

Supporting information for

**Monomer Controlled Self-switchable
Polymerization: A Metal-free Strategy for
Multiblock Copolymers from Epoxides, *O*-
phthalaldehyde, and CO₂**

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EXPERIMENTAL SECTION

Materials.

All manipulations of air or water sensitive compounds were carried out in glove box under argon. *O*-phthalaldehyde (OPA), Triethylborane (TEB) in THF solution (1.0 mol/L) and tetrabutylammonium chloride (TBAC) (>99%) were purchased from Macklin. 1,2-epoxybutane (BO), propylene oxide (PO) and 1,2-epoxyaladdin (HO) was purchased from Aladdin. 3,4-epoxy-1-butene (EB) was purchased from MERYER. CO₂ was purchased from Changchun Juyang Gas Company. OPA was purified by repeated recrystallization in dichloromethane/hexane (1:4 ratio) in an inert atmosphere. Tetrahydrofuran and hexane were stirred over sodium metal and then distilled under vacuum. Triethylborane (TEB) in THF solution (1.0 mol/L) and used without further purification. Tetrabutylammonium chloride (TBAC) was dried under vacuum at 35°C for 24h and stored in a glove box. Dichloromethane, EB, BO, PO and HO were stirred over CaH₂ for 2 days and then distilled under vacuum.

Measurements

The ¹H NMR spectrum was recorded on a Bruker AV-300 MHz at 25 °C. The DOSY spectrum was recorded on a Bruker AV-400 MHz at 25 °C. Gel permeation chromatography (GPC) measurements were conducted using a Waters 515 GPC and CH₂Cl₂ (DCM) as the eluent (flow rate: 1 mL/min, at 30 °C). Molecular weights were calculated using a calibration curve constructed from linear polystyrene standards. Diffraction scanning chromatogram (DSC) measurements were carried out under nitrogen flow on a TA Q100 thermal analyzer from -60 °C to 100 °C, -60 to 150 °C or

-80 to 50 °C at a heating rate of 10 °C/min, and the glass transition temperatures (T_g) of the samples were determined from the second run. Thermogravimetric analysis (TGA) measurements were performed on a TGA92 instrument in the temperature range from 40 °C to 600 °C at a heating rate of 10 °C/min in nitrogen.

Polymerization process.

The self-switch capability of OPA and CO₂ and the preparation of three diblock copolymers.

a. OPA-controlled self-switching process from ROP of BO to ROCOP of OPA/BO. All ampoules with a magnetic stir bar were dried in the oven at 125 °C for 8 h and immediately transferred to the glove box under argon. The ampoule was then charged with the initiator TBAC (27.8 mg, 0.1 mmol) and TEB (0.2 mL, 1 M solution in THF, 0.2 mmol). The monomer BO (2.62 mL, 30 mmol) was then added, the reactor was sealed with emulsion tube in glove box under argon and stirred at 25 °C. After 25 min, crude sample was withdrawn in the NMR tube with CDCl₃. Then, the monomer OPA (1.3413 g, 10 mmol) was added into the mixture in glove box under argon. The reactor was taken out of the glove box and sealed, followed by a further period of reaction at 25 °C. Crude sample was time-regularly withdrawn to monitor the reaction process by ¹H NMR. After a certain time, the mixture was diluted with dichloromethane and precipitated three times in methanol. Then, the polymer was dried under vacuum at 40 °C and the pure polymer was collected.

b. CO₂-controlled self-switching process from ROCOP of OPA/BO to ROCOP of CO₂/BO. The ampoule was replaced by autoclave and charged with the initiator TBAC

(27.8 mg, 0.1 mmol) and TEB (0.2 mL, 1 M solution in THF, 0.2 mmol). The monomer BO (2.62 mL, 30 mmol) and OPA (1.3413 g, 10 mmol) was then added, the reactor was sealed in glove box under argon and stirred at 25 °C. After a certain stirring time, the reactor was transferred to the glovebox where the sample was taken and the sample solution was prepared with CDCl₃ immediately, while the reactor was sealed and immediately transferred out of the glovebox. Then, the reactor charged with (2.5 MPa) CO₂ and stirred at 25 °C for another certain reaction time. Crude sample was time-regularly withdrawn in glove box under argon and dissolve into NMR tube with CDCl₃ to monitor the reaction process by ¹H NMR. Finally, the mixture was diluted with dichloromethane and precipitated three times in methanol. Then, the polymer was dried under vacuum at 40 °C and the pure polymer was collected.

c. CO₂-controlled self-switching process from ROP of BO to ROCOP of CO₂/BO. The autoclave was charged with the initiator TBAC (27.8 mg, 0.1 mmol) and TEB (0.2 mL, 1 M solution in THF, 0.2 mmol). The monomer BO (2.62 mL, 30 mmol) was then added, the reactor was sealed in glove box under argon and stirred at 25 °C for 30 min. Then, the reactor was transferred to the glovebox where the sample was taken and the sample solution was prepared with CDCl₃, while the reactor was sealed and immediately transferred out of the glovebox. Then, the reactor was charged with CO₂ (2.5 MPa), followed with another certain time of reaction at 25 °C. Crude sample was time-regularly withdrawn to monitor the reaction process by ¹H NMR. After a certain time, the mixture was diluted with dichloromethane and precipitated three times in methanol. Then, the polymer was dried under vacuum at 40°C and the pure polymer

was collected.

Synthesis of poly[(BO)-*b*-(OPA-*alt*-BO)-*b*-(CO₂-*alt*-BO)] (ABC), poly[(BO)-*b*-(OPA-*alt*-BO)-*b*-(BO)-*b*-(CO₂-*alt*-BO)] (ABAC) and poly[(BO)-*b*-(OPA-*alt*-BO)-*b*-(CO₂-*alt*-BO) -*b*-(OPA-*alt*-BO)-*b*-(CO₂-*alt*-BO)] (ABCBC).

As for a typical synthesis procedure of triblock polymer and tetrablock polymer for entry 1 (ABC), 10 (ABAC) and 11 (ABCBC), Table 1, the 25 mL autoclave with a magnetic stir bar was dried in the oven at 125 °C for 8 h and immediately transferred to the glovebox under argon. After cooling to room temperature, the autoclave was charged with the initiator TBAC (27.8 mg, 0.1 mmol), TEB (0.2 mL, 1 M solution in THF, 0.2 mmol) and monomer BO (2.62 mL, 30 mmol). The reactor was sealed in glove box under argon and stirred at 25 °C for a certain time. Then, the OPA (1.3413g, 10 mmol) was added to the mixture in the glove box and sealed. The reactor was stirred at 25 °C for a certain time. Then, the reactor was charged with CO₂ at a certain pressure and stirred at 25 °C for 24 h. Crude sample was time-regularly withdrawn during the polymerization process. Before moving the reactor into the glovebox, released the CO₂ and transferred the reactor immediately. Then, taking the sample and prepared the sample solution immediately, while sealed the reactor and transferred out of the glovebox. Then, the reactor was charged with CO₂ and maintained a particular pressure. The sample dissolved in the NMR tube with CDCl₃ to monitor the reaction process by ¹H NMR. After a certain time, the mixture was diluted with dichloromethane and precipitated three times in methanol. Then, the polymer was dried under vacuum at 40°C and the pure polymer was collected. Preparation of ABAC polymer by extending

the reaction time of the step II. Repeat steps II and III to prepare ABCBC polymer.

Synthesis of poly(acetal-*b*-carbonate).

The 25 mL autoclave with a magnetic stir bar was dried in the oven at 125 °C for 8 h and immediately transferred to the glove box under argon. After cooling to room temperature, the autoclave was charged with the initiator TBAC (27.8 mg, 0.1 mmol), TEB (0.2 mL, 1 M solution in THF, 0.2 mmol) and epoxides (30 mmol) and OPA (1.3413 g, 10 mmol) was added to the mixture in the glove box. The reactor was sealed in glove box under argon and stirred at 25 °C for a certain time. Then, the reactor was charged with CO₂ at a certain pressure and stirred at 25 °C for a certain time. Crude sample was withdrawn in glove box under argon and dissolved into the NMR tube with CDCl₃ to monitor the reaction process by ¹H NMR. After a certain time, the mixture was diluted with dichloromethane and precipitated three times in methanol. Then, the polymer was dried under vacuum at 40 °C and the pure polymer was collected.

Table S1. OPA/CO₂ controlled self-switchable copolymerization process.

Entry ^a	molar ratio		time (h)			Conv ^c (%)		Comp ^d (%)			<i>M</i> _{n,GPC} ^e (KDa)/ <i>D</i> ^e
	TBAC/TEB/BO/OPA /CO ₂ (MPa)	Step I ^b	Step II ^b	Step III ^b	BO	OPA	PBO	PBA	PBC		
1	1: 2: 300: 100: -	0.4	7.0	-	73	78	63	37	-	12.0/1.10	
2	1: 2: 300: -: 2.5	0.4	-	24.0	85	-	53	-	47	23.4/1.10	
3	1: 2: 300: 100: 2.5	-	3.7	25.5	49	58	-	47	53	19.9/1.05	

^aCopolymerizations were carried out in autoclaves or ampoules at 25°C under argon (Ar) or CO₂ (2.5 MPa). ^bThe reaction time (t) step I, step II and step III correspond to three steps in the Scheme 1: step I refers to the time of BO homopolymerization, step II refers to the time of BO/OPA copolymerization, step III refers to the time of BO/CO₂ copolymerization. ^cCalculated from the ¹H NMR spectrum of the crude reaction mixture. ^dEther linkage (PBO), acetal linkage (PBA) and carbonate linkage (PBC) were determined by integral ratios of the moieties in ¹H NMR spectrum. ^eObtained by GPC analysis (DCM) and calibrated against the polystyrene standard.

