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Organic Lewis Pairs for Selective Copolymerization of Epoxides with Anhydrides to Access Sequence-Controlled Block Copolymers

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1. Experimental sections

Chemicals

Unless otherwise stated, all chemicals are used without further purification. Propylene oxide (PO), phthalic anhydride (PA), BEt_3 and *rac*-1,2-propanediol were purchased from Acros. *L*-Lactide (*L*-LA) was purchased from Alfa Aesar. *S*-PO was purchased form Innochem. 1,2-Butylene oxide (BO), 1,4-Benzenedimethanol (BDM) and 2-chloro-1,3,2-dioxaphospholane were purchased from TCI. 1-tert-butyl-2,2,4,4,4-pentakis(dimethylamino)-2Λ5,4Λ5-catenadi(phosphazene) (*t*-BuP_2) and 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2Λ5,4Λ5-catenadi(phosphazene) (*t*-BuP_4) were purchased from Sigma Aldrich. Bisphenol A and tris(2,4-pentanedionato)chromium(III) ($Cr(acac)_3$) were purchased from Aladdin. BO, PO and *S*-PO were dried over CaH_2 for 48 h, distilled and stored under nitrogen atmosphere. Toluene was purified by a solvent purification system (Etelux SPS800). PA was first dissolved in acetic anhydride and stirred at 120 ℃ overnight before recrystallization at room temperature and further purified by sublimation before use. *L*-LA were purified by sublimation before use. All manipulations were performed using a standard Schlenk technique or in a nitrogen-filled Etelux Lab2000 glovebox unless otherwise mentioned.

Methods

^1H, ^{13}C, ^{31}P, ^{11}B, COSY, HSQC and DOSY NMR spectra were recorded on a Bruker Avance III spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) at room temperature in chloroform-d_1 (purchased form Innochem), and chemical shifts were referenced to an internal standard. DOSY NMR tests were performed at a steady temperature of 25 ℃ with at least 16 gradient increments using the ledbpgp2s sequence. Homonuclear decoupled ^1H NMR of PLLA was carried out with the decoupler set at 1.60 ppm. Gel permeation chromatography (GPC) analyses were carried out at 40 ℃ and a flow rate of 1.0 mL/min, with THF as the eluent on an Agilent PL-GPC 50 instrument coupled with a refractive index (RI) detector with respect to polystyrene (PS) standards. The columns included a PLgel guard 5 μm 50 ×7.5 mm column, a PLgel mixed-B 300 × 7.5 mm column and a PLgel mixed-C 300 × 7.5 mm column. Samples for GPC analysis were filtered through 0.22 μm PTFE filters. Chiral gas chromatography (GC) analyses were carried out at an Agilent 7890A instrument equipped with an FID and a chiral GC column (Agilent CycloSil-B 30 m × 0.25 mm ID × 0.25 μm film). Liquid chromatography-mass spectrometry (LC-MS) analyses were performed on an Agilent LC 1200 and Bruker micrOTOF-Q II instrument with an Eclipse Plus C18 (3.5μm) column. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) study was performed at an Autoflex III smart beam mass spectrometry from Bruker

company. The polymer samples were obtained at a low PA conversion. Then the crude products were dissolved in THF at an 1 mg·mL^{-1} concentration. The cationization agent was sodium trifluoroacetate prepared as 5 mg·mL^{-1} solution in THF. And the matrix was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and was dissolved in THF at a concentration of 40 mg·mL^{-1}. Tested solution was mixed in a volume ratio of 4:1:4 of matrix, salt and polymer sample. Differential scanning calorimetry (DSC) analyses of polymer samples were carried out at a scanning speed of 10 ℃/min (from 0 ℃ to 200 ℃) on a TA instruments DSC Q2000 with three heating cycles. Wide angle X-ray diffraction (WAXD) analyses of polymer powder were performed on a Rigaku diffractometer with Cu KR radiation (λ = 1.54056 Å) over the 2θ range of 5-40^{o} with a scan speed of 7.5 ^{o}/min at room temperature. The samples for WAXD are from the isolated polymers after separation from methanol and drying under vacuum.

Block copolymer synthesis in a one-step procedure

A typical polymerization procedure was as follows: In a nitrogen-filled glovebox, *t*-BuP_2 (0.01 mmol, 1 equiv.), BEt_3 (0.02 mmol, 2 equiv.), BDM (0.01 mmol, 1 equiv.) and PA (0.5 mmol, 50 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by BO (1 mmol, 100 equiv.) and toluene (0.16 mL; $[BO]_0$ = 4 M). The tube was removed from the glovebox and placed in an aluminum heating block with predetermined temperature (60 ℃). During polymerization, a crude aliquot was time-regularly withdrawn from the system by syringe and monitored by ^{1}H NMR and GPC to determine monomer conversion and molar mass. After the prescribed time, the reaction mixture was diluted with approximately 2 mL dichloromethane and dropwise precipitated into 100 mL of methanol or alcohol acidified by hydrochloric acid with vigorous stirring, then the methanol or alcohol were filtrated or poured out. The resulting polymers were dried under vacuum at 40 ℃. All analyses and further chemical modification were performed on the crude samples.

Random copolymer synthesis

A typical polymerization procedure was as follows: In a nitrogen-filled glovebox, the appropriate amount of *t*-BuP_2 (0.01 mmol, 1 equiv.), BEt_3 (0.02 mmol, 2 equiv.), BDM (0.01 mmol, 1 equiv.) and PA (0.5 mmol, 50 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by BO (5 mmol, 500 equiv.). The tube was removed from the glovebox and placed in an aluminum heating block with predetermined temperature (60 ℃). After the prescribed time (2 h), the reaction mixture was diluted with approximately 2 mL dichloromethane and dropwise precipitated into 100 mL of methanol or alcohol acidified by hydrochloric acid with vigorous stirring, then the methanol or alcohol were filtrated or poured

out. The resulting polymers were dried under vacuum at 40 ℃. All analyses were performed on the crude samples.

Polyester synthesis

A typical polymerization procedure was as follows: In a nitrogen-filled glovebox, the appropriate amount of *t*-BuP_2 (0.01 mmol, 1 equiv.), BEt_3 (0.02 mmol, 2 equiv.), BDM (0.01 mmol, 1 equiv.) and PA (0.5 mmol, 50 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by BO (1 mmol, 100 equiv.) and toluene (0.16 mL; $[BO]_0$ = 4 M). The tube was removed from the glovebox and placed in an aluminum heating block with predetermined temperature (60 ℃). During polymerization, a crude aliquot was time-regularly withdrawn from the system by syringe and monitored by ^{1}H NMR and GPC to determine monomer conversion and molar mass. Before full consumption of PA, the reaction was quenched (0.5 h of reaction for MALDI-TOF MS). Subsequently, the mixture was diluted with approximately 2 mL dichloromethane and dropwise precipitated into 100 mL of methanol or alcohol acidified by hydrochloric acid with vigorous stirring, then the methanol or alcohol were filtrated or poured out. The resulting polymers were dried under vacuum at 40 ℃. All analyses and further chemical modification were performed on the crude samples.

Polyether synthesis

A typical polymerization procedure was as follows: In a nitrogen-filled glovebox, the appropriate amount of *t*-BuP_2 (0.01 mmol, 1 equiv.), BEt_3 (0.02 mmol, 2 equiv.) and BDM (0.01 mmol, 1 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by BO (2 mmol, 200 equiv.) and toluene (0.32 mL; $[BO]_0$ = 4 M). The tube was removed from the glovebox and placed in an aluminum heating block with predetermined temperature (60 ℃). After 1.5 h, the reaction mixture was cooled to room temperature and the resulting products were dried under vacuum at 40 ℃. The resulting polymers were dried under vacuum at 40 ℃. All analyses were performed on the crude samples.

Pentablock copolymer synthesis in a tandem polymerization procedure

A typical polymerization procedure was as follows: In a nitrogen-filled glovebox, the appropriate amount of *t*-BuP_2 (0.01 mmol, 1 equiv.), BEt_3 (0.02 mmol, 2 equiv.), BDM (0.01 mmol, 1 equiv.) and PA (0.5 mmol, 50 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by BO (1 mmol, 100 equiv.) and toluene (0.16 mL; $[BO]_0$ = 4 M). The tube was removed from the glovebox and placed in an aluminum heating block with predetermined temperature (60 ℃). During polymerization, a crude aliquot was time-regularly withdrawn from the system by syringe and monitored by ^{1}H NMR and GPC to determine monomer conversion and molar mass. After the prescribed time (5 h), a batch of *L*-LA

(1 mmol, 100 equiv.) was added. Finally, the reaction mixture was diluted with approximately 2 mL dichloromethane and dropwise precipitated into 100 mL of methanol or alcohol acidified by hydrochloric acid with vigorous stirring, then the methanol or alcohol were filtrated or poured out. The resulting polymers were dried under vacuum at 40 ℃. All analyses were performed on the crude samples.

End-group assays

The similar procedure was previously reported in the literature.[1] First, a stock solution containing Bisphenol A (400 mg), $Cr(acac)_3$ (5.5 mg) and 10 mL of pyridine was prepared. Second, the polymer or model chemical was dissolved in $CDCl_3$ (50 mg/0.5 mL) and 40 μL of the stock solution were added to an NMR tube. Finally, the phosphorus agent of 2-chloro-1,3,2-dioxaphospholane (30 μL) was added to the NMR tube in a nitrogen-filled glovebox. The mixture was allowed to react for at least 0.5 h and then analyzed by ^{31}P NMR spectroscopy after calibration with the internal standard (bisphenol A & phosphorus agent).

Determination of regioselective ring-opening of *S*-PO[2]

A round-bottomed flask was charged with polyesters obtained from enantiopure *S*-PO (100 mg), THF (10 mL), MeOH (2 mL) and NaOH (4 mol/L, 2 mL). The resultant mixture was stirred at room temperature for 24 h. Then, it was concentrated to about 8 mL by evaporation. The solution was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$; and then the mixture was filtered and evaporated to colorless or yellow oil with small amount of ethyl acetate. The enantiomeric excess (*ee*) of the resultant diols was determined by an Agilent 7890A gas chromatography (GC) instrument equipped with a hydrogen flame ionization detector (FID) and a chiral GC column (Agilent CycloSil-B 30 m × 0.25 mm ID × 0.25 μm film). Retention time of diols and separation methods were showed as follows:

1,2-Propanediol: Injection temperature 275 ℃; FID detection temperature 275 ℃; Oven temperature 60 ℃. Retention time of *S*-1,2-propanediol = 29.0 min; Retention time of *R*-1,2-propanediol = 30.6 min.

