Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Self-Switchable Polymerization Catalysis from Monomer Mixtures: Using a Metal-Free Commercial Thiourea Catalyst to Deliver Block Polyesters

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Experimental Details

Materials

All reagents were purchased from Macklin and used as received unless otherwise specified. Cyclohexene oxide (CHO, 98%), Propylene oxide (PO, 98%), allyl glycidyl ether (AGE, 98%), styrene oxide (SO, 98%), ε-caprolactone (*ε*-CL, 98 %), δ-valerolactone (*δ*-VL, 98%) were distilled over CaH_2 under reduced pressure and stored under nitrogen atmosphere. Phthalic anhydride (PA, 99%), 5-norbornene-2,3-dicarboxylic anhydride (NA, 95%), 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 inertatmosphere. PPNCl ([PPN]=bis(triphenylphosphine) iminium, 96%) was recrystallized from chloroform and diethyl ether. The purity of all materials were 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.

Fourier Transform Infrared Spectroscopy (FTIR): The FTIR spectra of block polymer films were obtained using a Thermo Scientific Nicolet iS20 Fourier Transform Infrared Spectrometer and the transmittance mode was used. The spectra were recorded after 32 scans in a range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS): The MALDI-TOF MS were recorded on Bruker rapiflex MALDI Tissuetyper. The polymer sample in THF (10 mg/mL), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), THF as matrix (10 mg/mL) and sodium trifluoroacetate in methanol (1 mg/mL) were mixed in a 10:1:1 volume ratio, and then 1 µL of mixed solution was spotted onto the sample plate before being air-dried.

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 −70 °C to 100 °C at the rate of 10 °C/min under a N_2 atmosphere. Subsequently, the samples were cooled from 100 °C to −70 °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.

Thermogravimetric Analyses (TGA): Thermogravimetric analyses (TGA) were performed on a TGA 5500 (TA Instruments) apparatus under a N_2 atmosphere at the heating rate of 10 °C/min from 30 °C to 1000 °C.

Tensile Tests: Dumbbell-shaped sample bars were prepared from the cross-linking film (35 mm in length, 2.0 mm in gauge width as described in the standard, ISO 527-2-2002) using a ZS-405 Punch with a cutting blade. The mechanical properties of cross-linking films were measured on an CR-10 (Transcell) electronic universal testing machine at ambient temperature with a cross-head speed of 10 mm/min according to the standard GB/T 1040.3-2006. The results were analyzed using EVOTest software. Each value was reported as the average of three samples with confidence limits.

Synthesis the 1,3-Bis[3,5-bis(trifluoromethyl)phenyl]thiourea [TU]

To a mixture of dry methanol (3 mL) and 3,5-bis(trifluoromethyl) aniline (0.4580 g, 2.000 mmol) was added the solution of 3,5-bis(trifluorophenyl)phenyl isothiocyanate (0.5400 g, 2.000 mmol) in 2 mL DCM, and the resulting mixture was stirred at room temperature. After 30 min, the reaction mixture was concentrated in vacuum. The white solid product was purified by recrystallization from dry *n*-hexane/DCM. Then the product was dried under vacuum for 48 h at 50 °C (0.8900 g, yield: 89%). ^{1}H NMR (δ in $CDCl_3$, ppm): 7.87 (s, -N*H*), 8.21 (s, -NHCC*H*C-), 10.66 (s, -CF_3CC*H*CCF_3-).

Typical Polymerization Procedures

A typical procedure is given as follows: In an N_2-filled glovebox, TU (0.006300 g, 0.0125 mmol, 1 equiv.), PPNCl (0.007100 g, 0.01250 mmol, 1 equiv.), CHD (0.002900 g, 0.02500 mmol, 2 equiv.), AGE (1.141 g, 10.00 mmol, 800 equiv.) PA (0.1851 g, 0.6250 mmol, 100 equiv.), *ε*-CL (0.1427 g, 1.125 mmol, 200 equiv.) were placed in an oven-dried reaction vessel with a magnetic stir bar. Then the reaction mixture was stirred at 110 °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.

Transesterification

Block polyester (138.8 mg, 10.00 μmol, M_n = 13.88 kg/mol, 1 equiv.), TBD (2.800 mg, 20.00 μmol, 2 equiv.) were dissolved in 0.55 mL of toluene-d_8 in an oven-dried tube equipped with a magnetic stir. Then the tube was placed in a heating block at 60 °C. After 48 h, the reaction mixture was characterized by ^{13}C NMR spectroscopy.

Preparation of Multi-block Polymer Thermosets

A typical procedure is given as follows: In an N_2-filled glovebox, TU (6.300 mg, 12.50 μmol, 1 equiv.), PPNCl (7.100 mg, 12.50 μmmol, 1 equiv.), CHD (2.900 mg, 25.00 μmol, 2 equiv.), AGE (1.141 g, 10.00 mmol, 800 equiv.) PA (0.1851 g, 0.6250 mmol, 100 equiv.), and *ε*-CL (0.1427 g, 1.125 mmol, 200 equiv.) were placed in an oven-dried reaction vessel with a magnetic stir bar. Then the reaction mixture was stirred at 110 °C under an N_2 atmosphere in an oil bath for 3 h, resulting in the formation of triblock polymer. After complete conversion, the vessel was cooled to room temperature and transferred into the glovebox. PA (0.1851 g, 0.6250 mmol, 100 equiv.) and PA (0.1851 g, 0.6250 mmol, 100 equiv.)/*ε*-CL (0.1427 g, 1.125 mmol, 200 equiv.) were added into the vessel seperatly to produced PAGPE-*b*-PCL-*b*-PAGPE-*b*-PCL-*b*-PAGPE (~ 30 min) and PCL-*b*-PAGPE-*b*-PCL-*b*-PAGPE-*b*-PCL-*b*-PAGPE-*b*-PCL (~ 3 h). All the block polymer was precipitated using cold methanol. The purified polymers were dried under vacuum for 24 h at room temperature.

The multi-block polymer thermosets were prepared by solvent-cast method. Firstly, polyester (2 mmol) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 4% molar fraction of alkene groups of AGE moiet) were added into 5 mL DCM, the mixture was stirred for 30 min in a dark box, resulting in a yellow solution. Then, the mixture was poured into a Teflon mold. The solvent was slowly evaporated, in the fume hood, at room temperature for 1 day. Then the molds were irradiated under a UV lamp (365 nm, 10 W) for 2 hours and dried in vacuum oven for 2 days.

Results

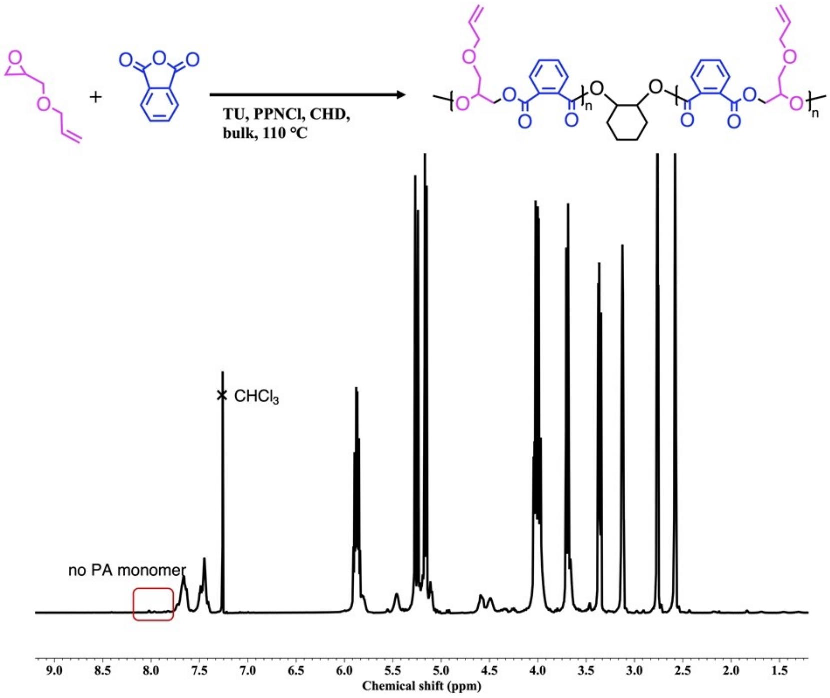

Figure S1. The ^{1}H NMR spectrum of AGE, PA ring-opening polymerization with TU/PPNCl as catalyst, CHD as CTA (in $CDCl_3$, entry 2 in Table 1). PA almost completely converted in 30 min. (Reaction conditions: AGE / PA / TU / PPNCl / CHD = 800 : 100 : 1 : 1 : 2, 110 °C, 30 min.)

