

Supporting information

Highly Selective and Productive Synthesis of Carbon Dioxide-based Copolymer upon Zwitterionic Growth

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Materials and methods.

Materials.

Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under nitrogen atmosphere or in a nitrogen-filled glovebox. Triethylamine (TEA) and N,N,N',N'-Tetramethylethylenediamine (TMED) was bought from J&K Chemical. N,N,N',N'-tetraethyl ethylenediamine (TEED) was purchased from Energy Chemical. All tertiary amines were purified by distillation after stirring with calcium hydride for 3 days in nitrogen. Triethyl borane (TEB) in tetrahydrofuran solution (1.0 mol/L) and tributyl borane (TBB) in tetrahydrofuran solution (1.0mol/L) was bought from Sigma-Aldrich and used without further purifications. Propylene oxide (PO) was purified by distillation after stirring with calcium hydride for 3 days. Carbon dioxide (> 99.99%) was used as received. Following purification, materials were stored in a nitrogen-filled glovebox prior to use unless otherwise specified.

Methods.

^1H and ^{13}C NMR spectra were performed on a Bruker Advance DMX 400 MHz in CDCl_3 . And chemical shift values were referenced to CHCl_3 at 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR. The number-average molecular weight (M_n) and molecular weight distribution ($\text{Đ} = M_w/M_n$) 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 0.4 wt %, and the injection volume was 50 µL. Calibration was performed using monodisperse polystyrene standards. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric measurements were performed on a Bruker Ultraflex MALDI TOF mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 99%, Alfa) was used as the matrix.

Representative procedure for copolymerization reactions.

A 10mL autoclave with magnetic stirrer was dried in an oven at 120°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 CO₂ with PO described below is taken from entry 2 in Table 1 as an example. triethylamine (TEA, 20 µl, 0.143 mmol) was firstly added into the reactor. Afterwards, propylene (PO, 1ml, 14.3 mmol) and triethyl borane (TEB, 143 µL, 0.143 mmol), was added into the autoclave respectively. The reactor was sealed and taken out from the glove box and charged with 1.26 g CO₂ (CO₂ : epoxide = 2:1, molar ratio, 2 MPa). The copolymerization was carried out at 60°C for 4 h. In the first 5 minutes of the reaction, the pressure was increased to 2.7 MPa. During the copolymerization process, the pressure drops gradually. When PO conversion was up to 80%, the pressure finally drops to around 2.1 MPa. At the end of the polymerization, the autoclave was cooled in ice-water bath and return to room temperature with decreased pressure to 1.8MPa. The unreacted CO₂ was slowly released. A spot of crude product was taken

for the determination of PO conversion and the molar ratio of copolymer/cyclic products by ^1H NMR spectrum. The crude product was quenched with HCl in ethanol (1mol/L). Next, the polymer was dissolved with CH_2Cl_2 and then precipitated in ethanol. The final product was dried in vacuum at 50°C until a constant weight.

Table S1. Copolymerization of CO_2 with PO catalyzed by TEA or TEB respectively.^[a]

Entr	LA	LB	LA/LB/PO	t/h	Conv.	PPC	F_{CO_2}	M_n	PDI
y					[%] ^[b]	Selec. [%] ^[b]	[%] ^[c]	[kg/mol] ^[d]	$[M_w/M_n]$ ^[d]
1	-	TEA	0:1:100	4	-	-	-	-	-
2	TEB	-	1:0:100	4	-	-	-	-	-

^[a] The reactions were performed in bulk in a 10 ml autoclave, 60°C , $[\text{CO}_2]:[\text{PO}]=2:1$.

^[b] Determined by ^1H NMR spectroscopy of crude product. ^[c] Determined by ^1H NMR spectroscopy of the purified product. ^[d] Determined by gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.

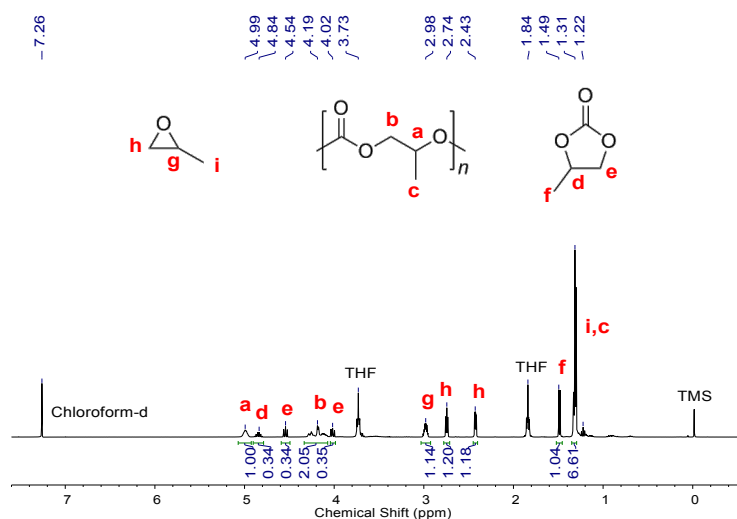


Figure S1. ^1H NMR spectrum of the crude product of entry 1, Table 1.

