Supplementary Information (SI) for Faraday Discussions.

Supporting Information

Dual-Selective Polymerization: Achieving Chemoselectivity and Stereoselectivity in a Single Catalytic System

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Experimental Details

Materials

All reagents were purchased from Macklin and used as received unless otherwise specified. Propylene oxide (PO, 98%), were distilled over CaH_2 under reduced pressure and stored under nitrogen atmosphere. Phthalic anhydride (PA, 99%), succinic anhydride (SA, 98%) were recrystallized and then purified by the way of sublimation before use. L-lactide (L-LA; 98%) were purified by recrystallization from dry toluene. trans-cyclohexane-1,2-diol (CHD, 98%) was recrystallized from ethyl acetate and stored under an inert atmosphere. The purity of all materials was confirmed by ^1H NMR spectroscopy in $CDCl_3$ or DMSO-d_6. All manipulations were performed using a standard Schlenk technique under N_2 atmosphere or in a nitrogen-filled MIKROUNA SUPER glovebox unless otherwise mentioned.

Measurements

Nuclear Magnetic Resonance (NMR): ^1H and ^{13}C NMR were recorded on Bruker 400 AV MHz spectrometers. All chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated using TMS. NMR spectra were processed and analyzed using MestReNova software.

^{1}H Diffusion-ordered Spectroscopy (DOSY): DOSY spectra was recorded on Bruker AVANCEIIIHD500 spectrometers. DOSY experiments were performed at a steady temperature of 298 K with at least 32 gradient increments using the ledbpgp2s sequence. Complete diffusion was ensured using the T1/T2 module of Topspin and DOSY transformations using either mono, bis- or tri-exponential fitting were performed using the same software after zero filling.

Size Exclusion Chromatography (SEC): SEC was conducted in THF at 40 °C and a flow rate of 1.0 mL/min using a SHIMADZU LC-20AD system equipped with a PSS SDV combination mediumlow (8 × 300 mm, 3 μm) column. The polyesters were dissolved in HPLC grade THF and filtered prior to analysis. Near monodispersed polystyrene standards were used to calibrate the instrument to achieve the molecular weight (M_n) and polydispersity index ($Đ$) of the polymers.

***In-situ* IR:** The switch polymerization was monitored using a Mettler-Toledo ReactIR 702L spectrometer equipped with a MCT detector and a AgX DiComp probe.

Differential Scanning Calorimeter (DSC): Glass transition temperatures (T_g) of block polymer were measured using a DSC Q100 (TA Instruments). The samples were heated from −60 °C to 200 °C at the rate of 10 °C/min under a N_2 atmosphere. Subsequently, the samples were cooled from 200 °C to −60 °C under the same condition. This cycle was repeated for three times. The T_g values were taken from the third heating curve, using the TA Universal Analysis Software. Each sample was entry for three heating/cooling cycles. To erase thermal history, glass transitions and melting endotherms are reported upon the third heating cycle.

Circular Dichroism (CD): CD spectra were recorded using a Jasco J-815 CD spectrometer. The samples were prepared by first vacuum-drying a small amount of the reaction solution to remove the toluene solvent. The residue was then dissolved in acetone, and the solution was slowly drop-cast onto a quartz slide, ensuring a uniform film formation upon solvent evaporation. CD measurements were performed under standard conditions (room temperature, wavelength range from 190 to 250 nm), and the resulting spectra were analyzed to evaluate the chiral properties of the materials.

Typical Polymerization Procedures: A typical procedure is given as follows: In a N_2-filled glovebox, 0.0115 g of CHD was weighed and dissolved in 5 mL of toluene to obtain a pre-prepared solution with a concentration of 0.02 M. Then (*S,S*)-TUC (0.020 g, 0.05 mmol, 5 equiv.) catalyst was added, followed by 0.5 mL of the CHD toluene solution, and the mixture was stirred for 10 minutes. Subsequently, *rac*-LA (0.072 g, 0.5 mmol, 50 equiv.) and TMC (0.052 g, 0.5 mmol, 50 equiv.) monomers were added sequentially, and the reaction was conducted outside the glovebox. Then the reaction mixture was stirred at 40 °C under an N_2 atmosphere in an oil bath. During polymerization, crude aliquots were taken at predetermined time intervals from the reaction mixture and characterized by ^{1}H NMR spectroscopy and SEC to determine monomer conversion and the molecular weight of the polymers. The block polymer was precipitated using cold methanol. The purified polymers were dried under vacuum for 24 h at room temperature for further analysis.

Results

Table S1. Copolymerization of *rac*-LA and TMC mediated by (*S,S*)-TUC catalyst at 40 °C in toluene.[a]

Entry	*t* [h]	*Conv.*[b] $_{\text{LA}}$ [%]	*Conv.*[b] $_{\text{TMC}}$ [%]	$M_{\text{n, theo}}$ (kg mol^{-1})[c]	$M_{\text{n, SEC}}$[d] (*Đ*) (kg mol^{-1})
1	2	18	0	1.3	3.3 (1.05)
2	4	30	0	2.2	3.9 (1.09)
4	12	48	0	3.5	7.4 (1.11)
5	24	77	10.6	6.0	9.3 (1.11)
6	48	95	19	-	- (-)
7	72	99	29	8.3	10.7 (1.10)
8	96	99	32	8.7	11.3 (1.10)
9	120	99	46	9.5	11.6 (1.16)
10	144	99	53	9.8	14.0 (1.11)
12	192	99	72	10.8	- (-)
13	288	99	89	11.6	12.0 (1.29)
14	336	99	90	11.7	10.2 (1.33)

[a] The polymerization were performed at 40 °C in toluene with the feed ratio [*rac*-LA]/[TMC]/[(*S,S*)-TUC]/[CHD] = 50/50/5/1, unless otherwise noted. [b] Determined by ^{1}H NMR analysis of the obtained samples in $CDCl_3$. [c] Determined on the basis of {(MW$_{rac\text{-LA}}$ + MW$_{\text{TMC}}$) × (Conv.% of *rac*-LA)}/{[CHD]} + {(MW$_{\text{TMC}}$) × (Conv.% of TMC)}/{[CHD]}, with units of kg/mol. [d] Determined by SEC analysis of the obtained polymer in THF using polystyrene calibration.

Table S2. Copolymerization of *rac*-LA and TMC mediated by (*S,S*)-TUC catalyst at 80 °C in toluene.[a]

Entry	*t* [h]	*Conv.*[b] $_{\text{LA}}$ [%]	*Conv.*[b] $_{\text{TMC}}$ [%]	$M_{\text{n, theo}}$ (kg mol^{-1})[c]	$M_{\text{n, SEC}}$[d] (*Đ*) (kg mol^{-1})
1	2	32	0	2.3	2.8 (1.15)
2	4	38	0	2.7	4.1 (1.11)
3	8	56	0	4.0	6.4 (1.10)
4	12	71	10	5.6	7.4 (1.11)
5	24	94	20	7.8	9.3 (1.11)
6	48	97	36	8.8	9.5 (1.18)
7	72	99	54	9.9	9.9 (1.27)
8	144	99	76	11.0	11.0 (1.29)
9	168	99	88	11.6	11.6 (1.27)
10	208	99	89	11.6	11.7 (1.30)
11	240	99	91	11.7	11.8 (1.25)
12	288	99	93	11.8	11.6 (1.49)

[a] The polymerization were performed at 80 °C in toluene with the feed ratio [*rac*-LA]/[TMC]/[(*S,S*)-TUC]/[CHD] = 50/50/5/1, unless otherwise noted. [b] Determined by ^{1}H NMR analysis of the obtained samples in $CDCl_3$. [c] Determined on the basis of {(MW$_{rac\text{-LA}}$ + MW$_{\text{TMC}}$) × (Conv.% of *rac*-LA)}/{[CHD]} + {(MW$_{\text{TMC}}$) × (Conv.% of TMC)}/{[CHD]}, with units of kg/mol. [d] Determined by SEC analysis of the obtained polymer in THF using polystyrene calibration.

Table S3. Copolymerization of *rac*-LA and TMC mediated by the (*S,S*)-TUC catalyst, initially conducted at 40 °C and subsequently increased to 80 °C after complete consumption of LA.[a]

Entry	t [h]	*Conv.*[b] LA [%]	*Conv.*[b] TMC [%]	$M_{n,\text{ theo}}$ (kg mol^{-1})[c]	$M_{n,\text{ SEC}}$ ($Đ$)[d] (kg mol^{-1})
1	8	43	0	3.1	4.5 (1.10)
2	24	77	6	5.9	8.4 (1.08)
3	48	91	17	7.4	9.5 (1.13)
4	72	99	29	8.6	10.4 (1.12)
5	96	99	32	8.8	10.8 (1.16)
6	120	99	47	9.5	11.4 (1.11)
7	144	99	53	9.8	13.5 (1.13)
8	168	99	67	10.6	10.8 (1.28)
9	192	99	71	10.7	11.5 (1.27)

[a] The polymerization were performed in toluene with the feed ratio [*rac*-LA]/[TMC]/[(*S,S*)-TUC]/[CHD] = 50/50/5/1. The reaction temperature was switched from 40 to 80 °C once the *rac*-LA conversion reached 99 %. [b] Determined by ^{1}H NMR analysis of the obtained samples in $CDCl_3$. [c] Determined on the basis of {($MW_{rac\text{-LA}}$ + MW_{TMC}) × (Conv.% of *rac*-LA)}/{[CHD]} + {(MW_{TMC}) × (Conv.% of TMC)}/{[CHD]}, with units of kg/mol. [d] Determined by SEC analysis of the obtained polymer in THF using polystyrene calibration.