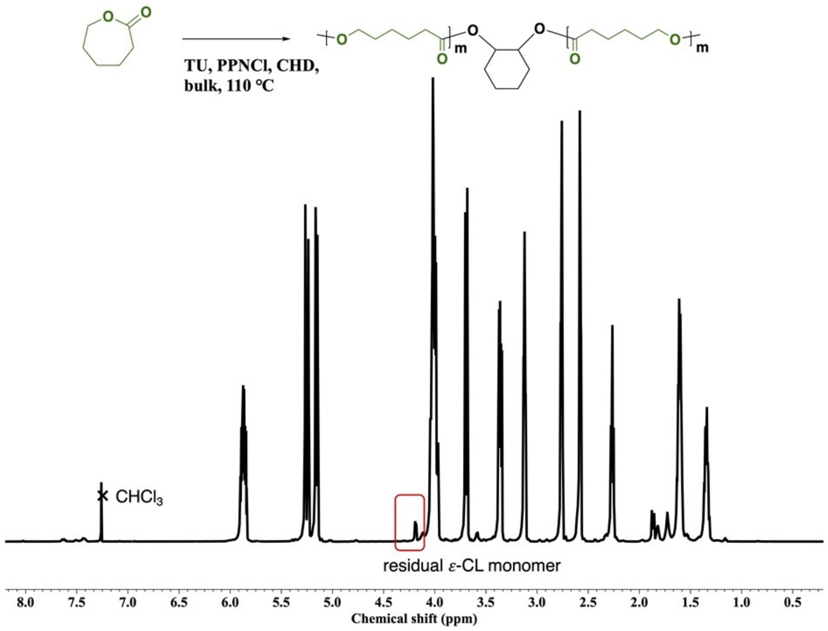

Figure S2. The ^{1}H NMR spectrum of ε-CL ring-opening polymerization with TU/PPNCl as catalyst, CHD as CTA (in $CDCl_3$, entry 3 in Table 1). After 3 hours, only a few ε-CL monomers remained. (Reaction conditions: AGE / ε-CL / TU / PPNCl / CHD = 800 : 200 : 1 : 1 : 2, 110 ℃, 180 min.)

End group analysis by ^{31}P NMR spectroscopy

^{31}P NMR spectroscopy was used to monitor the PAGPE polymer end groups.[1] The polymers were reacted excess 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphopholane and bisphenol A was used as an internal reference.

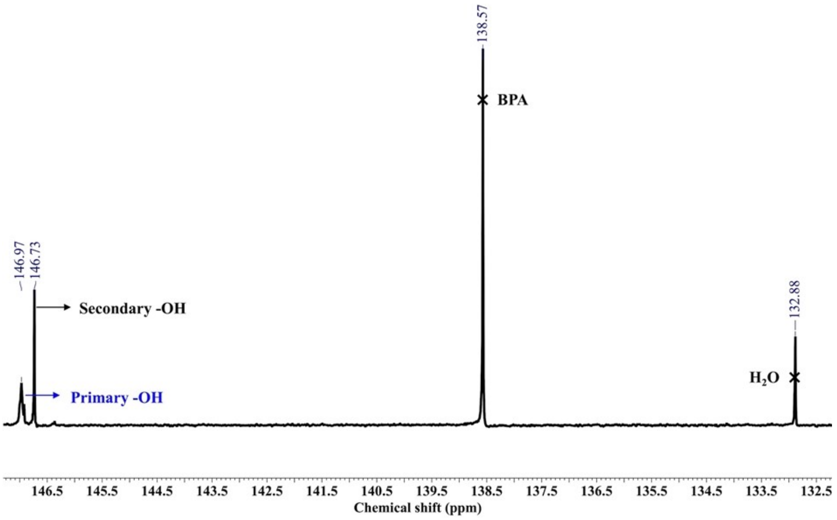

Figure S3. ^{31}P NMR spectrum ($CDCl_3$) of PAPGE after being reacted with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphopholane (using bisphenol A as internal reference). The signals at 146.97 and 146.73 ppm are attributed to primary and secondary hydroxyl groups of PAPGE polymer chain end, respectively.

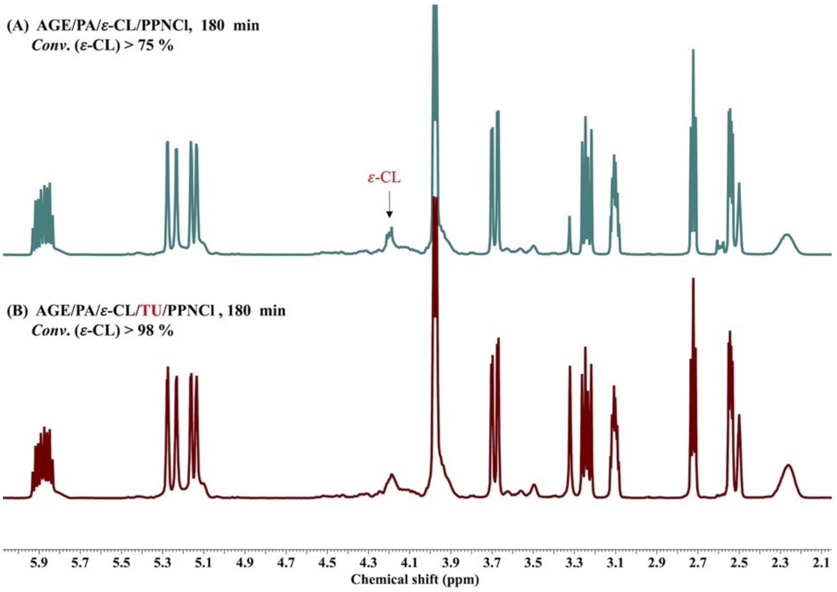

Figure S4. ^{1}H NMR spectra of crude aliquots withdraw from the reaction system for monitoring the conversion of CL within ~ 30 min: (A) AGE/PA/CL/PPNCl (entry 2 in Table S1); (B) AGE/PA/CL/TU/PPNCl (entry 3 in Table 1).

Table S1 Switchable polymerization of AGE, PA and ε-CL by TU or PPNCl binary catalysts[a]

Entry	[AGE]/[PA]/[ε-CL]/ [CHD]/[PPNCl]/[TU]	t [min]	T [°C]	Conv.[b] [%] PA	Conv.[b] [%] ε-CL	$M_{n,\ theo}$[c] (kg/mol)	$M_{n,\ SEC}$[d] ($Đ$) (kg/mol)
1	800/100/0/2/0/1	180	110	0	—	—	—
2	800/100/0/2/1/0	30	110	>99	—	8.6	2.0(1.54)
3	800/100/200/2/1/0	180	110	>99	>75	14.3	5.1 (1.84)

[a] Polymerization conditions: in the bulk under N_2 atmosphere. [b] Determined by ^{1}H NMR analysis of the obtained polymer in $CDCl_3$ or DMSO-d_6. [c] Determined on the basis of {(MW_{PA}+MW_{AGE}) × (Conv.% of PA)}/[CHD + PPNCl] + {($MW_{ε\text{-}CL}$) × (Conv.% of ε-CL)}/[CHD + PPNCl]. [d] Determined by SEC analysis of the obtained polymer in THF using polystyrene calibration.

