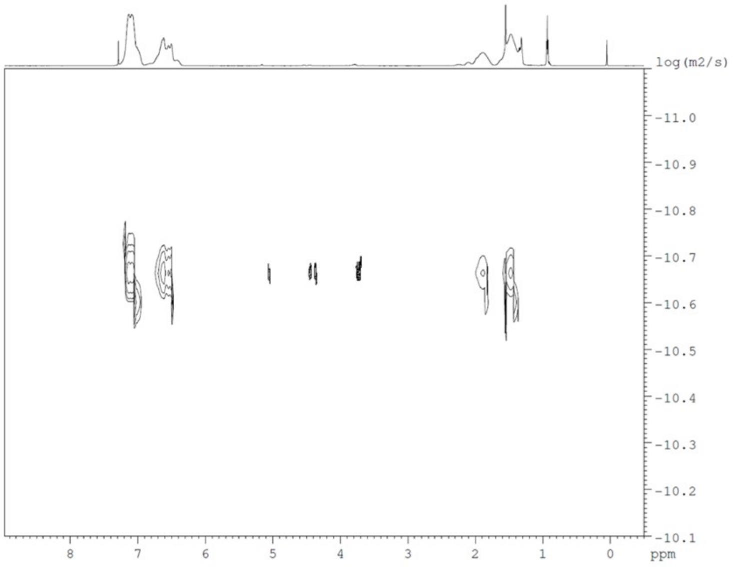

**Fig. S6.** The DOSY-NMR spectrum of P($CO_2$/ECH)-g-PS7 (Diffusion coefficient: $1.358 \times 10^{-11}$ $cm^2$ $s^{-1}$).