

## Electronic Supplementary Information

### Construction of triblock copolyesters via one-step switchable terpolymerization of epoxides, phthalic anhydrides and $\epsilon$ -caprolactone using dual urea/organic base catalysts

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### Experimental Procedures

#### Materials

All chemicals were used as received from Energy Chemical (Guangzhou, China) unless otherwise stated. Cyclohexene oxide (CHO), propylene oxide (PO), allyl glycidyl ether (AGE) and  $\epsilon$ -caprolactone (CL) were refluxed over CaH<sub>2</sub> for 24 h and vacuum-distilled prior to use. Phthalic anhydride (PA, J&K, 98%) was purified by sublimation. N,N'-dicyclohexylurea (U1, TCI, 98%), 1-cyclohexyl-3-phenyl-urea (U2, Fuyuan Technology company, 98%), triclocarban (U3, TCI, 98%), 1-cyclohexyl-3-phenyl-thiourea (TU, J&K, 98%) and bis(triphenylphosphine) iminium chloride (PPNCl) (Alfa, 97%) were dried in vacuum. 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 7-methyl-1,5,7-triazacycle [4.4.0] dec-5-ene (MTBD, TCI, >95.0%), 1,5, 7-triazacycle [4.4.0] dec-5-ene (TBD, TCI, >98.0%) and benzenedimethanol (BDM, 98%) were used as received.

## Measurements

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and diffusion-ordered NMR spectroscopy (DOSY) spectra were obtained on a Bruker DRX-500 MHz NMR spectrometer using  $\text{CDCl}_3$  as solvent and tetramethylsilane as the internal standard. Molecular weight determinations were carried out using a Waters gel permeation chromatography (GPC) system with chloroform as eluent. The GPC system was calibrated by a series of polystyrene standards with polydispersity of 1.02. In situ ATR-IR spectroscopy measurements were performed on a Mettler Toledo ReactIR 45 spectrometer equipped with a MCT detector and a DiComp probe. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) were recorded on Bruker ultrafleXtreme type. The polymer sample in THF (10 mg/mL), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) in 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  $\mu\text{L}$  of mixed solution was spotted onto the sample plate before being air-dried.

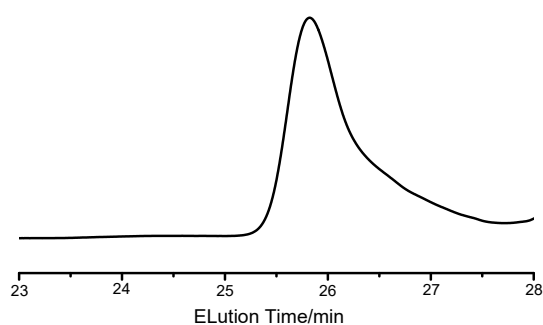
## General Procedure of Polymerization

Polymerizations were performed in a 25 mL vial using an external heating bath. The vial was charged with a predetermined amount of (thio)urea (0.05mmol, 1 equiv), organic base (0.05mmol, 1 equiv), benzenedimethanol (BDM, 0.10mmol, 2 equiv), epoxide (25mmol, 500 equiv), anhydride, (5mmol, 100 equiv) and  $\epsilon$ -caprolactone (CL, 5mmol, 100 equiv), which were kept stirring for 5 min at room temperature in an  $\text{N}_2$ -filled glovebox. The vial was sealed, taken out of glovebox, and then immersed in the heating bath under the predetermined temperature. After equilibration at the desired polymerization temperature, the polymerization started. After a desired period of time, the vial was removed from heat block and a 0.2 mL of aliquot was taken from the reaction mixture and prepared for  $^1\text{H}$  NMR analysis. Then the mixture was dissolved in  $\text{CHCl}_3$  and precipitated into 10-fold excess of methanol or hexane, filtered, washed with methanol to remove unreacted monomer, and dried in a vacuum oven at room temperature to a constant weight.

**Table S1** Homopolymerization of CL, copolymerization of CHO/PA and CHO/PA/CL using different catalyst systems.

Entry	Catalyst	Monomer	t /min	PA conv./% <sup>d</sup>	CL conv./% <sup>d</sup>	$M_n$ /kDa (theory)	$M_n$ /kDa <sup>e</sup>	PDI <sup>e</sup>
1 <sup>a</sup>	U1+PPNCl	CL	120	-	8	0.9	-	-
2 <sup>a</sup>	U1+PPNCl+BDM	CL	20	-	88	5.1	5.4	1.50
3 <sup>b</sup>	U1+PPNCl+BDM	CHO+PA	10	99	-	6.0	3.8	1.18
4 <sup>c</sup>	U1 +BDM	CHO+PA+ CL	40	0	0	-	-	-
5 <sup>c</sup>	U1+PPNCl	CHO+PA+ CL	40	100	70	16.2	11.7	1.85

<sup>a</sup> Homopolymerization of CL, performed at [U1]/[PPNCl]/[CL]=1:1:100 with or without 2 equiv BDM in bulk at 100 °C. <sup>b</sup> Copolymerization of CHO/PA, performed at [U1]/[PPNCl]/[BDM]/[PA]/[CHO]= 1:1:2:50:250 in bulk at 100°C. <sup>c</sup> The reaction was performed at [U1]/[BDM]/[CL]/[PA]/[CHO]=1:2:50:50:250 or [U1]/[PPNCl]/[CL]/[PA]/[CHO]=1:1:50:50:250 in bulk at 100 °C. <sup>d</sup> Conversion was determined by <sup>1</sup>H NMR. <sup>e</sup>  $M_n$  and PDI were determined by GPC.