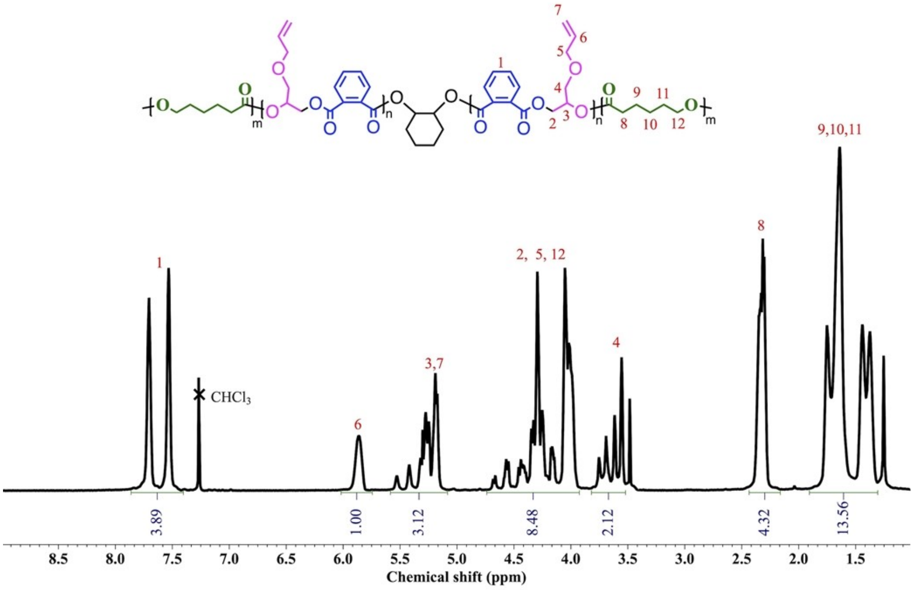

Figure S5 ^{1}H NMR spectrum of the isolated block polymer PCL-*b*-PAPGE-*b*-PCL isolated from the mixture by precipitation, in $CDCl_3$.

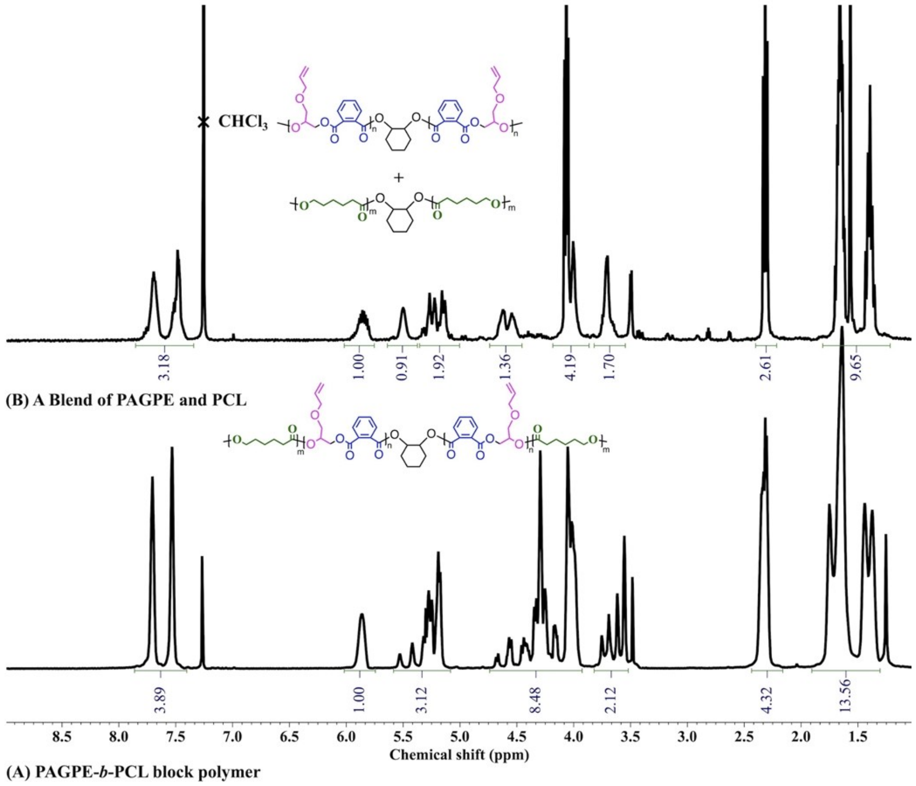

Figure S6. The comparison of the ^{1}H NMR spectra of the resultant PCL-*b*-PAPGE-*b*-PCL and the mixture of PAPGE and PCL homopolymer, in CDCl$_3$.

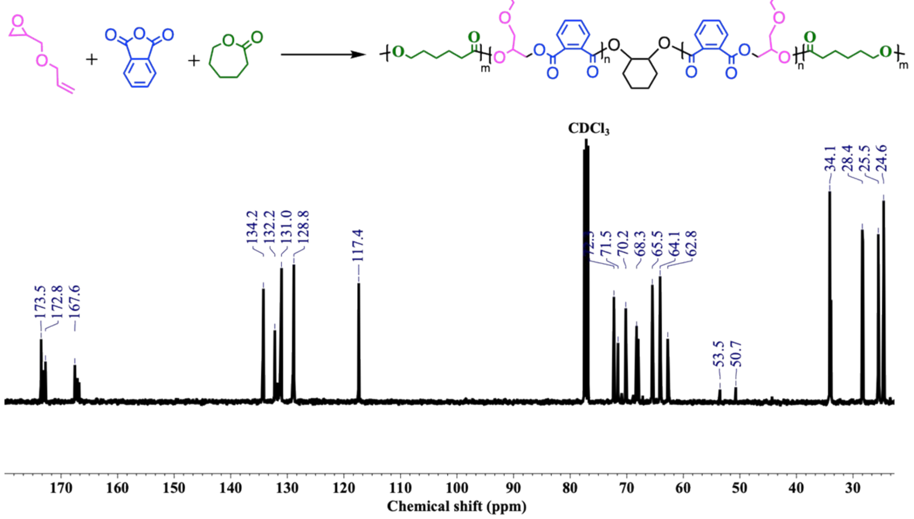

Figure S7. The ^{13}C NMR spectrum of the triblock polymer of PCL-*b*-PAPGE-*b*-PCL in CDCl$_3$, isolated from the reaction mixture by precipitation.

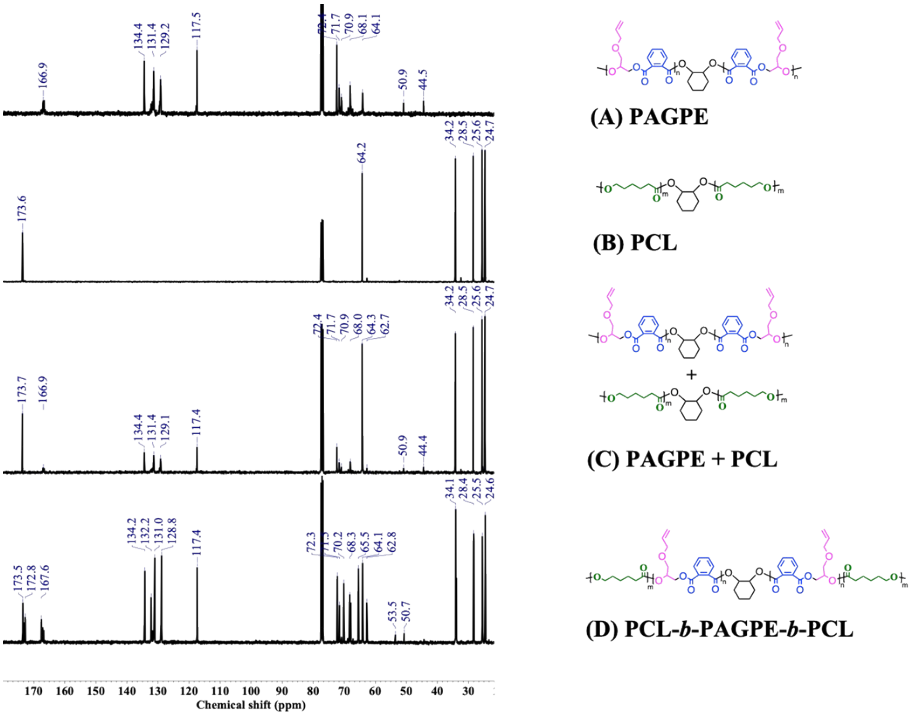

Figure S8. The comparison of the ^{13}C NMR spectra of the (A) PAGPE; (B) PCL; (C) the mixture of PAGPE and PCL homopolymer; (D) PCL-*b*-PAPGE-*b*-PCL triblock polyester in $CDCl_3$, isolated from the reaction mixture by precipitation.

