Supporting Information for

Chemoselective Ring-Opening Copolymerization of δ-Lactone Derived from CO_2 and Butadiene via Transesterification to Synthesize Bifunctional Copolyesters

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Experimental Section

Materials.

The monomer EVP was prepared according to previously reported procedure,[1] dried over CaH_2 for 24 h and distilled under reduced pressure. TMC was purchased from Aladdin Co., and recrystallized from toluene period to used. THF was purified by first purging with dry nitrogen, then by passing through columns of activated alumina. 3-Chloroperoxybenzoic acid (75%) and benzyl mercaptan (98%) were obtained from Aladdin and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 98%) from Energy Chemical Co. Benzenedimethanol (BDM) was purchased from TCI and recrystallized from toluene period to used. CTPB and ureas (U1−U4) were synthesized according to the literatures.[2, 3] All other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted.

Instruments.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). ^{1}H detected heteronuclear multiple bond correlation (HMBC) and heteronuclear single-quantum coherence (HSQC) techniques were used to assist in the assignment of ^{1}H and ^{13}C NMR spectra. The molar mass (M_n) and dispersity ($Đ = M_w/M_n$) were determined by size exclusion chromatography (SEC) equipped with an Agilent HPLC system, a 1260 Hip degasser, a 1260 Iso pump and a 1260 differential refractometer detector. One

PLgel 5 μm guard column and three Mz-Gel SD_{plus} (10^3 Å, 10^4 Å, and 10^5 Å) columns were connected in series. The SEC columns were eluted with THF at 1.0 mL/min at 40 °C. The sample concentration used for SEC analysis was 5 mg/mL. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex MALDI-TOF MS spectrometer equipped with a 337 nm nitrogen laser. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) was used as the matrix and CF_3COONa as the ionization agent. The post-functionalization experiments were carried out in an ultraviolet lamp box, using an ultraviolet high-pressure mercury lamp (GGZ250) with a wavelength of 365 nm and a power of 250 W.

General procedure for the copolymerization of EVP and TMC (Table 1, run 4).

In a glove-box, CTPB (0.02 mmol, 24 mg), BDM (0.02 mmol, 2.8 mg), U1 (0.02 mmol, 12.0 mg) were mixed in 0.87 mL THF in a Schlenk tube. After stirring for 5 minutes, the mixture of TMC (1.0 mmol, 102 mg) and EVP (1.0 mmol, 0.13 mL) was added into the Schlenk tube to begin the polymerization. After the desired reaction time, a few drops of acetic acid in chloroform were added to quench the reaction and a small portion of the solution was taken and used to determine the polymerization selectivity and the conversions of EVP and TMC by ^1H NMR. The conversion of the EVP monomer was calculated based on the integration (I) ratio $I_{poly(EVP)}/[I_{poly(EVP)} + I_{EVP}]$ of the protons of unsaturated C=C double bonds of poly(EVP) (6.94-6.77 ppm) and EVP (7.17-7.07

ppm), while the conversion of TMC was calculated by the ratio of $I_{PTMC}/[I_{PTMC} + I_{TMC}]$ of the methylene protons (-OCH_2) of PTMC (4.39-4.13 ppm) and TMC (4.50 ppm). The selectivity of the EVP monomer was calculated based on the integration (*I*) ratio $I_{poly(EVP)}/[I_{poly(EVP)} + I_{Di\text{-}EVP}]$ of the protons of unsaturated C=C double bonds of poly(EVP) (6.94-6.77 ppm) and Di-EVP (7.10-6.95 ppm). The remaining solution was poured into cold methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by SEC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 4 H, Ar-H of initiator), 6.94-6.77 (m, 8 H), 5.89-5.75 (m, 8 H), 5.34-5.21 (m, 16 H), 5.14 (s, 4 H, H of initiator), 5.07-4.97 (m, 8 H), 4.35-4.15 (m, 194 H), 2.45-2.30 (m, 16 H), 2.12-1.97 (m, 97 H), 1.87-1.70 (m, 40 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.13, 154.87, 154.45, 138.59, 135.55, 131.85, 128.52, 117.80, 78.56, 77.32, 77.20, 76.68, 64.72, 64.25, 64.05, 60.72, 33.06, 28.01, 21.97, 14.21 ppm. M_n = 5.4 kDa, $Đ$ = 1.77.

Preparation of PTMC.

In a glove-box, DPP (0.02 mmol, 5 mg), BDM (0.02 mmol, 2.8 mg) were mixed in 0.4 mL toluene in a Schlenk tube. After stirring for 5 minutes, TMC (0.5 mmol, 51 mg) was added into the Schlenk tube to begin the polymerization under room temperature. After 24 h, a few drops of acetic acid in chloroform were added to quench the reaction and a small portion of the solution was taken and used to determine the conversion of TMC by ^{1}H NMR. The remaining solution was poured into cold methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by SEC. M_n = 2.9 kDa, $Đ$ = 1.11.

Preparation of poly(TMC-*co*-EVP) copolymer (Table 2, run 1).

In a glove-box, 102 mg PTMC (M_n = 2.9 kDa, $Đ$ = 1.11), 24 mg CTPB (0.02 mmol), and 12 mg U1 (0.02 mmol) were mixed in 0.37 mL THF in a Schlenk tube. After stirring for 10 minutes, 0.13 mL EVP (1.0 mmol) was added into the Schlenk tube to begin the polymerization. After 1 h, a few drops of acetic acid in chloroform were added to quench the reaction and a small portion of the solution was taken and used to determine the polymerization selectivity and the conversion of EVP by ^{1}H NMR. The remaining solution was poured into cold methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by ^{1}H NMR and SEC. M_n = 6.2 kDa, $Đ$ = 1.39.

Preparation of PLLA.

In a glove-box, Sn(oct)$_2$ (0.001 mmol, 0.4 μL), BDM (0.02 mmol, 2.8 mg) were mixed in 2.5 mL toluene in a Schlenk tube. After stirring for 5 minutes, *L*-LA (1.0 mmol, 144 mg) was added into the Schlenk tube to begin the polymerization under 130 °C. After 2 h, a few drops of acetic acid in chloroform were added to quench the reaction and a small portion of the solution was taken and used to determine the polymerization selectivity and the conversion of *L*-LA by ^{1}H NMR. The remaining solution was poured into methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by SEC. M_n = 7.2 kDa, $Đ$ = 1.15.

Preparation of poly(LLA-*co*-EVP) copolymer (Table 2, run 4).

In a glove-box, 144 mg PLLA (M_n = 7.2 kDa, $Đ$ = 1.15), 24 mg CTPB (0.02 mmol), and 12 mg U1 (0.02 mmol) were mixed in 0.37 mL THF in a Schlenk tube. After stirring for 10 minutes, 0.13 mL EVP (1.0 mmol) was added into the Schlenk tube to begin the polymerization. After 6 h, a few drops of acetic acid in chloroform were added to

quench the reaction and a small portion of the solution was taken and used to determine the polymerization selectivity and the conversion of EVP by ^{1}H NMR. The remaining solution was poured into cold methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by ^{1}H NMR and SEC. M_n = 8.0 kDa, $Đ$ = 1.27.

Preparation of poly(LLA-*co*-EVP)$_{S1}$ via Michael addition reaction.

A mixture of 100 mg poly(LLA-*co*-EVP) (M_n = 8.0 kDa, 16 mol% EVP), 150 μL benzyl mercaptan (1.2 mmol, 10 equiv.), and 10 μL TEA (0.07 mmol, 0.6 equiv.) was dissolved in 0.5 mL chloroform. The reaction mixture was stirred at 20 °C for 20 h. An aliquot of the solution was withdrawn and used to determine the conversion by ^{1}H NMR. The remaining mixture was poured into excess hexane. Poly(LLA-co-EVP)$_{S1}$ was obtained as a precipitate, which was washed twice with hexane and then dried under vacuum at room temperature. The resulting polymer was analyzed by ^{1}H NMR and SEC. M_n = 9.6 kDa, $Đ$ = 1.22.

Preparation of poly(LLA-*co*-EVP)$_{S1+S2}$ via thiol-ene click reaction.

A flame-dried Schlenk tube was charged with 100 mg poly(LLA-*co*-EVP)$_{S1}$ (M_n = 9.6 kDa, 16 mol% EVP), 8 mg (0.03 mmol, 8 wt%) DMPA and 0.5 mL chloroform, then 33 μL isobutyl mercaptan (0.3 mmol, 3 equiv.) was added into the Schlenk tube via a gastight syringe. The tube was then irradiated by UV light at 365 nm for 5 h. The reaction mixture was poured into excess cold methanol and the precipitate obtained was washed twice with excess cold methanol and then dried under vacuum at room

temperature. The resulting polymer was analyzed by ^{1}H NMR and SEC. M_n = 16.3 kDa, $Đ$ = 2.07.

Preparation of poly(LLA-*co*-EVP) (Table 2, run 5) from commercially available PLA.

In a glove-box, 720 mg PLLA-LX175, 11.2 mg TBD (0.08 mmol), and 48 mg U1 (0.08 mmol) were mixed in 3 mL THF in a Schlenk tube. After stirring for 30 min, 0.52 mL EVP (4.0 mmol) was added into the Schlenk tube to begin the polymerization. After 2 h, a few drops of acetic acid in chloroform were added to quench the reaction and a small portion of the solution was taken and used to determine the polymerization selectivity and the conversion of EVP by ^{1}H NMR. The remaining solution was poured into cold methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by ^{1}H NMR and SEC. M_n = 18.2 kDa, $Đ$ = 1.54.