Table S2. Conversion of BO and OPA in three steps.

Entry ^a	molar ratio TBAC/TEB/BO/OPA /CO ₂ (MPa)	Step I		Step II			Step III		
		Time (h)	Conv. of BO (%)	Time (h)	Conv. of BO (%)	Conv. of OPA (%)	Time (h)	Conv. of BO (%)	Conv. of OPA (%)
1	1: 2: 300: 100: 1.5	0.5	45	8.5	65	74	24	83	77
2	1: 2: 300: 2.5	1	45	12	65	48	24	79	60
3	1: 2: 400: 100: 1.5	0.5	30	12	63	>99	24	81	>99
4	1: 2: 300: 100: 2.5	0.3	40	3+3	50/64	32/46	10+10	58/73	34/47

^aEntry 1 corresponding to the entry 1 in Table 1; entry 2 corresponding to the entry 9 in Table 1; entry 3 corresponding to the entry 10 in Table 1; entry 4 corresponding to the entry 11 in Table 1

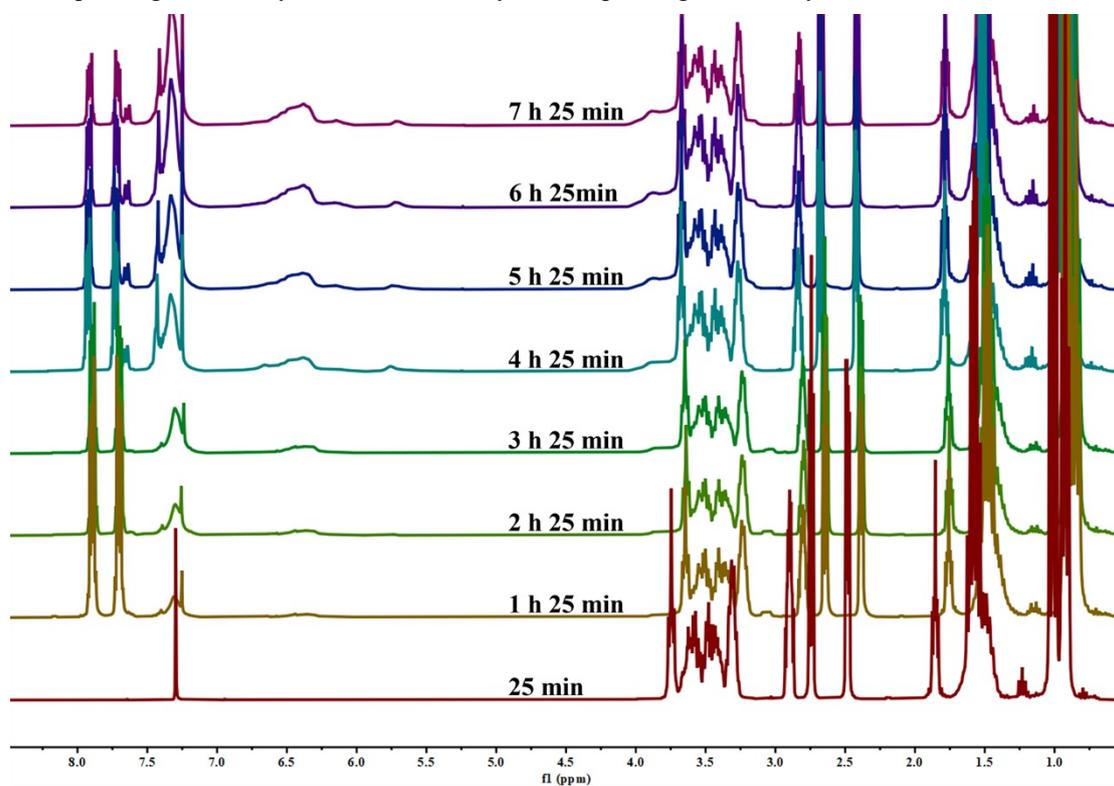


Figure S1. ¹H NMR (CDCl₃) characterization of the crude reaction mixture at different stages of self-switching polymerization before and after the addition of OPA at 25 °C without solvent (Table S1, entry 1).

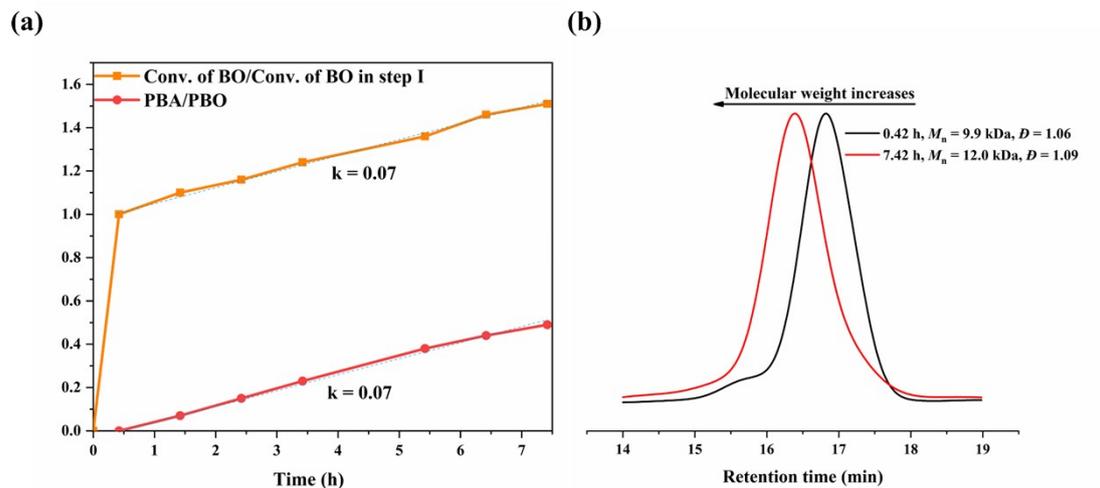


Figure S2. (a) Conv. of BO/Conv. of BO in step I: ratio of the full conversion of BO at each stage to the conversion of BO in step I; PBA/PBO: ratio of the content of polyacetal to the content of polyester in the polymer; the slopes of the curves were obtained by a linear fitting of the conversion curves. (b) GPC traces of polyether and poly[(BO)-*b*-(OPA)-*alt*-BO] using DCM as eluent showing increasing molecular weight but retaining narrow D after the addition of OPA (Table S1, entry 1).

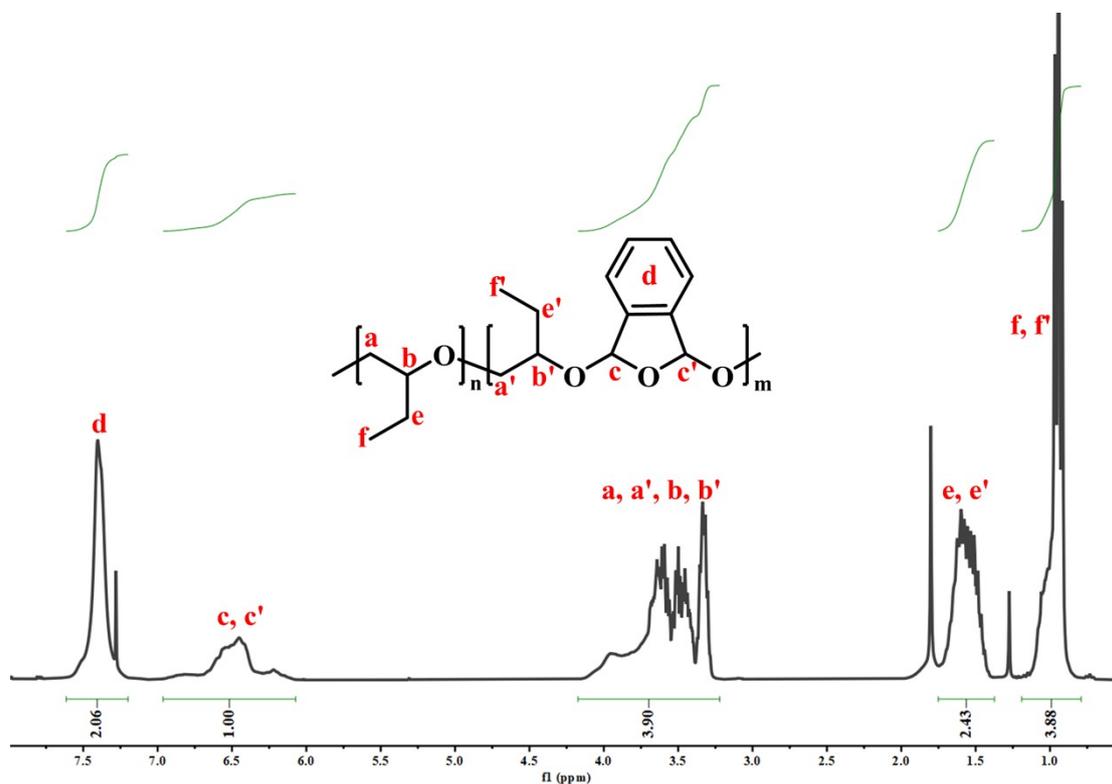


Figure S3. ^1H NMR spectrum of poly[(BO)-*b*-(OPA-*alt*-BO)] in CDCl_3 (Table S1, entry 1).

