

One-pot Synthesis of Crystalline Polycarbonate-*block*- polyester

Bingkai Shang^a, Min Xiao^a, Shuanjin Wang^a, Dongmei Han^b, Sheng Huang^a, Hui
Guo^{b,*}, and Yuezhong Meng^{a,b,c,d*}

^a The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong
Province/State Key Laboratory of Optoelectronic Materials and Technologies, School
of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, P.
R. China

^b School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai
519000, P. R. China

^c Institute of Chemistry, Henan Academy of Sciences, Zhengzhou, 45000, P.R. China

^d College of Chemistry, Zhengzhou University, Zhengzhou, 450001, P.R. China

*Corresponding authors:

guoh37@mail.sysu.edu.cn (H. Guo)

mengyzh@mail.sysu.edu.cn (Y. Meng)

EXPERIMENTAL SECTION

Materials

All chemicals were applied as received unless otherwise stated. Triethyl borane (TEB; 1 M in THF, Energy), bis(triphenylphosphine)iminium chloride (PPNCl; Alfa, 97%), tetrabutylammonium chloride (TBACl; Alfa, 97%), tetrachlorophthalic anhydride (TCPA; Alfa ; > 99%) was stirred in a mixed solution of ether and toluene for 24 hours before use, filtered to remove the filtrate, and then dried in a vacuum oven for use, ethylene oxide (EO; Huate Gas Co. Ltd., > 99.9%) and high purity CO₂ (Guangqi Gas Co. Ltd., > 99.999%) were used as received, dioxane (99%, from Energy) was stirred thoroughly with NaH under a nitrogen atmosphere for 24 hours.

Characterizations

The ¹H NMR, ¹³C NMR spectra were recorded on a Bruker Advanced III 400 MHz NMR spectrometer using CDCl₃ as solvent. The molar mass (M_n) and dispersity (PDI) were tested on a Shimadzu size exclusion chromatography (SEC) system equipped with Shodex GPC KF-804, KF-802.5, KF-801, and Refractive Index Detector. The tests were operated at 40°C using chloroform (CHCl₃) as an eluent and a series of polystyrene (PDI = 1.02) as a standard with a flow rate of 1.0 mLmin⁻¹, the concentration of the sample in CHCl₃ solvent is 5 mg mL⁻¹.

Differential scanning calorimeter (DSC) was tested on a DSC model 204 (Netzsch) under N₂ flow. The sample was heated at a rate of 10 K min⁻¹ from 25 °C to 110 °C, held for 3 minutes, and then cooled at a rate of 10 K min⁻¹ from 110 °C to -50 °C. Finally, it was heated twice at a rate of 10 K min⁻¹ from -50 to 190 °C, with each cycle held at -50 °C and 190 °C for 3 minutes.

TGA analysis was studied in a Perlin Elmer Pyris Diamond TG/ DTA analyzer under an N₂ atmosphere with a heating rate of 10°C min⁻¹ in the temperature range of 30-600°C.

The X-ray diffraction (XRD) of the TPU films was measured on the D8ADV ANCE instrument of Bruker, Germany, from 5 to 50° at the speed of 10° min⁻¹.

Mechanical property tests were performed using a universal testing machine (CMT 4204, SANS, Shenzhen, China) according to the ASTM D638 standard. The sample for the test was standard 25 × 4 × 0.5 mm³ dumbbell-shaped specimens. The average results were recorded by testing five specimens of each sample.

Synthesis of crystalline block copolymers

All polymerizations were carried out in a 50 mL autoclave equipped with a magnetic stirrer. The autoclave was dried overnight at 120°C and transferred to a glovebox. A typical reaction procedure, as illustrated by the synthesis of entry 3 from Table 1, involved adding TBACl (27.79 mg, 0.075 mmol), TCPA (2.85 g, 10 mmol), and dioxane (20 g) to the reactor. This was followed by the addition of TEB (300 µL, 0.3 mmol). The reactor was sealed, removed from the glovebox, and loaded with EO (17.62 g, 400 mmol). CO₂ was then introduced until a pressure of 2 MPa was achieved. The copolymerization proceeded at 60°C for 6 hours under constant CO₂ pressure (2 MPa). After completion, the reactor was cooled in an ice bath, unreacted CO₂ was slowly released, and a small sample of the reaction mixture was taken for ¹H NMR analysis. The reaction was quenched using ethanol containing 1 M HCl. The crude polymer was dissolved in dichloromethane (CH₂Cl₂) and precipitated in 8 volumes of ethanol. The product was collected and dried under vacuum at 110°C until a constant weight was reached.

Purification and Induced Crystallization of Polymers

The dried polymer sample was re-dissolved in CH_2Cl_2 , precipitated in ethanol, and the purification process was repeated three times. To induce crystallization, the purified polymer was dissolved in CH_2Cl_2 and the solvent evaporated in an 85°C oven to obtain the crystalline polymer.