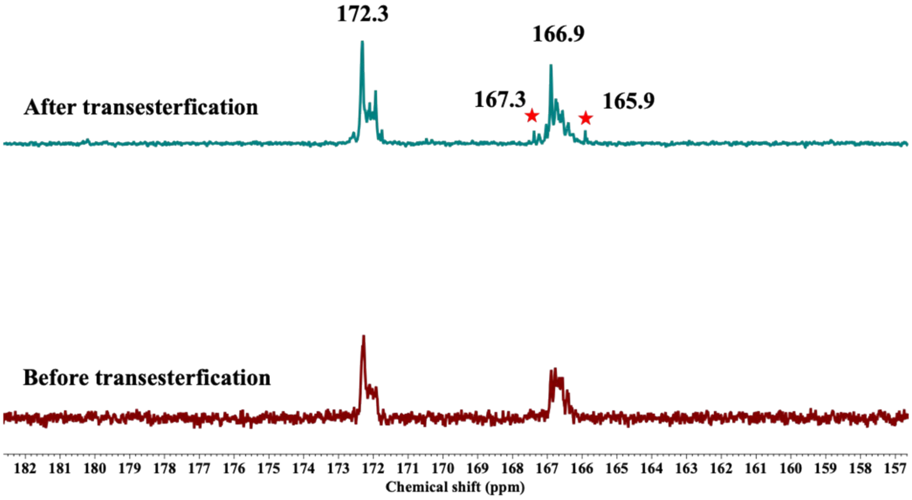

Figure S9. The ^{13}C NMR spectra of the PCL-*b*-PAGPE-*b*-PCL triblock polyester treated with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) at 60 °C for 48 h in a NMR tube, using toluene-d_8 as solvent, under N_2.

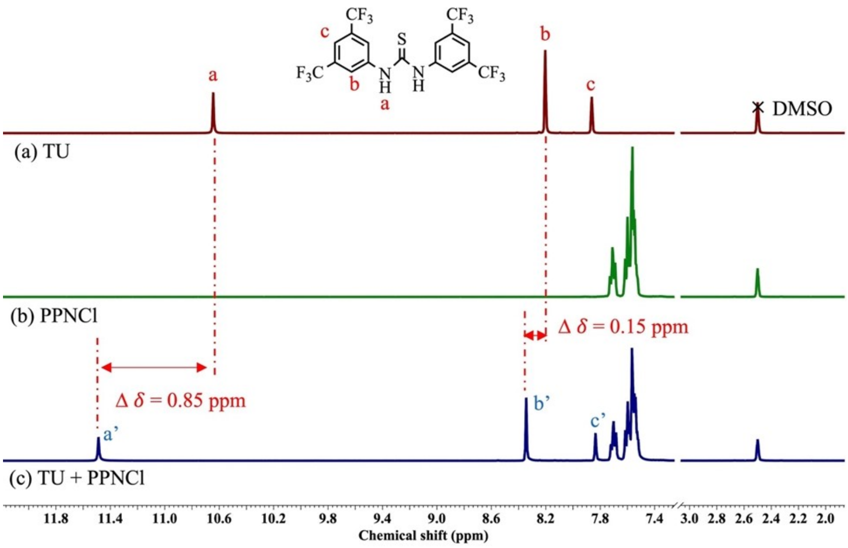

Figure S10. Stacked ^{1}H NMR spectra of (a) TU; (b) PPNCl and (c) TU/ PPNCl (1: 1) in DMSO-d_6 at room temperature.

Extension to Other Monomers

Table S2. Switchable polymerization of different epoxides, cyclic anhydrides and cyclic esters by TU/PPNCl binary catalysts [a]

Entry	Monomer	T (℃)	t (h)	*Conv.*[b] [%]		$M_{n, theo}$ [c] (kg/mol)	$M_{n, SEC}$ [d] ($Đ$) (kg/mol)
				(cyclic anhydride)	(cyclic ester)		
1	CHO/PA/ε-CL	110	0.67	99	0	8.1	5.8 (1.18)
			7	99	19	9.6	7.4 (1.36)
2	CHO/PA/δ-VL	110	0.67	99	0	8.1	3.6 (1.09)
			7	99	72	12.9	7.8 (1.38)
3[e]	CHO/PA/L-LA	110	0.67	62	0	5.1	2.1 (1.18)
			3	99	87	12.3	3.6 (1.22)
4	CHO/SA/ε-CL	110	0.67	15	0	1.0	0.5 (1.23)
			3	99	0	6.5	1.7 (1.27)
5	CHO/NA/ε-CL	110	1	15	0	1.3	1.1 (1.20)
			6	99	68	13.8	6.5 (1.27)
6	PO/PA/ε-CL	80	1	56	0	3.8	1.2 (1.15)
			6	99	95	14.0	9.7 (1.55)
7	PO/PA/δ-VL	80	1	76	0	5.2	1.3 (1.19)
			6	99	90	9.8	5.7 (1.54)
8	PO/SA/ε-CL	80	1	0	0	—	—
			7	99	52	9.2	3.8 (1.39)
9	SO/PA/ε-CL	110	1	99	0	8.8	3.9 (1.15)
			6	99	90	15.6	7.7 (1.40)

[a] The polymerization were performed at bulk with the feed ratio [epoxide]/[cyclic anhydride]/[cyclic ester]/[CHD]/[TU]/[PPNCl] = 800/100/200/2/1/1, unless otherwise noted. [b] Determined by ^{1}H NMR analysis of the obtained polymer in CDCl$_3$. [c] Determined on the basis of {($MW_{cyclic\ anhydride}$ + $MW_{epoxide}$) × (*Conv.*% of cyclic anhydride)}/{[CHD] + [PPNCl]} + {($MW_{cyclic\ ester}$) × (*Conv.*% of cyclic ester)}/{[CHD]+[PPNCl]}, with units of kg/mol. [d] Determined by SEC analysis of the obtained polymer in THF using polystyrene calibration. [e] The polymerization were performed at bulk with the feed ratio [CHO]/[PA]/[L-LA]/[CHD]/[TU]/[PPNCl] = 800/100/100/2/1/1.