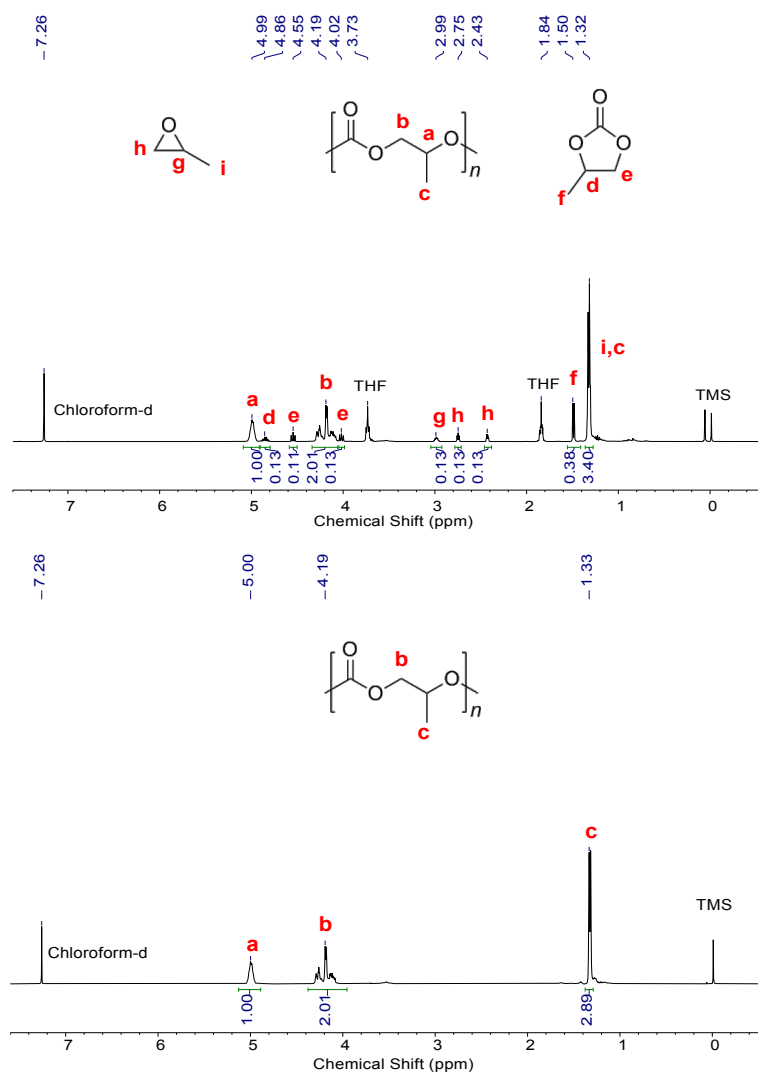


Figure S2. ^1H NMR spectrum of the crude product of entry 2, Table 1.

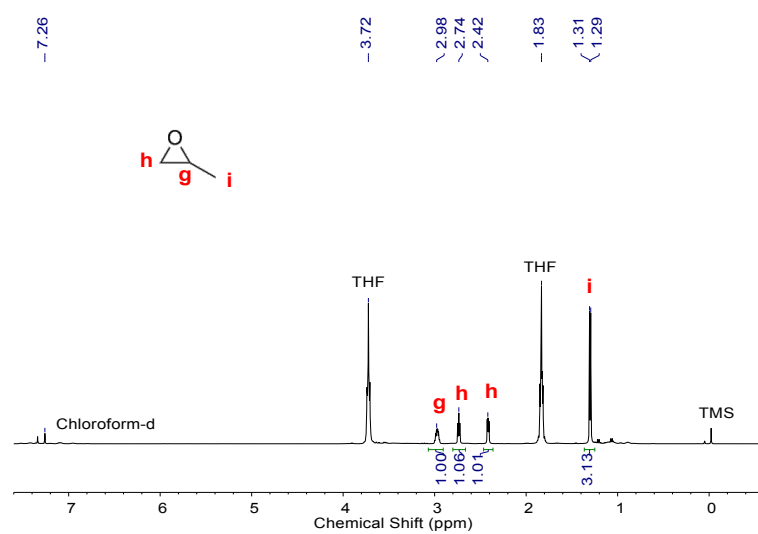


Figure S3. ^1H NMR spectrum of the crude product of entry 3, Table 1.

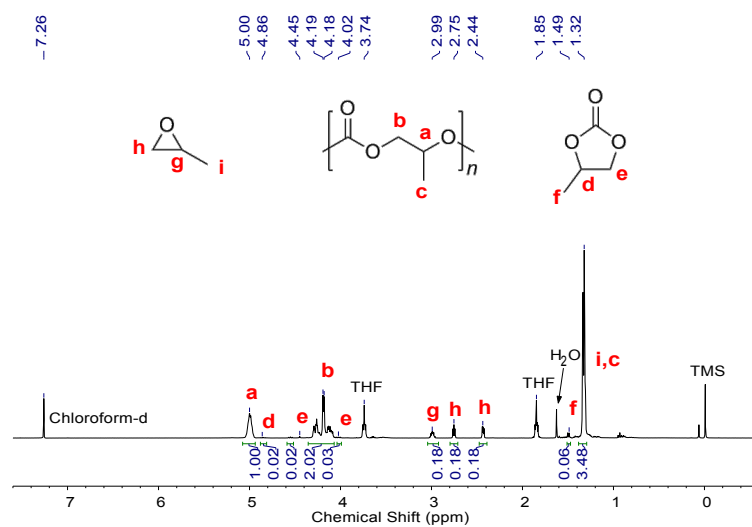


Figure S4. ^1H NMR spectrum of the crude product of entry 4, Table 1.

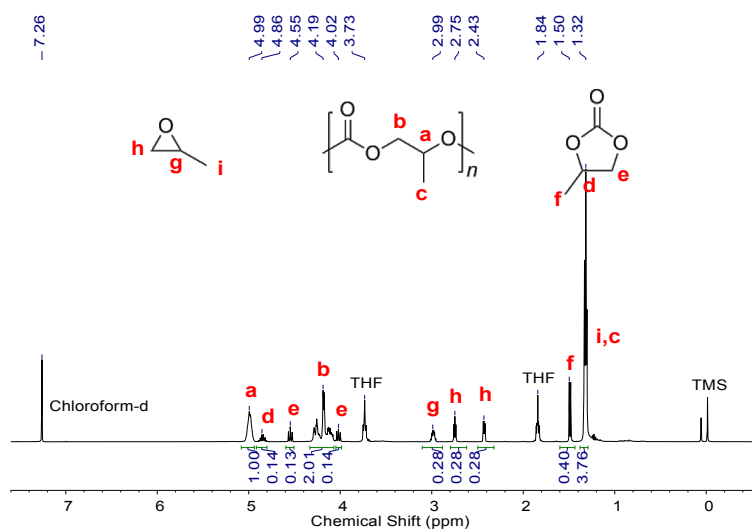


Figure S5. ^1H NMR spectrum of the crude product of entry 5, Table 1.