LC-MS analyses

The presence of *t*-BuP_2 residual was detected by liquid chromatography-electrospray ionization time of flight mass spectrometry (ESI TOF MS) with a positive ion polarity mode. The *t*-BuP_2 standard was dissolved in MeCN at *ca.* 5 $\mu g \cdot mL^{-1}$ concentration. The reaction mixture and precipitated crude copolymer were dissolved in MeCN at *ca.* 10 mg mL^{-1} concentration, and then were centrifuged at 10 kr/min. Retention time and separation methods were showed as follows:

t-BuP$_2$: Flow rate 0.4 mL/min; Eluent MeCN; Oven temperature 35 ℃; Retention time of *t*-BuP$_2$ = 21.4 min.

2. Optimization of catalysts and reaction conditions

The general principles and recommendations for a practicable catalyst were described as follows: (i) the selected catalyst should be effective for two different types of polymerization, which could be tested by independent polymerization experiments; (ii) growing active chains should be compatible with each discrete polymerization in the system, ensuring the formation of a copolymer rather than polymer mixtures; (iii) the conversion of one monomer is remarkably faster than another one in view of both kinetic and thermodynamic control, which guarantees a high chemoselectivity with very little tapering structure between two blocks; and (iv) there should be negligible chain transfer and chain termination side reactions in the polymerization, in which a living/controlled polymerization is highly desired.

Following the abovementioned guidelines, we attempted a series of organocatalysts for such a selective copolymerization. The model copolymerization of phthatic anhydride (PA) with 1,2-butylene oxide (BO) was firstly investigated. The symmetrical structure and fewer protons in PA facilitate NMR analyses. Meanwhile, high boiling point (63 ℃) of BO is in favor of real-time NMR and GPC experiments at the polymerization temperature (60 ℃). In the catalyst optimization, single phosphazene base *t*-BuP$_2$ (pK$_a$ = 33.5 in MeCN) was unable to catalyze the ROP of BO, and transesterifications were observed in the ROAC of PA/BO. Other organic catalysts like *N*-Heterocyclic Olefins (NHOs) displayed a pretty slow polymerization rate for the ROP of epoxides.

Scheme S1. Illustration of the possible polymeric products by ring-opening copolymerization of mixed feedstocks containing anhydrides and excess epoxides.

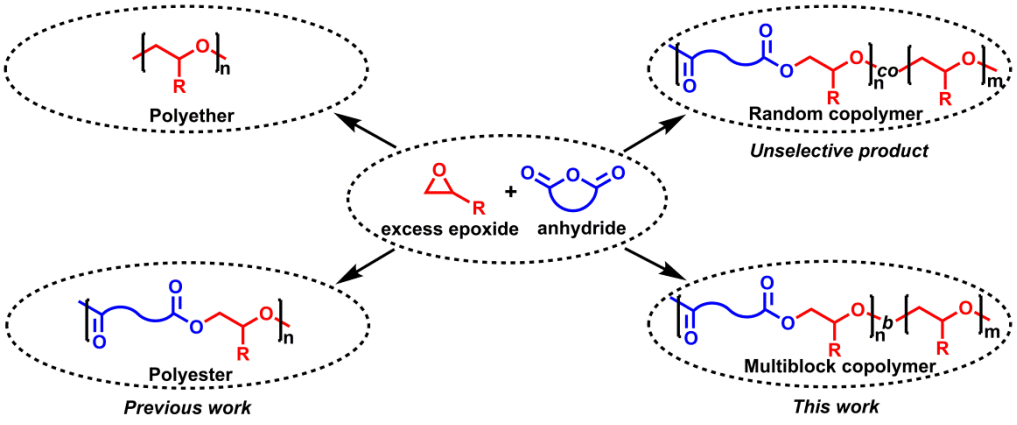


Table S1. Optimization of catalysts and conditions for selective copolymerization of anhydride with BO.[a]

entry	Temp. (℃)	Solvent	Time (h)	%Conv. (PA)[b]	%Conv. (BO)[c]	Ether (%)[d]	$M_{n,\,theo}$ (kDa)[e]	$M_{n,\,GPC}$ (kDa)[f]	$Đ$[f]
1	r.t.	Tol	6	49	25	<1	5.6	5.0	1.06
			20	>99	56	11	11.6	10.1	1.08
2	40	Tol	4	87	43	<1	9.7	8.5	1.05
			20	>99	66	24	12.3	10.8	1.06
3	60	Tol	1	87	44	< 1	9.8	9.3	1.07
			7	>99	85	41	13.7	13.5	1.07
4	80	Tol	0.33	97	48	<1	10.8	9.9	1.10
			16	>99	89	44	14.0	12.8	1.11
5	100	Tol	0.1	78	39	<1	8.7	8.0	1.09
			16	>99	93	46	14.2	12.9	1.12
6	60	2-MeTHF	1	76	38	<1	8.5	7.3	1.07
			7	>99	74	32	12.9	9.8	1.10
7	60	γBL	1	47	24	<1	5.3	4.4	1.05
			7	>99	63	21	12.1	10.2	1.09
8[g]	60	Tol	1	<1	39	>99	2.9	1.7	1.21
9[h]	60	Tol	1	gelation	-	-	-	-	-

[a]Unless otherwise stated, the polymerizations were performed with the 1:2:1:50:100 molar ratio of [*t*-BuP_2]/[BEt_3]/[BDM]/[PA]/[BO]. [b]Conversion of PA was determined by ^{1}H NMR spectroscopy. [c]Conversion of BO was determined by ^{1}H NMR spectroscopy. [d]The content of polyether in the corresponding copolymer. [e]$M_{n,\,theo} = M_{BDM} + M_{PA} \times$ mol(PA)/mol(BDM) $\times$ Conv.(PA) + $M_{BO} \times$ mol(BO)/mol(BDM) $\times$ Conv.(BO). [f]M_n and $Đ$ were determined by GPC analysis in THF calibrated by PS standards. [g]$B(C_6F_5)_3$ served as Lewis acid with the 1:2:1:50:100 molar ratio of [*t*-BuP_2]/[$B(C_6F_5)_3$]/[BDM]/[PA]/[BO]. [h]Maleic anhydride (MA) served as comonomer with the 1:2:1:50:100 molar ratio of [*t*-BuP_2]/[BEt_3]/[BDM]/[MA]/[BO].

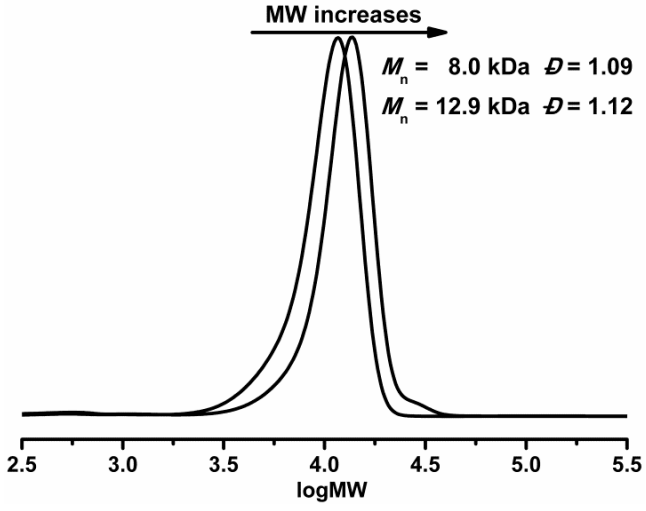


Figure S1. Evolution of GPC traces. The copolymerization was performed at 100 ℃ and quenched at 0.1 h (Conv.(PA) = 78%) and 16 h (Conv.(PA) > 99%), respectively.

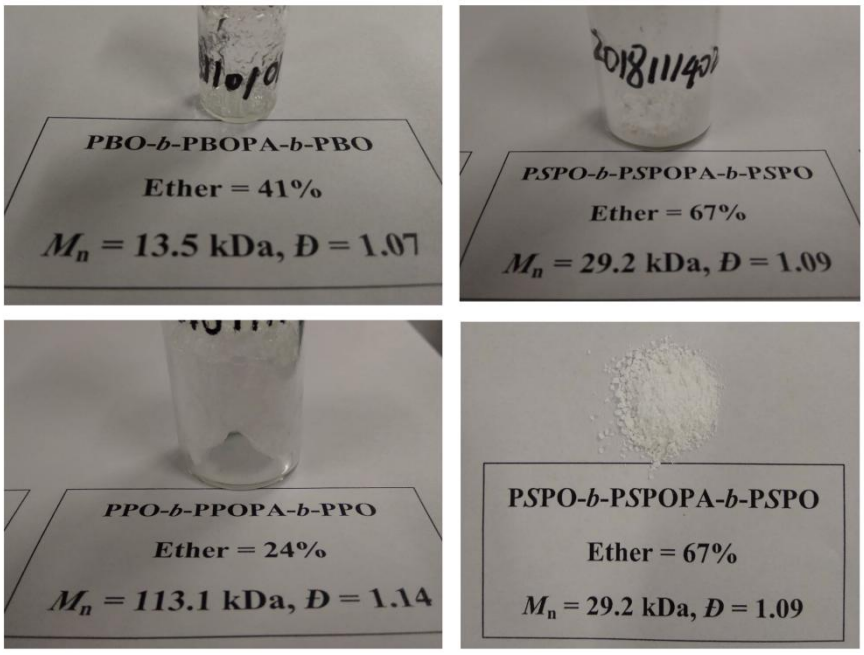


Figure S2. Images of the corresponding block copolymers.