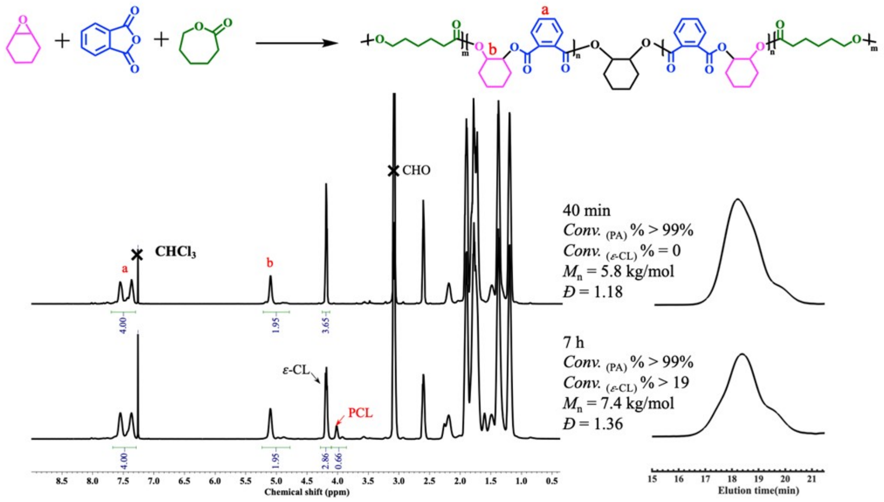

Figure S11. The ^{1}H NMR spectra (in $CDCl_3$) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of PA and *ε*-CL and the formation of PCL-*b*-PCHPE-*b*-PCL.

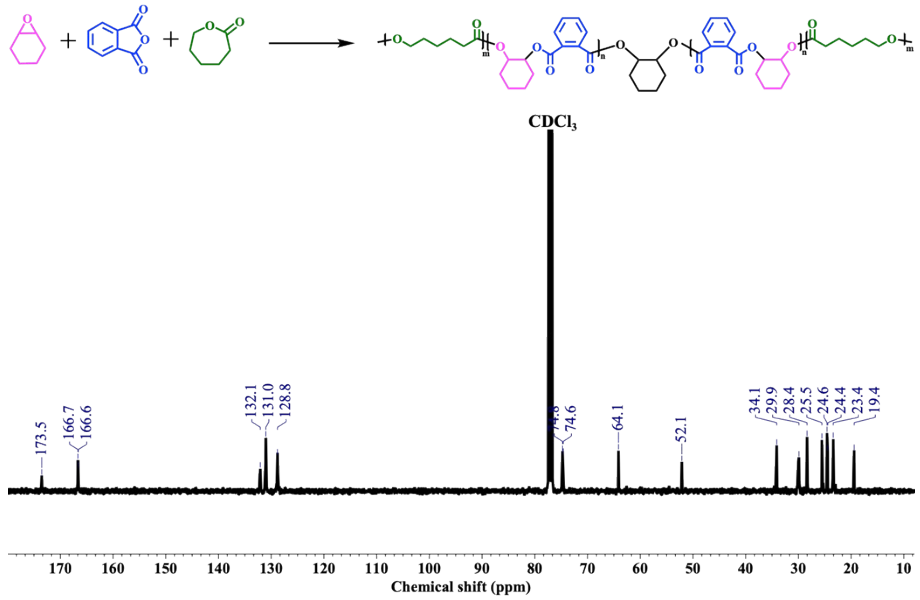

Figure S12. The ^{13}C NMR spectrum of the resultant PCL-*b*-PCHPE-*b*-PCL in $CDCl_3$, isolated from the reaction mixture by precipitation.

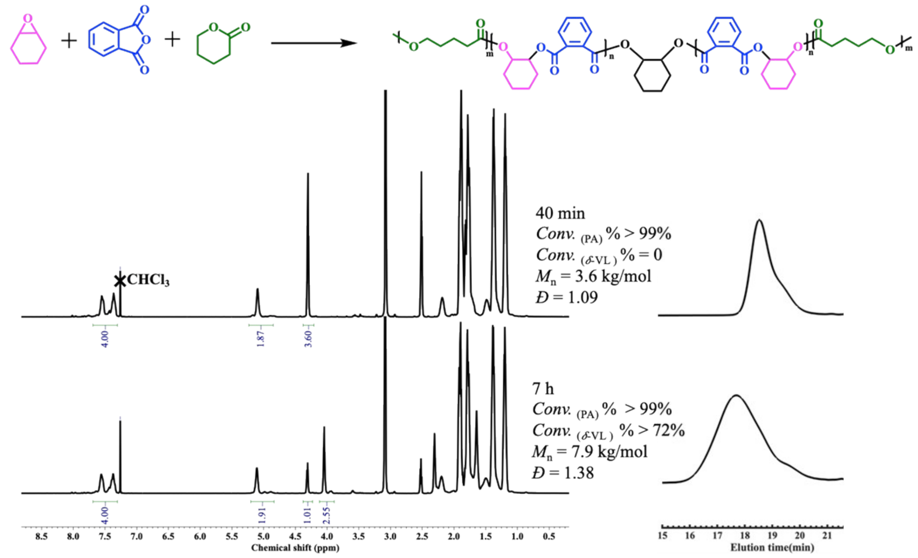

Figure S13. The ^{1}H NMR spectra (in $CDCl_3$) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of PA and *δ*-VL and the formation of PVL-*b*-PCHPE-*b*-PVL.

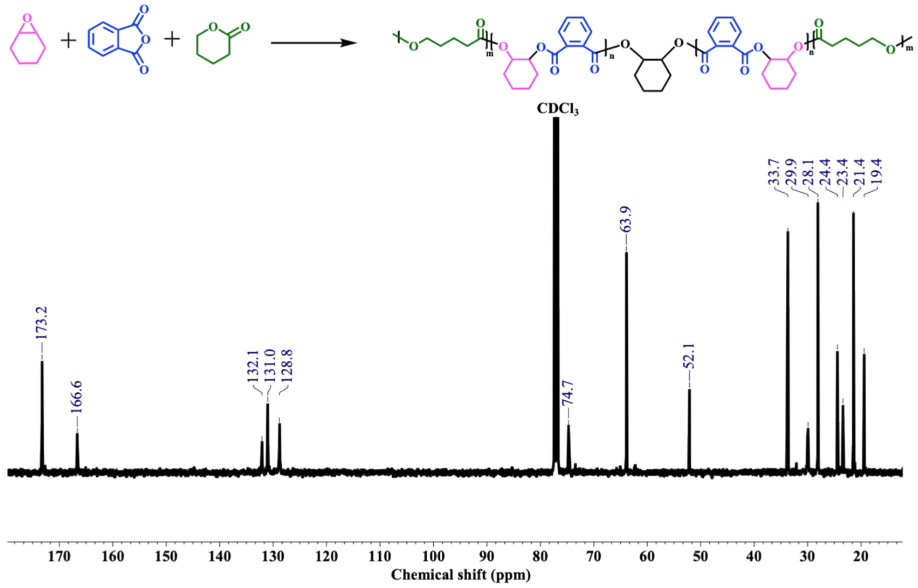

Figure S14. The ^{13}C NMR spectrum of the resultant PVL-*b*-PCHPE-*b*-PVL in $CDCl_3$, isolated from the reaction mixture by precipitation.

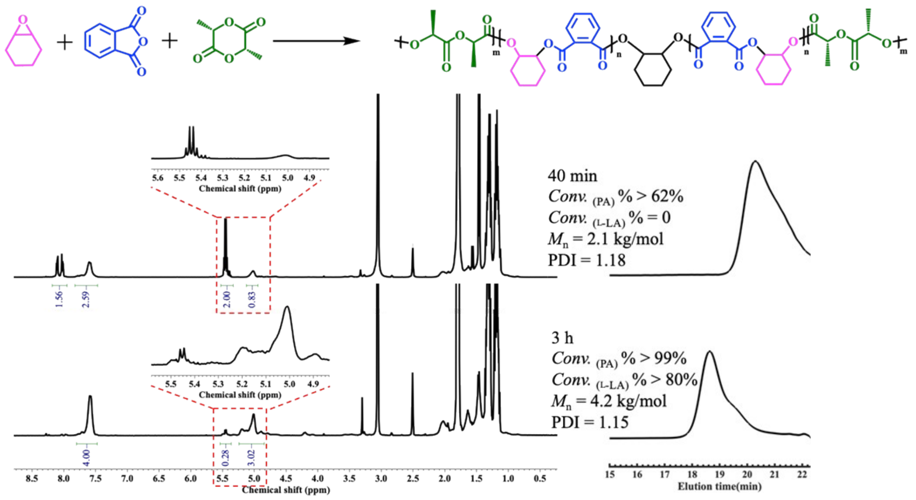

Figure S15. The ^{1}H NMR spectra (in DMSO-d_6) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of PA and L-LA and the formation of PLLA-*b*-PCHPE-*b*-PLLA.