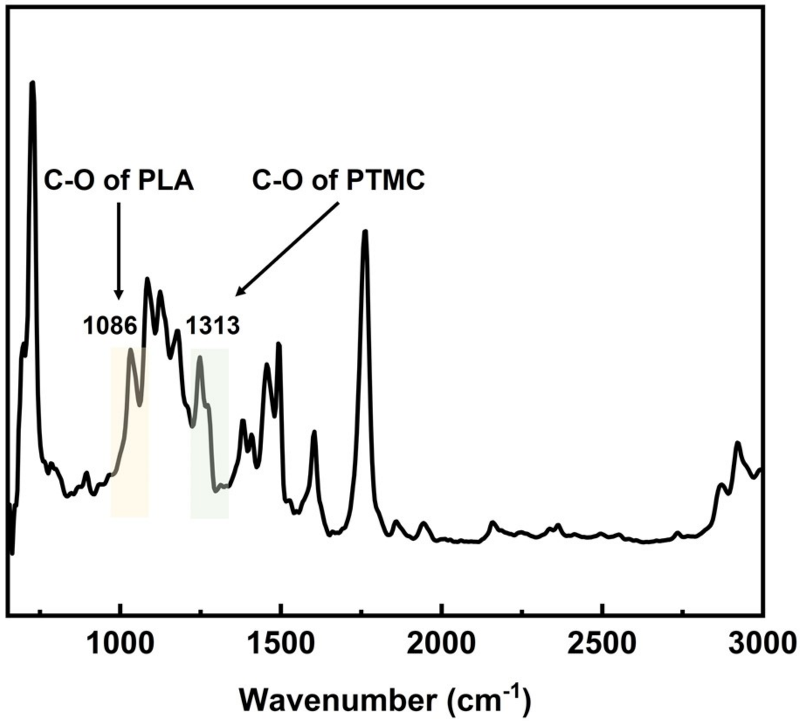


Figure S1. Infrared spectrum of the rac-LA/TMC copolymerization at 72 h (Table S1, entry 7).

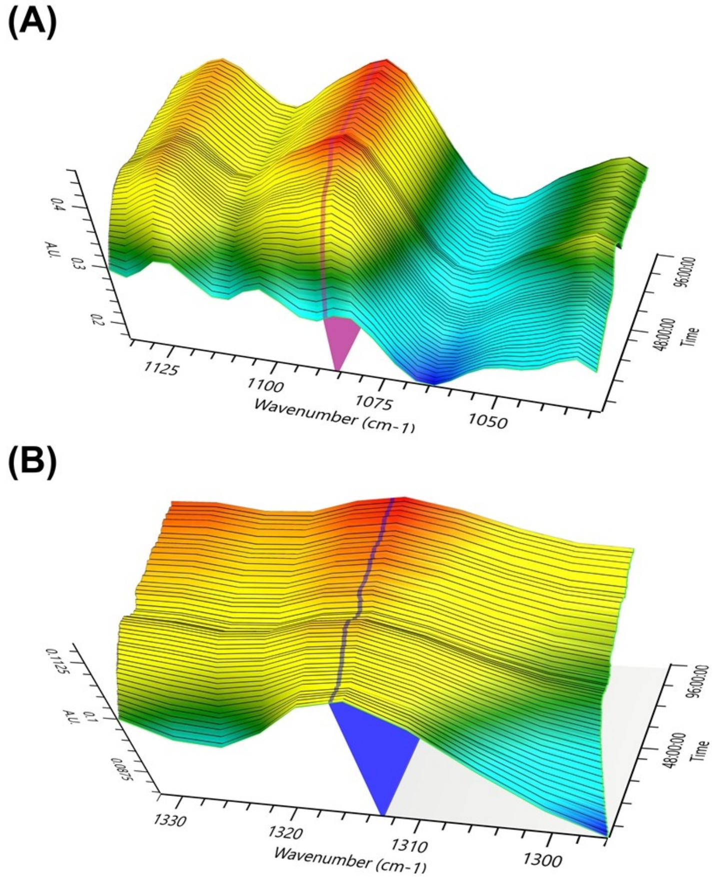


Figure S2. The *in-situ* IR curve shows the trend of (A) PLA formation at 1086 cm⁻¹ and (B) PTMC formation at 1313 cm⁻¹.

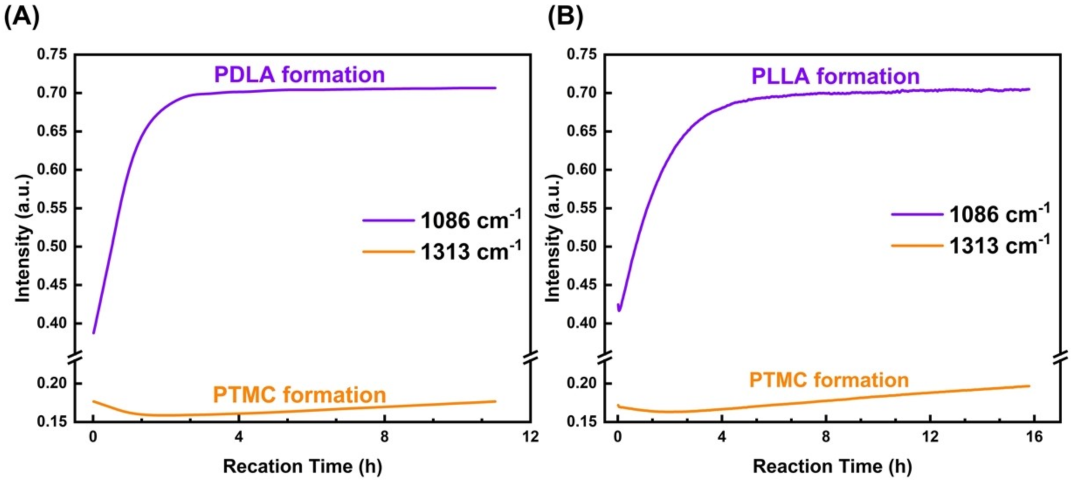
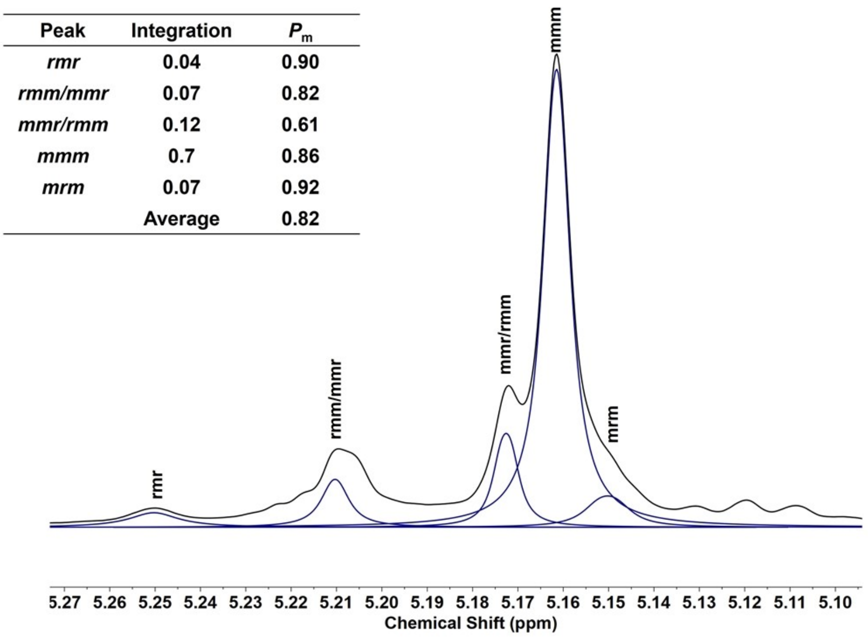


Figure S3. *In-situ* ATR-IR spectroscopy monitoring: (A) Copolymerization of D-LA/TMC. Reaction conditions: [CHD]/[(S,S)-TUC]/[D-LA]/[TMC] = 1/5/20/20, at 80 °C, in toluene. (B) Copolymerization of L-LA/TMC. Reaction conditions: [CHD]/[(S,S)-TUC]/[L-LA]/[TMC] = 1/5/20/20, at 80 °C, in toluene.



Peak	Integration	P_m
rmr	0.04	0.90
rmm/mmr	0.07	0.82
mmr/rmm	0.12	0.61
mmm	0.7	0.86
mrm	0.07	0.92
	Average	0.82

Figure S4. Homonuclear decoupled $^1H\{^1H\}$ NMR spectrum (400 MHz, $CDCl_3$) of the methine region of PLA obtained from (*S,S*)-TUC at 25 °C NMR (Table 1, entry 3).