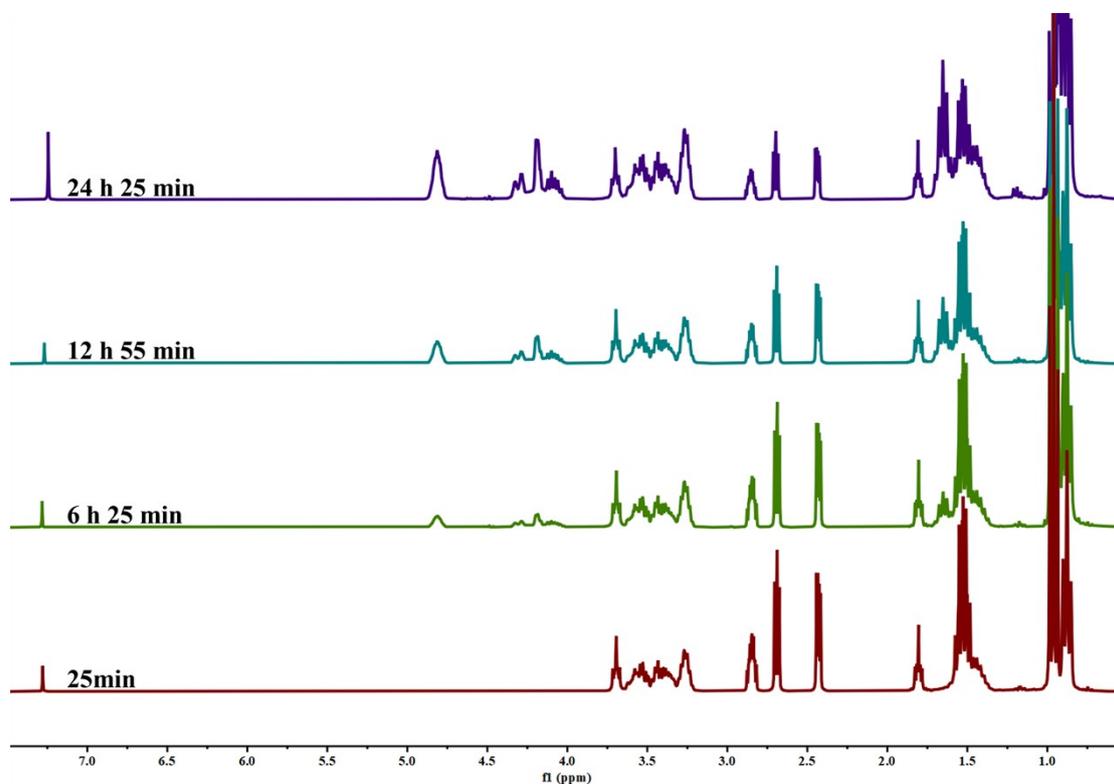


Figure S4. ^1H NMR (CDCl_3) characterization of the crude reaction mixture at different stages of self-switching polymerization before and after the addition of CO_2 at 25°C without solvent (Table S1, entry 2).

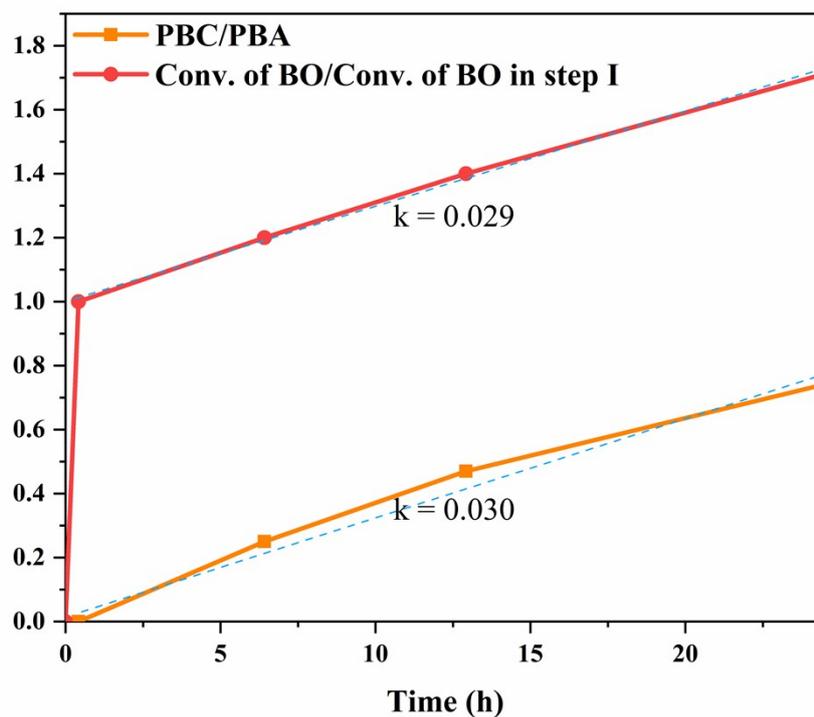


Figure S5. Conv. of BO/Conv. of BO in step I: ratio of the conversion of BO at each stage to the conversion of BO in step I; PBC/PBO: ratio of the content of polycarbonate to the content of polyester in the polymer; the slopes of the curves were obtained by a linear fitting of the conversion curves (Table S1, entry 2).

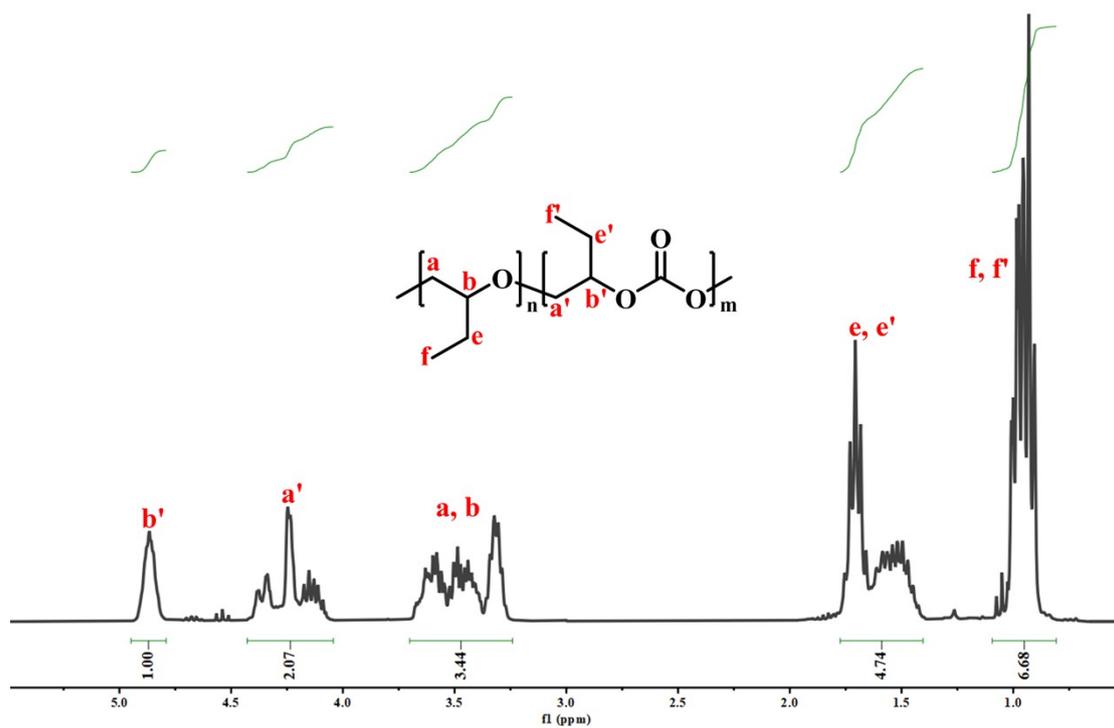


Figure S6. ^1H NMR spectrum of poly[(BO)-*b*-(CO₂-*alt*-BO)] in CDCl₃ (Table S1, entry 2).