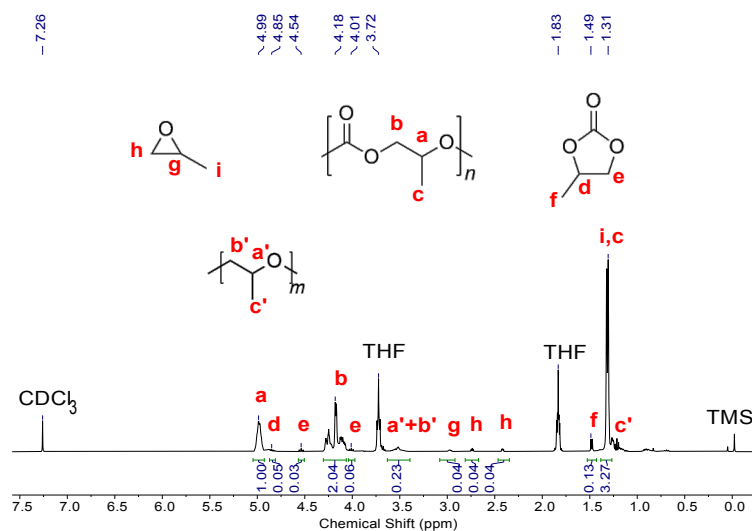


Figure S6. ^1H NMR spectrum of the crude product of entry 6, Table 1.

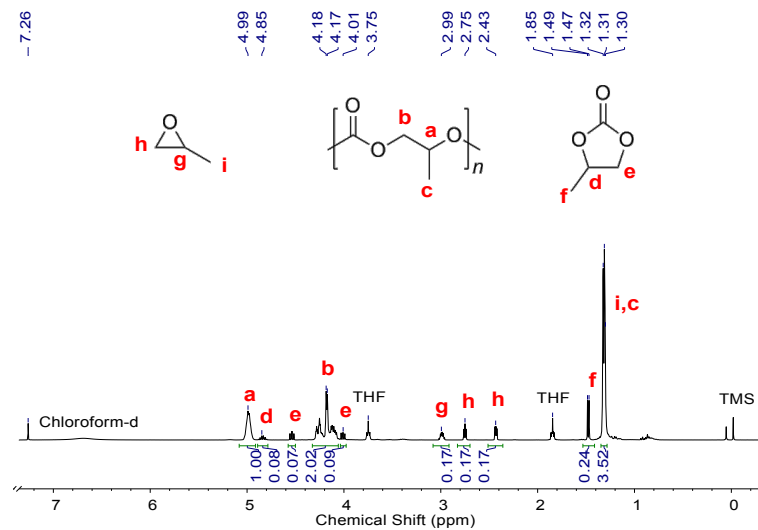


Figure S7. ^1H NMR spectrum of the crude product of entry 7, Table 1.

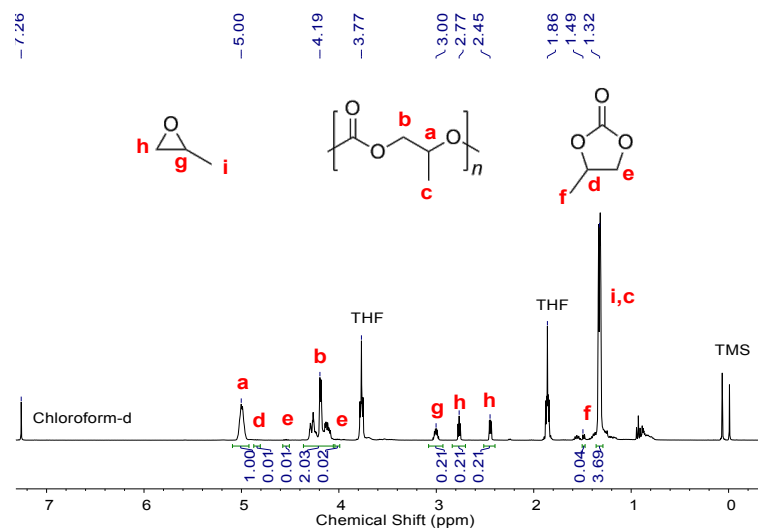


Figure S8. ^1H NMR spectrum of the crude product of entry 8, Table 1.