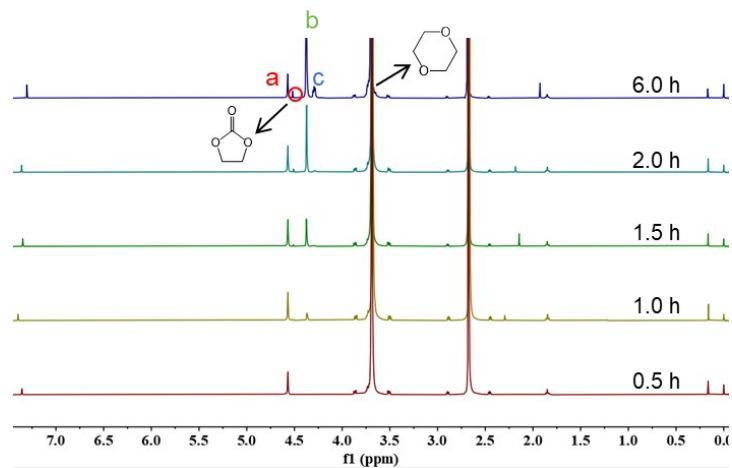


Figure S1 ^1H NMR spectrum of the reaction solution at different reaction durations.

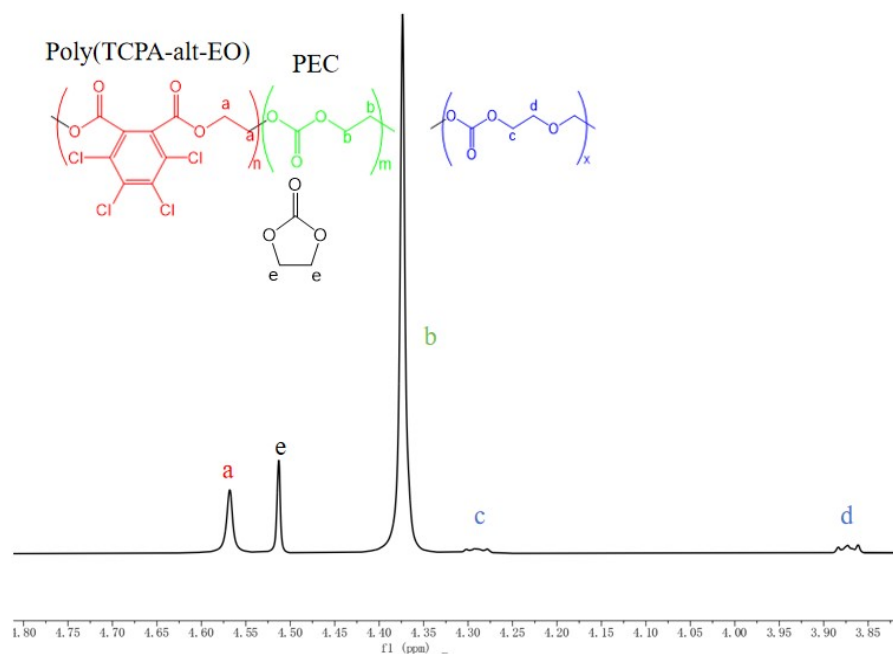


Figure S2 ^1H NMR spectrum of the reaction solution

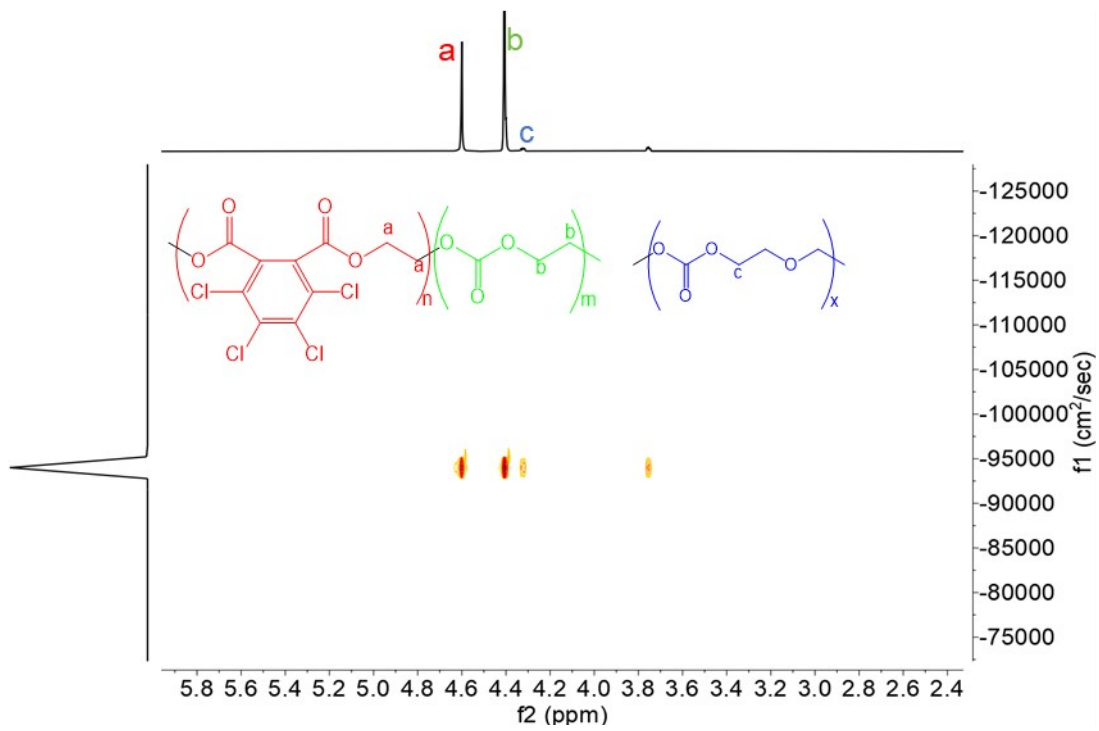


Figure S3 2D DOSY NMR spectra of EO/TCPA/CO₂ copolymerization.

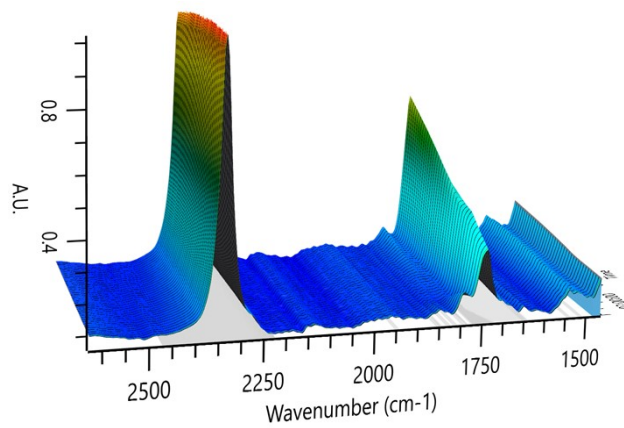


Figure S4 In situ infrared spectroscopy results

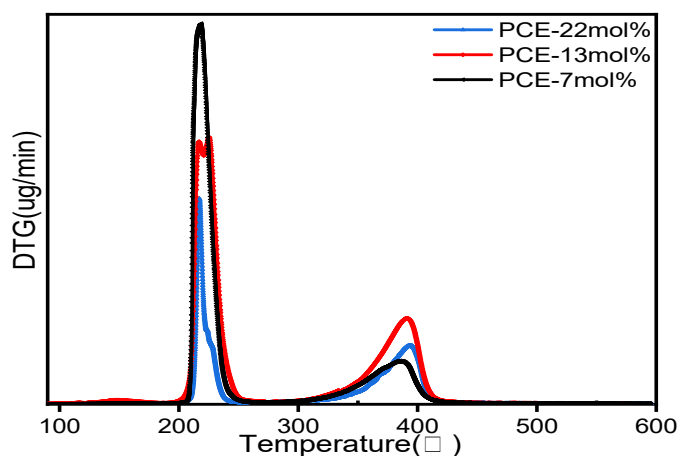


Figure S5 DTG curves of copolymers with different polyester contents

Table S1 Results of EO/TCPA/CO₂ copolymerization at different durations^a

Entry	EO/TCPA/TEB/TBACl (mol)	T (°C)	t (h)	PE/PEC/PEO (mol%)	CC(mol%)	M _n (kg/mol)/PDI ^b	EO Conv. (%) ^b
1	4000:100:4:1	60	0.5	100/0/0	0	5.63/1.12	2
2	4000:100:4:1	60	1	65/29/6	0	10.2/1.16	4
3	4000:100:4:1	60	1.5	46/49/5	1	14.4/1.17	5
4	4000:100:4:1	60	2	29/65/5	2	19.5/1.17	9