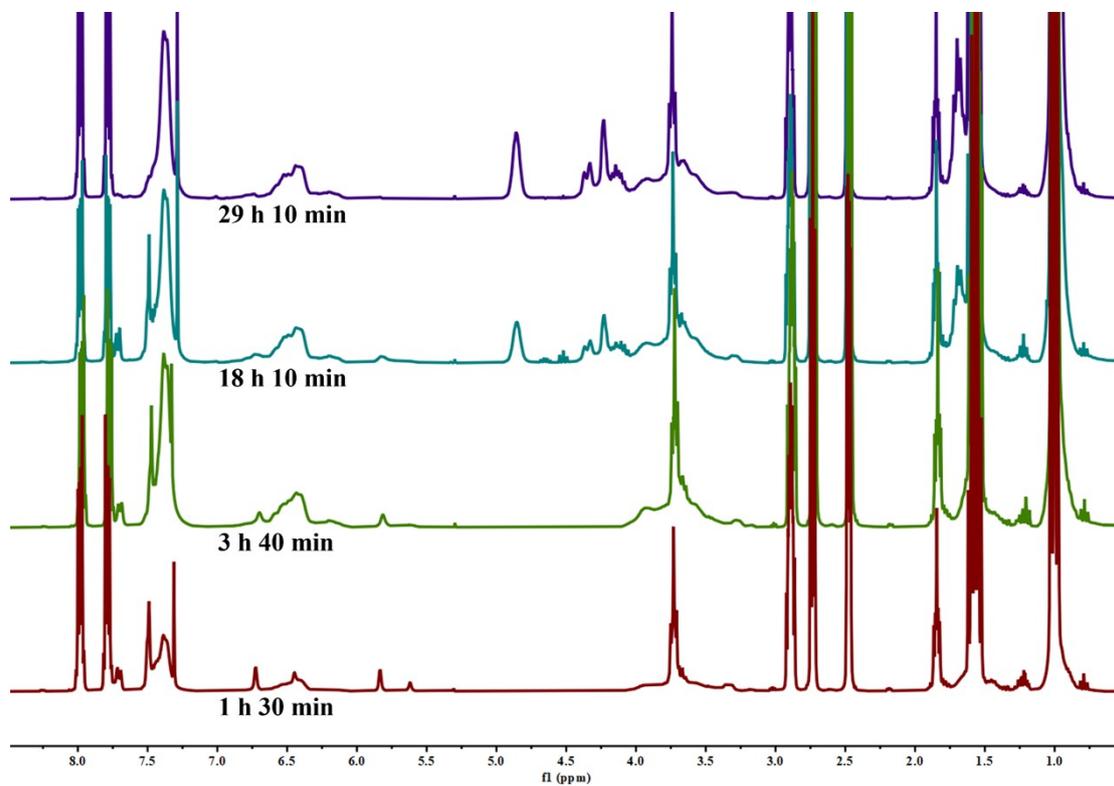


Figure S7. (a) ^1H NMR (CDCl₃) characterization of the crude reaction mixture at

different stages of self-switching polymerization at 25 °C without solvent (Table S1, entry 3).

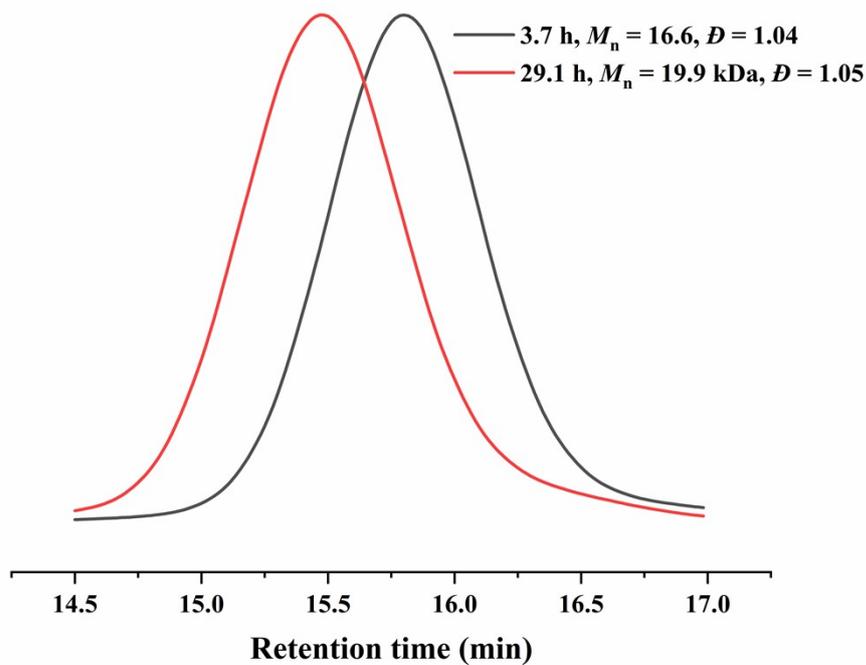


Figure S8. GPC traces of polyacetal and poly[(OPA-*alt*-BO)-*b*-(CO₂-*alt*-BO)] using dichloromethane as eluent showing increasing molecular weight but retaining narrow D after the addition of OPA (Table S1, entry 3).

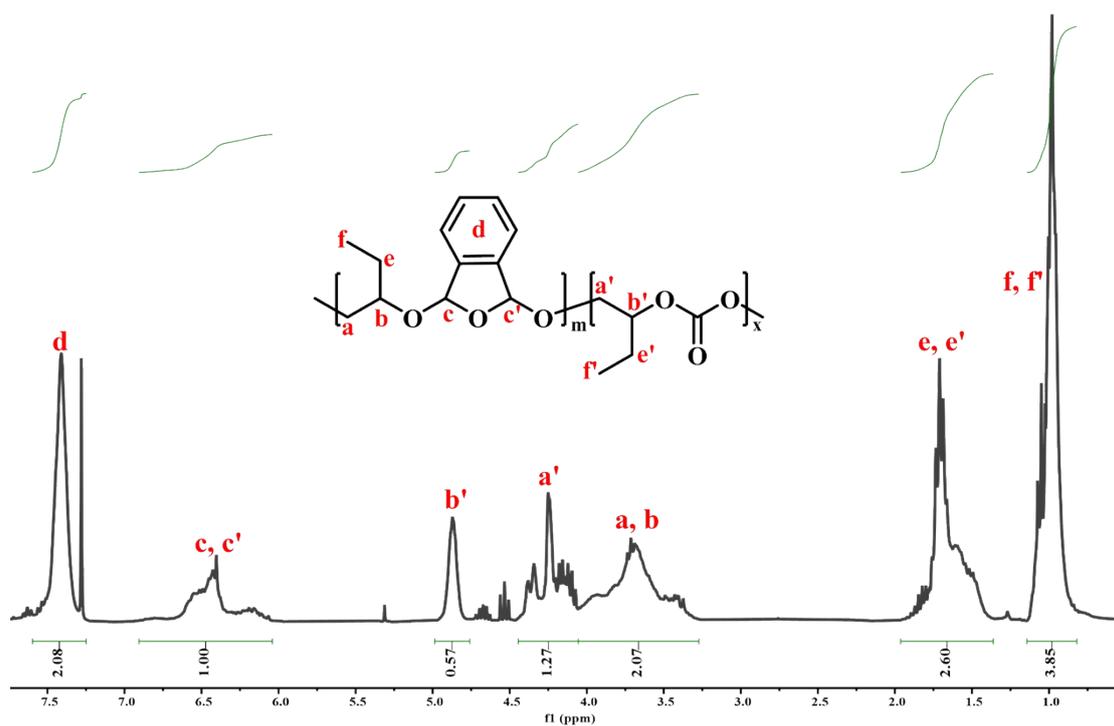


Figure S9. ^1H NMR spectrum of poly[(OPA-*alt*-BO)-*b*-(CO₂-*alt*-BO)] in CDCl₃

(Table S1, entry 3).

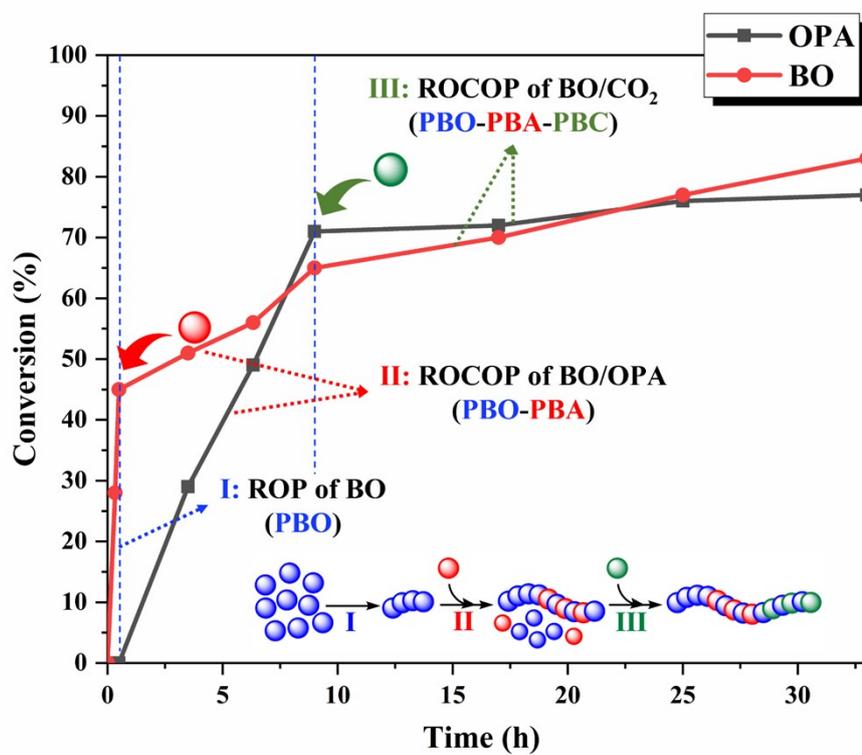


Figure S10. Conversion of BO/OPA with time calculated directly from ^1H NMR (Table 1, entry 1).