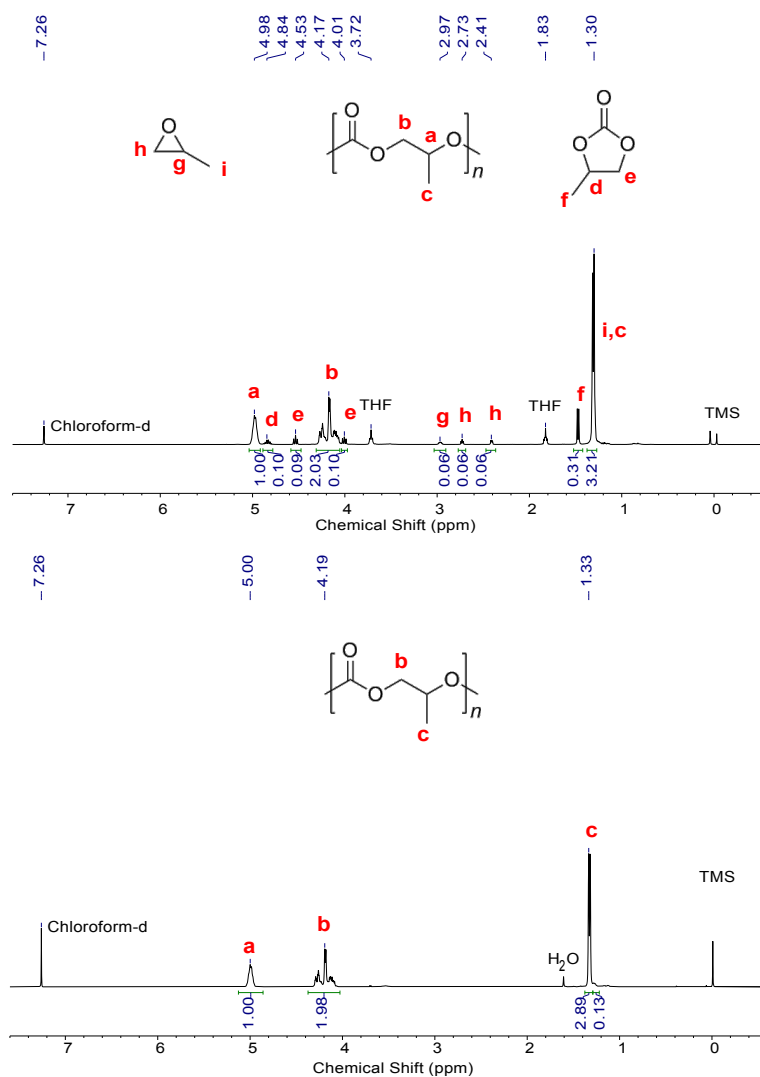
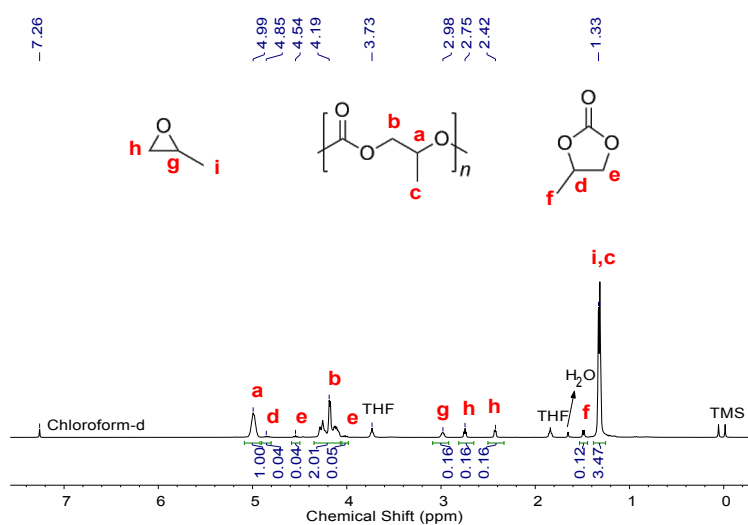


Figure S9. ¹H NMR spectrum of the crude product of entry 9, Table 1.



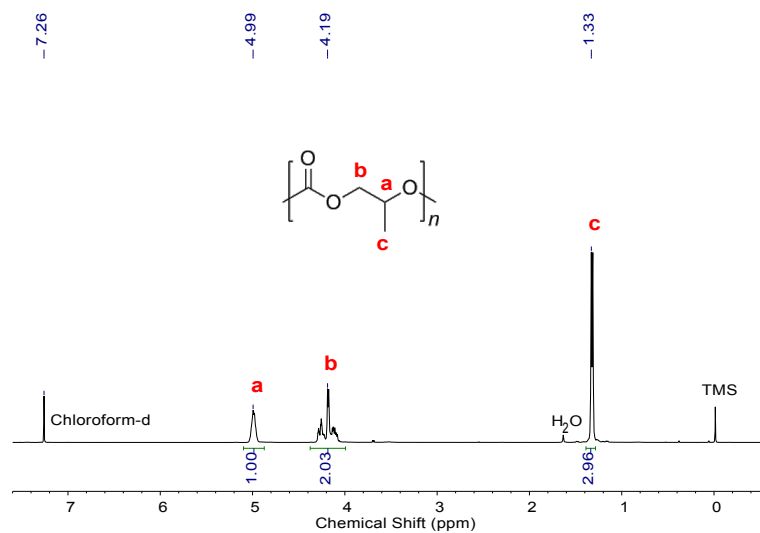


Figure S10. ^1H NMR spectrum of the crude product of entry 10, Table 1.