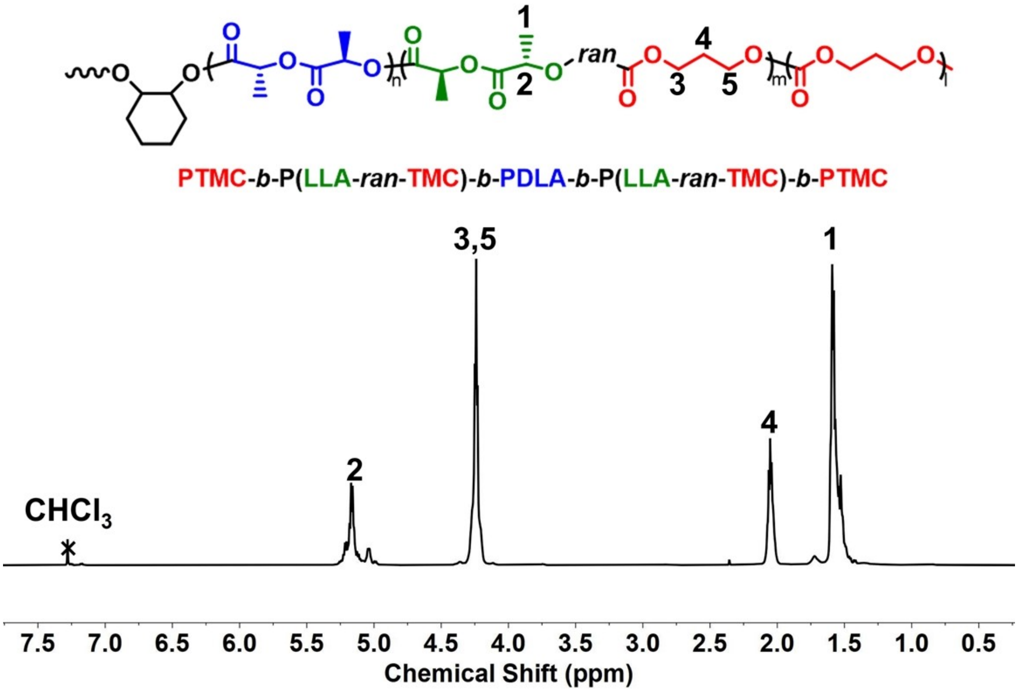


Figure S5. ^1H NMR spectrum of the block polymer PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC isolated from the mixture by precipitation, in $CDCl_3$ (Table 1, entry 3).

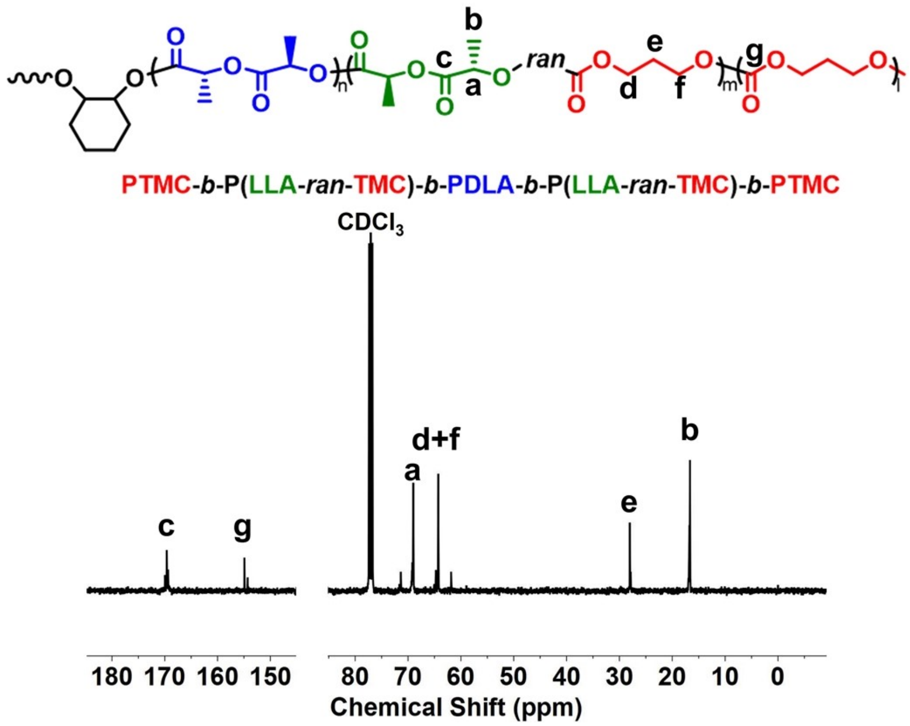


Figure S6. ^{13}C NMR spectra of the block polymer PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC copolymers isolated from the reaction mixture by precipitation, in $CDCl_3$ (Table 1, entry 3).

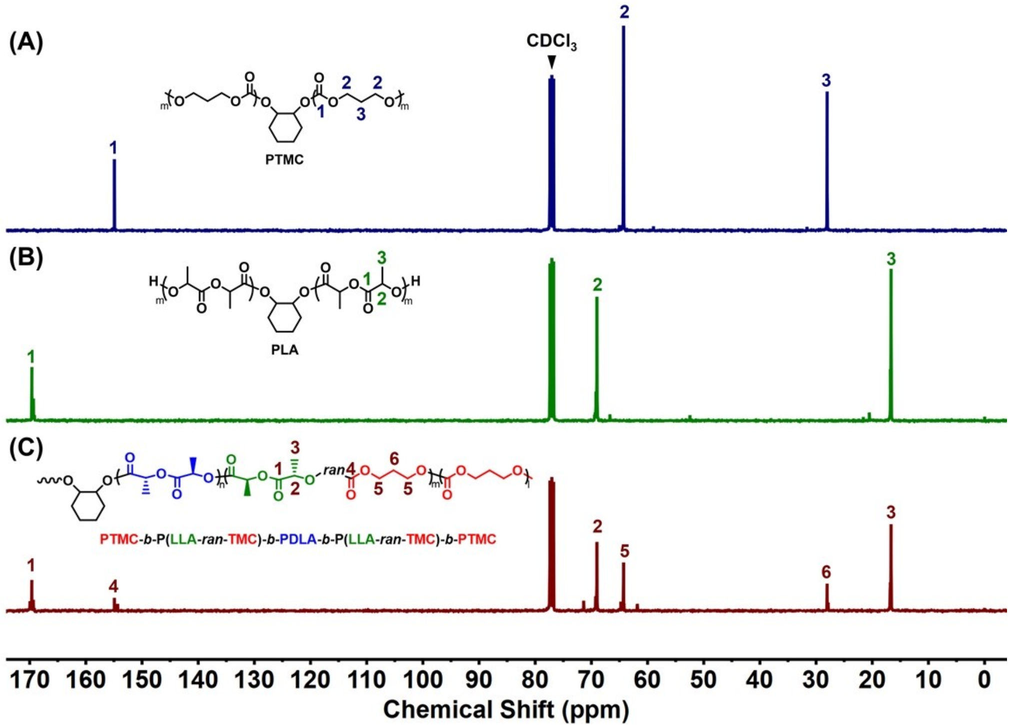


Figure S7. The comparison of the ^{13}C NMR spectra of the (A) PTMC; (B) PLA; (C) PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC, isolated from the reaction mixture by precipitation.

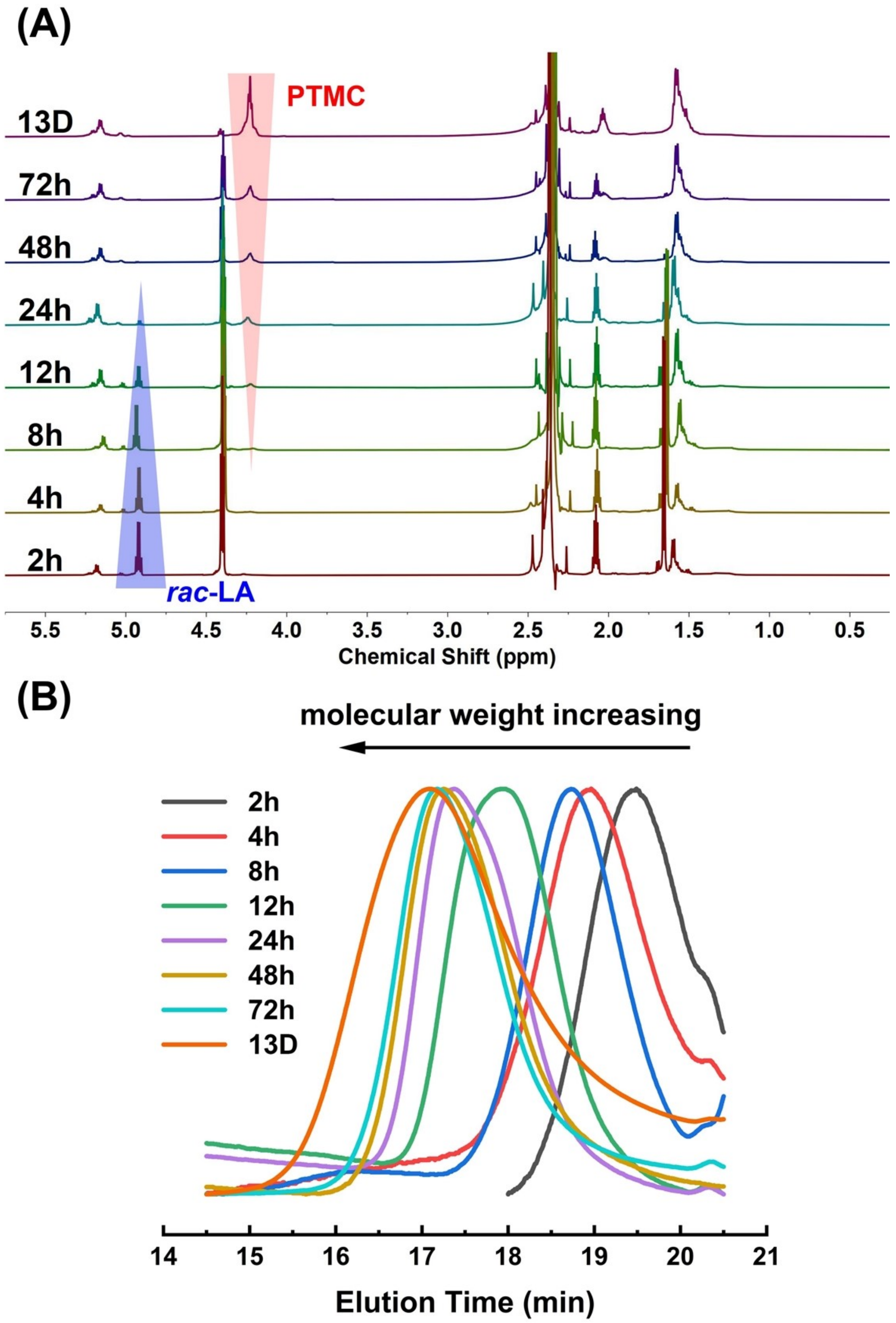


Figure S8. (A) The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of *rac*-LA and TMC and the formation of PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC in $CDCl_3$ ([*rac*-LA]$_0$/[TMC]$_0$/[(*S,S*)-TUC]/[CHD]= 50/50/5/1, at 80 °C) (B) Evolution of SEC traces over time.