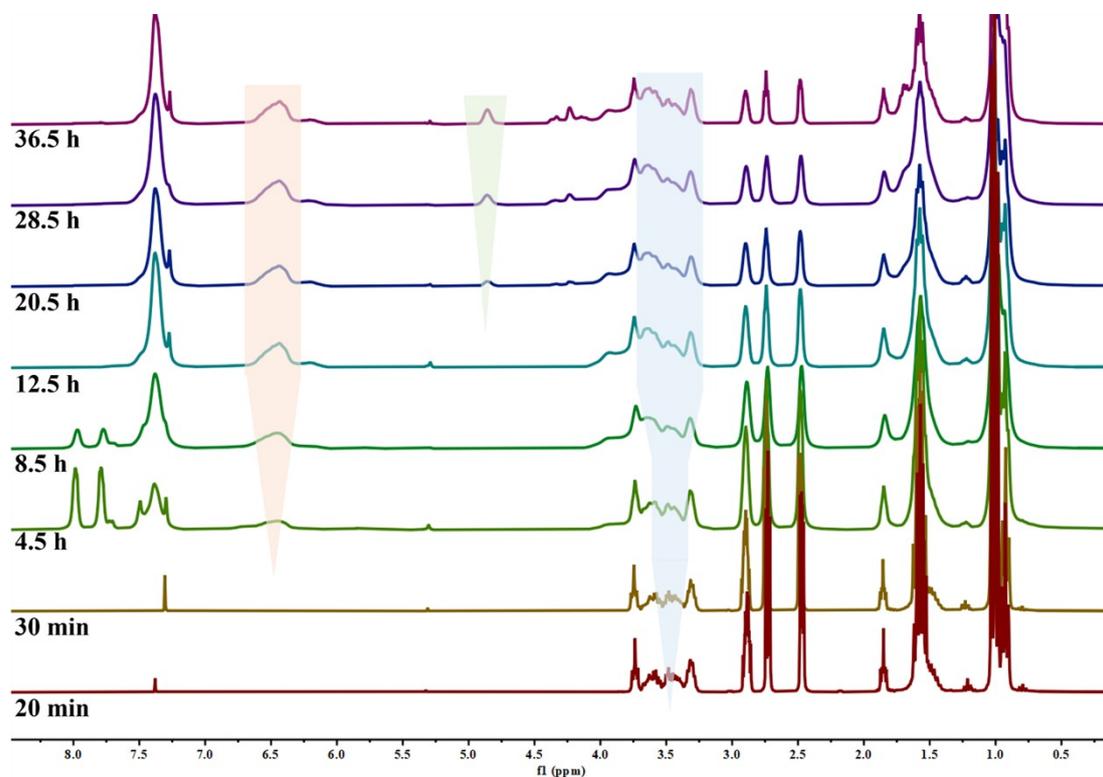


Figure S11. ^1H NMR (CDCl_3) characterization of the crude reaction mixture at different stages of self-switching polymerization of ABAC tetrablock copolymer at 25 $^\circ\text{C}$ without solvent (Table 1, entry 10).

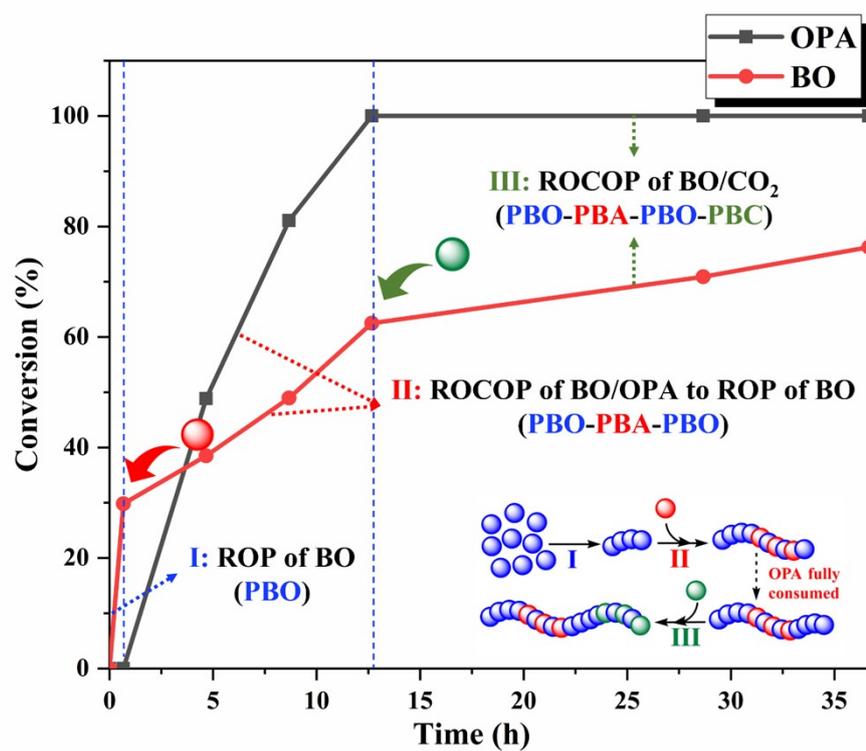


Figure S12. Conversion of BO/OPA with time calculated directly from ¹H NMR (Table 1, entry 10).

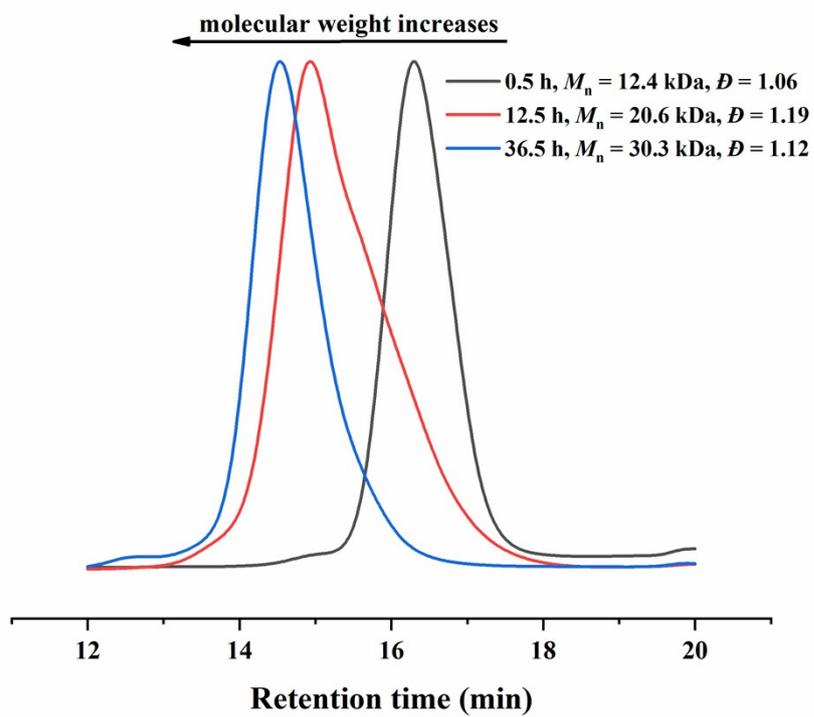


Figure S13. GPC traces of polymers obtained at different stages using DCM as eluent showing an increasing molecular weight but maintaining a narrow \mathcal{D} (Table 1, entry 10).