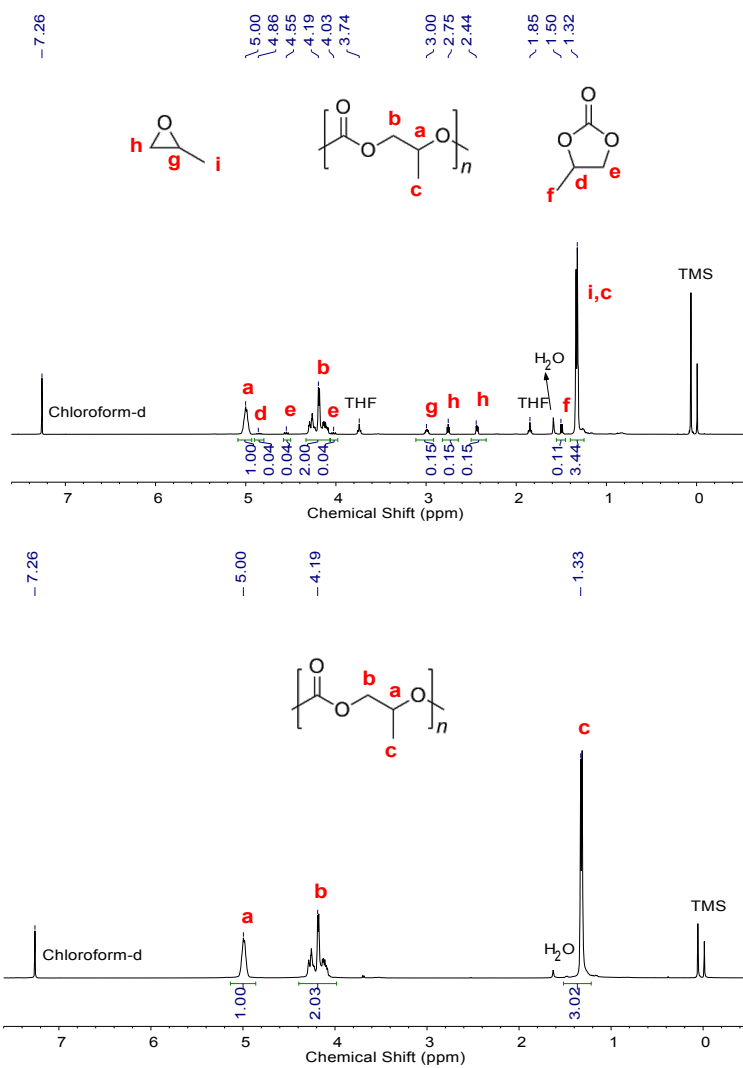


Figure S11. ^1H NMR spectrum of the crude product of entry 11, Table 1.

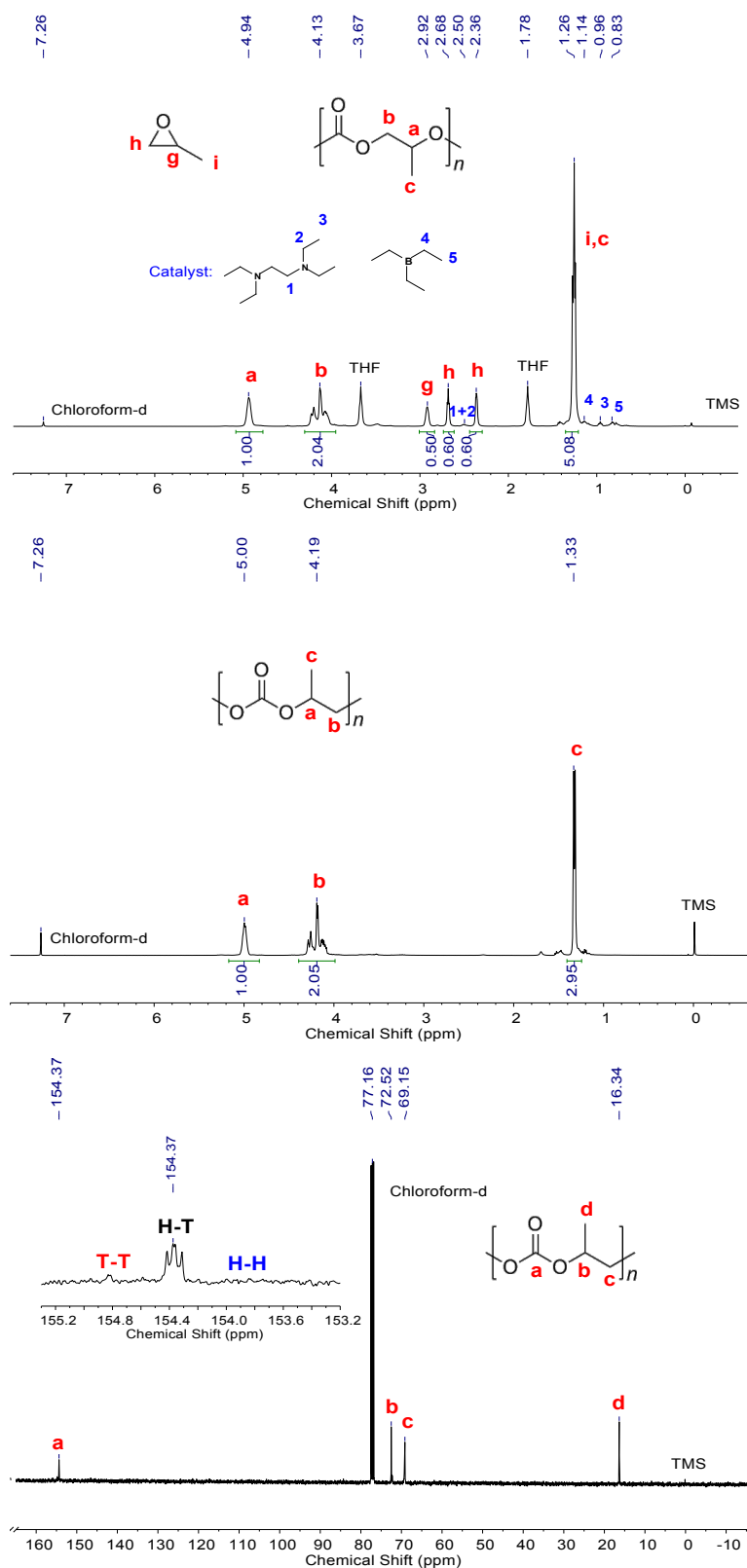


Figure S12. (1) ¹H NMR spectrum of the crude product of entry 1 Table 2; (2) ¹H NMR spectrum of the purified product of entry 1, Table 2; (3) ¹³C NMR spectrum of the purified product of entry 1, Table 2.