Preparation of with functional PLA with antibacterial properties via thiol-ene click reaction from commercially available PLA.

A flame-dried Schlenk tube was charged with 300 mg LX175-EVP-5% (18.2 kDa, 5 mol% EVP), 24 mg (8 wt%) DMPA and a mixed solvent of 3 mL chloroform and 1 mL methanol, then 138 mg $NMe_2(CH_2)_{14}$-SH (0.36 mmol, 10 equiv.) was added into the Schlenk tube via a gastight syringe. The tube was then irradiated by UV light at 365 nm for 18 h. The reaction mixture was poured into excess cold methanol and the precipitate obtained was washed twice with excess cold methanol and then dried under vacuum at room temperature. The resulting polymer was analyzed by ^{1}H NMR.

Preparation of PCL.

In a glove-box, CTPB (0.01 mmol, 12 mg), BDM (0.02 mmol, 2.8 mg), U1 (0.02 mmol, 12.0 mg) were mixed in 4 mL THF in a Schlenk tube. After stirring for 5 minutes, CL (4.0 mmol, 0.52 mL) was added into the Schlenk tube to begin the polymerization. After 3 h, a few drops of acetic acid in chloroform were added to quench the reaction and a small portion of the solution was taken and used to determine the polymerization selectivity and the conversion of CL by ^{1}H NMR. The remaining solution was poured into cold methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by SEC. M_n = 24.6 kDa, $Đ$ = 1.13.

Preparation of PVL.

In a glove-box, CTPB (0.01 mmol, 12 mg), BDM (0.02 mmol, 2.8 mg), U1 (0.02 mmol, 12.0 mg) were mixed in 4 mL THF in a Schlenk tube. After stirring for 5 minutes, VL (6.0 mmol, 102 mg) was added into the Schlenk tube to begin the polymerization. After 6 h, a few drops of acetic acid in chloroform were added to quench the reaction and a small portion of the solution was taken and used to determine the polymerization selectivity and the conversion of VL by ^{1}H NMR. The remaining solution was poured into cold methanol to precipitate the polymer, which was dried overnight under vacuum in an oven. The resulting polymer was analyzed by SEC. M_n = 34.4 kDa, $Đ$ = 1.60.

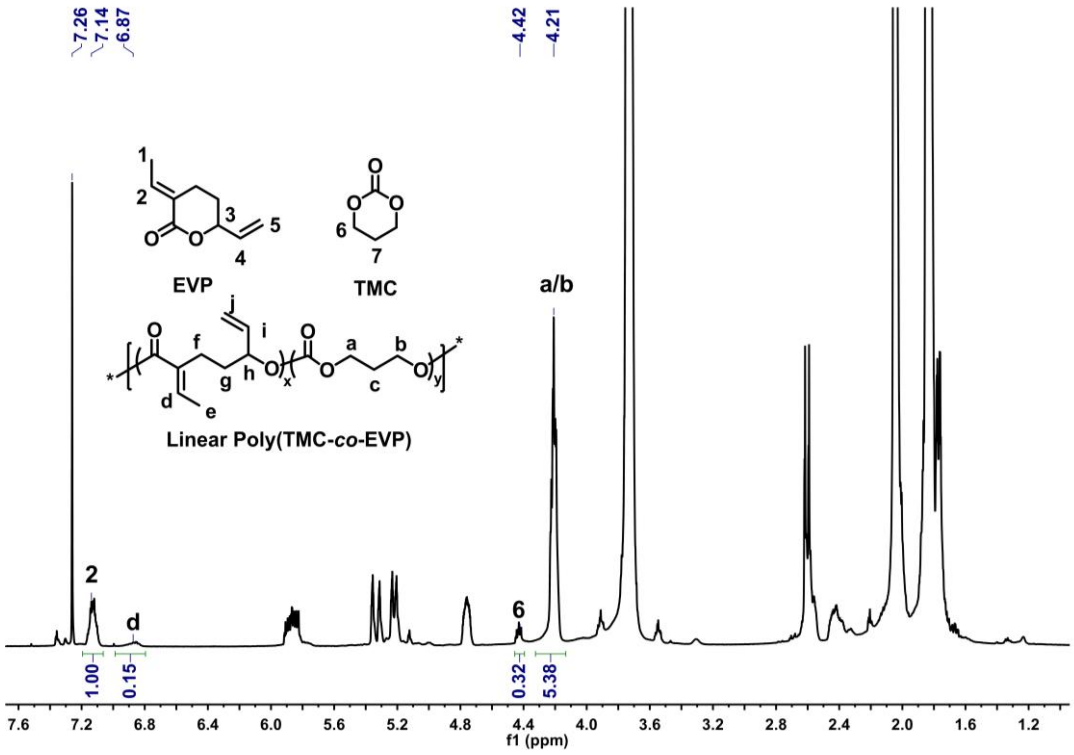

Figure S1. ^{1}H NMR spectrum of the crude reaction mixtures obtained in Table 1 run 1.

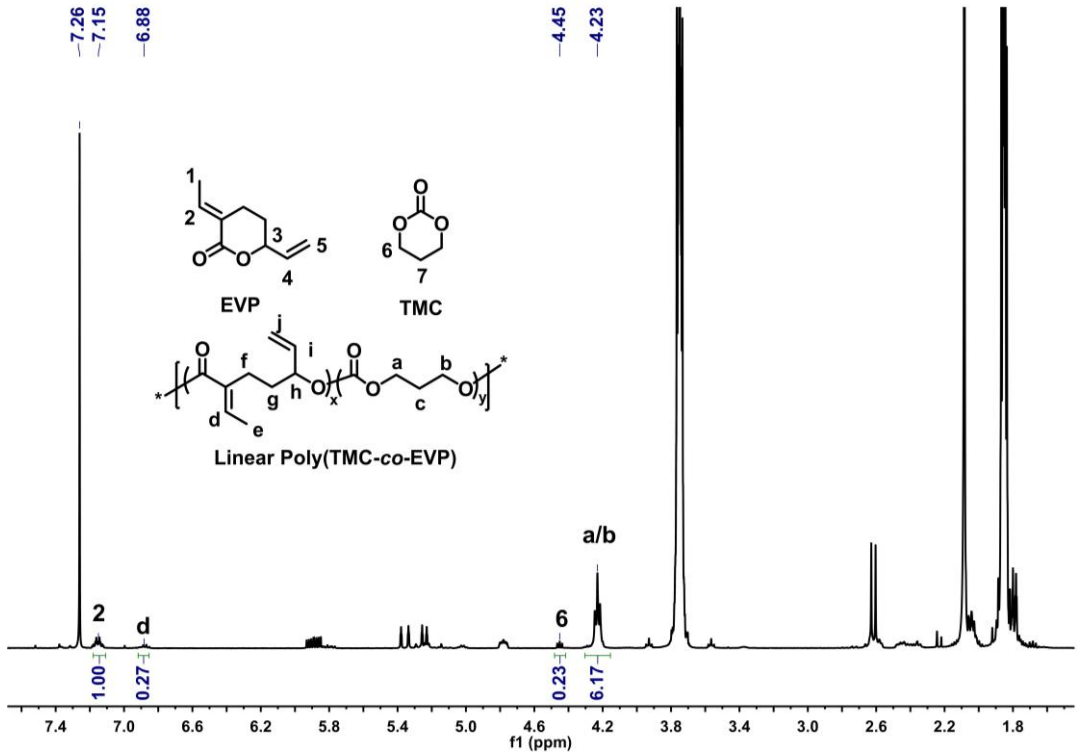

Figure S2. ^{1}H NMR spectrum of the crude reaction mixtures obtained in Table 1 run 2.

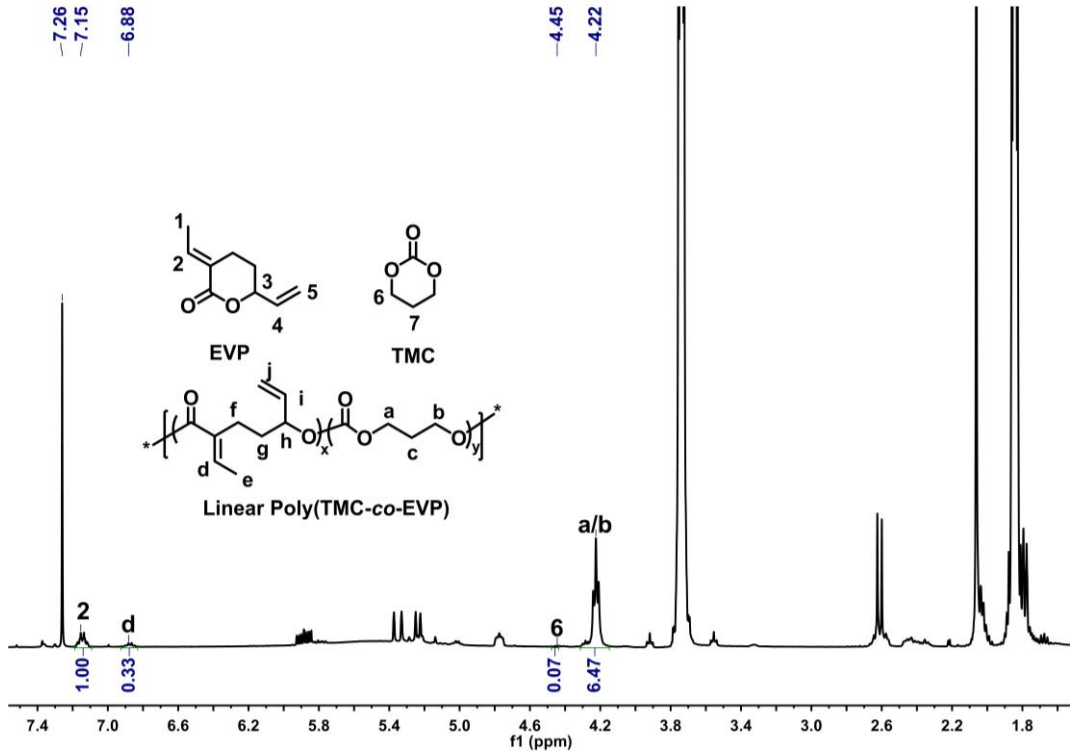

Figure S3. [1]H NMR spectrum of the crude reaction mixtures obtained in Table 1 run 3.