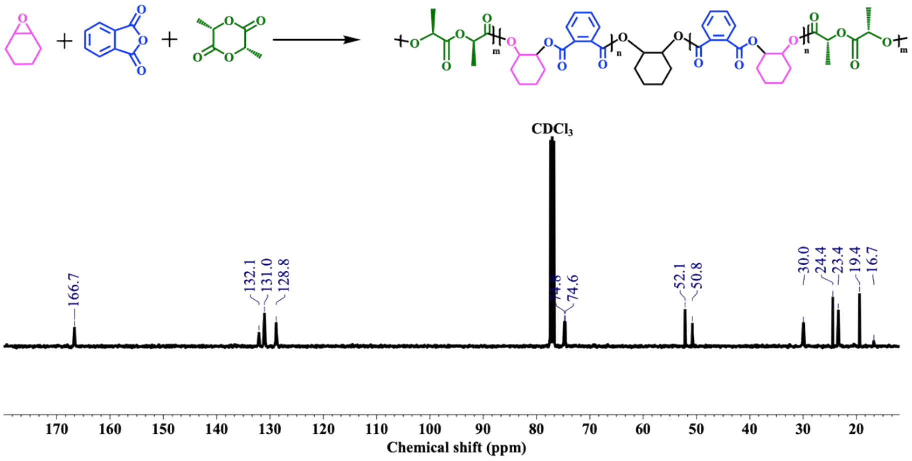

Figure S16. The ^{13}C NMR spectrum of the resultant PLLA-*b*-PCHPE-*b*-PLLA in CDCl$_3$, isolated from the reaction mixture by precipitation.

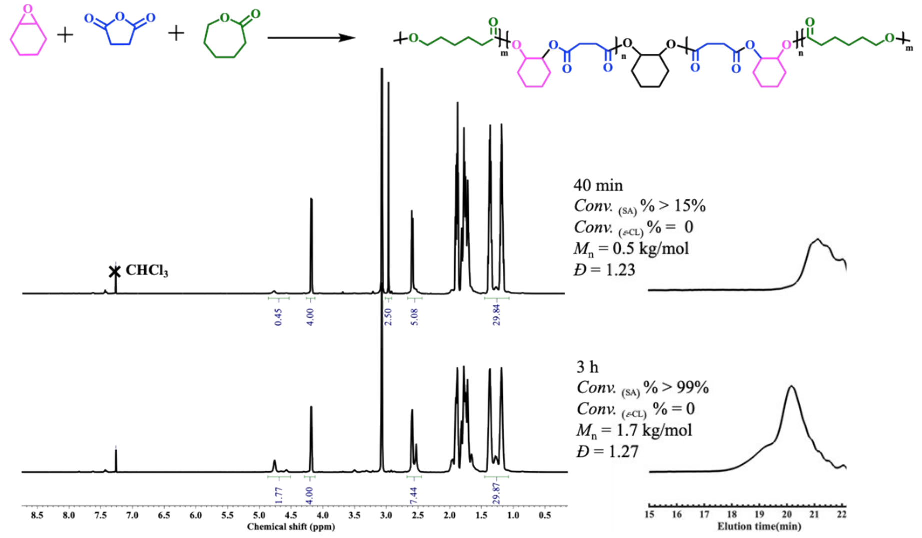

Figure S17. The ^{1}H NMR spectra (in CDCl$_3$) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of PA and *ε*-CL and the formation of PCL-*b*-PCHSE-*b*-PCL.

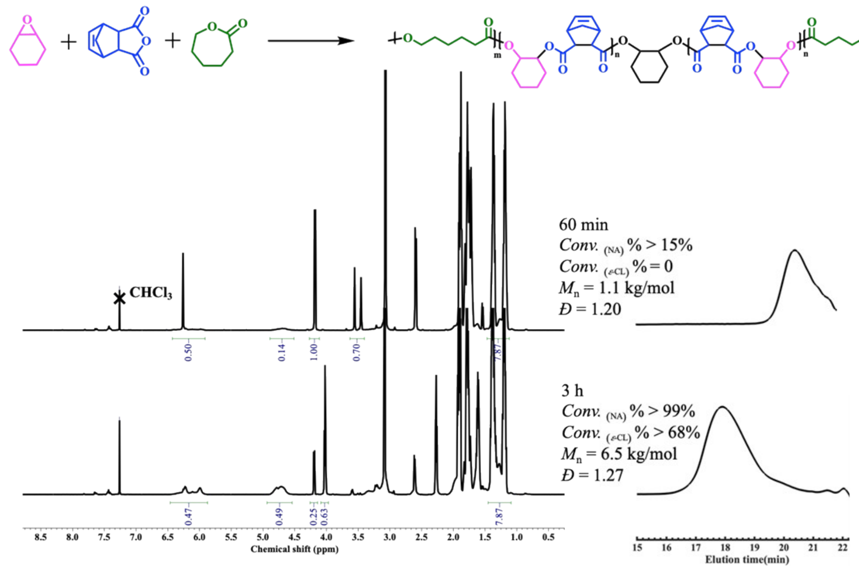

Figure S18. The ^{1}H NMR spectra (in CDCl$_3$) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of NA and *ε*-CL and the formation of PCL-*b*-PCHNE-*b*-PCL.

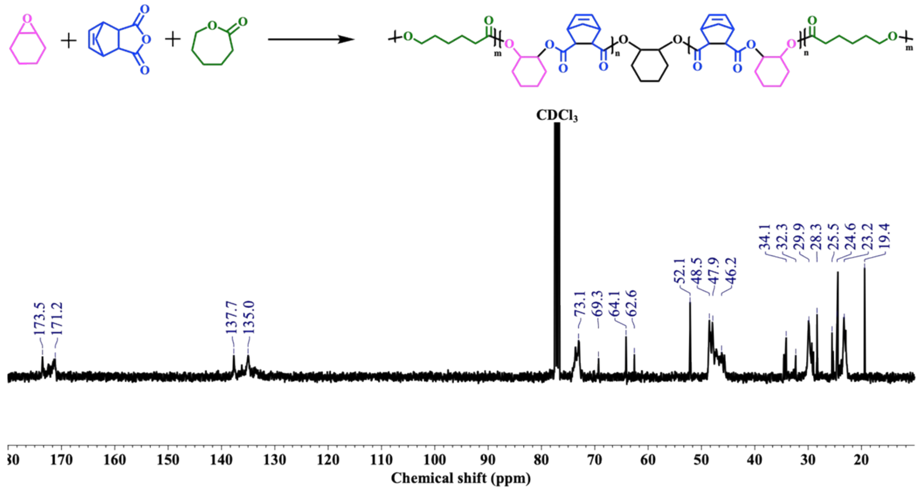

Figure S19. The ^{13}C NMR spectrum of the resultant PCL-*b*-PCHNE-*b*-PCL in CDCl$_3$, isolated from the reaction mixture by precipitation.