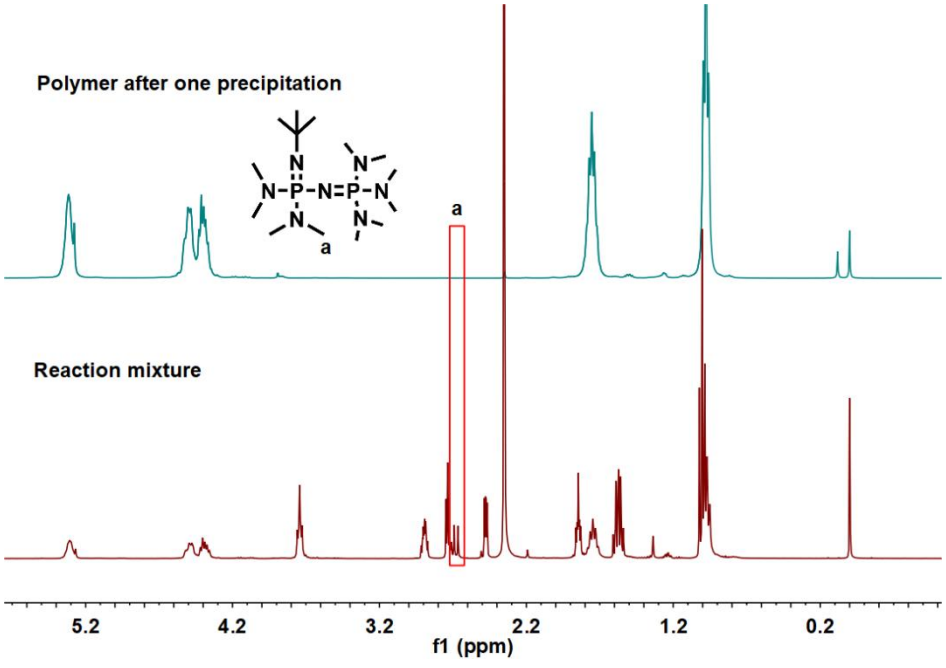


Figure S3. The ^{1}H NMR spectra of the reaction mixture and the precipitated copolymer. *t*-BuP_2 was not detected in the precipitated polymers.

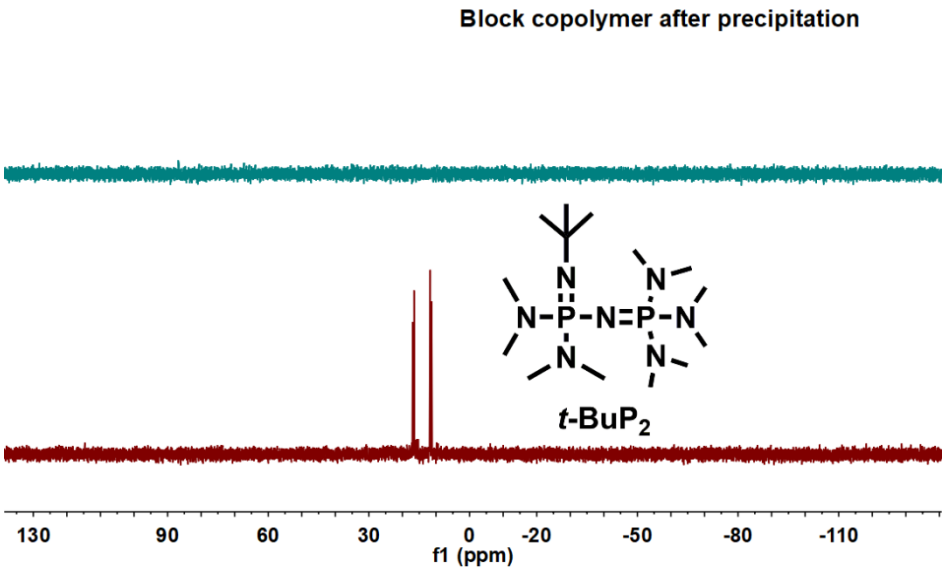


Figure S4. The ^{31}P NMR spectra of the precipitated copolymer and *t*-BuP_2 standard.

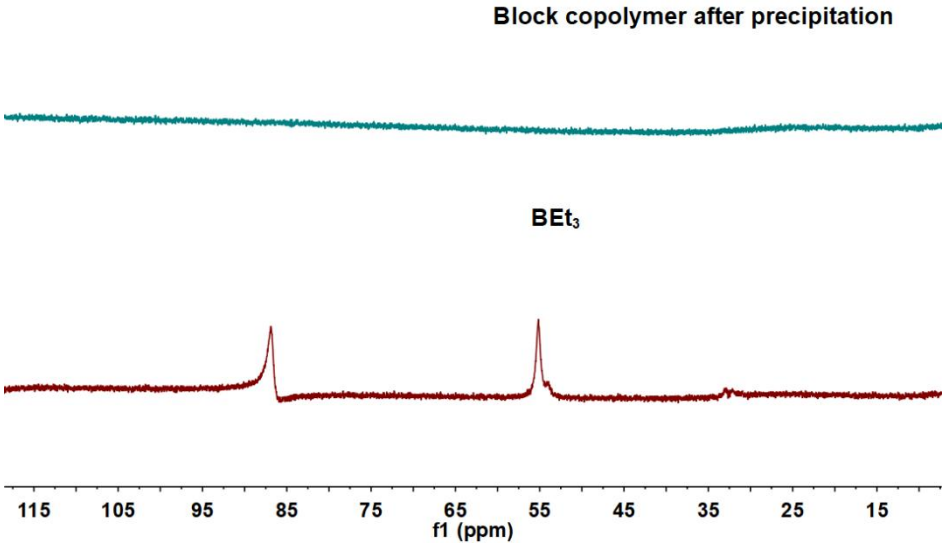


Figure S5. The ^{11}B NMR spectra of the precipitated copolymer and BEt_3 standard.

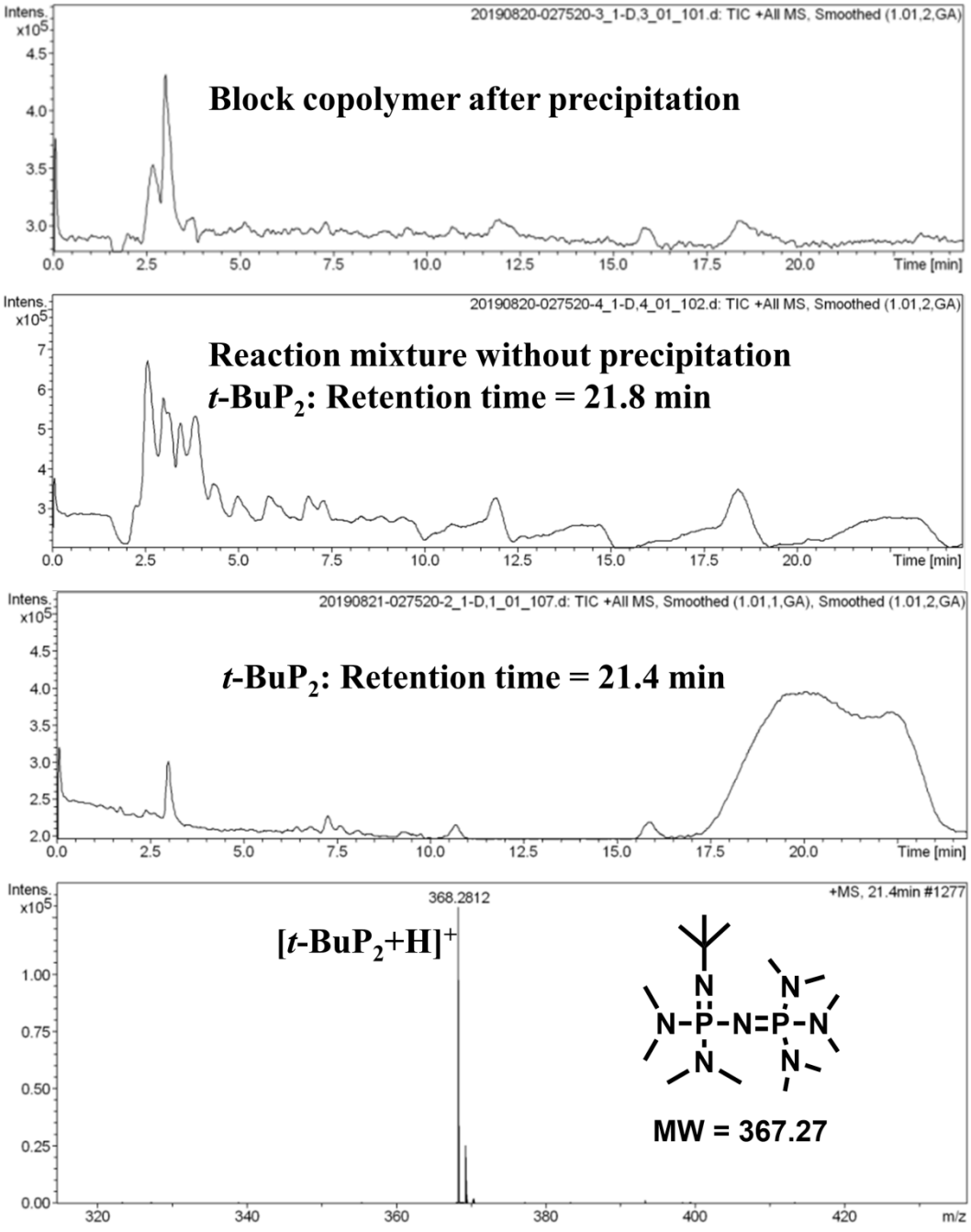


Figure S6. LC-MS analyses of the precipitated copolymer, reaction mixture and *t*-BuP_2 standard.

3. Alternating copolymerization of BO and PA

The ring-opening alternating copolymerization (ROAC) of PA with BO catalyzed by *t*-BuP_2/BEt_3 was investigated firstly. Previously, we found that the incorporation of BEt_3 can remarkably accelerate the copolymerization rate. However, the same equivalent of BEt_3 versus base failed to catalyze the ROP of BO, though it is very effective for the ROAC. In this contribution, we further increased the content of BEt_3 since it could activate epoxides for easily ring-opening with an 1:2:1 molar ratio of [BEt_3]/[*t*-BuP_2]/[BDM]. BO and PA as model comonomers are used, because high boiling point of BO (63 ^oC) allows for the time-regular monitoring of crude aliquots withdrawn from the reaction system to analyze monomer conversions and molecular weights.