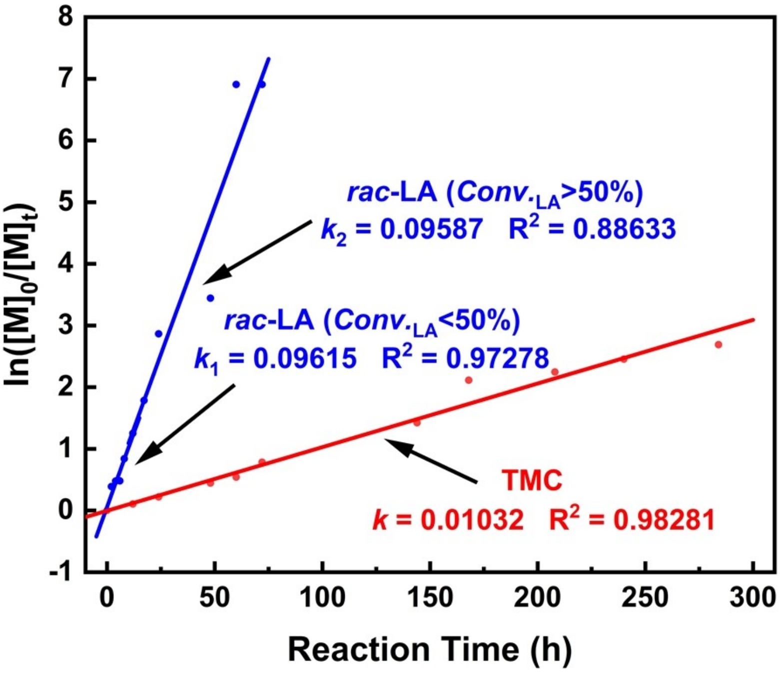
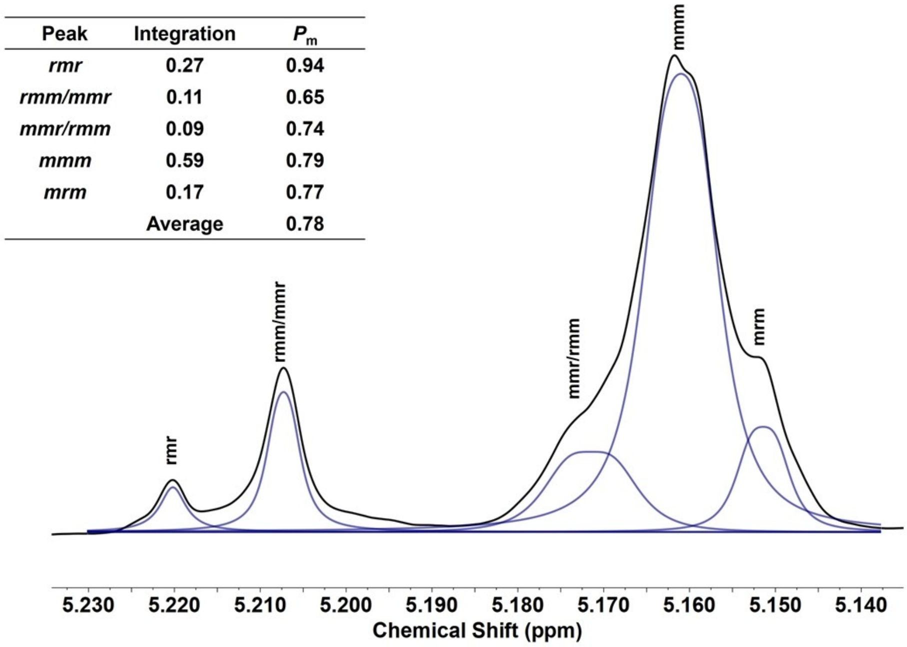


Figure S9. Kinetic plots of the copolymerization of *rac*-LA/TMC catalyzed by (*S,S*)-TUC in toluene at 80 °C in the presence of CHD as an initiator: [*rac*-LA]$_0$/[TMC]$_0$/[(*S,S*)-TUC]/[CHD] = 50/50/5/1. *rac*-LA: k_1 = 0.09615, k_2 = 0.09587, (k_1/ k_2 ≈ 1), TMC: k = 0.01032.



Peak	Integration	P_m
rmr	0.27	0.94
rmm/mmr	0.11	0.65
mmr/rmm	0.09	0.74
mmm	0.59	0.79
mrm	0.17	0.77
	Average	0.78

Figure S10. Homonuclear decoupled $^1H\{^1H\}$ NMR spectrum (400 MHz, $CDCl_3$) of the methine region of PLA obtained from (*S,S*)-TUC at 25 °C NMR (Table 1, entry 7).

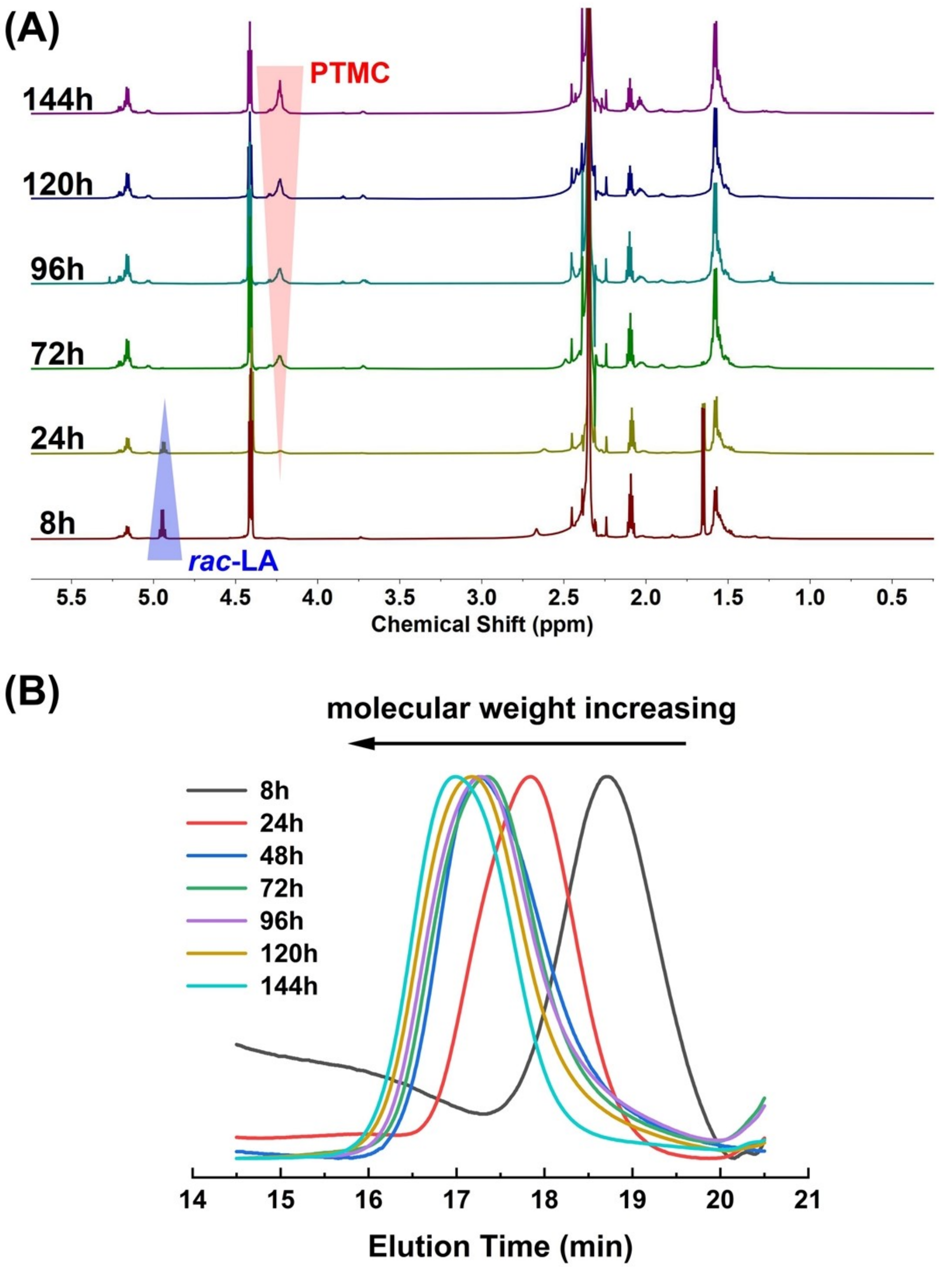


Figure S11. (A) The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of *rac*-LA and TMC and the formation of PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC in $CDCl_3$. ([*rac*-LA]$_0$/[TMC]$_0$/[(*S,S*)-TUC]/[CHD]= 50/50/5/1, The reaction temperature was initially set at 40 °C and raised to 80 °C once the *rac*-LA conversion exceeded 99%) (B) Evolution of SEC traces over time.