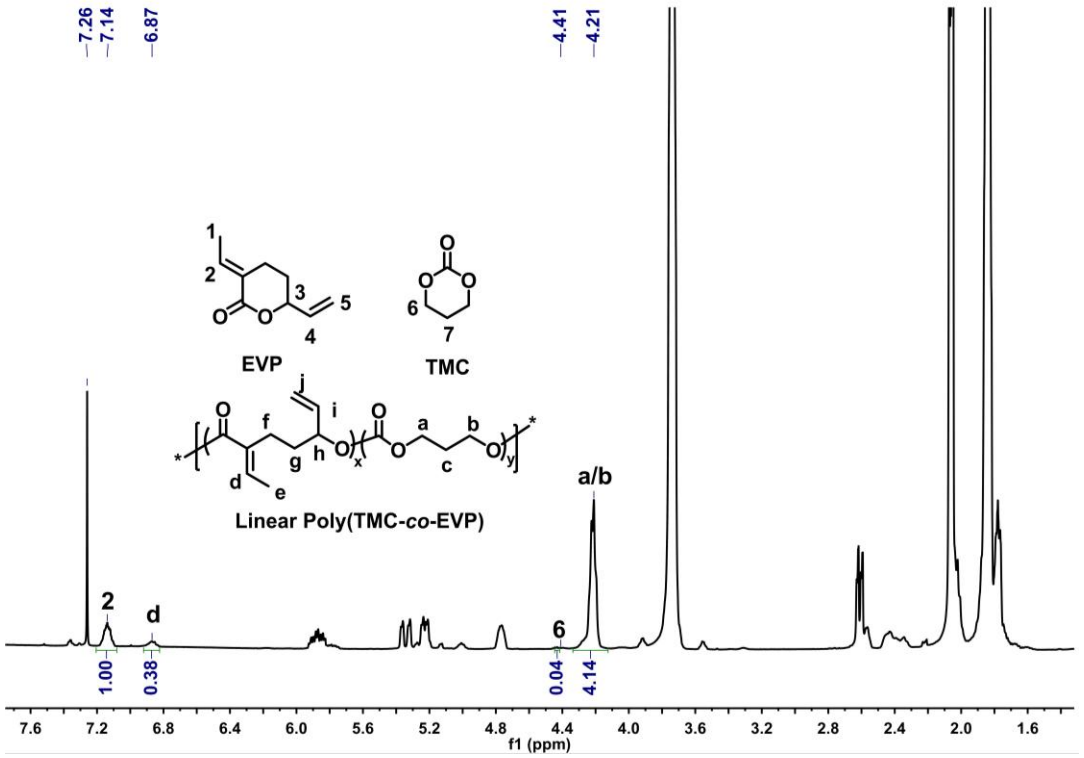

Figure S4. [1]H NMR spectrum of the crude reaction mixtures obtained in Table 1 run 4.

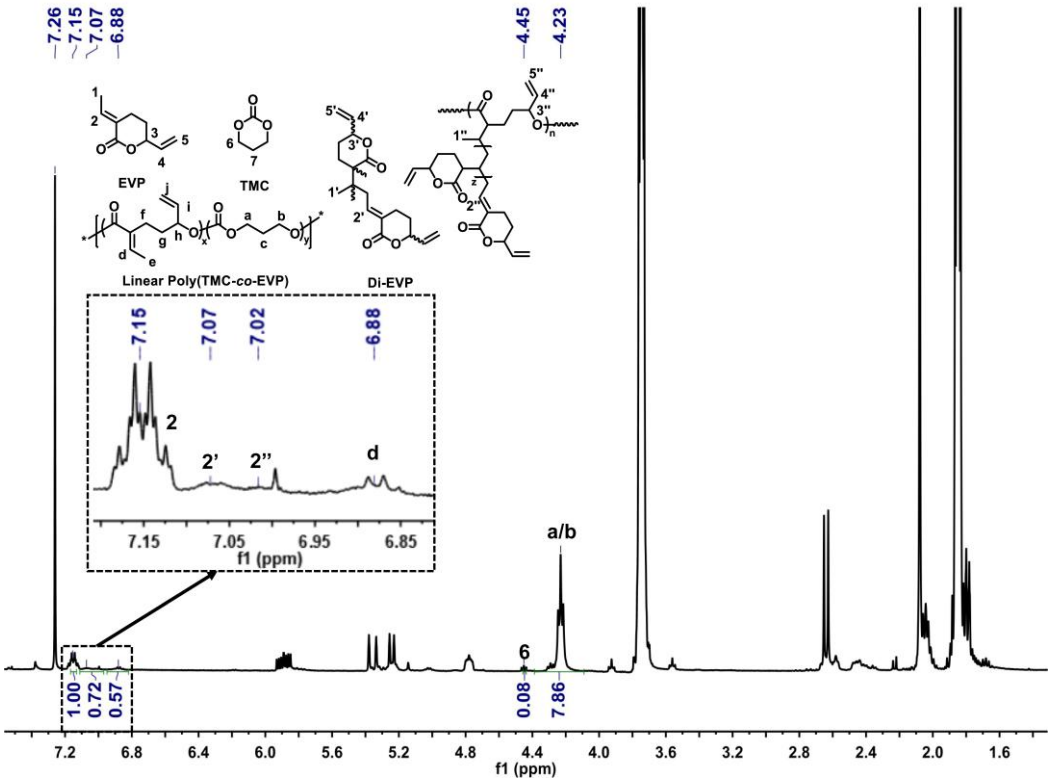

Figure S5. ^{1}H NMR spectrum of the crude reaction mixtures obtained in Table 1 run 5.

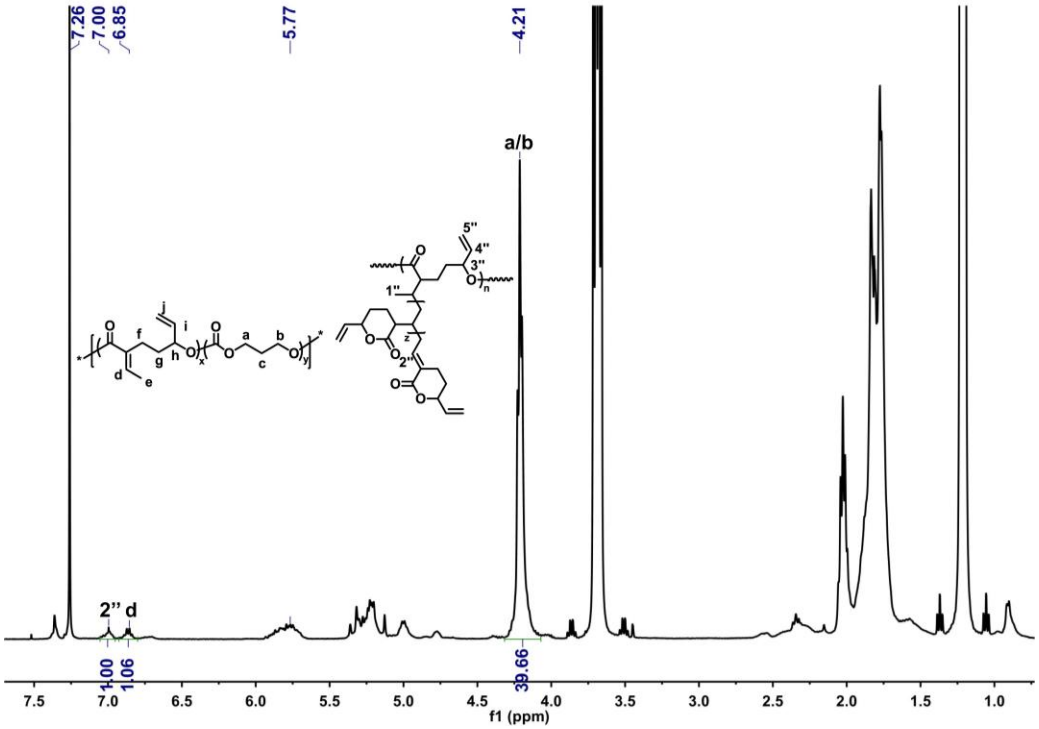

Figure S6. ^{1}H NMR spectrum of the purified copolymer obtained in Table 1 run 5.