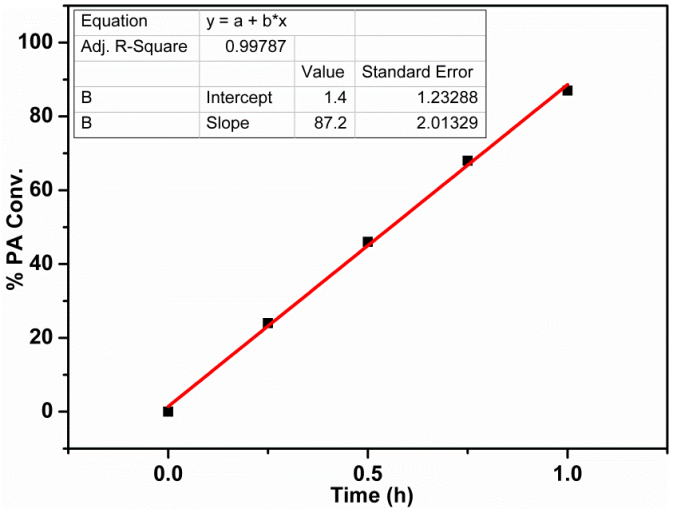


Figure S7. The zero-order kinetic of PA/BO copolymerization with respect to the concentration of PA.

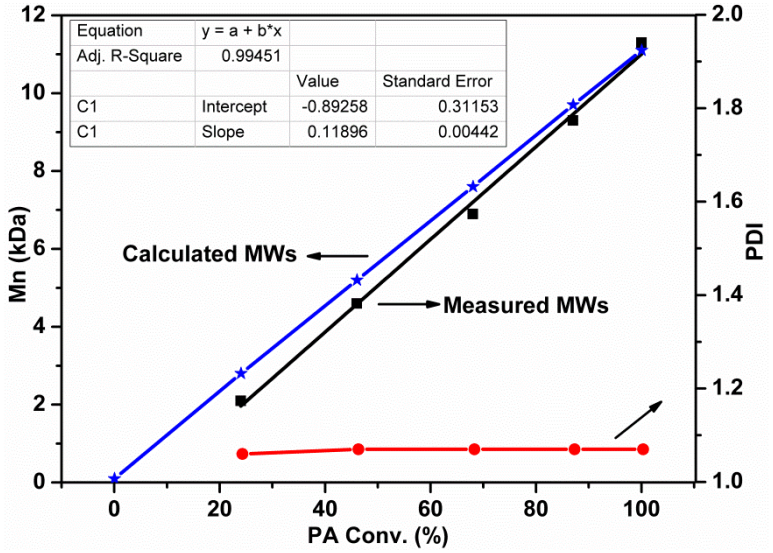


Figure S8. The plots of calculated and measured MWs and *Đ* versus PA conversion in the ROAC, indicating a living/controlled polymerization catalyzed by *t*-BuP_2/BEt_3. Calculated MWs = M_{BDM} + M_{PA} × mol(PA)/mol(BDM) × Conv. (PA) + M_{BO} × mol(BO)/mol(BDM) × Conv. (BO).

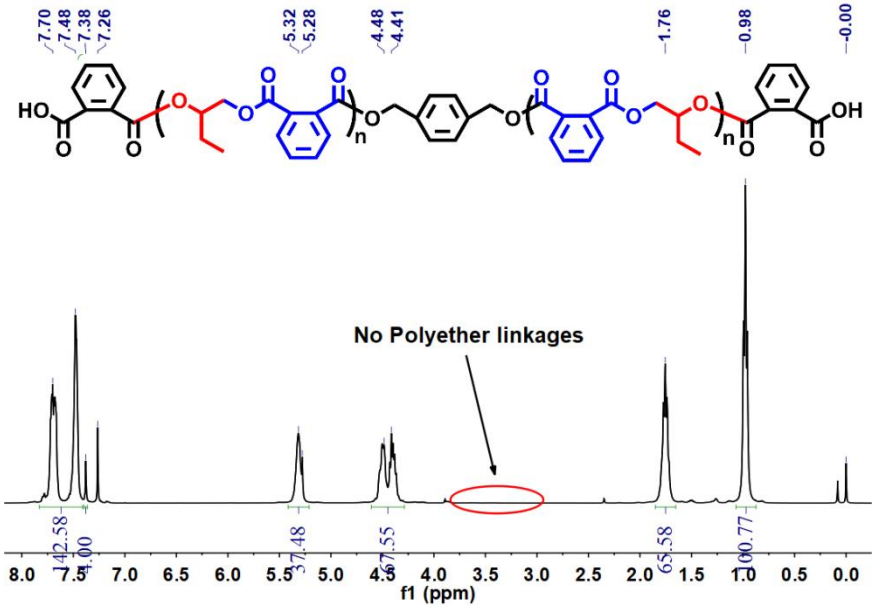


Figure S9. The ^{1}H NMR spectrum of the resultant PBOPA isolated from the mixture.

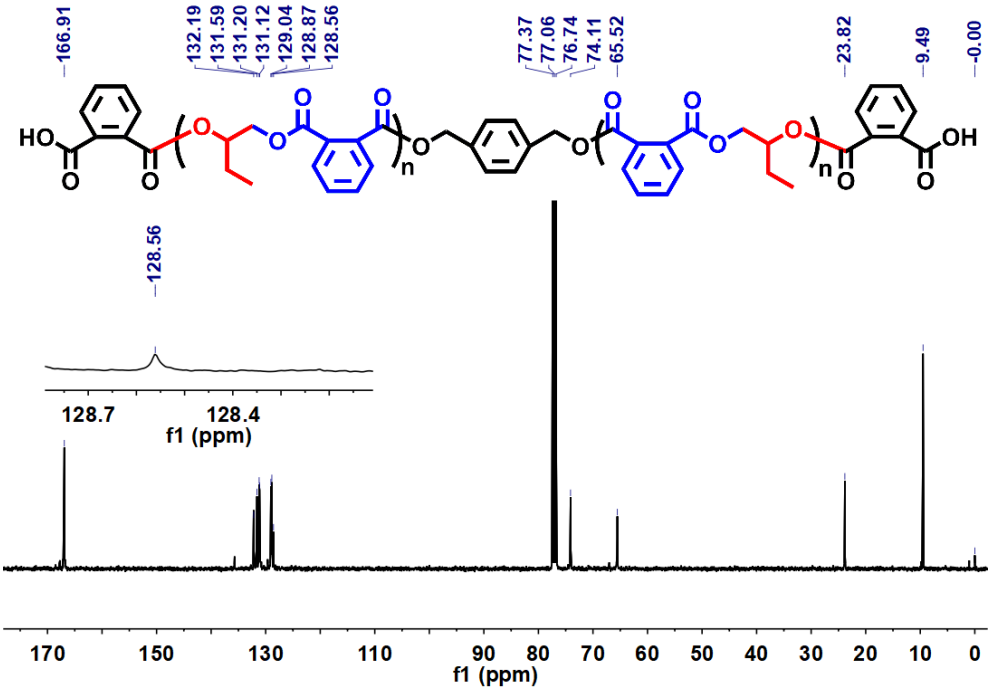


Figure S10. The ^{13}C NMR spectrum of the resultant PBOPA precipitated from the mixture.

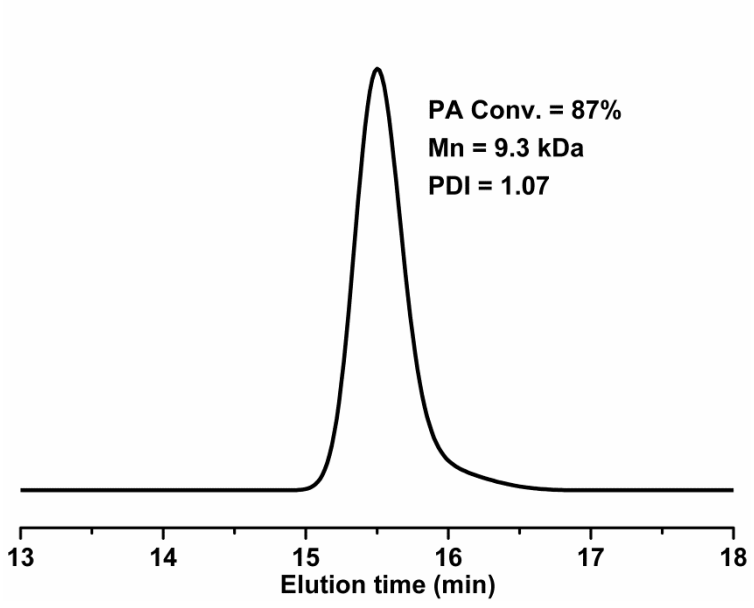


Figure S11. The GPC profile of the resultant PBOPA.

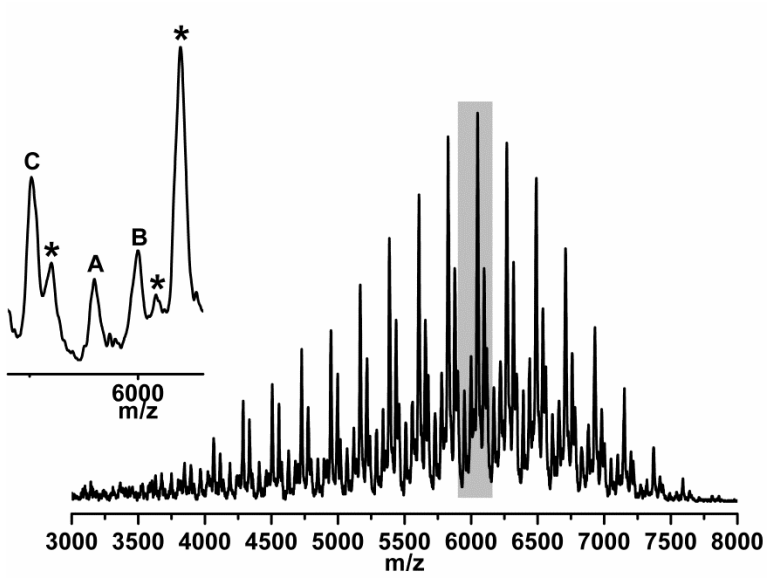


Figure S12. Positive ion MALDI-TOF MS analyses of the resultant copolymers obtained from different conditions before full consumption of PA. Polymerizations were conducted in toluene with [*t*-BuP_2]/[BEt_3]/[BDM]/[PA]/[BO] = 1:2:1:50:100 and quenched at 0.5 h. Continuous PBO repeating units was detected by ^{1}H NMR in the resultant copolymer with $[BO]_0$ = 6 M; $[M + H^+]$ for carboxyl-terminated chains and $[M + Na^+]$ for hydroxyl-terminated chains.[4]