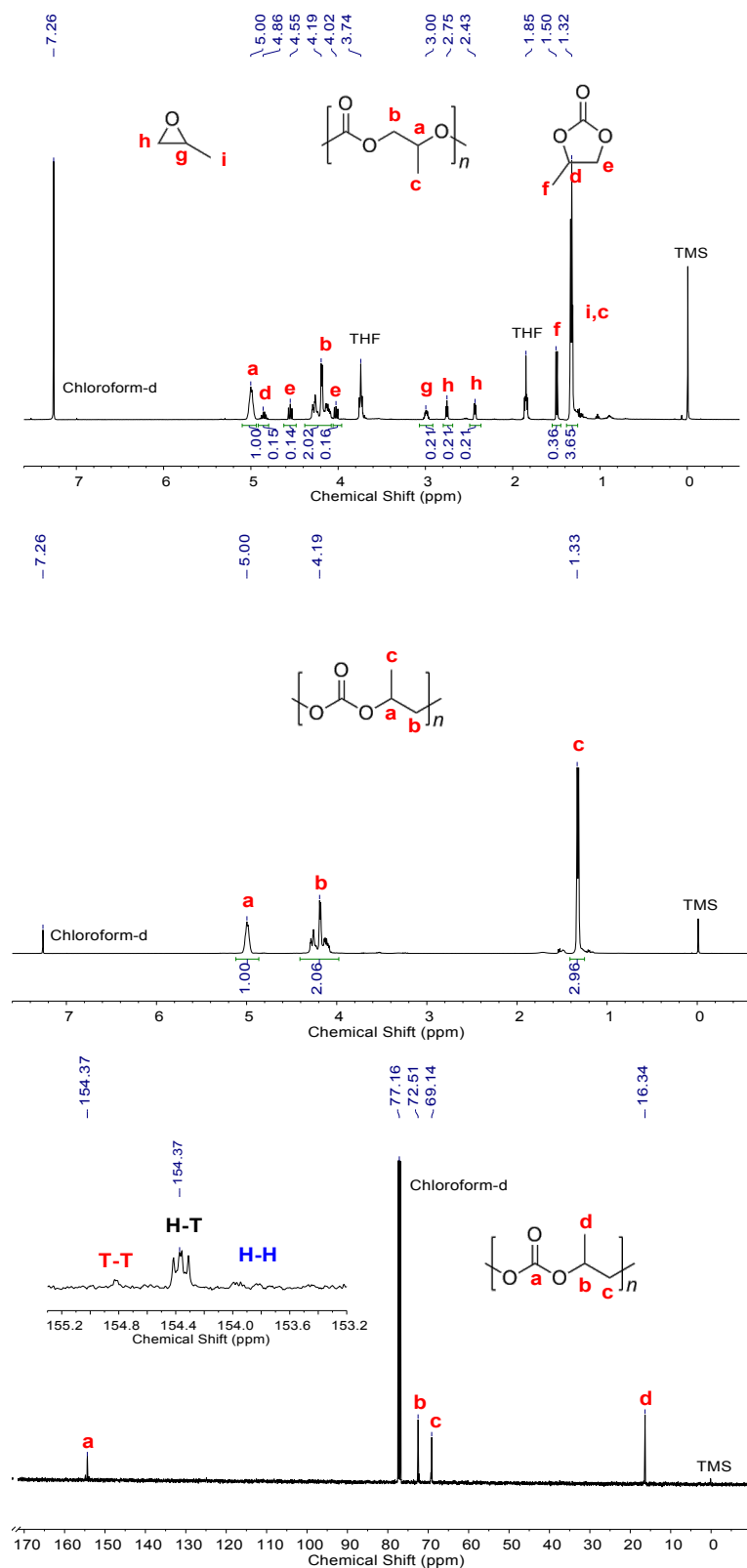


Figure S13. (1) ^1H NMR spectrum of the crude product of entry 2 Table 2; (2) ^1H NMR spectrum of the purified product of entry 2, Table 2; (3) ^{13}C NMR spectrum of the purified product of entry 2, Table 2.

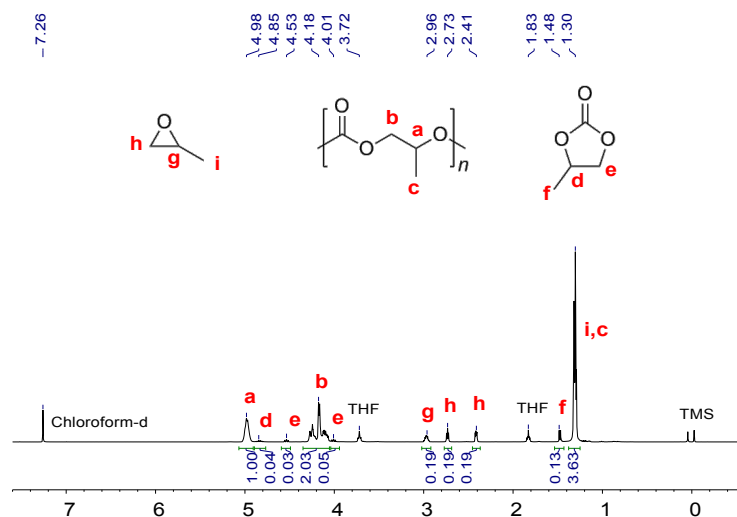


Figure S15. ^1H NMR spectrum of the crude product of entry 4 Table 2.

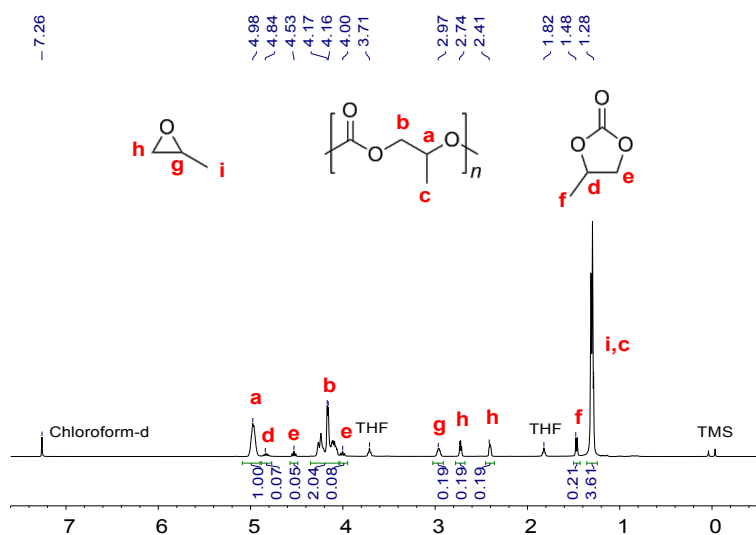


Figure S16. ^1H NMR spectrum of the crude product of entry 5 Table 2.