5	4000:100:4:1	60	6	13/83/4	2	41.8/1.15	19

^a All polymerizations (17.6 g EO + 2.85 g TCPA) were carried out in 50 mL autoclaves with 20

g Dioxane. ^b Determined by GPC in chloroform with polystyrene standard. ^c Calculated by ¹H

NMR.

Table S2 Results of EO/TCPA/CO₂ copolymerization^a

Entry	EO/TCPA/TEB/TBACl (mol)	T (°C)	t (h)	PE/PEC/PEO (mol%)	CC (mol%)	Mn (kg/mol)/PDI ^b	EO Conv. (%) ^b
1	1000:100:4:1	60	6	35/61/4	9	20.6/1.66	37
2	2000:100:4:1	60	6	22/76/3	6	33.4/1.23	31
3	4000:100:4:1	60	6	13/83/4	2	41.8/1.15	19
4	1000:100:4:1	60	12	19/77/4	11	22.2/1.25	45
5	1000:100:4:1	60	15	17/79/4	10	36.3/1.41	63
6	1000:100:4:1	60	21	13/84/3	8	41.0/1.32	70

^a All polymerizations (17.6 g EO + 2.85 g TCPA) were carried out in 50 mL autoclaves with 20

g Dioxane or under conditions otherwise mentioned. ^b Determined by GPC in chloroform with

polystyrene standard. ^c Calculated by ¹H NMR.