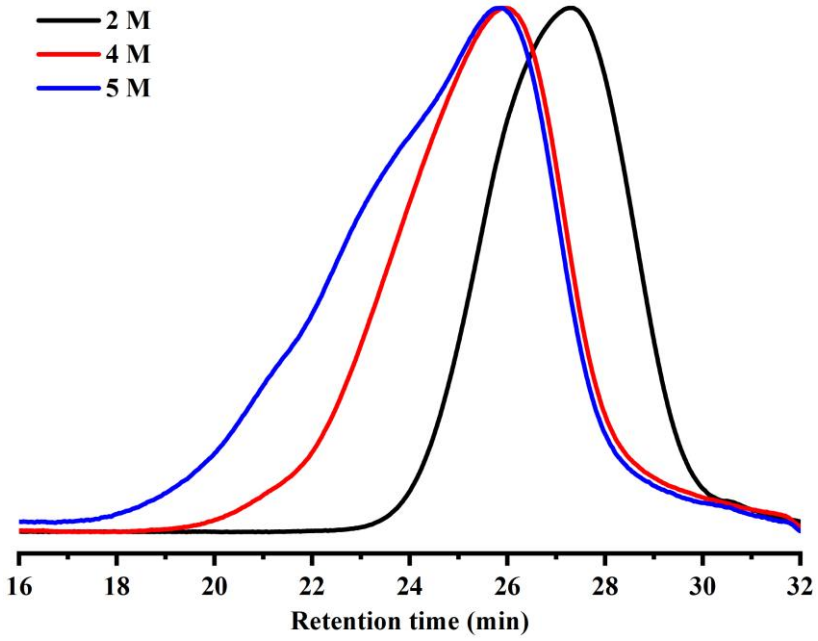

Figure S7. SEC traces for poly(TMC-*co*-EVP)s obtained at different monomer concentrations (data shown in Table 1, runs 4, 7, and 8).

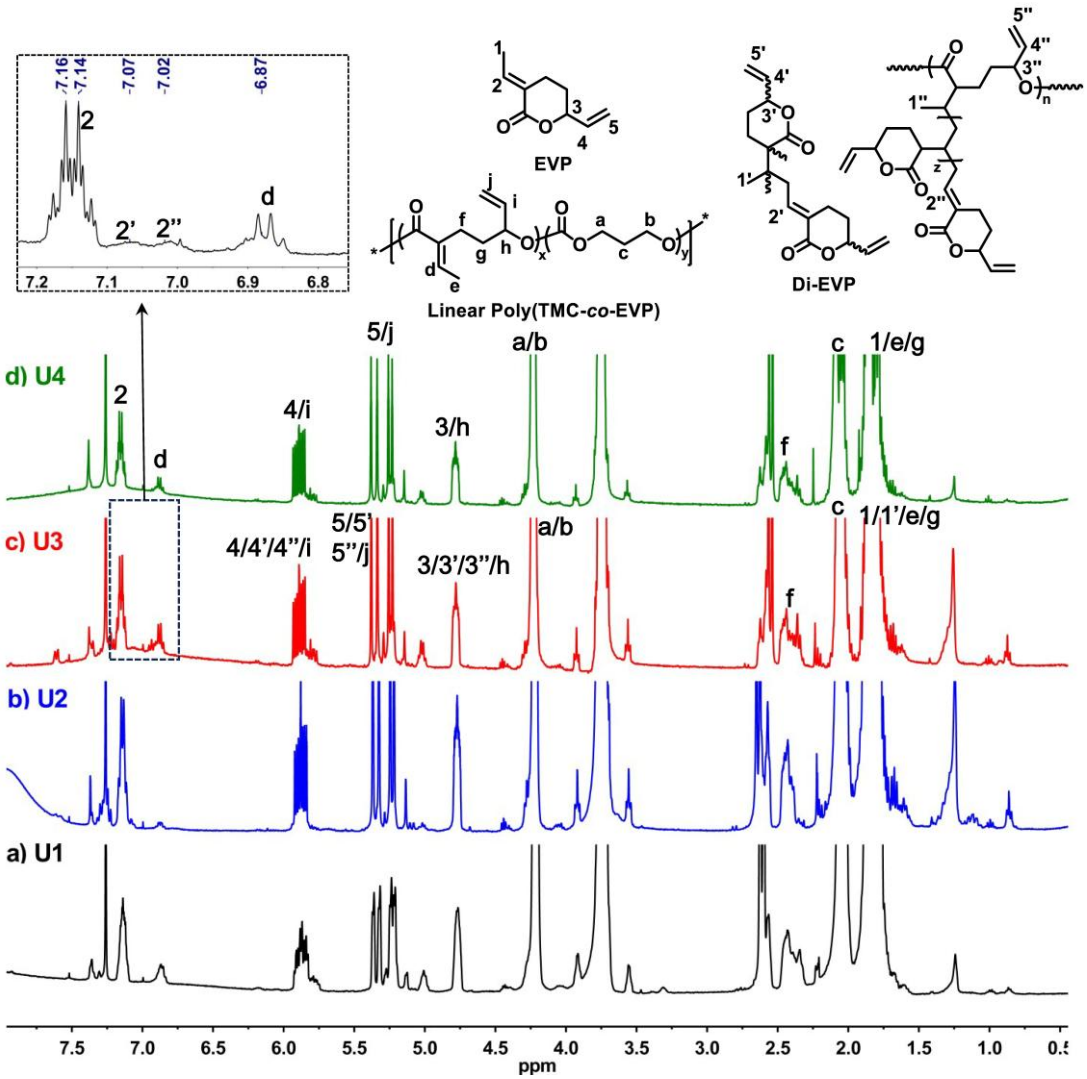

Figure S8. Stacked ^{1}H NMR spectra of the crude reaction mixtures obtained with different ureas and CTPB (Table 1, runs 4, and 9–11).

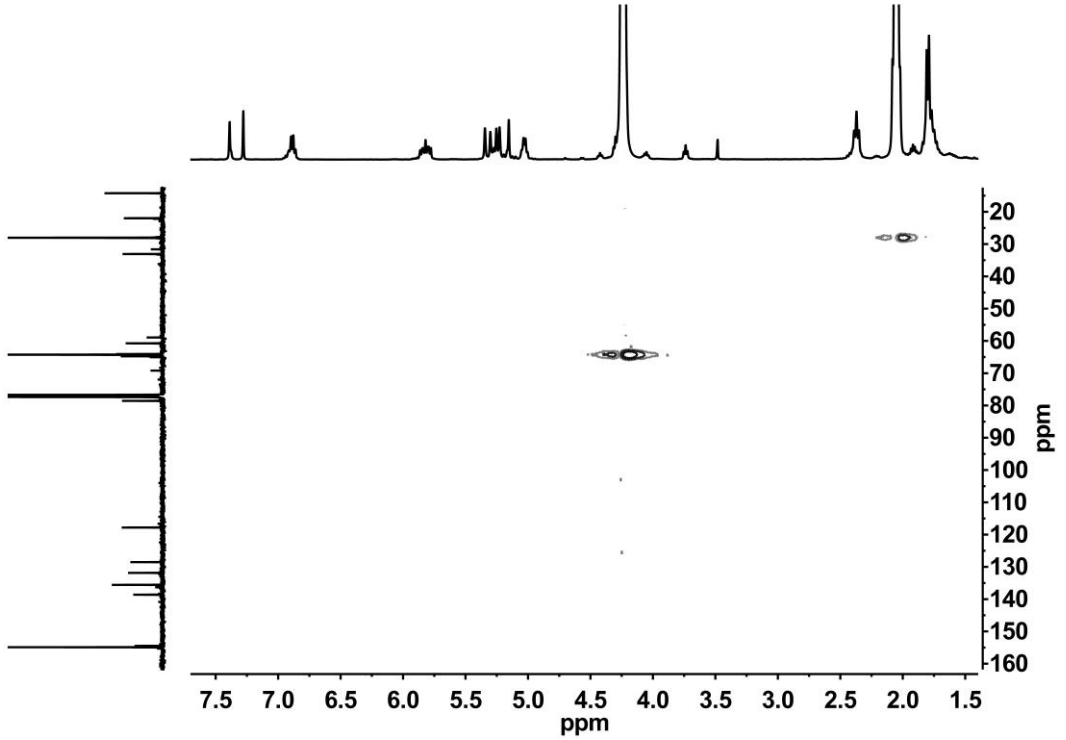

Figure S9. ^{1}H-^{13}C HSQC NMR ($CDCl_3$) of poly(TMC-*co*-EVP) obtained in Table 1 run 13.