**Fig. S1** GPC trace of resultant poly(CHO-*alt*-PA) performed at [U1]/[PPNCl]/[BDM]/[PA]/[CHO]= 1:1:2:50:250 in bulk at 100 °C (Table S1 entry 3)

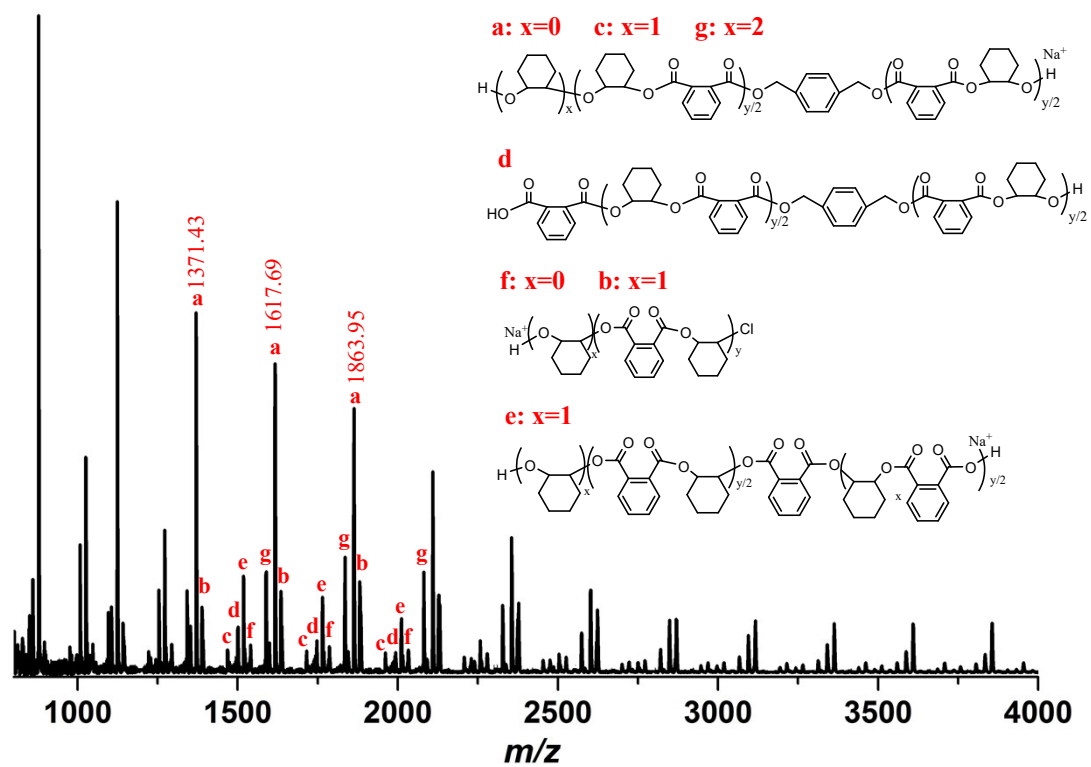
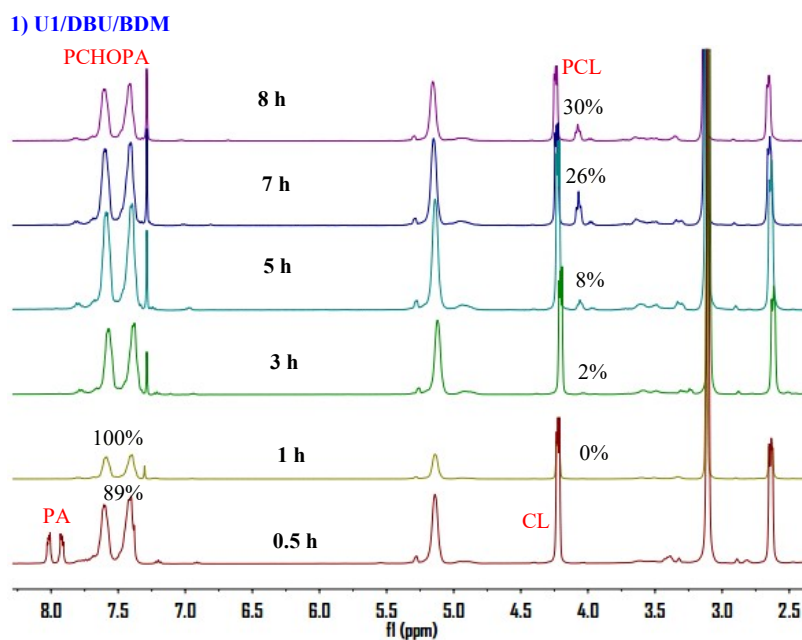
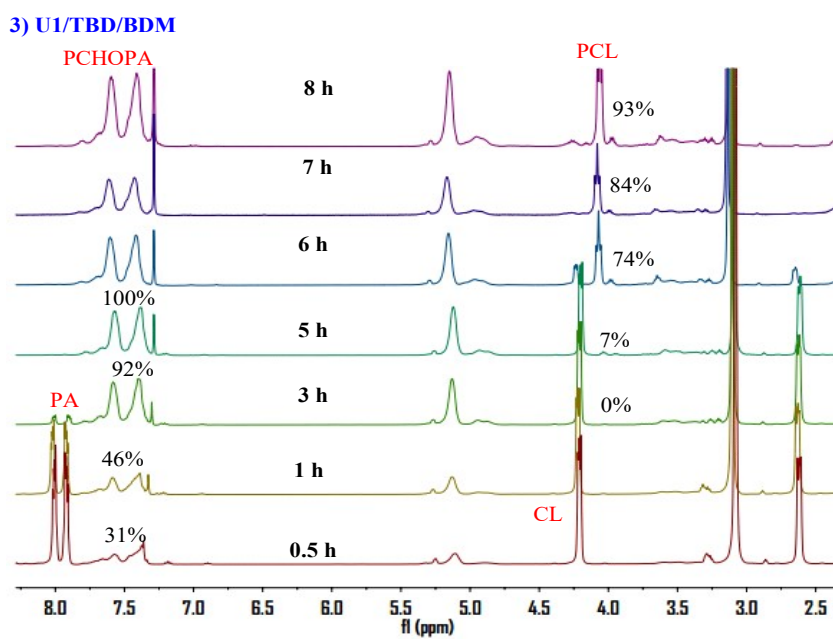
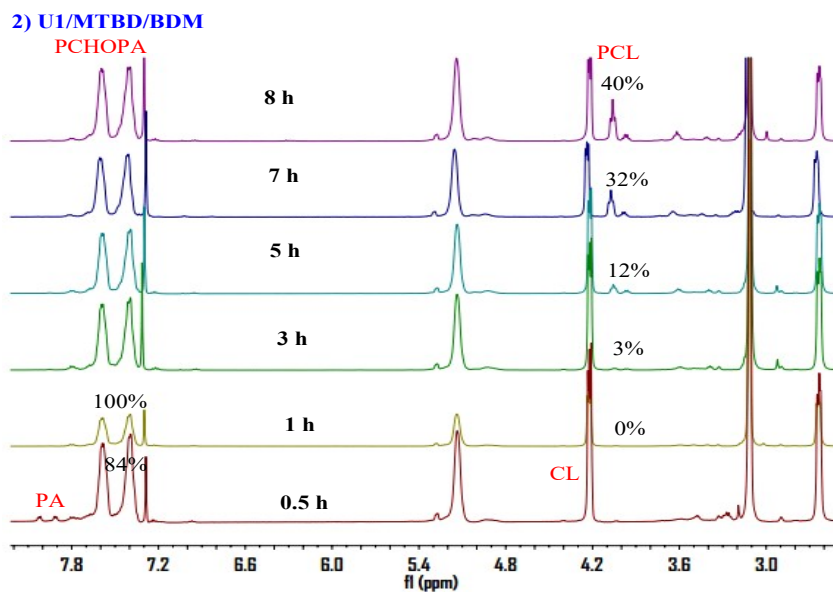
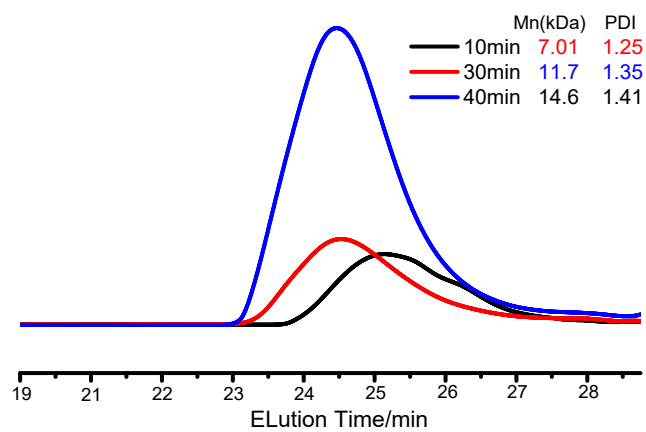


Fig. S2 MALDI-ToF MS spectrum of poly(CHO-*alt*-PA) (Table S1 entry 3).





**Fig. S3**  $^1\text{H}$  NMR spectra in situ of crude aliquots withdrawn from the reaction system for monitoring the conversion of PA and CL with various catalyst pair: 1) U1/DBU; 2) U1/MTBD; 3) U1/TBD (Table 2 entry 3 to 5).



**Fig. S4** GPC traces of polymers (Table 1 entry 4) synthesized with varying monomer conversion at different reaction time corresponding to Fig.3.