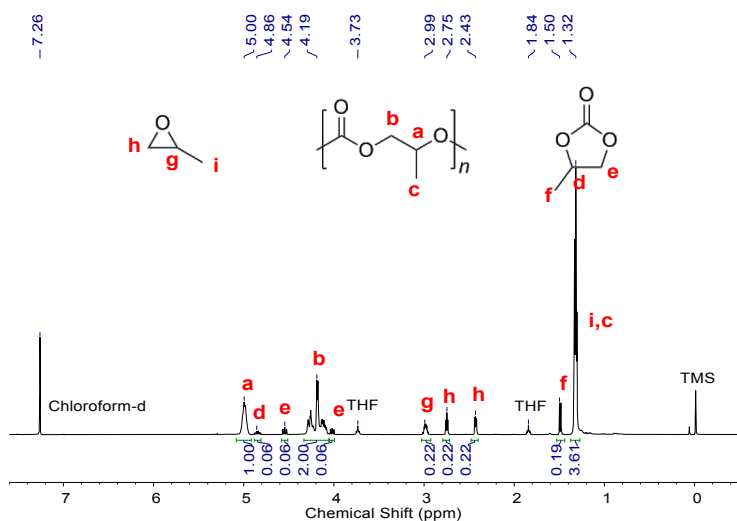


Figure S17. ^1H NMR spectrum of the crude product of entry 6 Table 2.

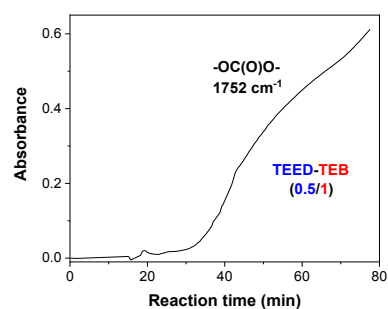
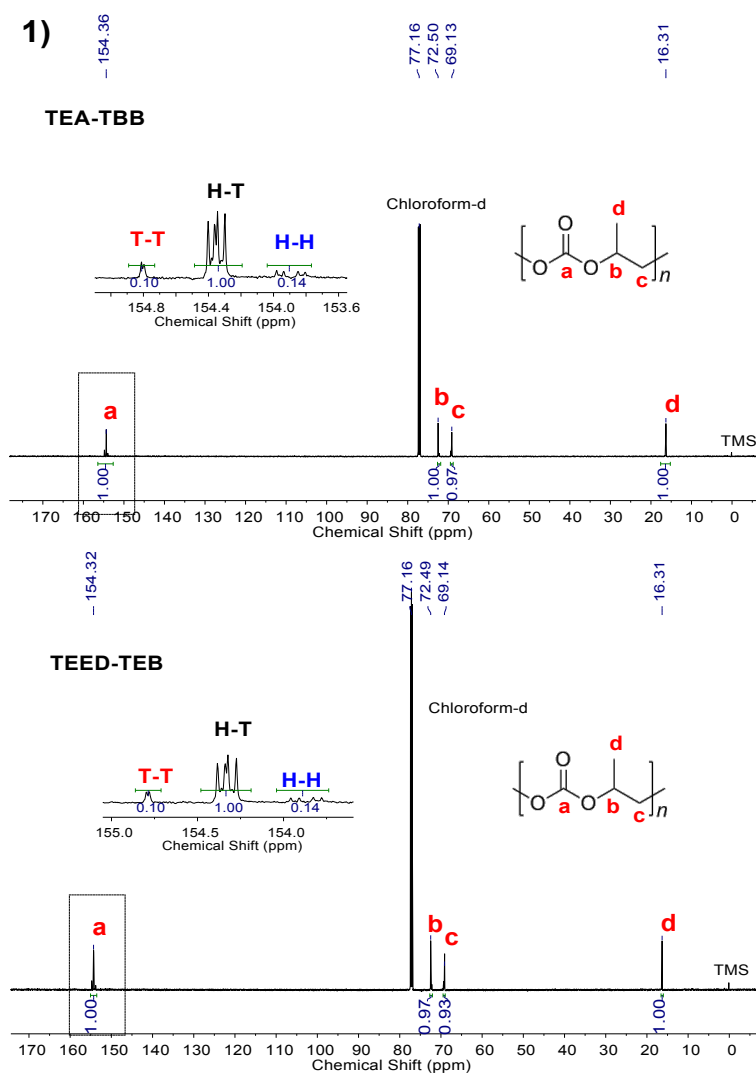


Figure S18. In situ infrared profiles of $-\text{OC}(\text{O})\text{O}-$ linkages in PPC catalyzed by TEED/TEB at 60°C .



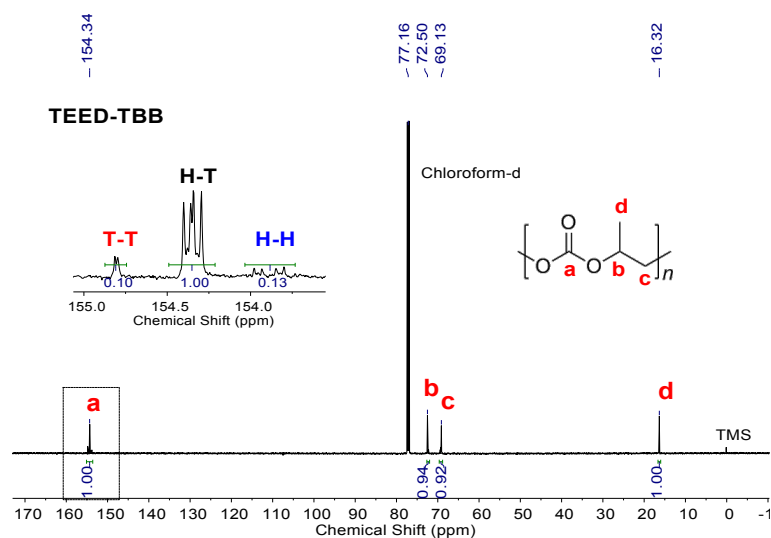


Figure S19. Quantitative ^{13}C NMR spectrum (CDCl_3) of the purified CO_2/PO copolymer catalyzed by 1) TEA-TBB; 2) TEED-TEB; 3) TEED-TBB.