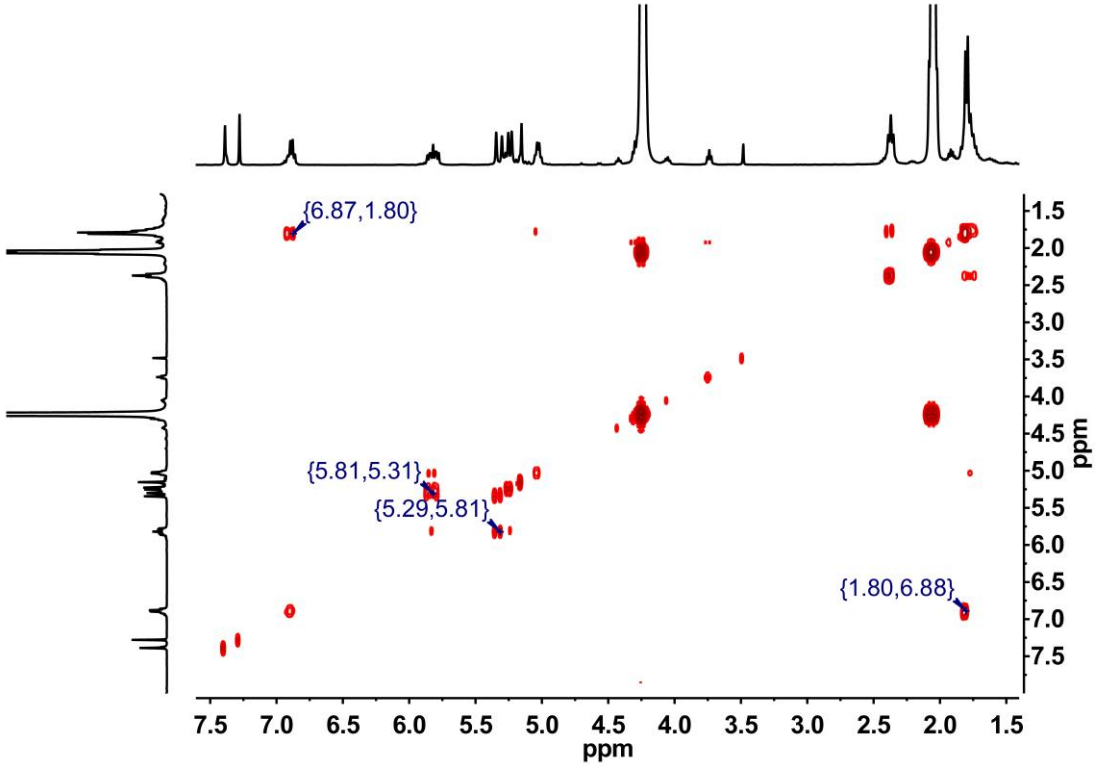

Figure S10. ^{1}H-^{1}H COSY NMR ($CDCl_3$) of poly(TMC-*co*-EVP) obtained in Table 1 run 13.

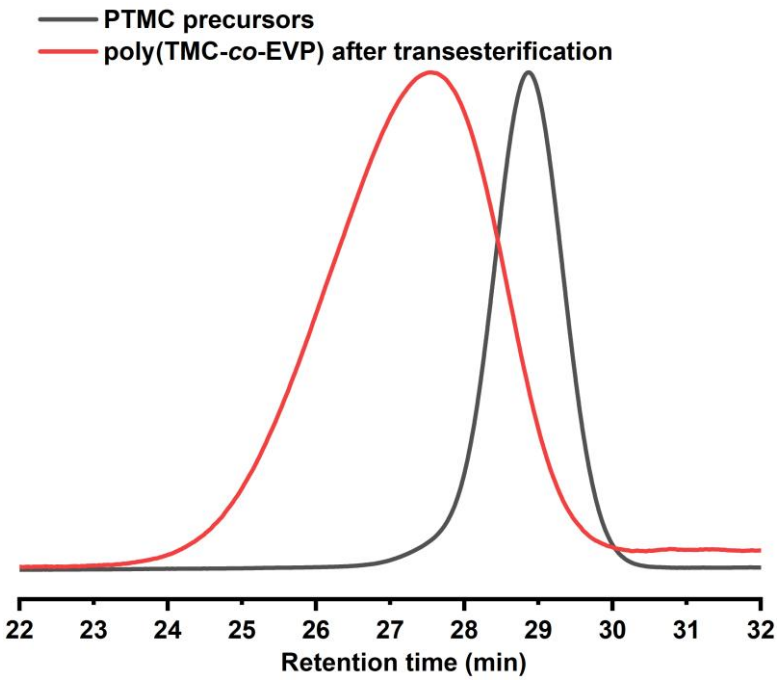

Figure S11. SEC traces for PTMC precursors and poly(TMC-*co*-EVP) after transesterification (Table 2 run 1).

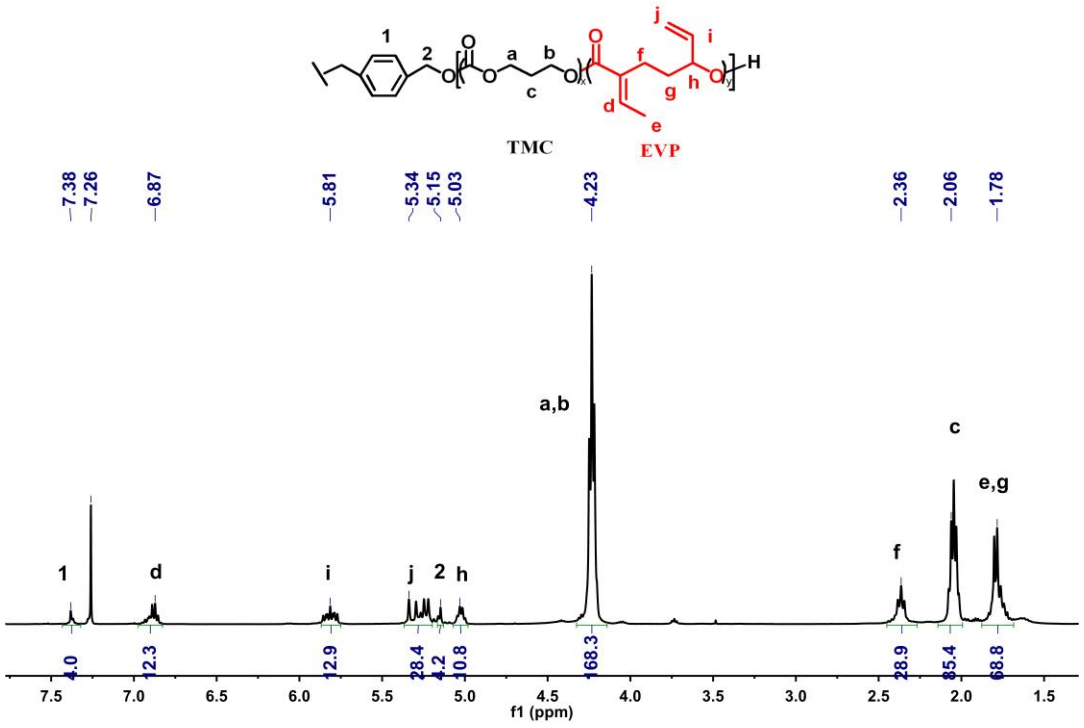

Figure S12. ^{1}H NMR spectrum of poly(TMC-*co*-EVP) obtained from EVP and PTMC precursors transesterification (Table 2 run 1).

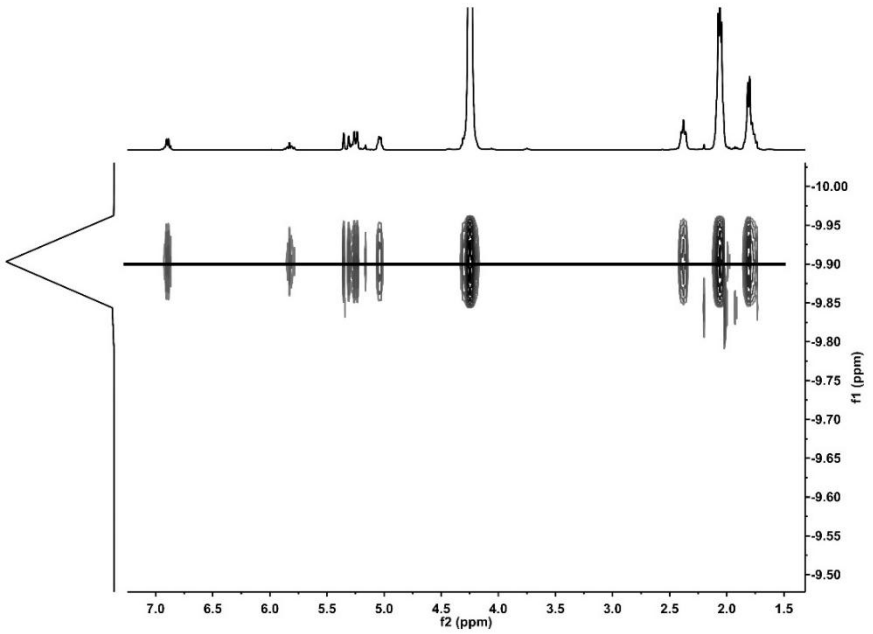

Figure S13. DOSY NMR of poly(TMC-*co*-EVP) obtained from EVP and PTMC precursors transesterification (Table 2 run 1).