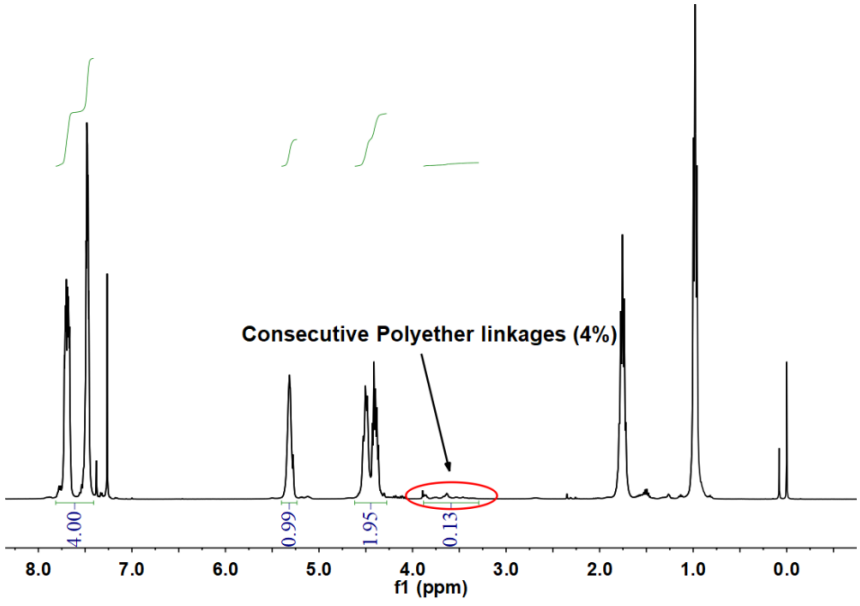
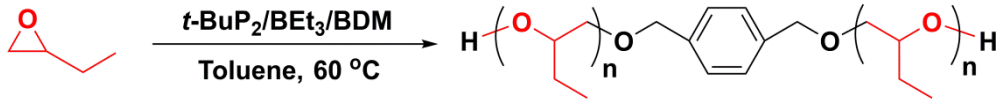


Figure S13. The ^{1}H NMR spectrum of the resultant PBOPA isolated from the mixture with $[BO]_0$ = 6 M. Consecutive PBO linkages was detected by ^{1}H NMR even though PA was not fully converted (t_{rxn} = 1h).

4. Homopolymerization of BO

The ring-opening polymerization (ROP) of BO catalyzed by *t*-BuP$_2$/BEt$_3$/BDM (1/2/1) system was further studied. Similar to the ROAC, the ROP of BO was performed in toluene ([BO]$_0$ = 4 M) at 60 ℃. The results suggested that the ROP of BO complied with the first-order dependence and a living/controlled ROP of BO was observed.

Table S2. The ROP of LA catalyzed by *t*-BuP$_2$/BEt$_3$[a]



entry	Time (h)	Conv. (%)[b]	TOF (h^{-1})	[BO]$_0$/[BO]$_t$	Ln{[BO]$_0$/[BO]$_t$}	$M_{n,\ calc.}$ (kDa)[c]	$M_{n,\ GPC}$ (kDa)[d]	$Đ$ [d]
1	0.5	40	80	1.667	0.511	3.0	3.0	1.04
2	1	51	51	2.041	0.713	3.8	3.8	1.05
3	1.5	58	39	2.381	0.868	4.3	4.4	1.05
4	2	63	32	2.703	0.994	4.7	5.0	1.05
5	2.5	67	27	3.030	1.109	5.0	5.5	1.06
6	3	70	23	3.333	1.204	5.2	5.8	1.06
7	3.5	72	21	3.571	1.273	5.3	5.9	1.06

[a]The copolymerization reactions were conducted in toluene ([BO]$_0$ = 4 M) at 60 ℃, [*t*-BuP$_2$]:[BEt$_3$]:[BDM]:[BO] = 1:2:1:100. [b]The conversion of BO was determined by ^{1}H NMR spectroscopy. [c]$M_{n,\ theo}$ = M_{BDM} + M_{PO} × n(BO)/n(BDM) × Conv. (BO). [d]$M_{n,\ GPC}$ and $Đ$ were determined by GPC analysis in THF calibrated with polystyrene standards.

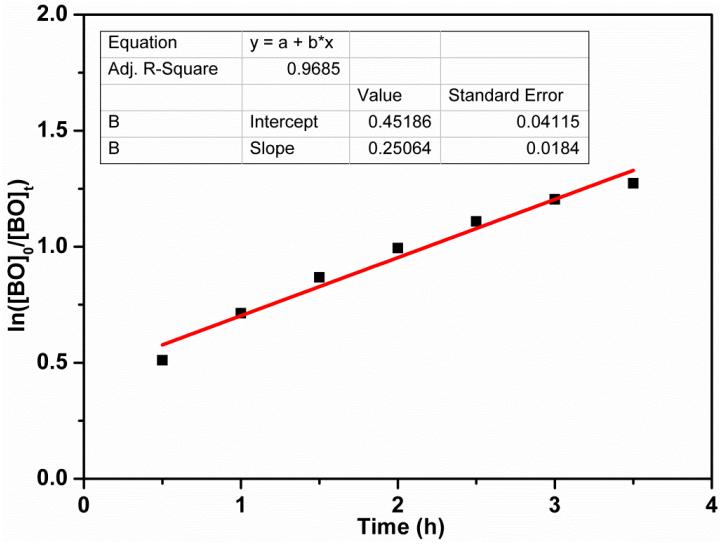


Figure S14. The first-order kinetic plots for ROP of BO with respect to the concentration of BO.

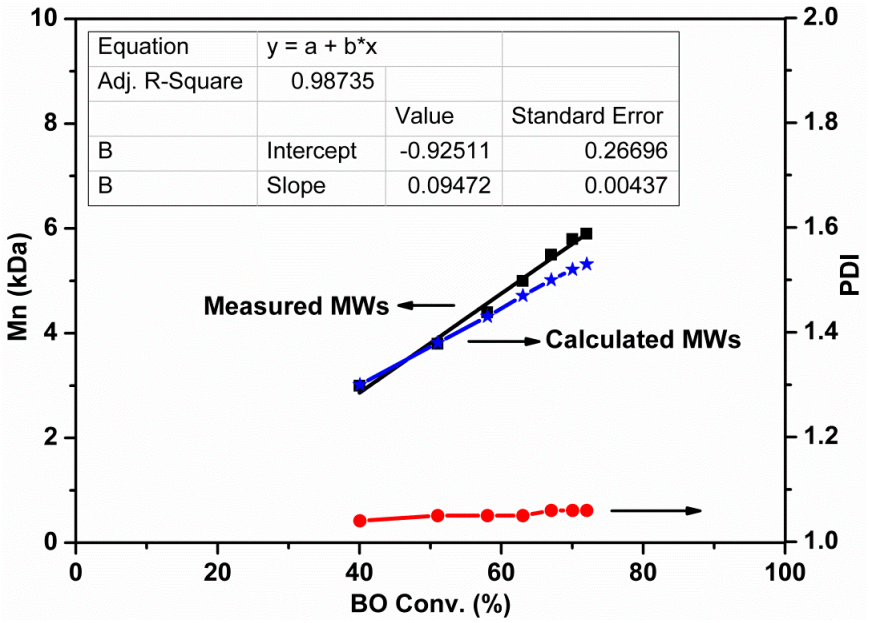


Figure S15. The plots of calculated and measured MWs and *Đ* versus BO conversion in the ROP of BO, indicating a living/controlled ROP of BO catalyzed by *t*-BuP$_2$/BEt$_3$. Calculated MWs = M_{BDM} + M_{BO} × mol(BO)/mol(BDM) × Conv. (BO).

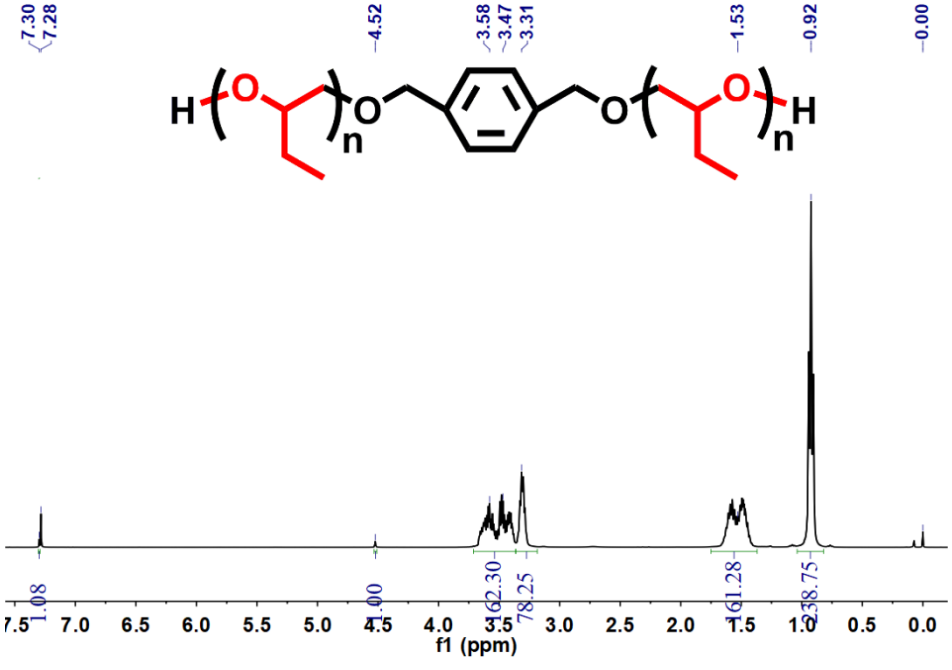


Figure S16. The ^{1}H NMR spectrum of the resultant PBO isolated from the mixture.