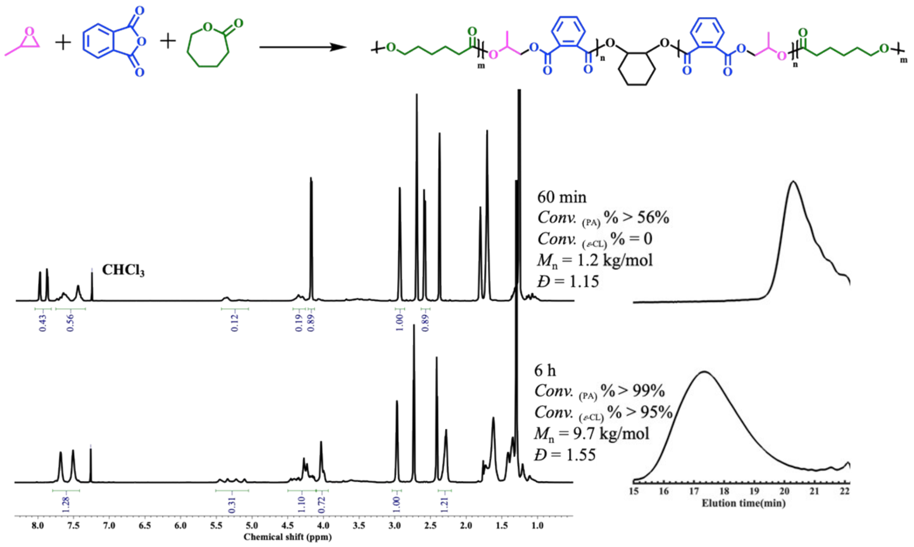

Figure S20. The ^{1}H NMR spectra (in $CDCl_3$) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of PA and *ε*-CL and the formation of PCL-*b*-PPPE-*b*-PCL.

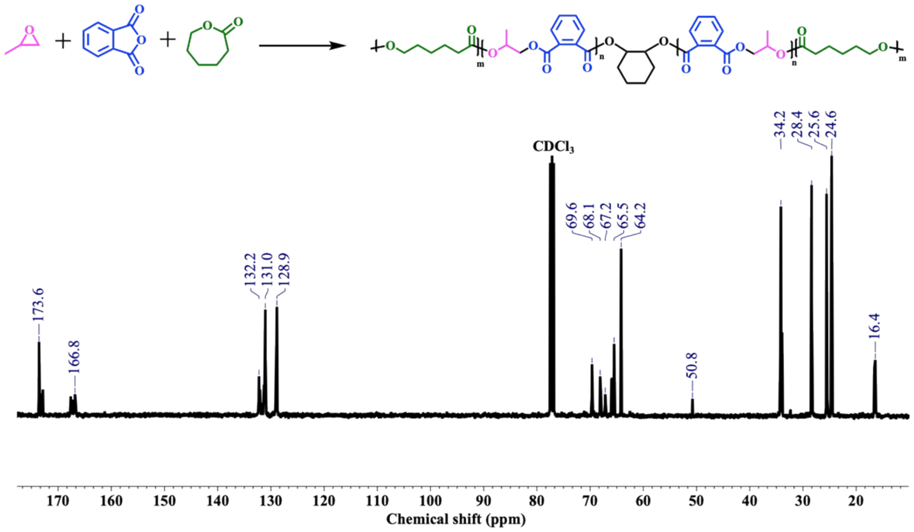

Figure S21. The ^{13}C NMR spectrum of the resultant PCL-*b*-PPPE-*b*-PCL in $CDCl_3$, isolated from the reaction mixture by precipitation.

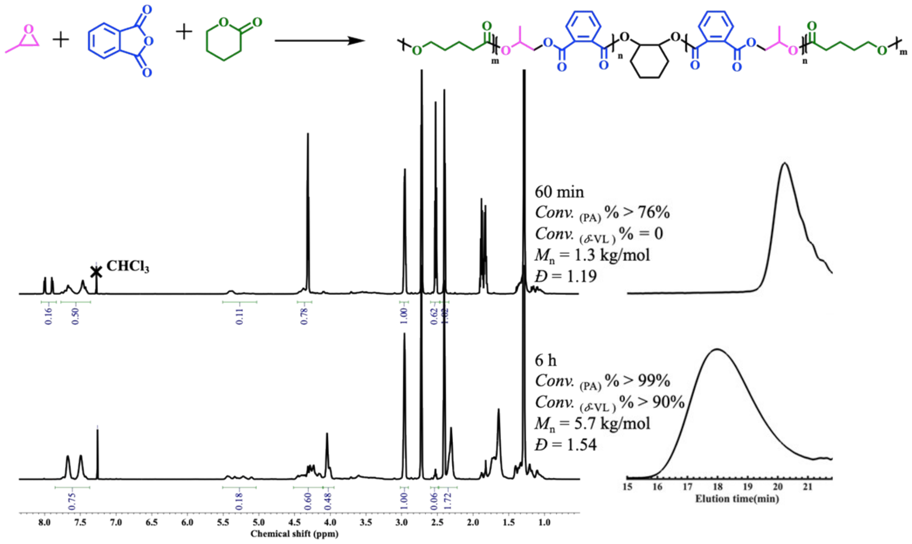

Figure S22. The ^{1}H NMR spectra (in CDCl$_3$) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of PA and *δ*-VL and the formation of PVL-*b*-PPPE-*b*-PVL.

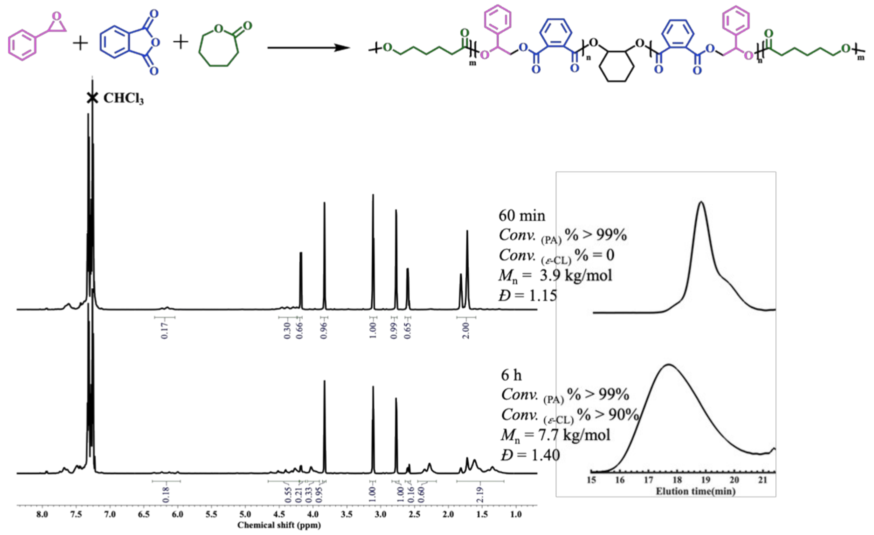

Figure S23. The ^{1}H NMR spectra (in CDCl$_3$) and SEC traces of crude aliquots taken from the reaction mixture for monitoring the conversion of PA and *ε*-CL and the formation of PCL-*b*-PSPE-*b*-PCL.

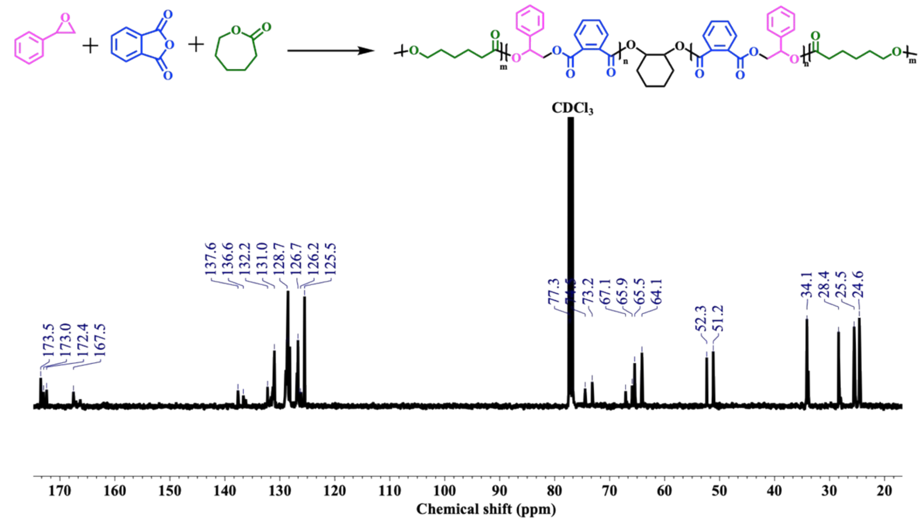

Figure S24. The ^{13}C NMR spectrum of the resultant PCL-*b*-PSPE-*b*-PCL in CDCl$_3$, isolated from the reaction mixture by precipitation.