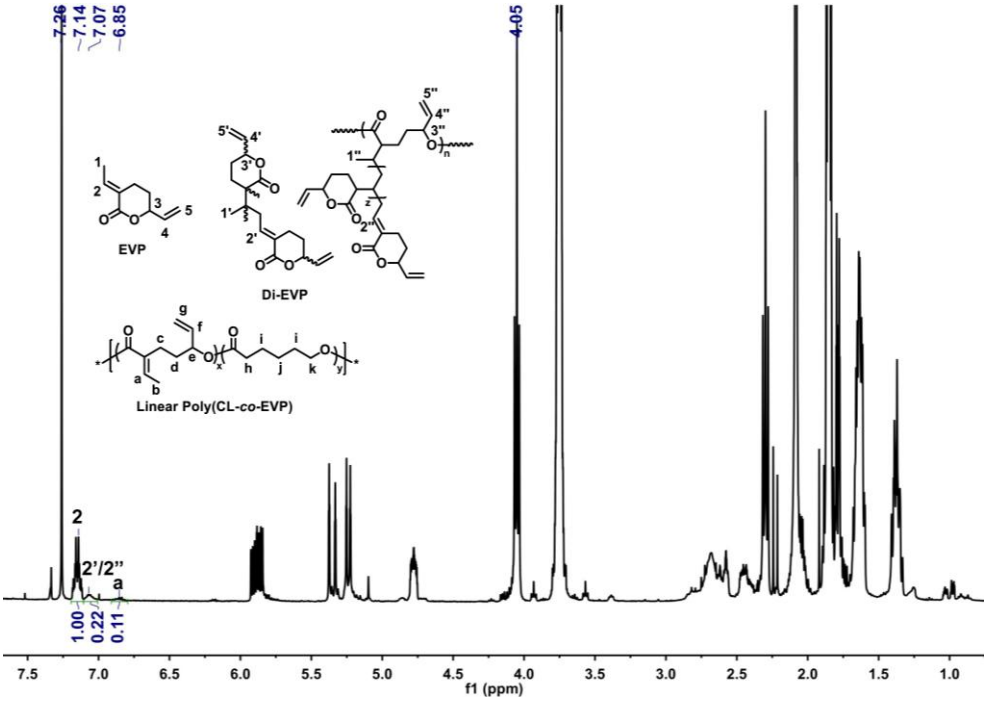

Figure S14. ^{1}H NMR spectrum of the crude mixtures obtained in Table 2 run 2.

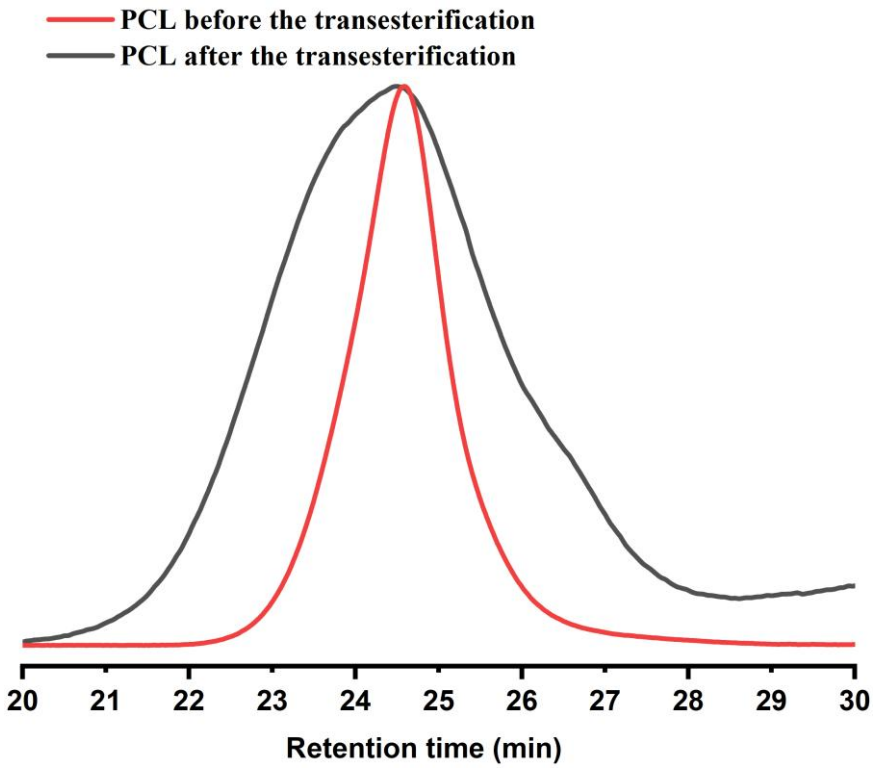

Figure S15. SEC traces for PCL before and after the transesterification (Table 2 run 2).

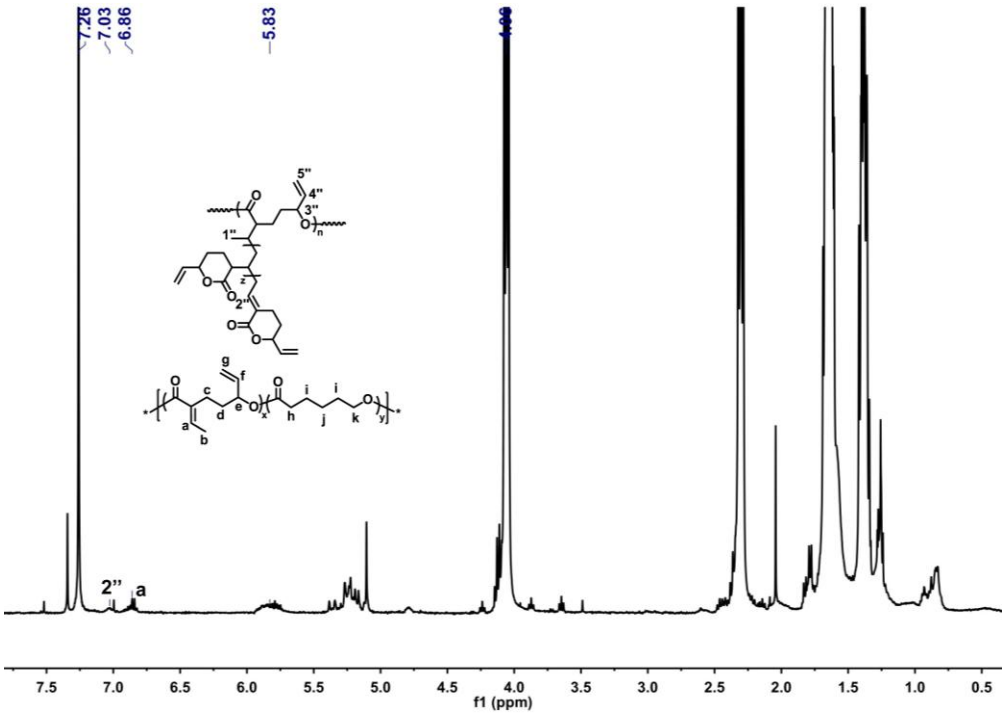

Figure S16. ^{1}H NMR spectrum of purified copolymer after the transesterification in Table 2 run 2.

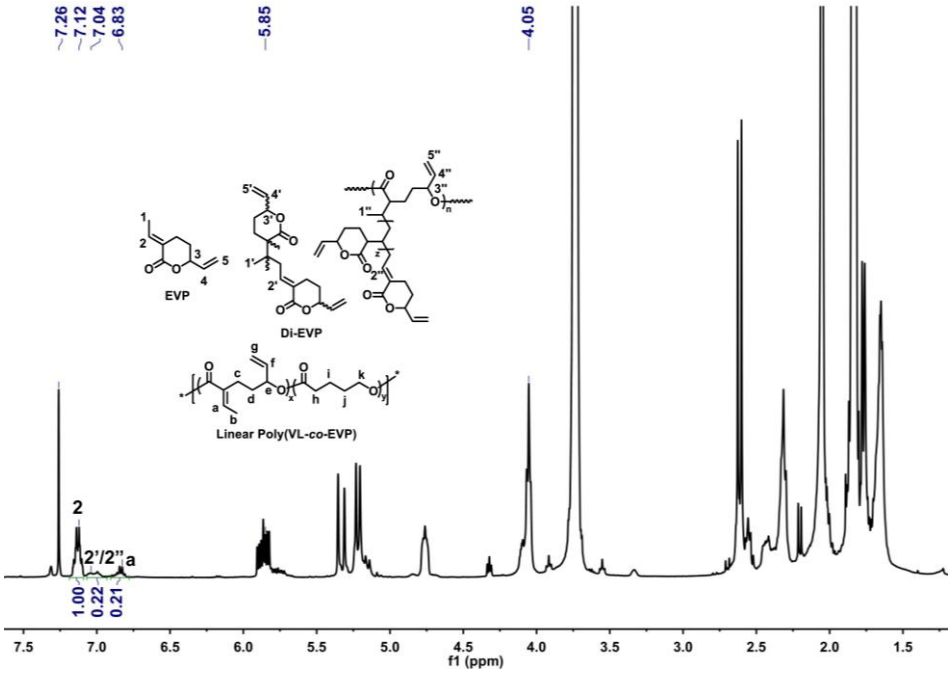

Figure S17. ^{1}H NMR spectrum of the crude mixtures obtained in Table 2 run 3.