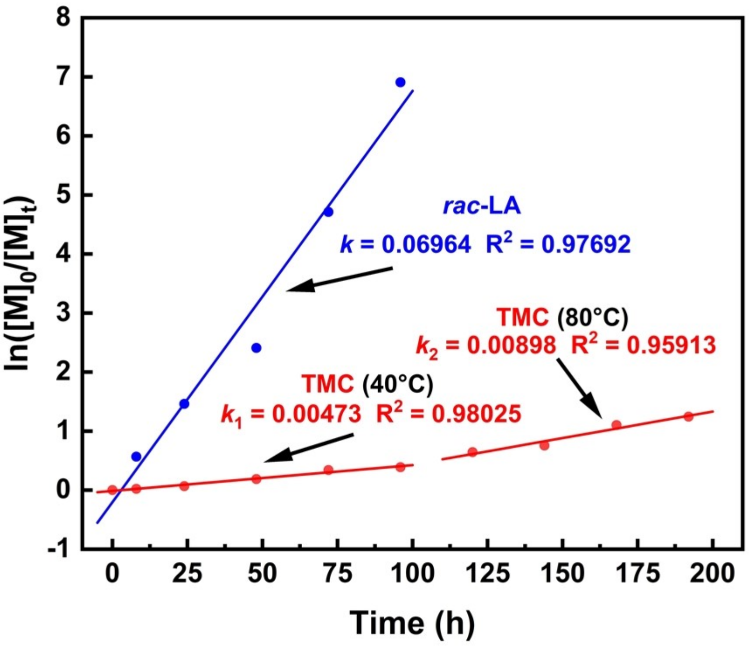
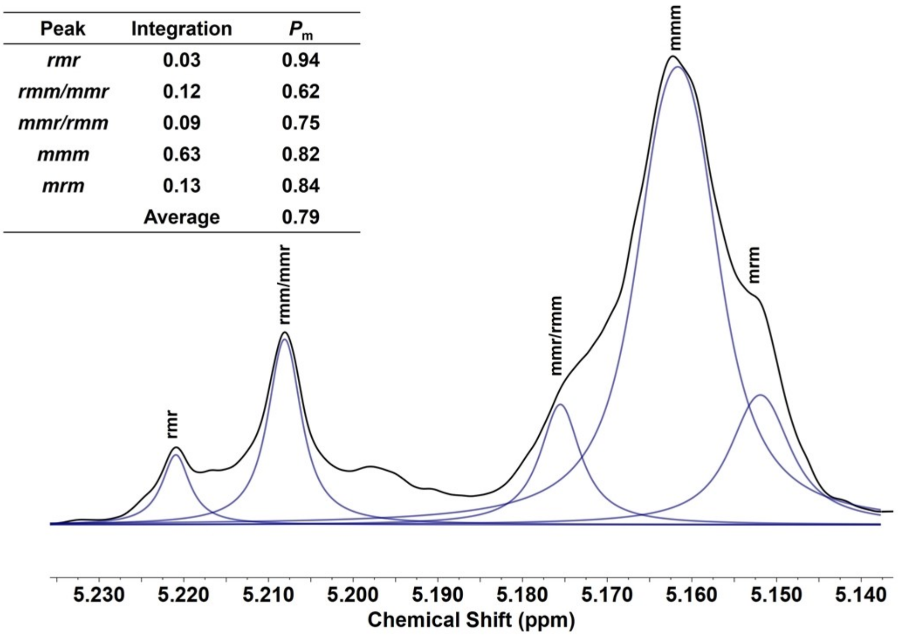


Figure S12. Kinetic plots of the copolymerization of *rac*-LA/ TMC catalyzed by (*S,S*)-TUC in toluene.in the presence of CHD as an initiator: [*rac*-LA]$_0$/[TMC]$_0$/[(*S,S*)-TUC]/[CHD] = 50/50/5/1. The reaction temperature was initially set at 40 °C and raised to 80 °C once the *rac*-LA conversion exceeded 99%. (A) *rac*-LA: *k* = 0.06964. (B) TMC: *k*$_1$ = 0.00473, *k*$_2$ = 0.00898, *k*$_2$/ *k*$_1$ ≈ 1.90.



Peak	Integration	P_m
rmr	0.03	0.94
rmm/mmr	0.12	0.62
mmr/rmm	0.09	0.75
mmm	0.63	0.82
mrm	0.13	0.84
	Average	0.79

Figure S13. Homonuclear decoupled ^{1}H {^{1}H} NMR spectrum (400 MHz, CDCl$_3$) of the methine region of PLA obtained from (*S,S*)-TUC at 25 °C (Table 1, entry 5).

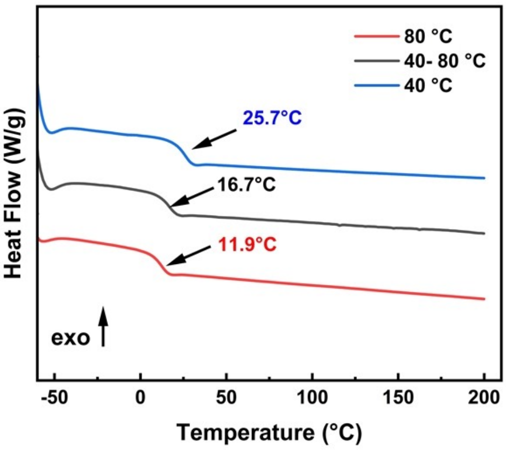


Figure S14. DSC traces of PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC obtained under different reaction temperature conditions. Blue line: consistently at 40 °C (Table 1, entry 8); black line: initially set at 40 °C and raised to 80 °C once the *rac*-LA conversion exceeded 99% (Table 1, entry 9); Red line: consistently at 80 °C (Table 1, entry 10).

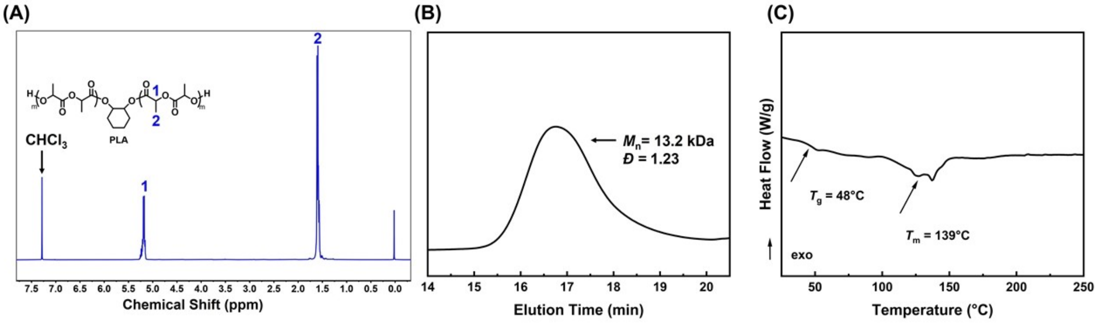


Figure S15. (A) ^{1}H NMR, (B) SEC and (C) DSC results of PDLA-*b*-PLLA synthesized by (*S,S*)-TUC in toluene at 40 °C in the presence of CHD as an initiator: [*rac*-LA]$_0$/[(*S,S*)-TUC]/[CHD] = 100/5/1.

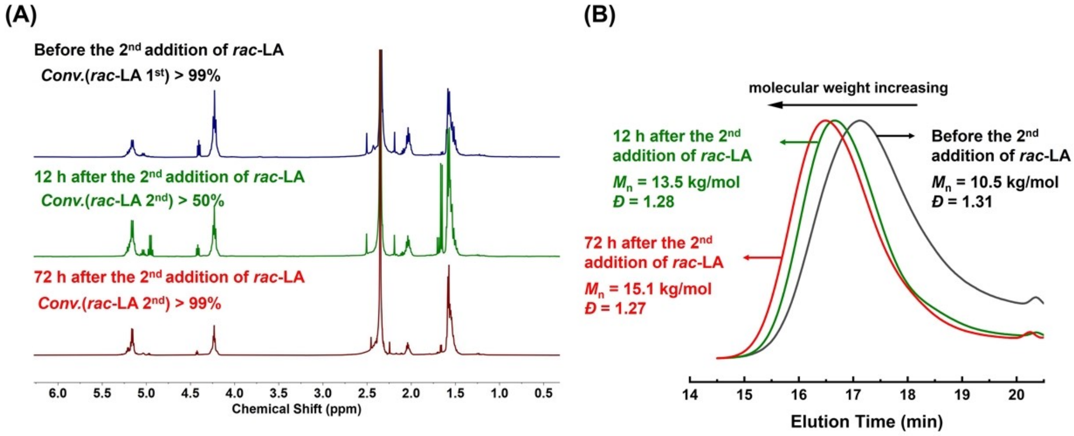


Figure S16. (A) ^{1}H NMR spectra (in $CDCl_3$) of PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC before the 2nd addition of *rac*-LA , 12 h after the 2nd addition of *rac*-LA and 72 h after the 2nd addition of *rac*-LA. [CHD]/[(*S,S*)-TUC]/[*rac*-LA 1st]/[*rac*-LA 2nd]/[TMC]= 1/5/50/50/50. (B) SEC traces of crude aliquots taken from the reaction mixture.