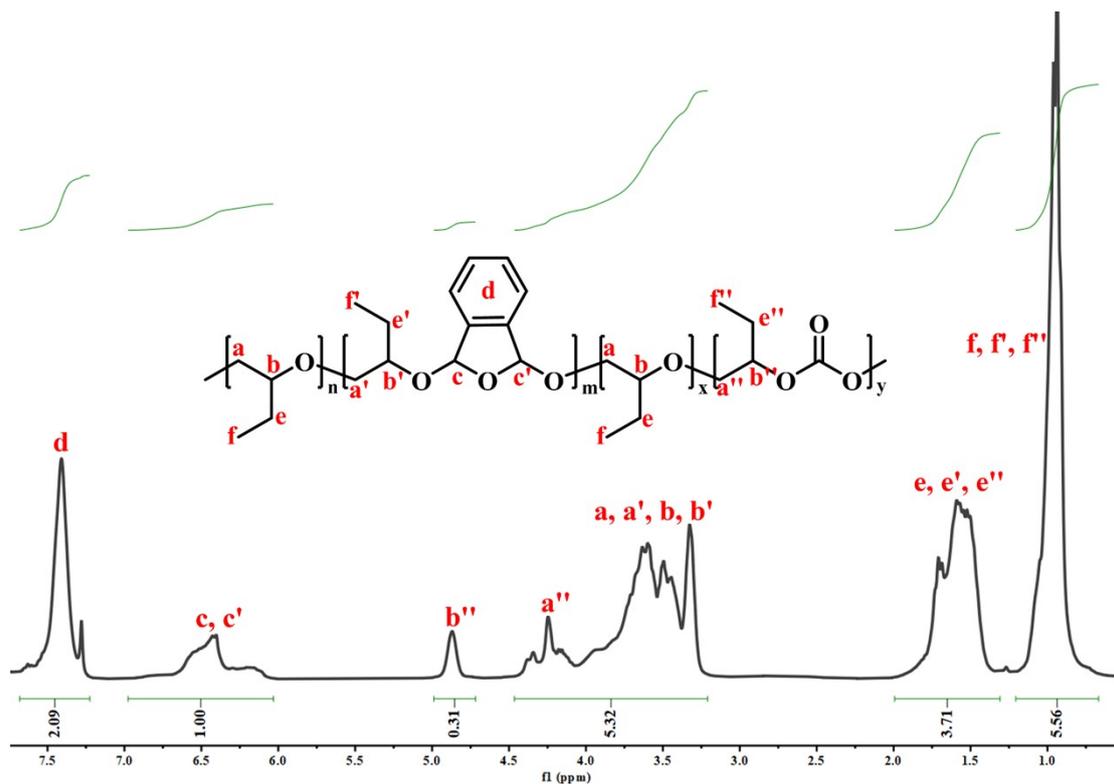


Figure S14. ^1H NMR spectrum (CDCl_3) of poly[(BO)-*b*-(OPA-*alt*-BO)-*b*-(BO)-*b*-(CO₂-*alt*-BO)] obtained in the sequential route (Table 1, entry 10).

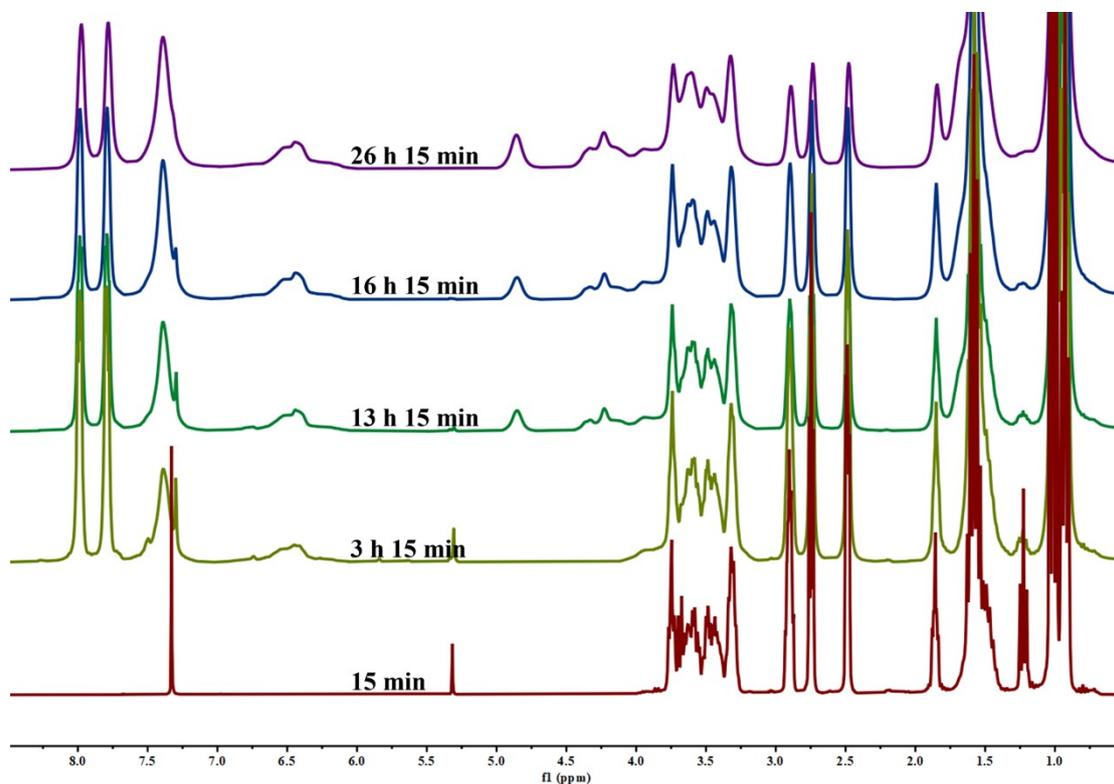


Figure S15. ^1H NMR (CDCl_3) characterization of the crude reaction mixture at

different stages of self-switching polymerization with gas shift (Ar-CO₂) at 25 °C

without solvent (Table 1, entry 11).

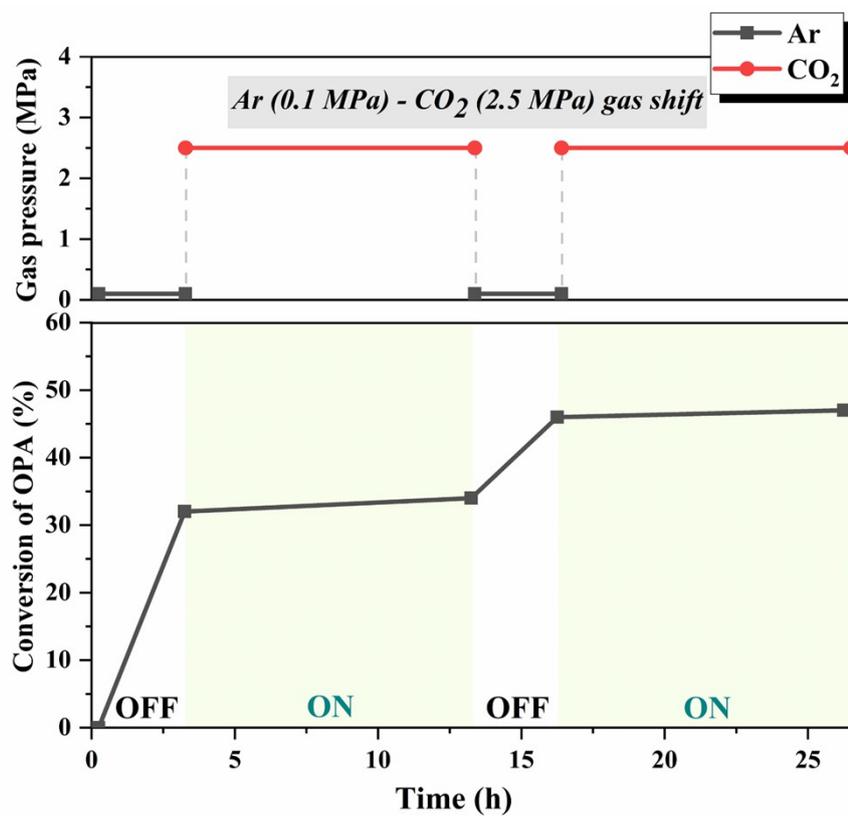


Figure S16. The conversion of OPA with time calculated directly from ¹H NMR in two Ar-CO₂ gas-shift cycle (Table 1, entry 11).

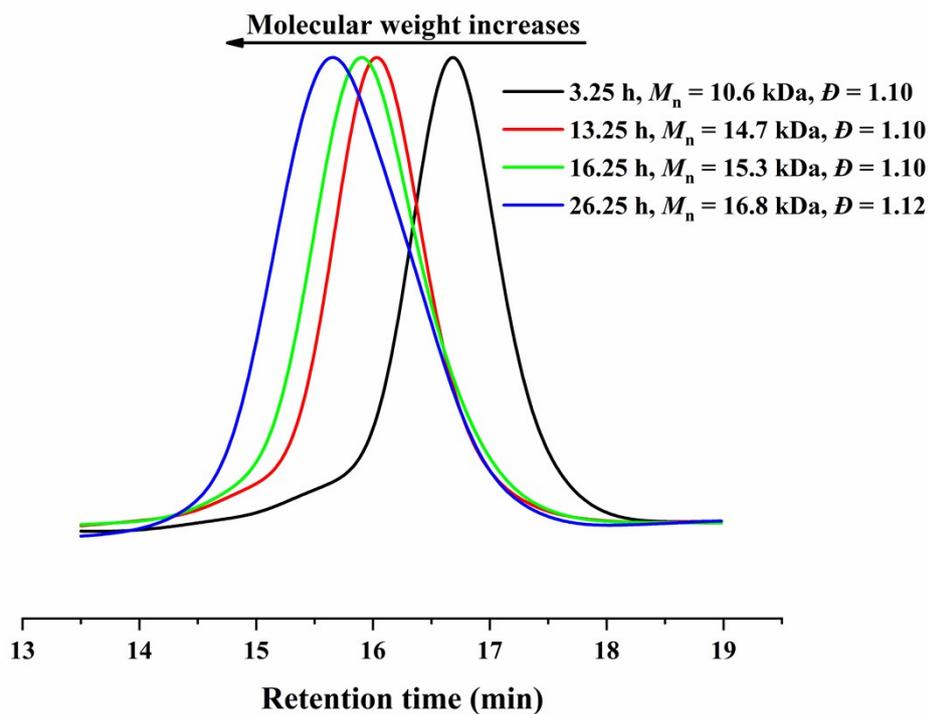


Figure S17. GPC traces of polymers obtained at different stages showing an increasing molecular weight but maintaining a narrow D (Table 1, entry 11).