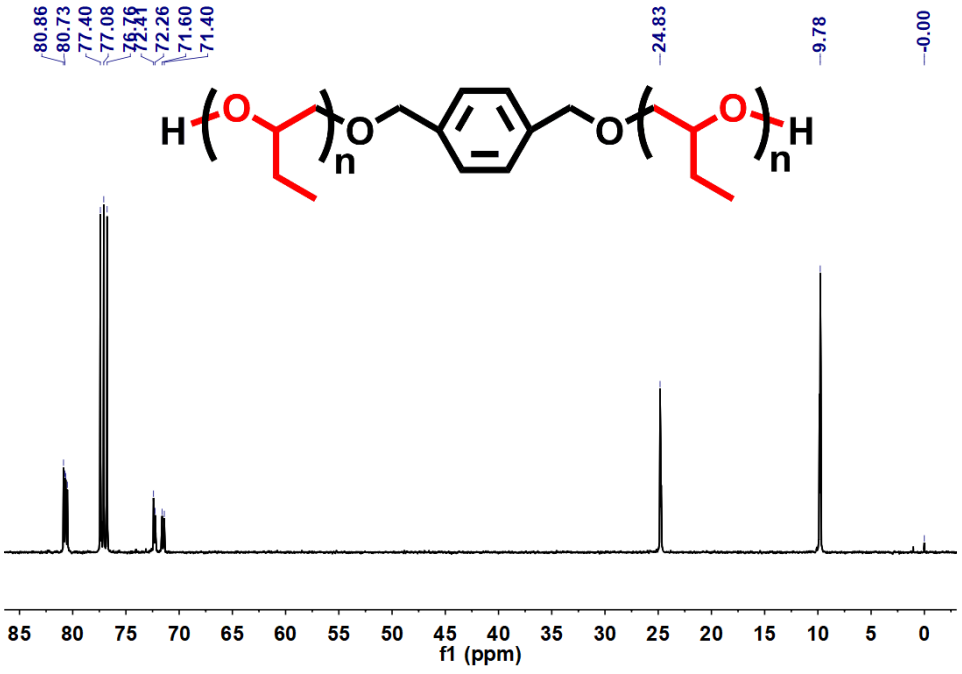


Figure S17. The ^{13}C NMR spectrum of the resultant PBO isolated from the mixture.

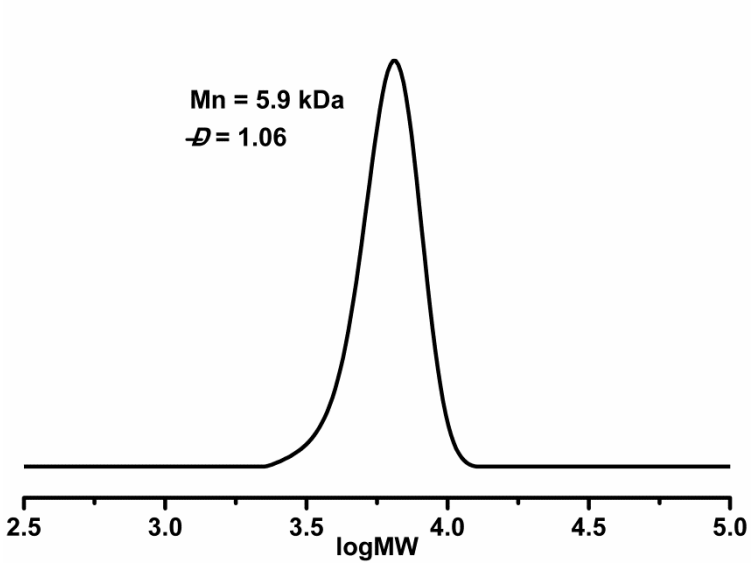


Figure S18. The GPC curve of the resultant PBO.

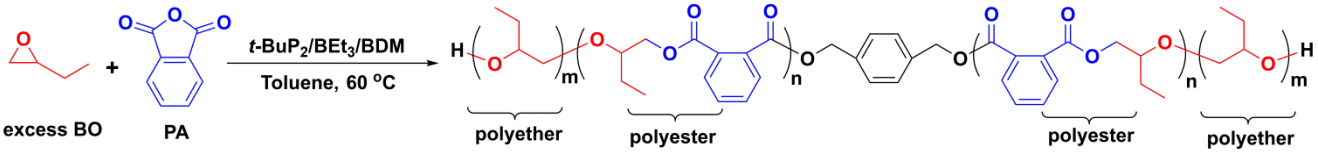
5. Selective copolymerization of BO and PA

In this section, polymerization of PA/BO mixed feedstocks in the presence of excess BO was performed in toluene ($[BO]_0$ = 4 M) at 60 ℃. The polymerization was monitored by ^1H NMR and GPC. The presence of PA in this system inhibited the ROP of BO. And the ROP of BO was switched on only after the full consumption of PA. The conversion of PA and BO versus time, as well as the precise

junction between polyester and polyether blocks suggested the formation of multi-block copolymers. The absence of transesterification and selective alternating insertion of PA in the *t*-BuP$_2$/BEt$_3$ catalytic system implied that random copolymers were nonexistent. The result could be further confirmed by comparing with the random copolymers of PA/BO and polymer blend. In order to characterize the polymer composition, a series of characterizations, including junctions analysis, end group assay, and DOSY were conducted.

5.1. Monitoring the polymerization process

Table S3. The selective copolymerization of BO and PA.[a]



entry	Time (h)	%Conv. (PA)[b]	%Conv. (BO)[c]	Ester forming[d]	Ether forming[e]	$M_{n,\ calc.}$ (kDa)	$M_{n,\ GPC}$ (kDa)[f]	$Đ$[f]
1	0.25	24	12	100	0	2.8	2.1	1.06
2	0.5	46	23	100	0	5.2	4.6	1.07
3	0.75	68	34	100	0	7.6	6.9	1.07
4	1	87	44	100	0	9.7	9.3	1.07
5	1.25	100	50	100	0	11.1	11.3	1.07
6	1.5	100	57	88	12	11.7	11.3	1.08
7	2	100	67	75	25	12.4	12.5	1.07
8	3	100	75	67	33	13.0	12.8	1.07
9	4	100	79	63	37	13.2	13.1	1.07
10	5	100	81	61	39	13.4	13.3	1.07
11	6	100	83	60	40	13.5	13.4	1.07
12	7	100	85	59	41	13.7	13.5	1.07

[a]The copolymerization reactions were conducted in toluene at 60 ℃, [*t*-BuP$_2$]:[BEt$_3$]:[BDM]:[PA]:[BO] = 1:2:1:50:100, $[BO]_0$ = 4 M. [b]The conversion of PA was determined by ^{1}H NMR spectroscopy. [c]The conversion of BO was determined by ^{1}H NMR spectroscopy. [d]The formation of ester was calculated by the ratio of detected polyester and polyether. [e]The formation of ether was calculated by the ratio of detected polyester and polyether. [f]M_n and $Đ$ were determined by GPC analysis in THF calibrated with polystyrene standards.

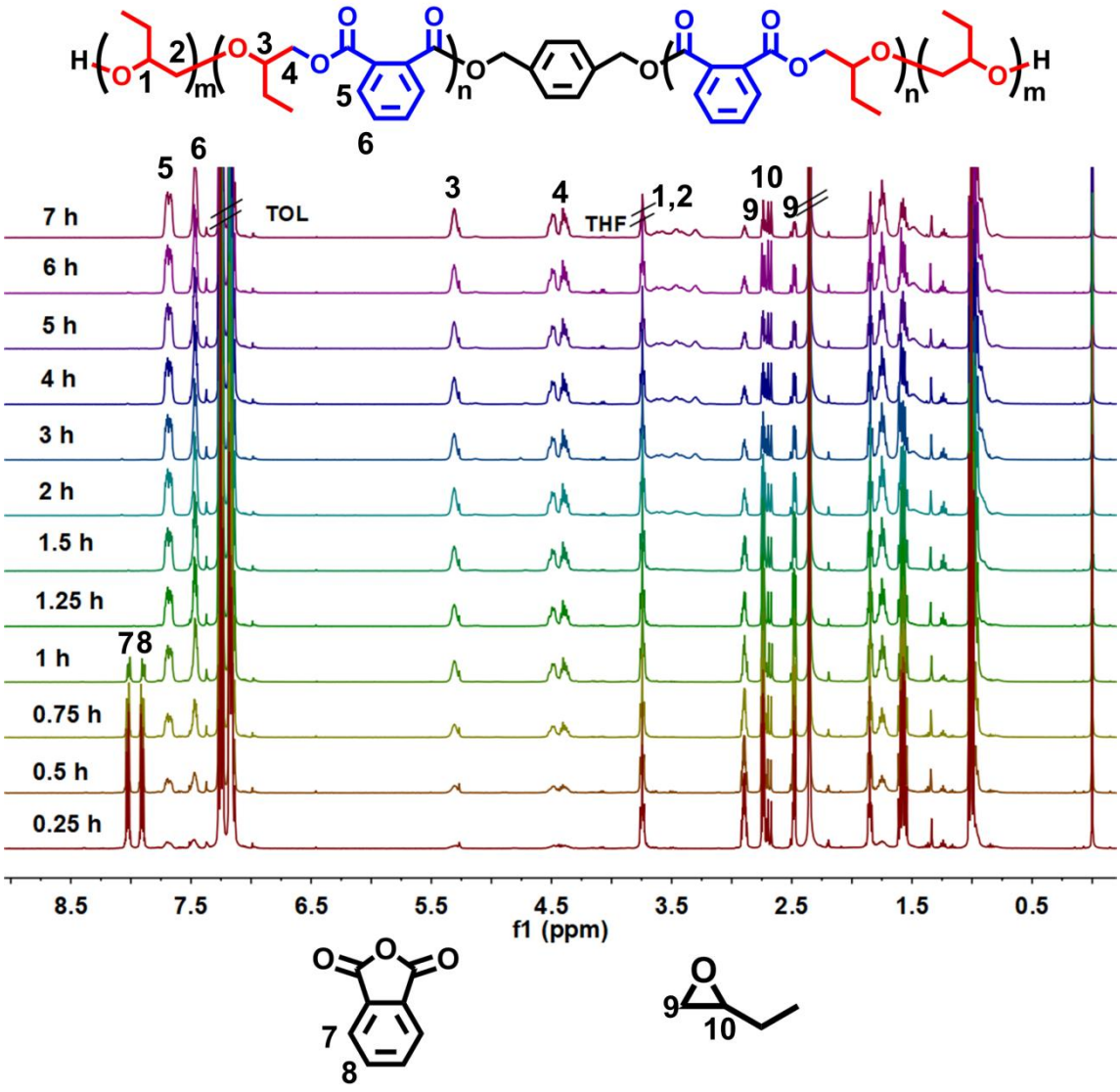


Figure S19. The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of PA and BO and the formation of PBO-*b*-PBOPA-*b*-PBO.