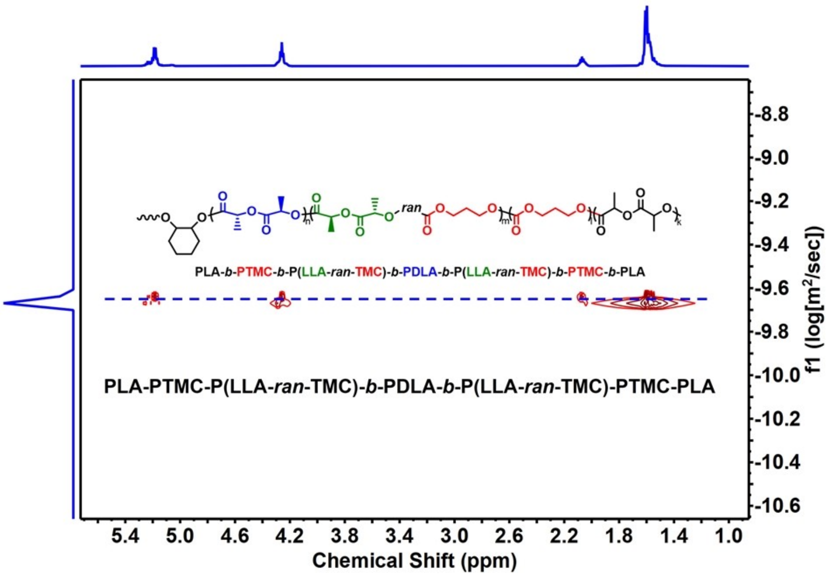


Figure S17. ^{1}H NMR DOSY spectra of PLA-*b*-PTMC-*b*-P(LLA-*ran*-TMC)-*b*-PDLA-*b*-P(LLA-*ran*-TMC)-*b*-PTMC-*b*-PLA heptablock copolyesters (Table 1, entry 11).

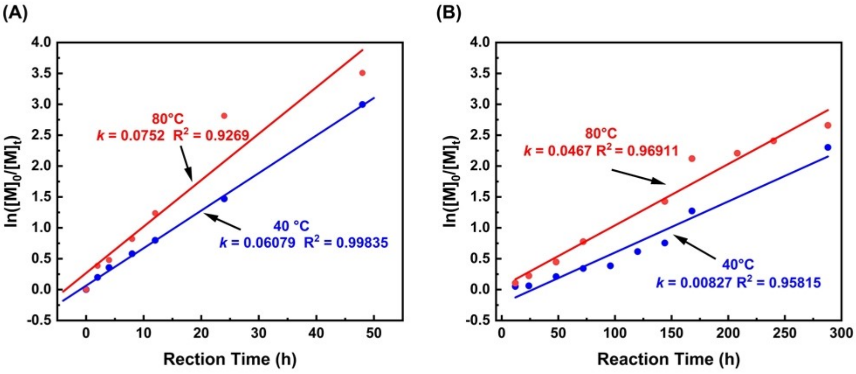


Figure S18. Kinetic plots of the copolymerization of *rac*-LA/TMC catalyzed by (*S,S*)-TUC in toluene at different temperatures in the presence of CHD as an initiator: [*rac*-LA]$_0$/[TMC]$_0$/[(*S,S*)-TUC]/[CHD] = 50/50/5/1. (A) *rac*-LA (Red line: 80 °C, Blue line: 40 °C) (B) TMC (Red line: 80 °C, Blue line: 40 °C).

Table S4. Copolymerization of D-LA and PA/PO mediated by (*S,S*)-TUC catalyst systems [a]

Entry	*t* [h]	*Conv.*[b] $_{\text{D-LA}}$[%]	*Conv.*[b] $_{\text{PA}}$[%]
1	24	0	45
2	44	8	99
3	72	73	99
4	96	95	99
5	120	94	99
6	144	96	99

[a] The polymerization were performed at 80 °C in toluene with the feed ratio [D-LA]/[PA]/[PO]/[(*S,S*)-TUC]/[CHD] = 200/100/200/5/1, unless otherwise noted. [b] Determined by ^{1}H NMR analysis of the obtained samples in $CDCl_3$.

Table S5. Copolymerization of L-LA and PA/PO mediated by (*S,S*)-TUC catalyst systems [a]

Entry	*t* [h]	*Conv.*[b] $_{\text{L-LA}}$[%]	*Conv.*[b] $_{\text{PA}}$[%]
1	24	13	39
2	44	63	99
3	68	96	99
4	76	97	99

[a] The polymerization were performed at 80 °C in toluene with the feed ratio [L-LA]/[PA]/[PO]/[(*S,S*)-TUC]/[CHD] = 200/100/200/5/1, unless otherwise noted. [b] Determined by ^{1}H NMR analysis of the obtained samples in $CDCl_3$.

Table S6. Copolymerization of *rac*-LA and PA/PO mediated by (*S,S*)-TUC catalyst systems [a]

Entry	*t* [h]	*Conv.*[b] $_{\text{LA}}$[%]	*Conv.*[b] $_{\text{PA}}$[%]
1	52	6	50
2	96	7	85
3	216	43	99
4	264	75	99
5	312	80	99
6	360	88	99

[a] The polymerization were performed at 80 °C in toluene with the feed ratio [*rac*-LA]/[PA]/[PO]/[(*S,S*)-TUC]/[CHD] = 200/100/200/5/1, unless otherwise noted. [b] Determined by ^{1}H NMR analysis of the obtained samples in $CDCl_3$.

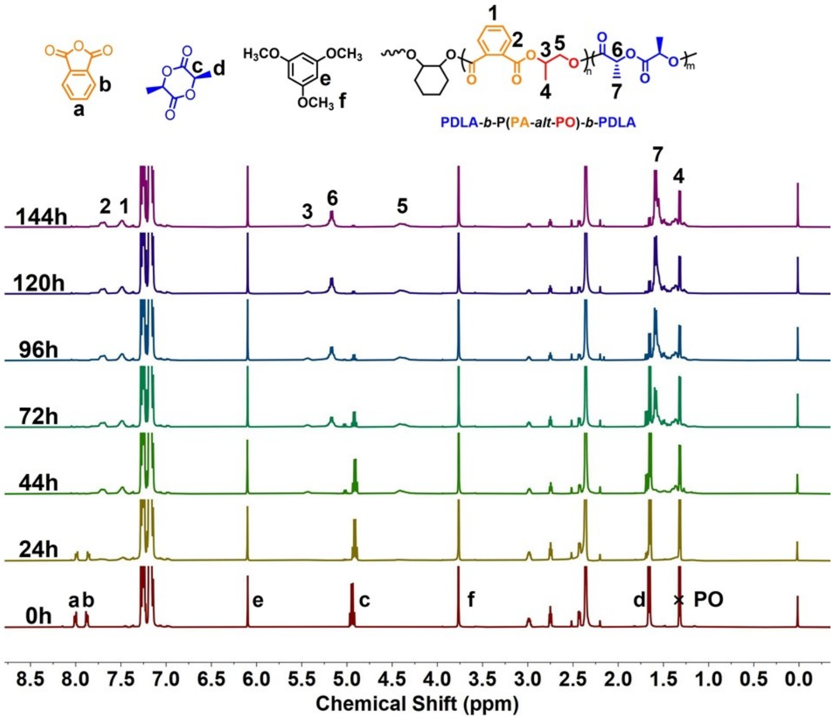


Figure S19. The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of D-LA/PA/PO and the formation of PDLA-*b*-P(PA-*alt*-PO)-*b*-PDLA in $CDCl_3$ ($[\text{D-LA}]_0/[\text{PA}]_0/[\text{PO}]_0/[(S,S)\text{-TUC}]/[\text{CHD}]$ = 200/100/200/5/1, at 80 °C in toluene). 1,3,5-Trimethoxybenzene was used as an internal reference.

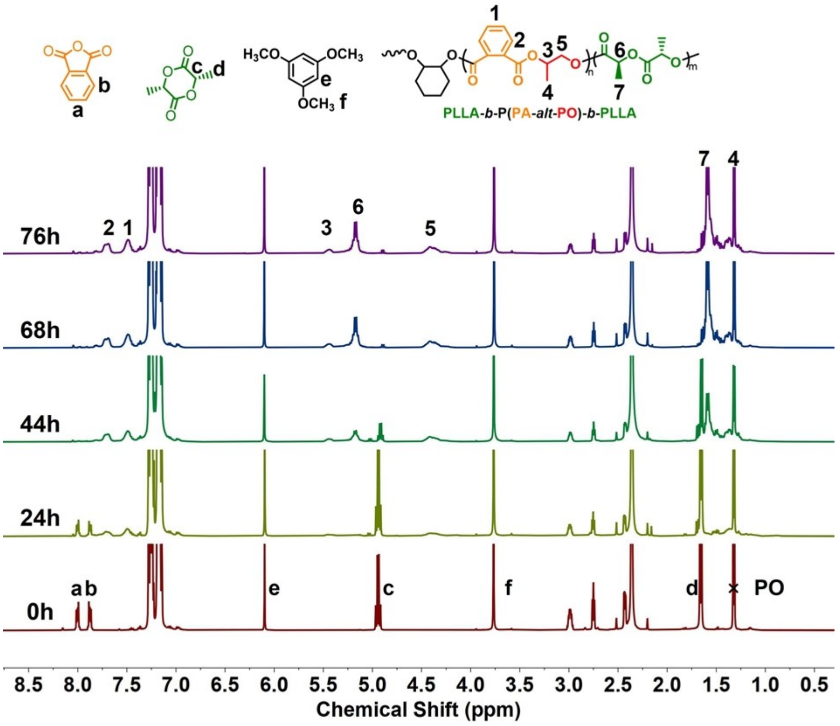


Figure S20. (A) The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of L-LA/PA/PO and the formation of PLLA-*b*-P(PA-*alt*-PO)-*b*-PLLA in $CDCl_3$ ($[\text{L-LA}]_0/[\text{PA}]_0/[\text{PO}]_0/[(S,S)\text{-TUC}]/[\text{CHD}]$ = 200/100/200/5/1, at 80 °C in toluene). 1,3,5-Trimethoxybenzene was used as an internal reference.