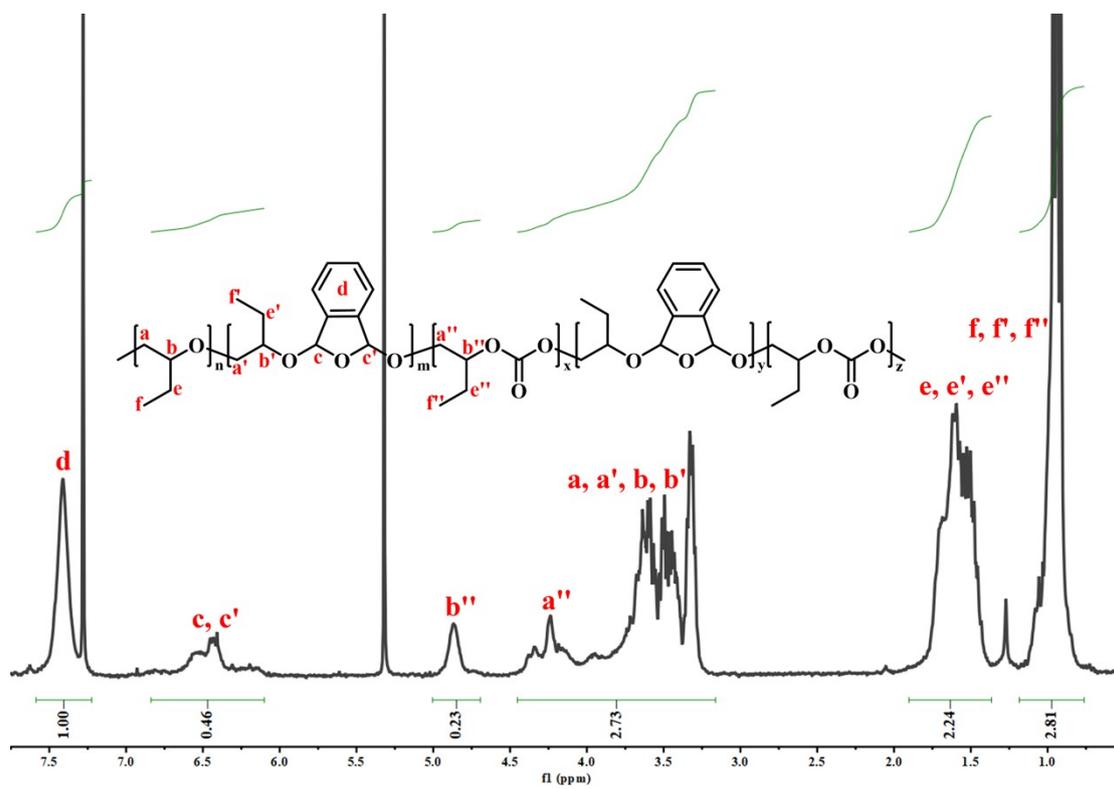


Figure S18. ^1H NMR spectrum of poly[(BO)-*b*-(OPA-*alt*-BO)-*b*-(CO₂-*alt*-BO)-*b*-(OPA-*alt*-BO)-*b*-(CO₂-*alt*-BO)] in CDCl₃ (Table 1, entry 11).

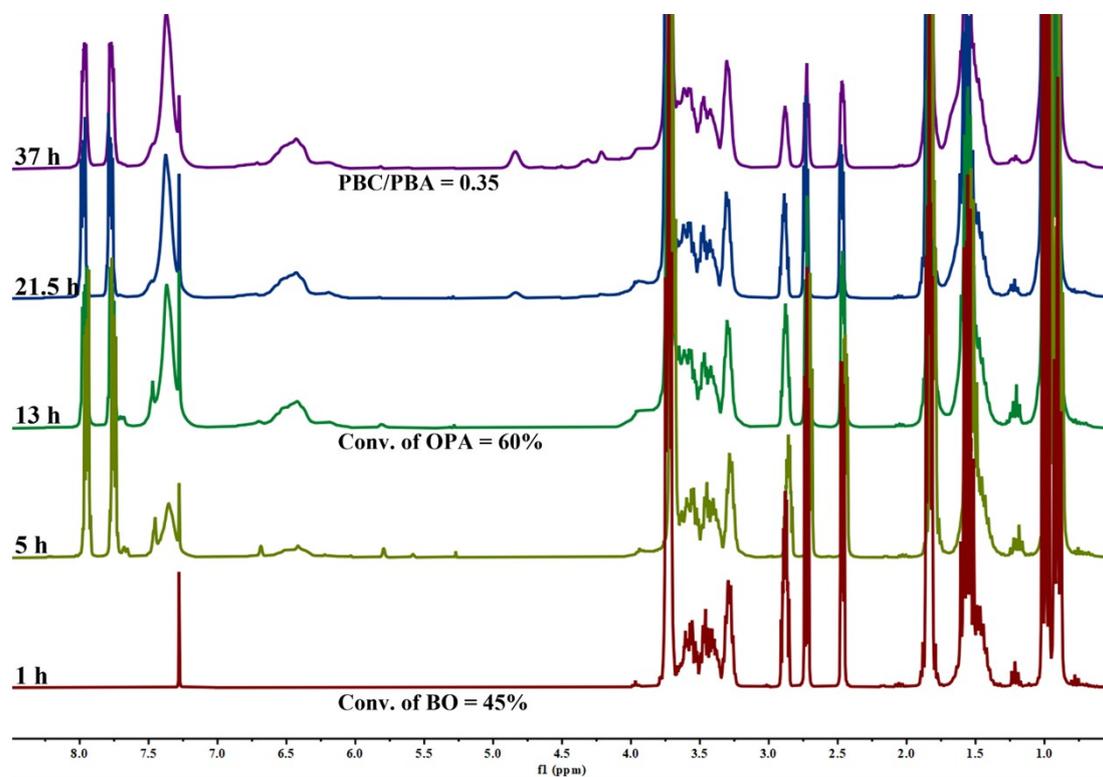


Figure S19. ^1H NMR (CDCl₃) characterization of the crude reaction mixture at different stages of self-switching polymerization at 25 °C (10 M in THF) (Table 1, entry 9).

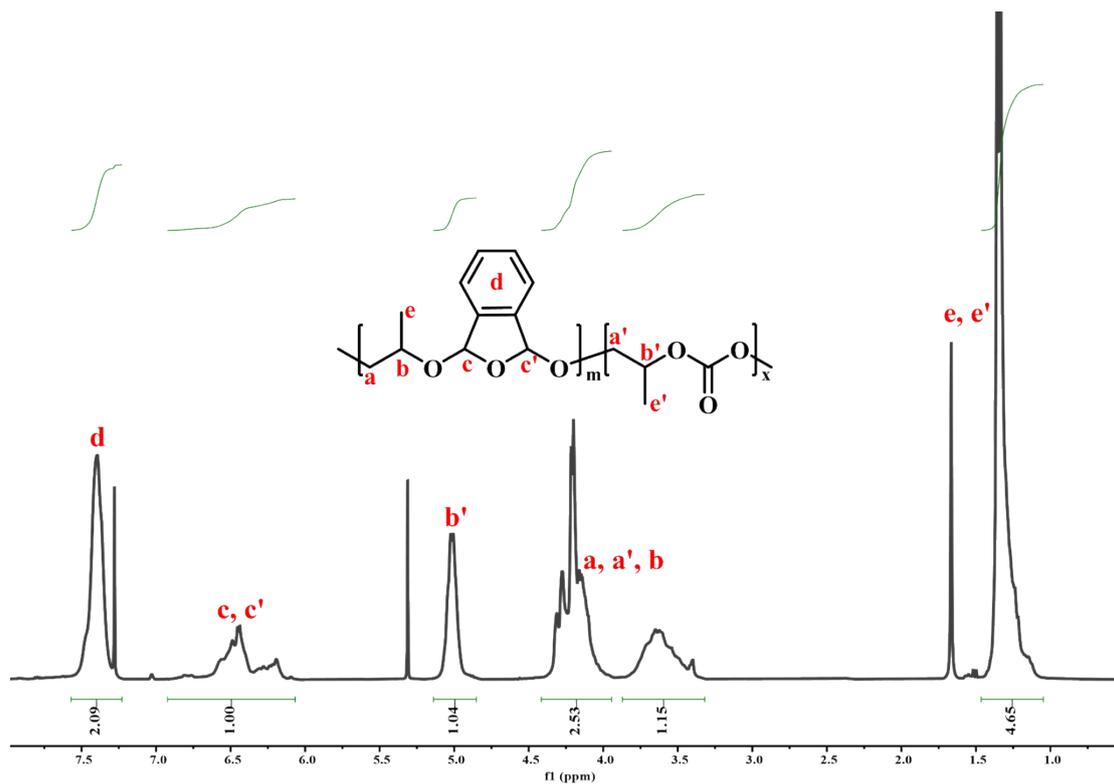


Figure S20. ¹H NMR spectrum of poly[(OPA-*alt*-PO)-*b*-(CO₂-*alt*-PO)] in CDCl₃

(Table 2, entry 1).