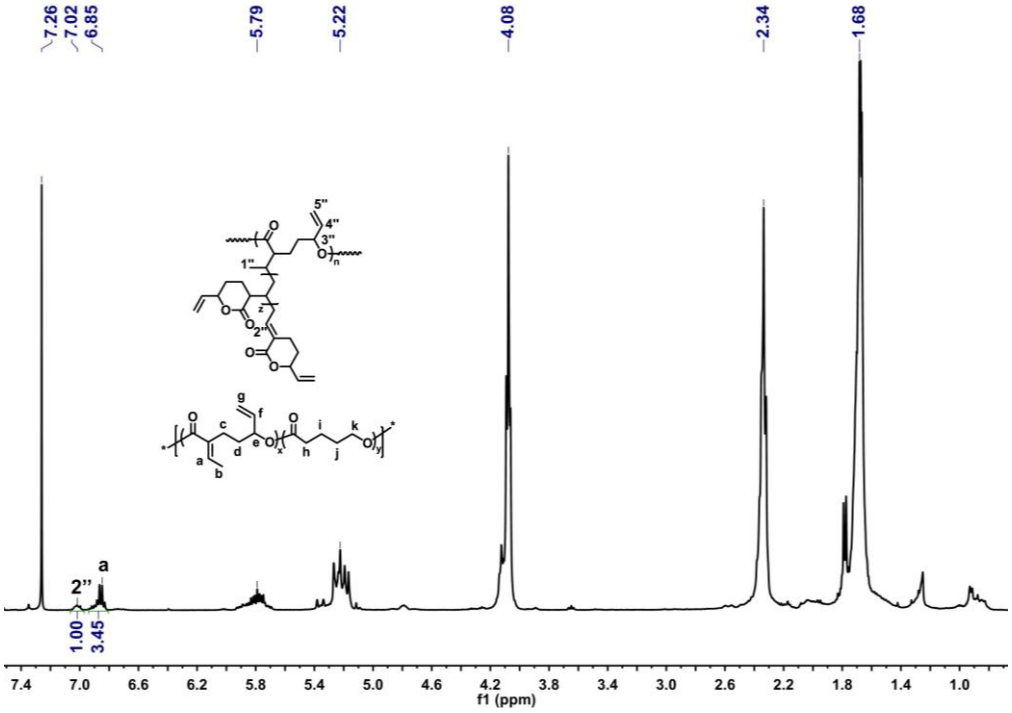

Figure S18. ^{1}H NMR spectrum of purified copolymer after the transesterification in Table 2 run 3.

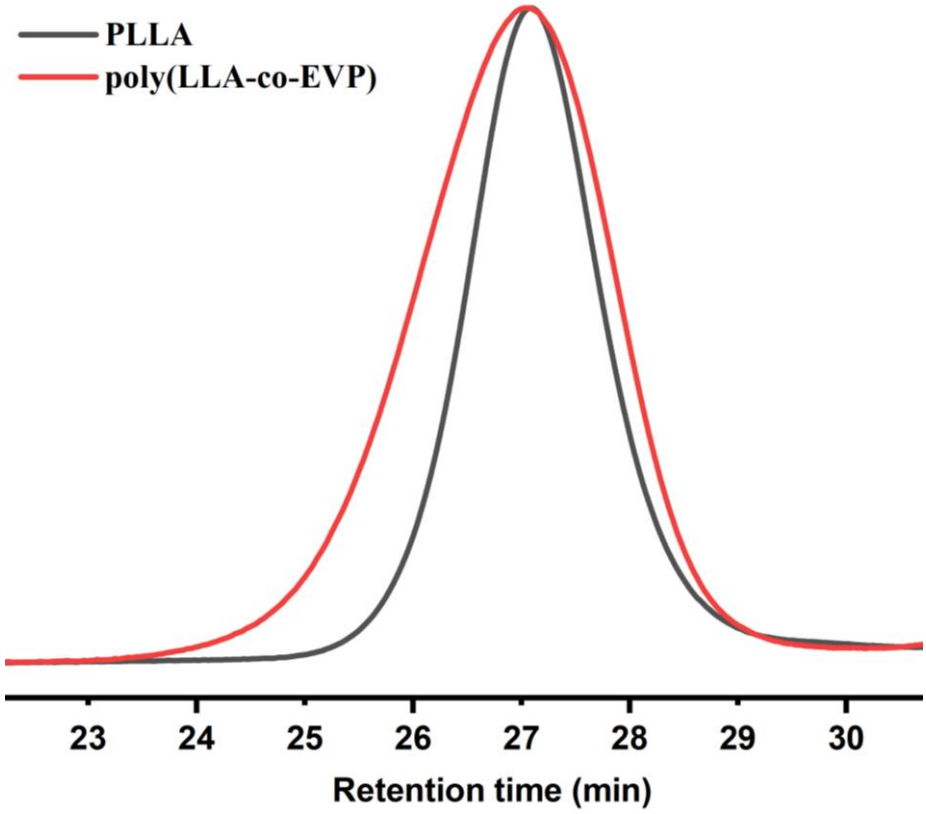

Figure S19. SEC traces for PLLA and poly(LLA-*co*-EVP) after the transesterification (Table 2 run 4).

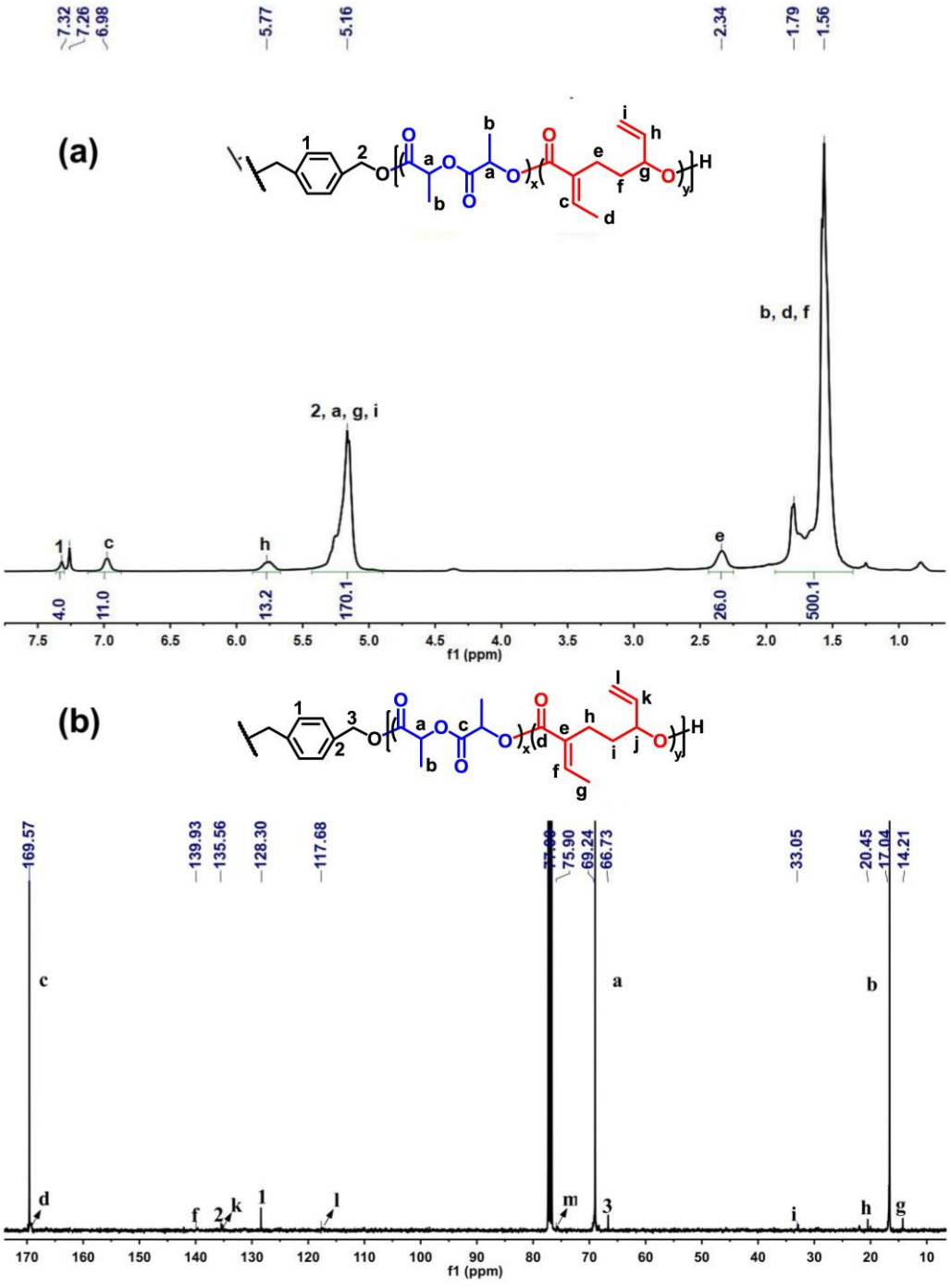

Figure S20. (a) ^{1}H NMR, and (b) ^{13}C NMR of purified poly(LLA-*co*-EVP) copolyester obtained in Table 2 run 4.