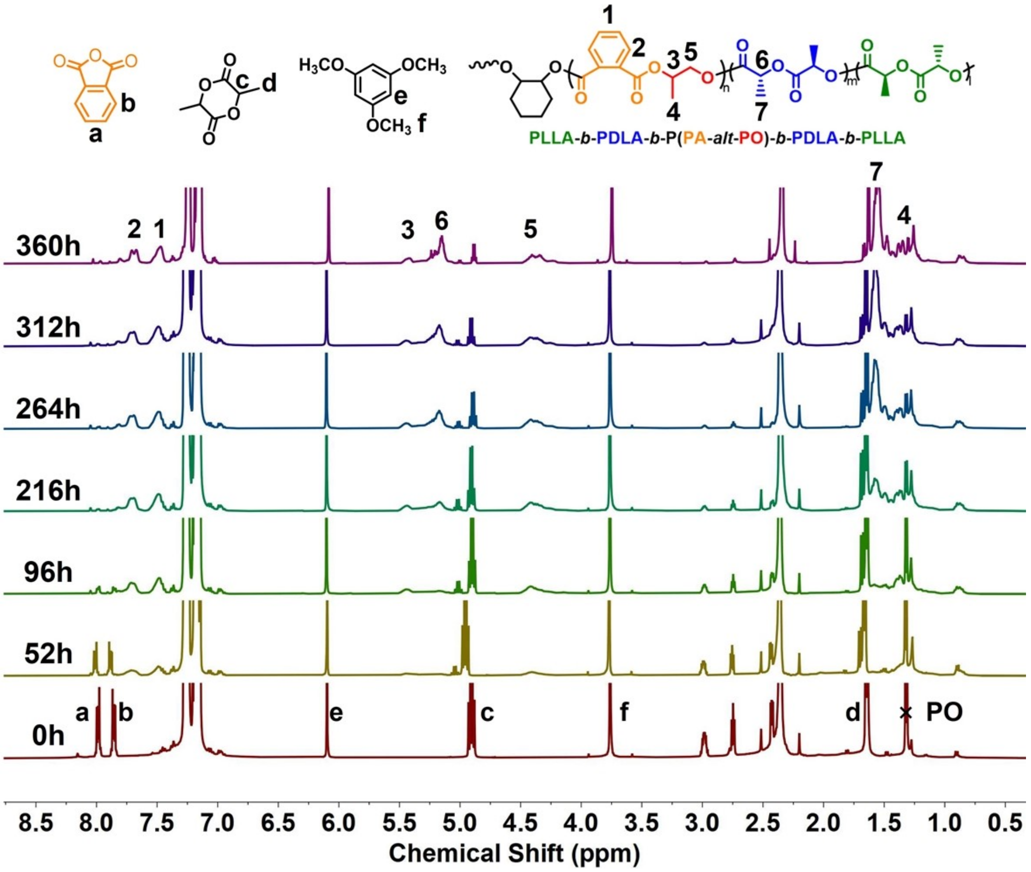


Figure S21. (A) The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of *rac*-LA/PA/PO and the formation of PLLA-*b*-PDLA-*b*-P(PA-*alt*-PO)-*b*-PDLA-*b*-PLLA in $CDCl_3$ ([*rac*-LA]$_0$/[PA]$_0$/[PO]$_0$/[(*S,S*)-TUC]/[CHD] = 200/100/200/5/1, at 80 °C in toluene). 1,3,5-Trimethoxybenzene was used as an internal reference.

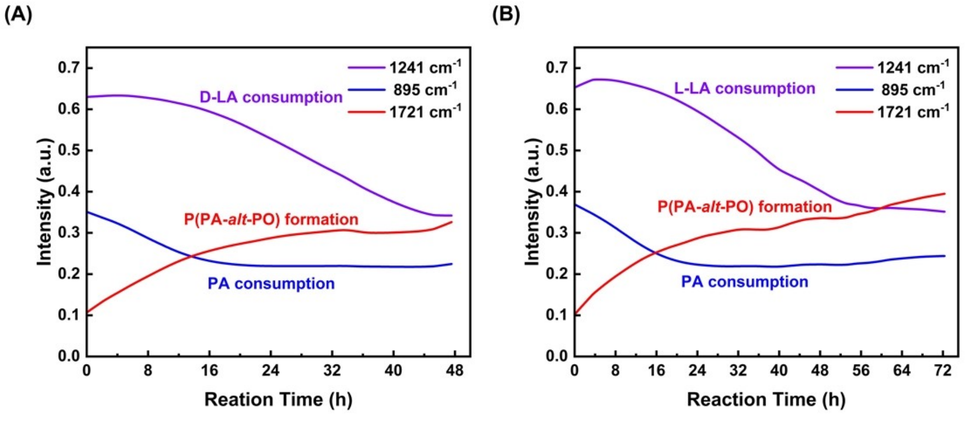
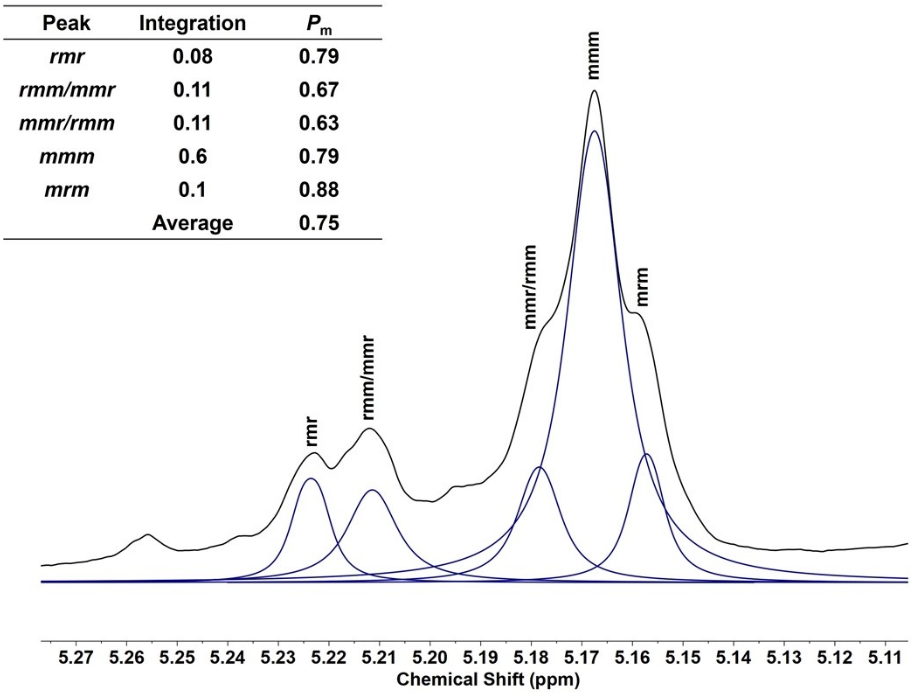


Figure S22. *In-situ* ATR-IR spectroscopy monitoring: (A) Copolymerization of PA/PO/D-LA. Reaction conditions: [CHD]/[(*S,S*)-TUC]/[PA]$_0$/[PO]$_0$/[D-LA]$_0$ = 1/5/100/200/200, 80 °C, and toluene as the solvent. (B) Copolymerization of /PA/PO/L-LA. Reaction conditions: [CHD]/[(*S,S*)-TUC]/[PA]$_0$/[PO]$_0$/[L-LA]$_0$ = 1/5/100/200/200, 80 °C, and toluene as the solvent.



Peak	Integration	P_m
rmr	0.08	0.79
rmm/mmr	0.11	0.67
mmr/rmm	0.11	0.63
mmm	0.6	0.79
mrm	0.1	0.88
	Average	0.75

Figure S23. Homonuclear decoupled ^{1}H {^{1}H} NMR spectrum (400 MHz, $CDCl_3$) of the methine region of PLA obtained from (*S,S*)-TUC at 25 °C (Table S6, entry 6).

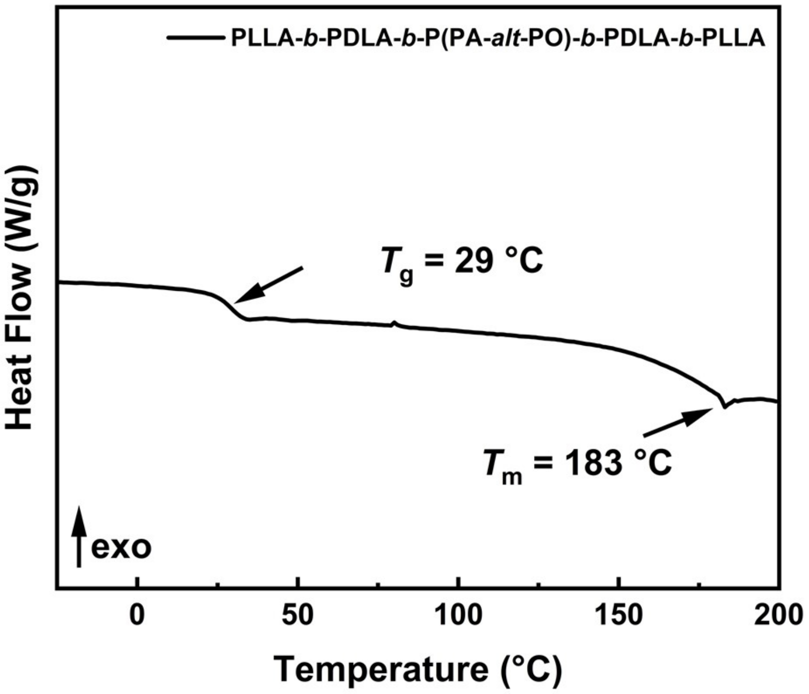


Figure S24. DSC traces of PLLA-*b*-PDLA-*b*-P(PA-*alt*-PO)-*b*-PDLA-*b*-PLLA (Table S6, entry 6).