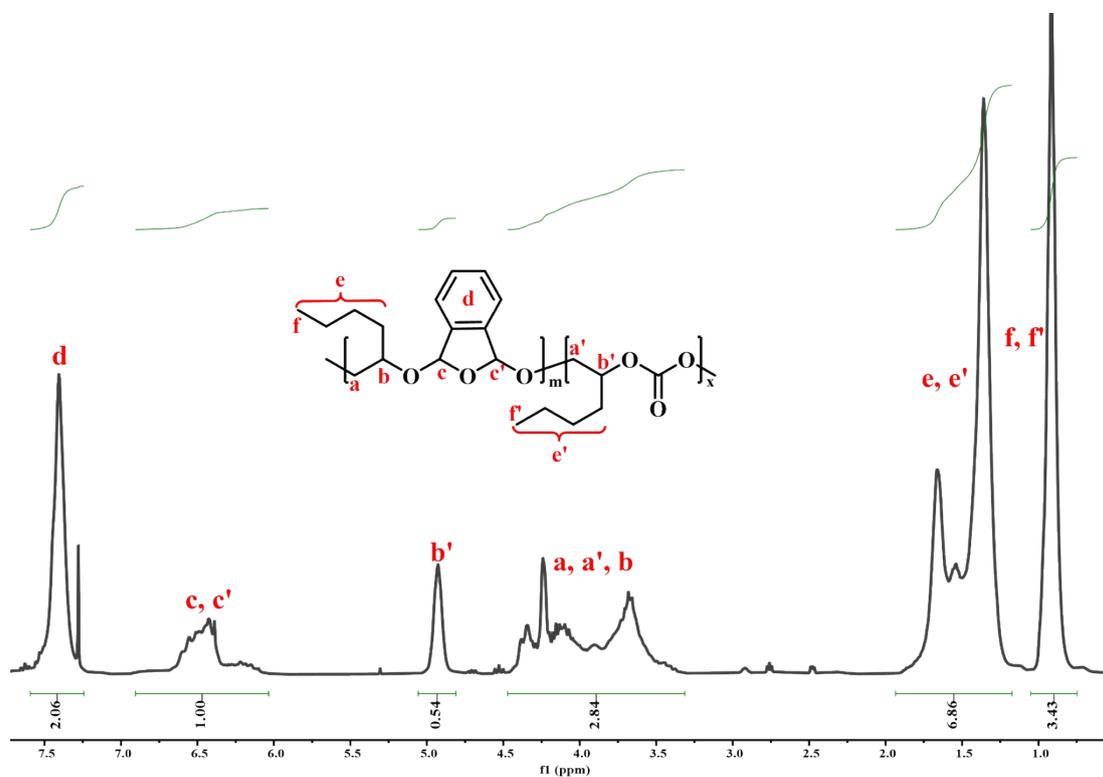


Figure S21. ¹H NMR spectrum of poly[(OPA-*alt*-HO)-*b*-(CO₂-*alt*-HO)] in CDCl₃

(Table 2, entry 2).

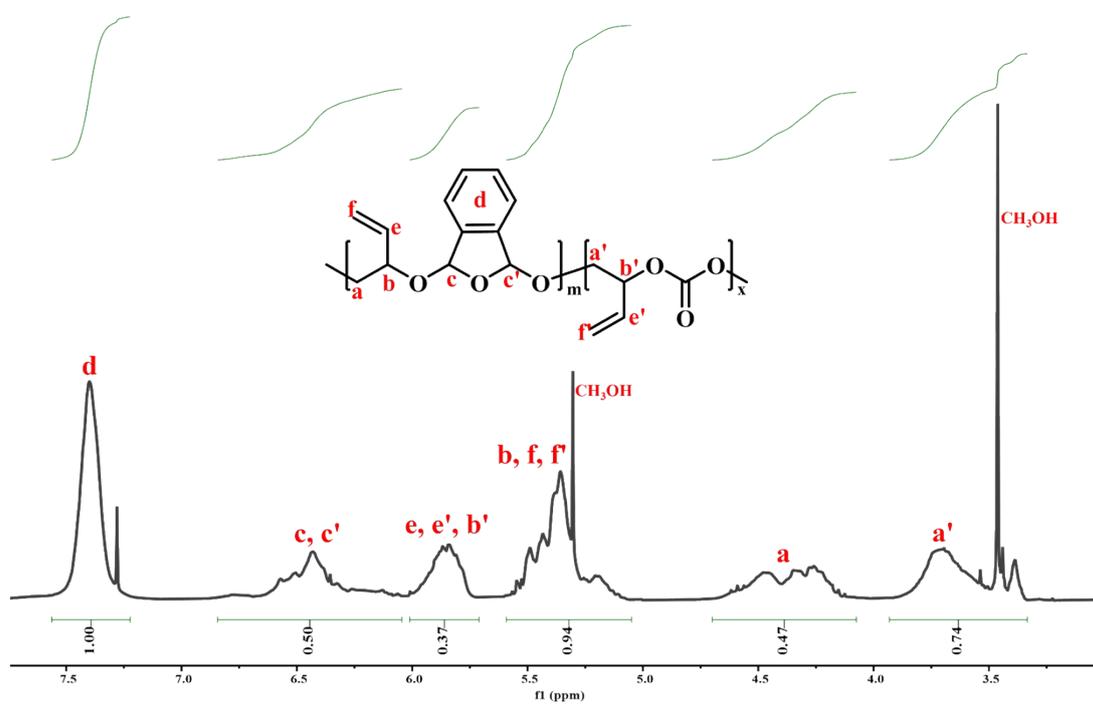


Figure S22. ^1H NMR spectrum of poly[(OPA-*alt*-EB)-*b*-(CO₂-*alt*-EB)] in CDCl₃

(Table 2, entry 3).

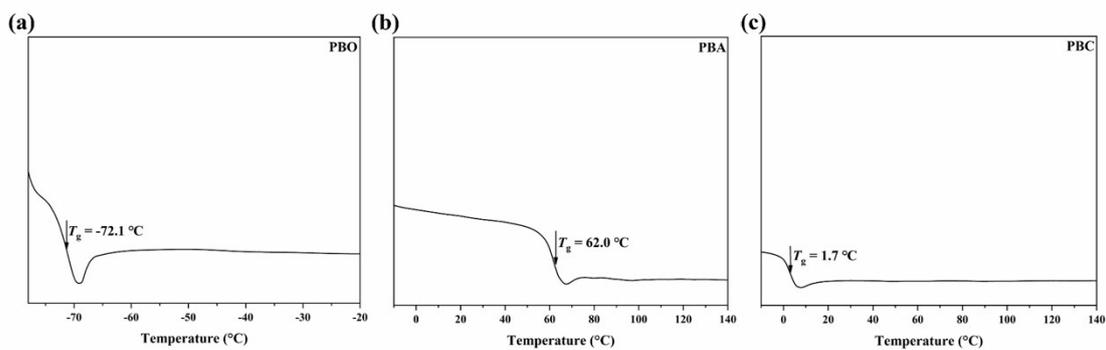


Figure S23. DSC curves for polymers: (a) PBO ($M_n = 22.3$ kDa, $D = 1.06$), (b) PBA

($M_n = 8.5$ kDa, $D = 1.13$), (c) PBC ($M_n = 16.9$ kDa, $D = 1.19$).

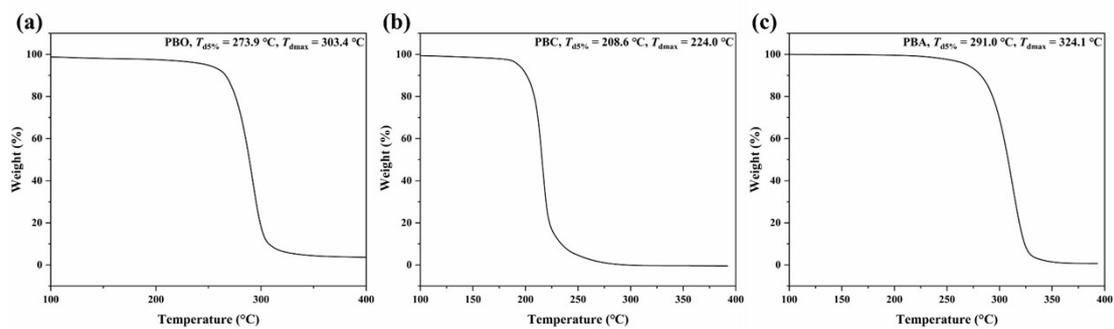


Figure S24. TGA curves for polymers: (a) PBO ($M_n = 22.3$ kDa, $\mathcal{D} = 1.06$), (b) PBA ($M_n = 8.5$ kDa, $\mathcal{D} = 1.13$), (c) PBC ($M_n = 16.9$ kDa, $\mathcal{D} = 1.19$).