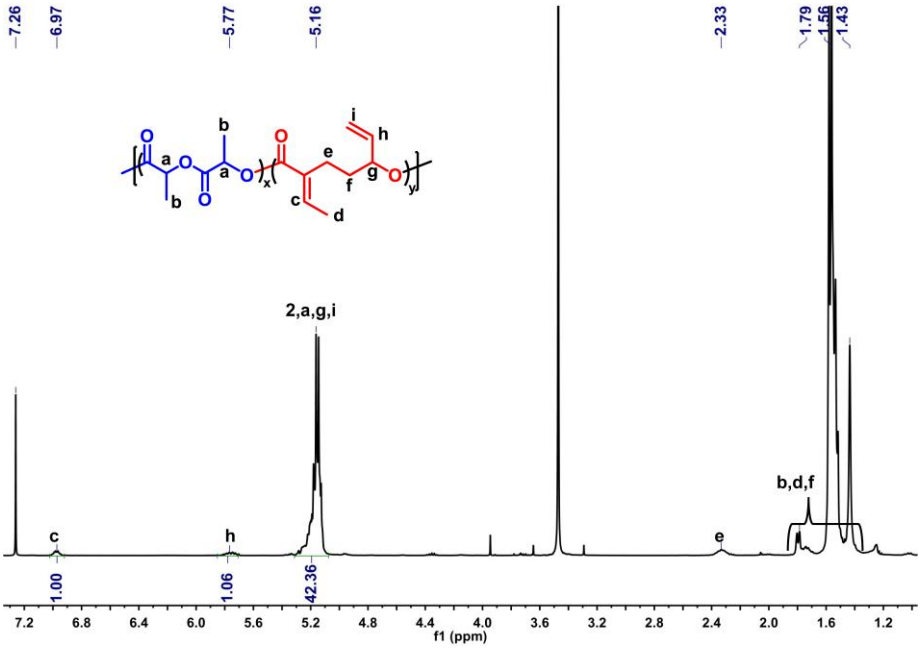

Figure S21. ^{1}H NMR spectrum of the poly(LLA-*co*-EVP) copolymer with 5 mol% EVP incorporation obtained from EVP and commercial PLLA-LX175 by transesterification in Table 2 run 5.

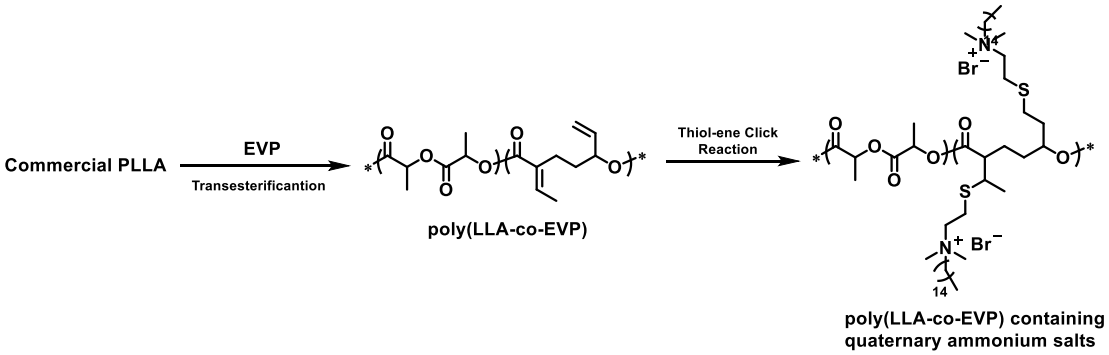

Figure S22. Synthesis of functionalized poly(LLA-*co*-EVP) containing quaternary ammonium salts via photo-triggered thiol-ene click reaction form commercial PLLA.

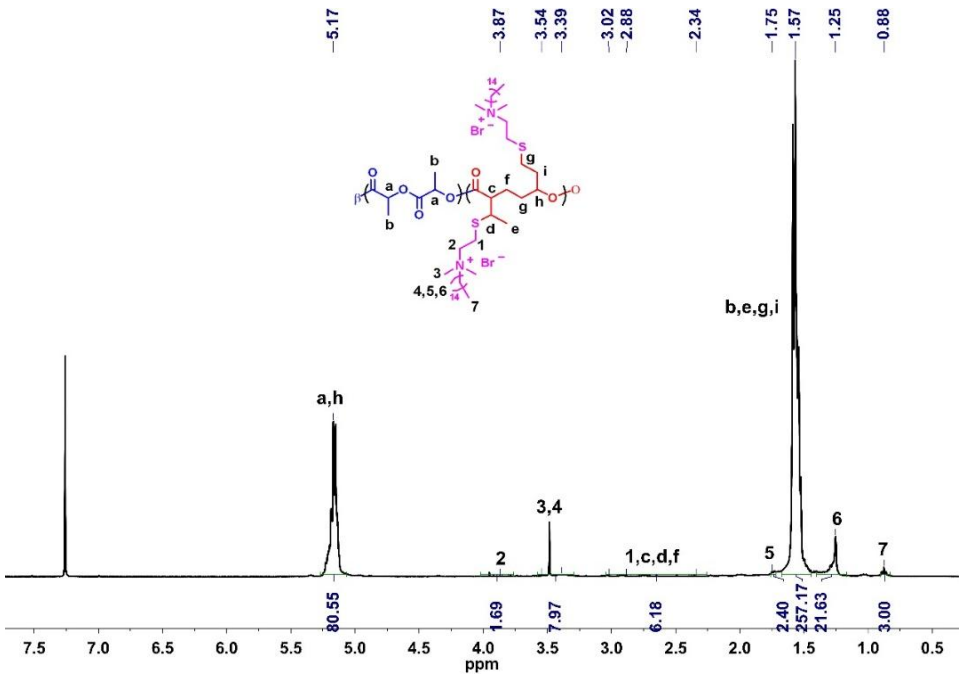

Figure S23. ^{1}H NMR spectrum of post-functionalized poly(LLA-*co*-EVP) containing quaternary ammonium salts.

Table S1. ROCOP of EVP and TMC with Different Feeding Ratios Catalyzed by CTPB/U1.[a]

run	EVP/TMC	conv.[b] (EVP %)	conv.[b] (TMC %)	select.[c] (%)	incorp.[b] (%)	$M_{n,theo}$[d] (kDa)	$M_{n,SEC}$[e] (kDa)	$Đ$.[e]
1	100/0	26	-	0	-	-	-	-
2	90/10	12	98	74	39	-	-	-
3	80/20	23	99	74	33	-	-	-
4	65/35	29	99	75	26	-	-	-
5	50/50	37	99	100	27	7.9	14.1	1.80
6	35/65	37	99	100	15	8.3	8.9	2.46
7	10/90	38	99	100	4	9.7	5.7	3.16
8	0/100	-	99	-	0	10.2	3.0	3.42

[a] Conditions: CTPB (0.02 mmol, 24 mg), 25 °C, 1 h, CTPB/U1/BDM = 1/1/1, THF was used as solvent, $[M]_0 = [EVP]_0 + [TMC]_0 = 4$ M. [b] Determined by ^{1}H NMR spectroscopy. [c] EVP polymerization selectivity via ROP pathway determined by ^{1}H NMR spectroscopy. [d] $M_{n,theo} = [EVP]_0/[I] \times conv.(EVP) \times M_{EVP} + [TMC]_0/[I] \times conv.(TMC) \times M_{TMC} + M_{BDM}$. [e] Determined by SEC in THF at 40 °C relative to PS standards.

Table S2. ROCOP of EVP and TMC Catalyzed by Organocatalysts.[a]

run	base	time (min)	conv.[b] (EVP %)	conv.[b] (TMC %)	select.[c] (%)	incorp.[b] (%)	$M_{n,theo}$[d] (kDa)	$M_{n,SEC}$[e] (kDa)	$Đ$[e]
1	TBD	60	22	99	100	18	6.8	5.1	1.52
2	TBD	180	30	99	100	23	7.4	7.1	1.37
3	DBU	60	6	99	100	6	5.6	4.4	1.17
4	DBU	180	8	99	100	7	5.7	4.7	1.20
5	DMAP	60	0	31	100	-	-	-	-
6	DMAP	180	3	46	100	-	-	-	-
7	CH_3OK	60	Crosslink						
8[f]	CH_3OK	60	18	99	100	15	6.4	5.0	1.54

[a] Conditions: CTPB (0.02 mmol, 24 mg), 25 °C, EVP/TMC/BDM/U1/base = 50/50/1/1/1, $[M]_0 = [EVP]_0 + [TMC]_0$, = 4 M, THF was used as solvent. [b] Determined by ^{1}H NMR spectroscopy. [c] EVP polymerization selectivity via ROP pathway determined by ^{1}H NMR spectroscopy. [d] $M_{n,theo} = [EVP]_0/[I] \times conv.(EVP) \times M_{EVP} + [TMC]_0/[I] \times conv.(TMC) \times M_{TMC} + M_{BDM}$. [e] Determined by SEC in THF at 40 °C relative to PS standards. [f] U1/base = 2/1.

Table S3. ROCOP of EVP and TMC at Low Concentration of Monomers with Different Times.[a]

run	Time (min)	conv.[b] (EVP %)	conv.[b] (TMC %)	select.[c] (%)
1	0.1	0	88	100
2	0.5	0	92	100
3	1	3	96	100
4	45	6	99	100
5	60	10	99	100
6	180	15	99	100

[a] Conditions: CTPB (0.02 mmol, 24 mg), 25 °C, EVP/TMC/BDM/U1/CTPB = 50/50/1/1/1, $[M]_0 = [EVP]_0 + [TMC]_0$, = 0.5 M, THF was used as solvent. [b] Determined by ^{1}H NMR spectroscopy. [c] EVP polymerization selectivity via ROP pathway determined by ^{1}H NMR spectroscopy.

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