5.2. Characterization of PBO-*b*-PBOPA-*b*-PBO

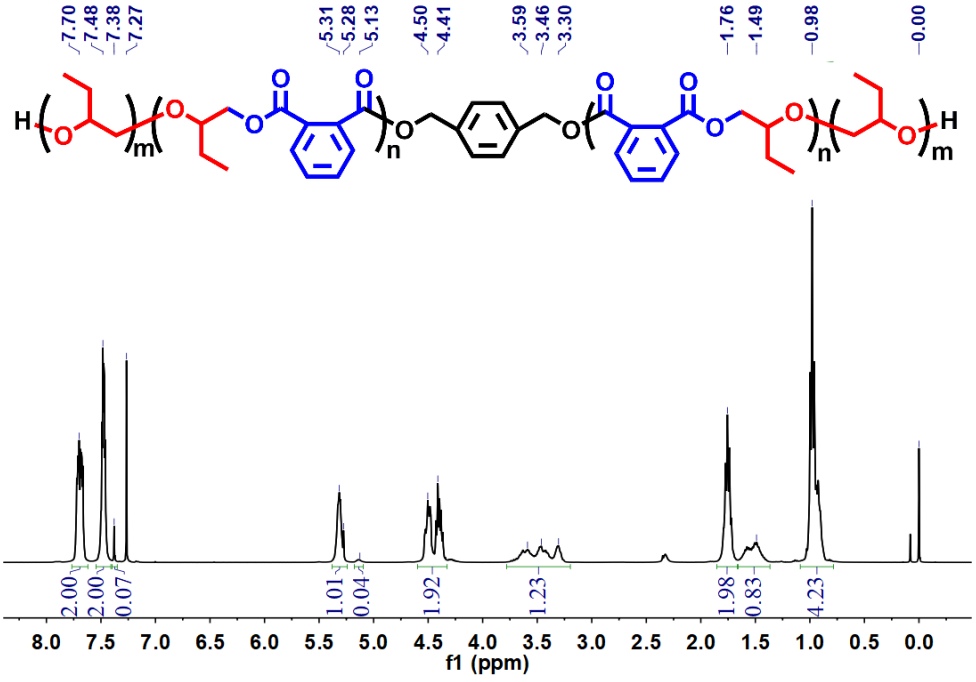


Figure S20. The ^{1}H NMR spectrum of the resultant PBO-*b*-PBOPA-*b*-PBO isolated from the mixture.

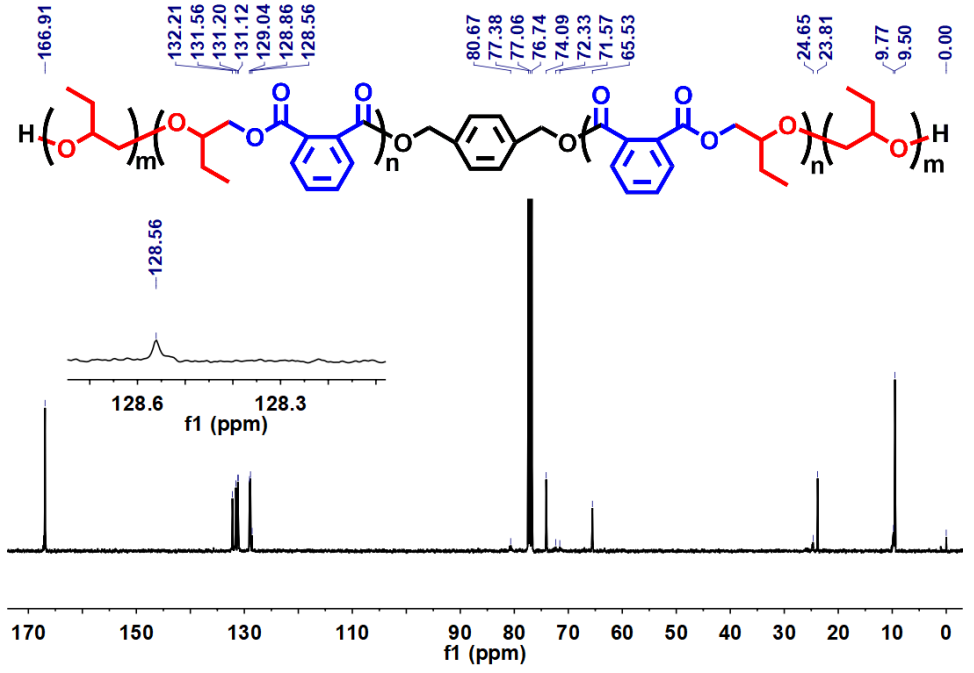


Figure S21. The ^{13}C NMR spectrum of the resultant PBO-*b*-PBOPA-*b*-PBO isolated from the mixture. Inset: the expanded region of phenyl ring of BDM initiator.

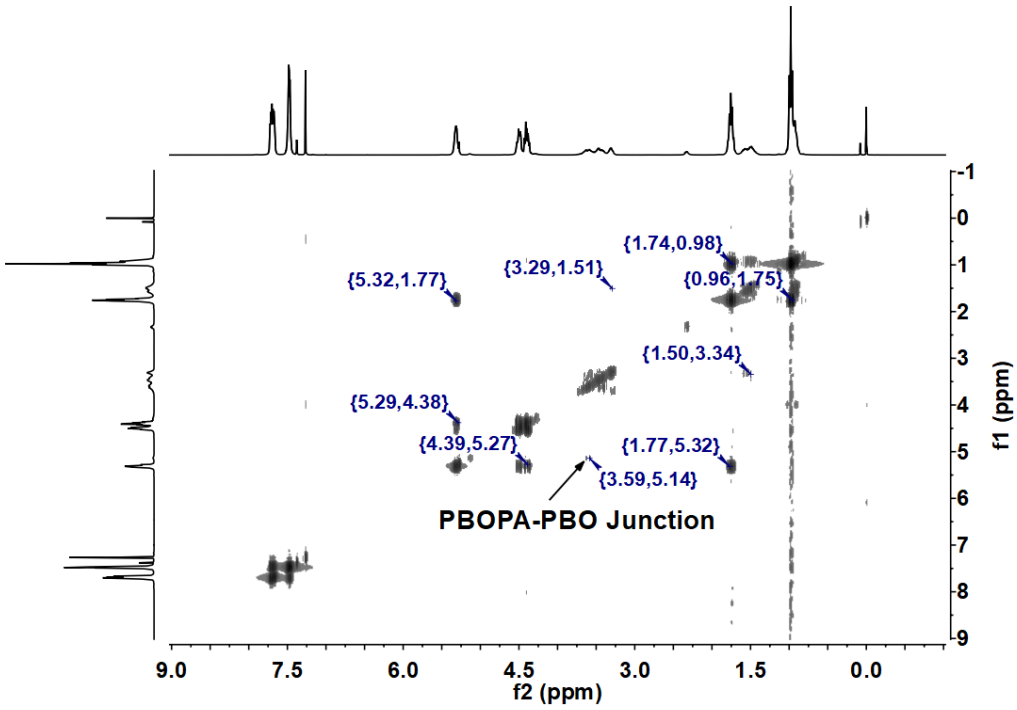


Figure S22. The COSY NMR spectrum of the resultant PBO-*b*-PBOPA-*b*-PBO isolated from the mixture.

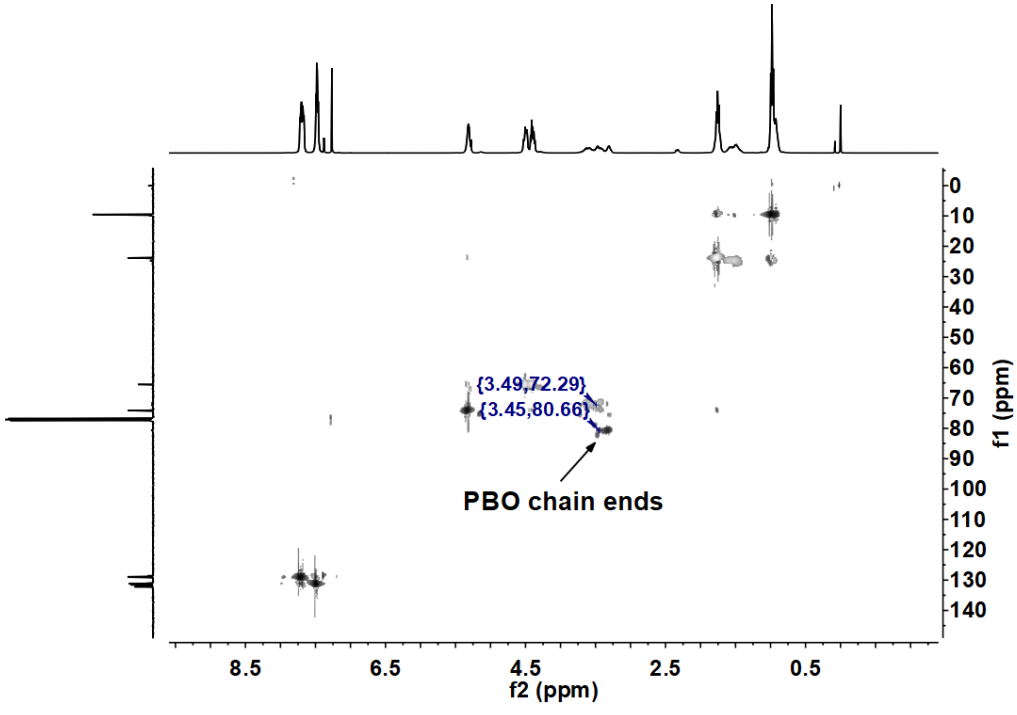


Figure S23. The HSQC NMR spectrum of the resultant PBO-*b*-PBOPA-*b*-PBO isolated from the mixture.