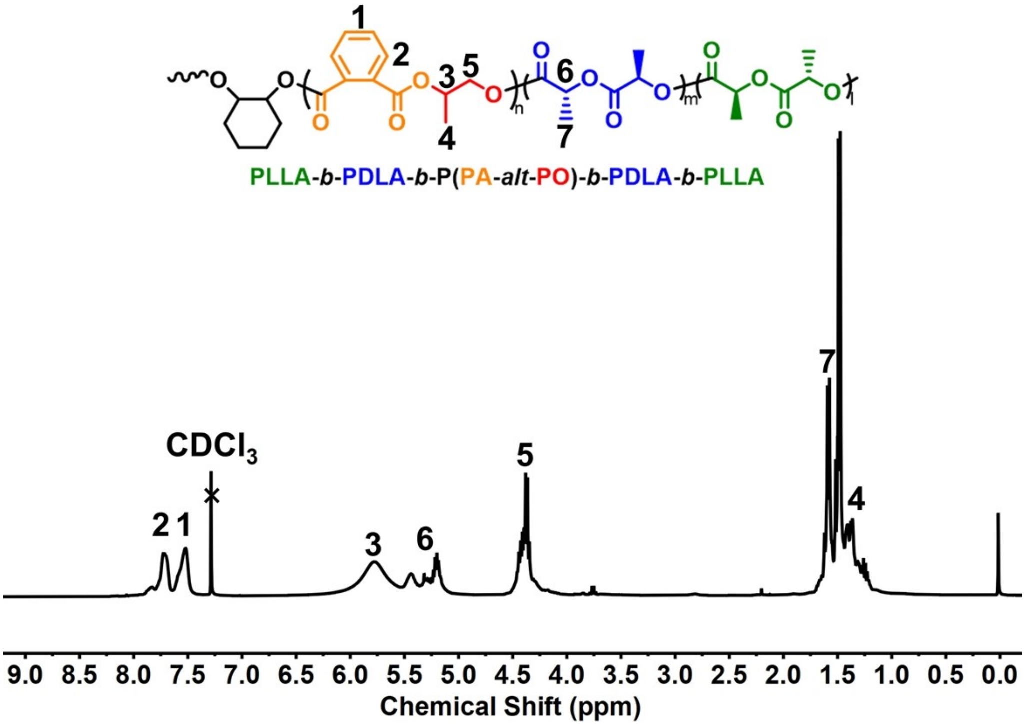


Figure S25. ^{1}H NMR spectrum of the block polymer PLLA-*b*-PDLA-*b*-P(PA-*alt*-PO)-*b*-PDLA-*b*-PLLA isolated from the mixture by precipitation, in CDCl$_3$ (Table S6, entry 6).

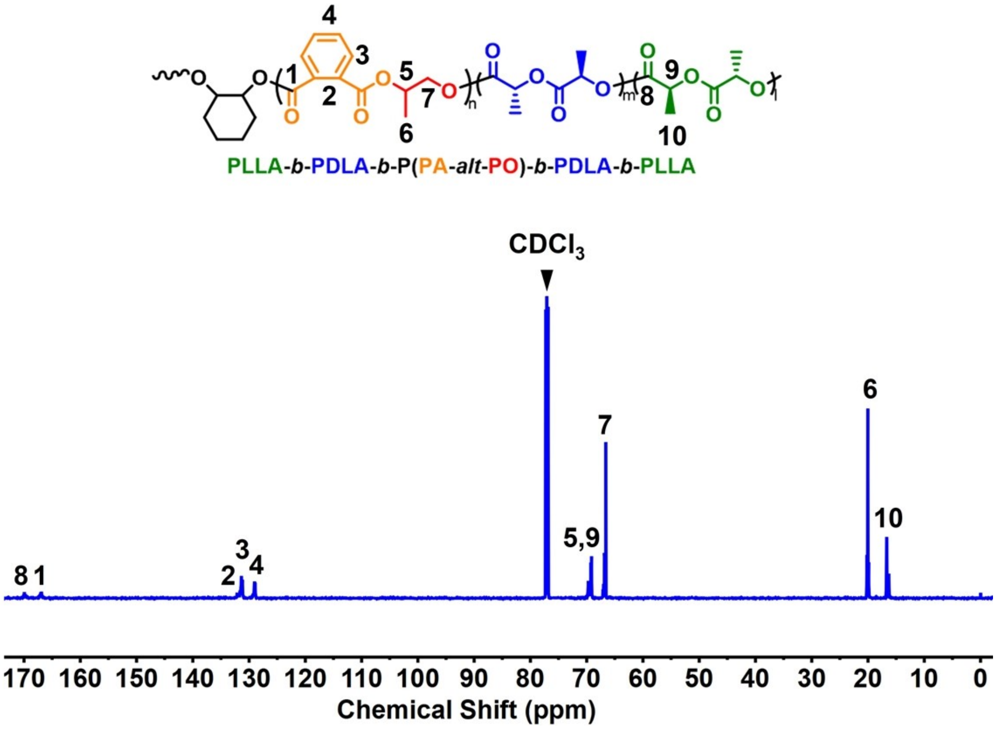


Figure S26. ^{13}C NMR spectra of the block polymer PLLA-*b*-PDLA-*b*-P(PA-*alt*-PO)-*b*-PDLA-*b*-PLLA isolated from the mixture by precipitation, in CDCl$_3$ (Table S6, entry 6).

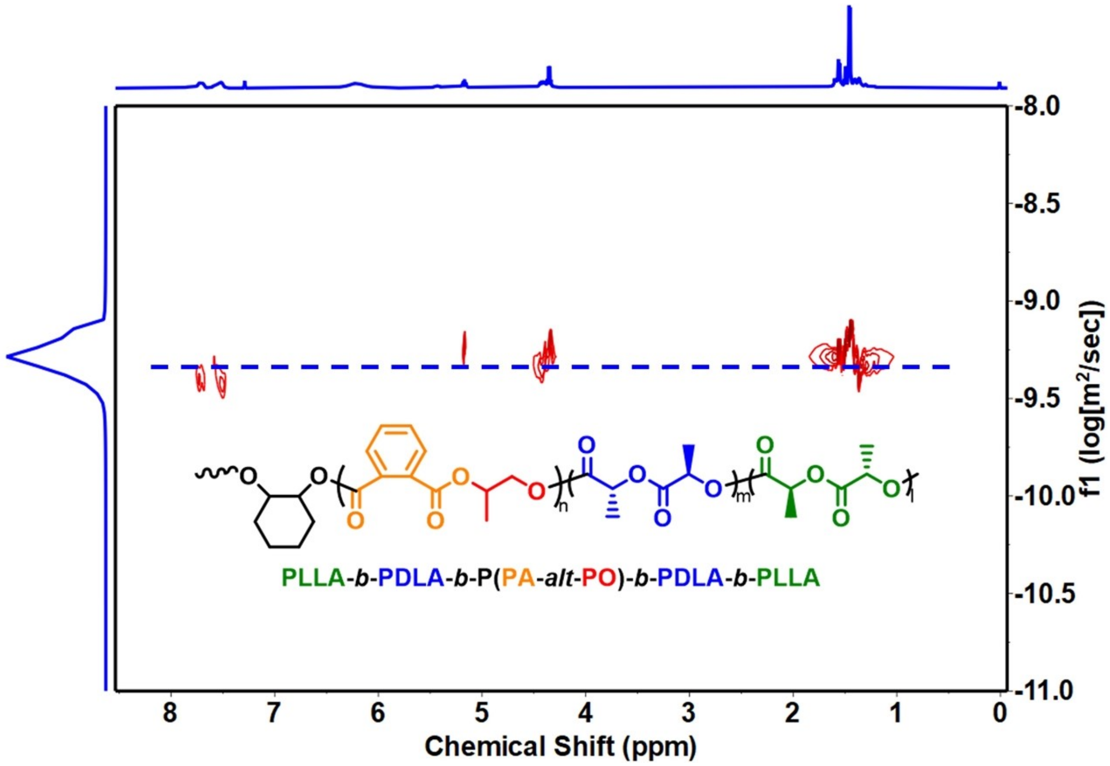


Figure S27. ^{1}H NMR DOSY spectra of PLLA-*b*-PDLA-*b*-P(PA-*alt*-PO)-*b*-PDLA-*b*-PLLA pentablock copolyesters (Table S6, entry 6).

Abbreviations

CHD	*trans*-cyclohexane-1,2-diol
CHO	cyclohexene oxide
Đ	polydispersity index
DOSY	^{1}H diffusion-ordered NMR spectrum
D-LA	D-lactide
L-LA	L-lactide
M_n	number average molar mass
M_w	weight average molar mass
NMR	nuclear magnetic resonance
PA	phthalic anhydride
PLA	polylactic acid
P_m	Probability of forming meso dyads
PO	propylene oxide
ROCOP	ring opening copolymerization
ROP	ring opening polymerization
SA	succinic anhydride
SEC	size exclusion chromatography
T_g	glass transition temperature
T_m	melting temperature
TMC	trimethylene carbonate1,3-Dioxan-2-one