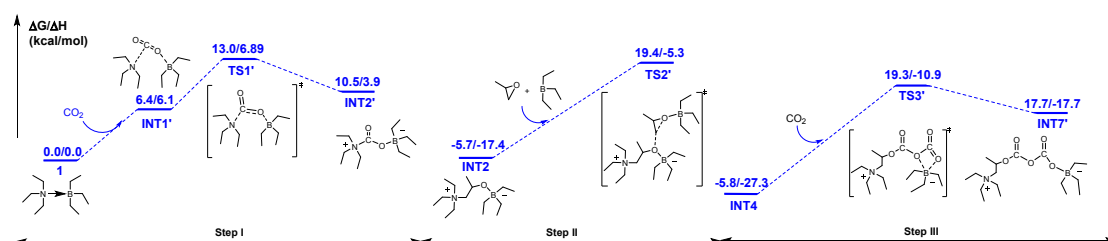


Figure S20. Free energies associated with the chain initiation and growth of the copolymerization of CO_2 with PO by the TEB/TEA pair by the unfavourable routes.

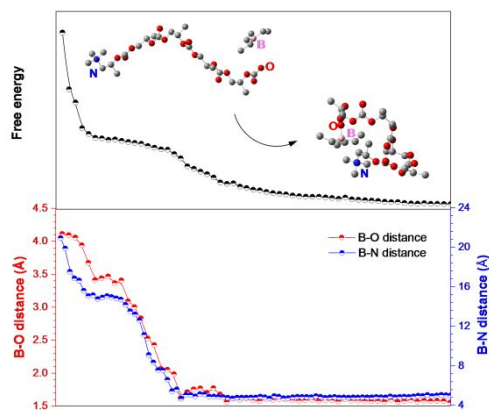


Figure S21. The free energy and corresponding B-O and B-N distance during changes of the conformation for CO₂/PO copolymer with 5 repeating units. Calculated by the method of m062x/6-31g(d,p), Gaussian 09 program.

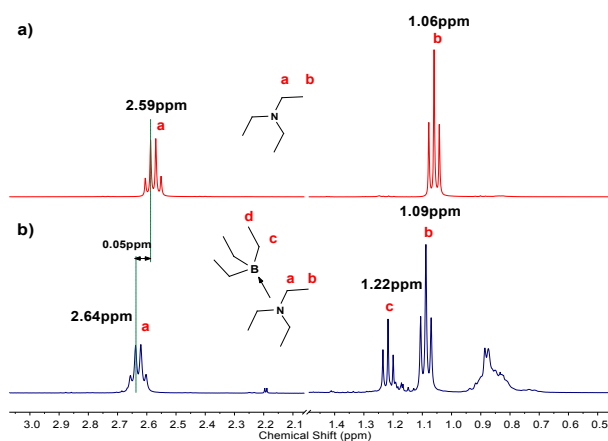


Figure S22. ¹H NMR spectra (CDCl₃) of a) TEA, b) TEA/TEB (1:1) pair.

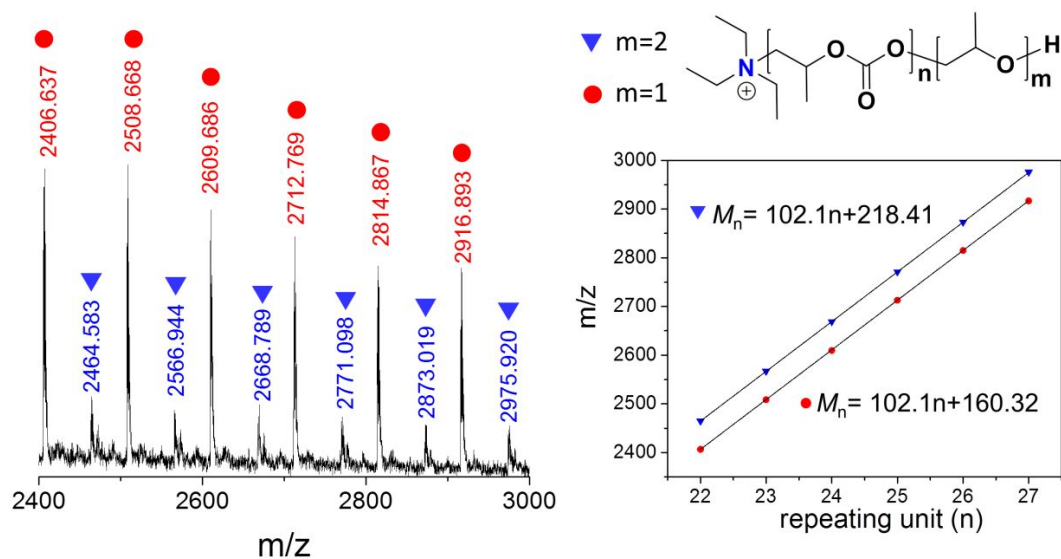


Figure S23. a) MALDI-TOF MS spectrum of PPC catalyzed by TEB/TEA (without termination). b) The fitting relationship of M_n of PPC vs. the numbers of the repeating unit.

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Figure S24. The elemental analysis result of PPC catalyzed by TEB/TEA ($M_n = 2500$ g/mol, terminated by dilute 1.0 M HCl in ethanol).