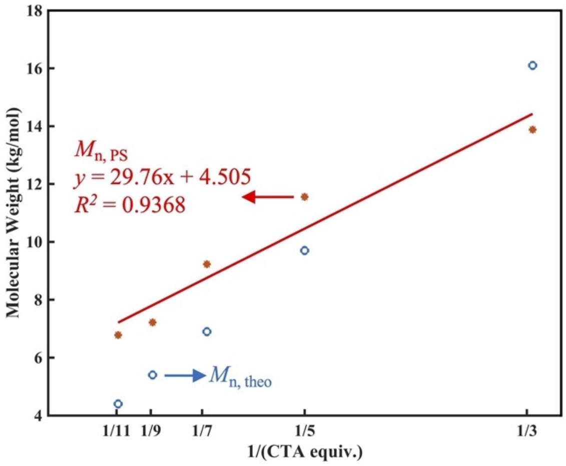

Figure S25. Plots showing the molecular weight of PCL-*b*-PAPGE-*b*-PCL (blue rings: theoretical M_n; red dots: experimental M_n determined by SEC analysis of the obtained polymer in THF using polystyrene calibration, see **entries 6-10** in **Table 1**) and the number of equivalents of CHD and PPNCl (as CTA) used during the self-switchable polymerization. (Red line: linear fittings of the experimental M_n).

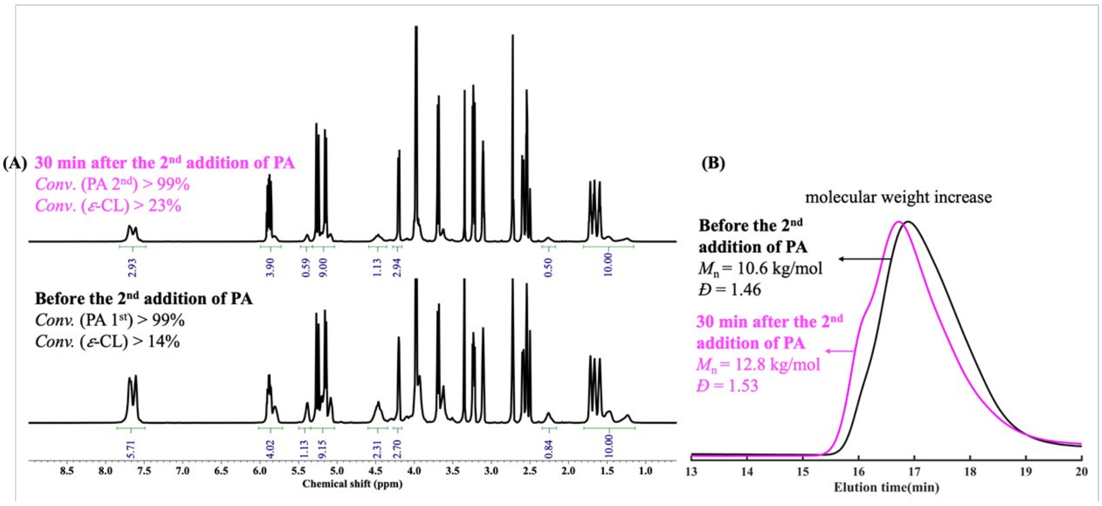

Figure S26. (A) ^{1}H NMR spectra (in DMSO-d_6) of PCL-*b*-PAGPE-*b*-PCL before the 2nd addition of PA (lower) and 30 min after the 2nd addition of PA (upper). [AGE]/[ε-CL]/[PA 1st]/[**PA 2nd**]/[TU]/[PPNCl]/[CHD] = 800/200/100/100/1:1/2. (B) SEC traces of crude aliquots taken from the reaction mixture.

Postmodification

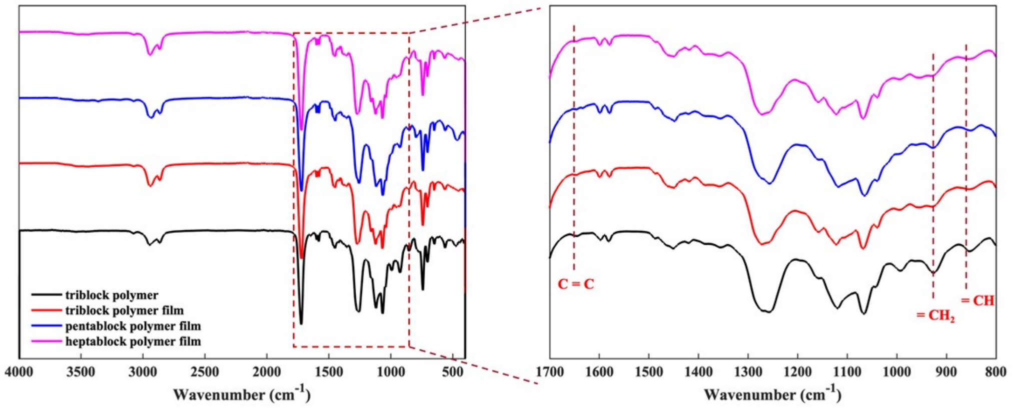

Figure S27. FTIR spectra of triblock polymer and different cross-linking films.

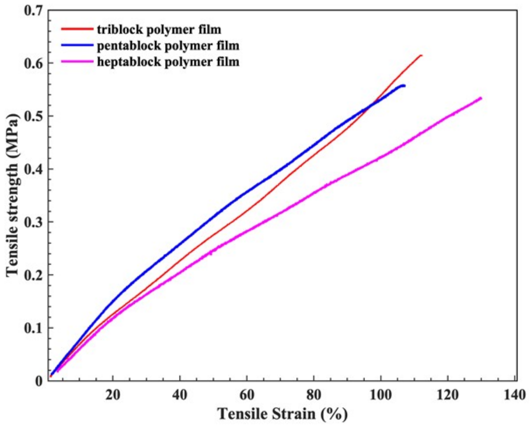

Figure S28. Mechanical properties characterization of different cross-linking films.

References

1 T. T. D. Chen, Y. Zhu, and C. K. Williams, *Macromolecules*, **2018**, *51*, 5346–5351.

Abbreviations

AGE	allyl glycidyl ether
CHD	*trans*-cyclohexane-1,2-diol
CHO	cyclohexene oxide
ε-CL	*ε*-caprolactone
CTA	chain transfer agent
Đ	polydispersity index
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
DMSO	dimethyl sulfoxide
DMPA	2,2-dimethoxy-2-phenylacetophenone
DOSY	^{1}H diffusion-ordered NMR spectrum
FTIR	fourier transform infrared spectroscopy
L-LA	L-lactide
M_n	number average molar mass
M_w	weight average molar mass
NA	5-norbornene-2,3-dicarboxylic anhydride
NMR	nuclear magnetic resonance
PA	phthalic anhydride
PCL	poly(*ε*-caprolactone)
PDI	polydispersity index
PLA	poly(L-lactide)
PO	propylene oxide
PPNCl	bis(triphenylphosphine)iminium chloride
PVL	poly(*δ*-valerolactone)
ROCOP	ring opening copolymerization
ROP	ring opening polymerization
SA	succinic anhydride
SEC	size exclusion chromatography
SO	styrene oxide
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
T_g	glass transition temperatures
TGA	thermogravimetric analyses
TU	1,3-bis[3,5-bis(trifluoromethyl)phenyl]thiourea
δ-VL	*δ*-valerolactone