5.3. Polymer blends of PBO and PBOPA

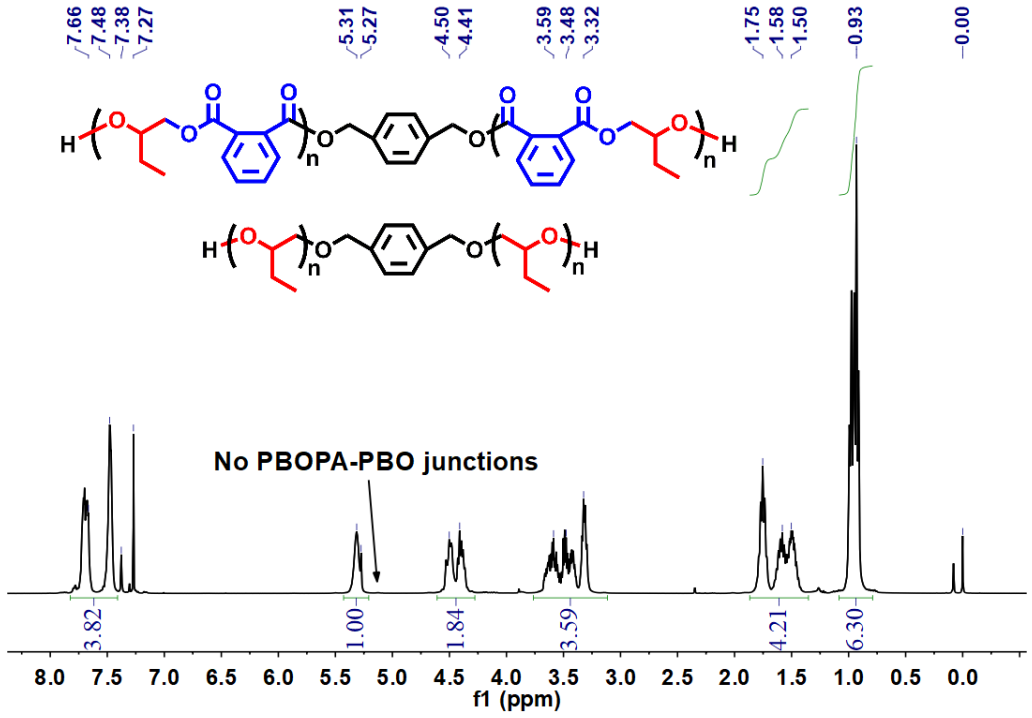


Figure S24. The ^{1}H NMR spectrum of the PBO/PBOPA blend.

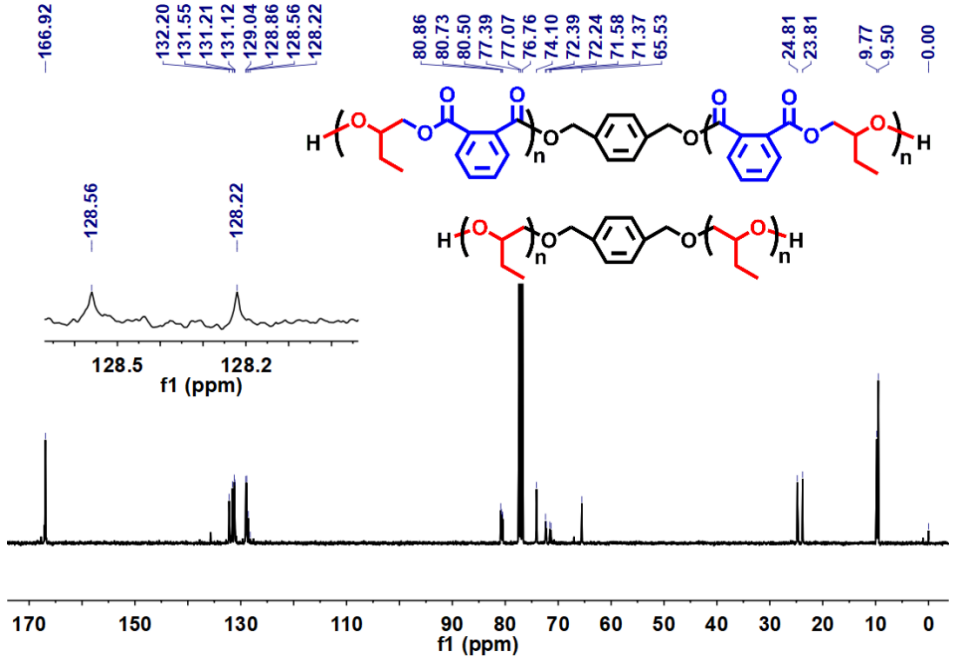


Figure S25. The ^{13}C NMR spectrum of the PBO/PBOPA blend. Inset: the expanded region of phenyl ring of BDM initiator.

5.4. Random copolymerization of BO and PA

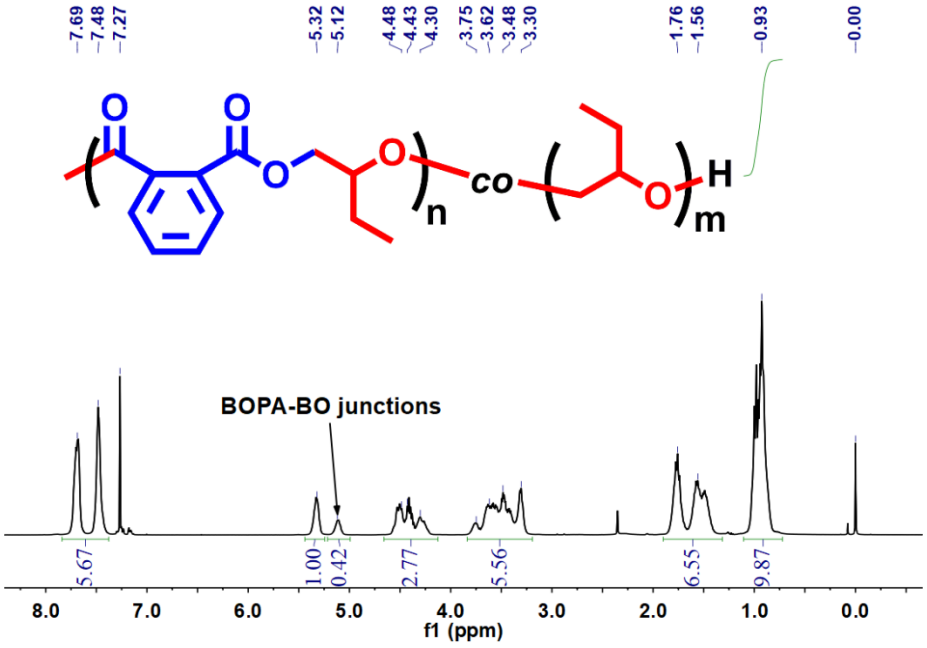


Figure S26. The ^{1}H NMR spectrum of the random PBO-*co*-PBOPA copolymer obtained from bulk polymerization.

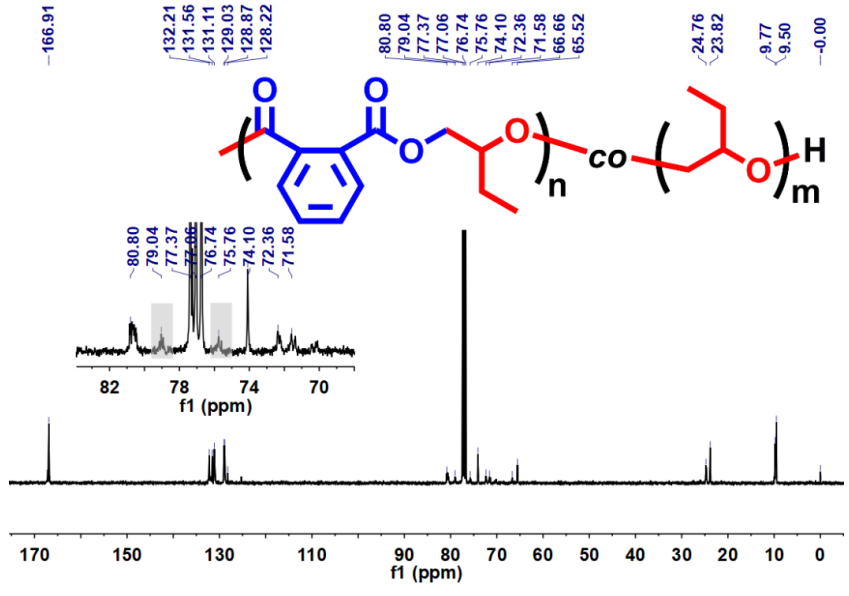


Figure S27. The ^{13}C NMR spectrum of the random PBO-*co*-PBOPA copolymer obtained from bulk polymerization.

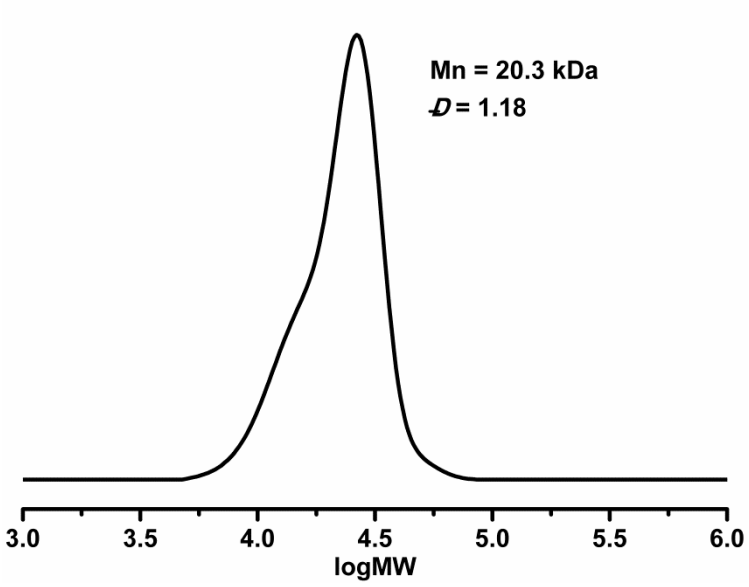


Figure S28. The GPC trace of the random PBO-*co*-PBOPA copolymer.

5.5. Junction group analyses

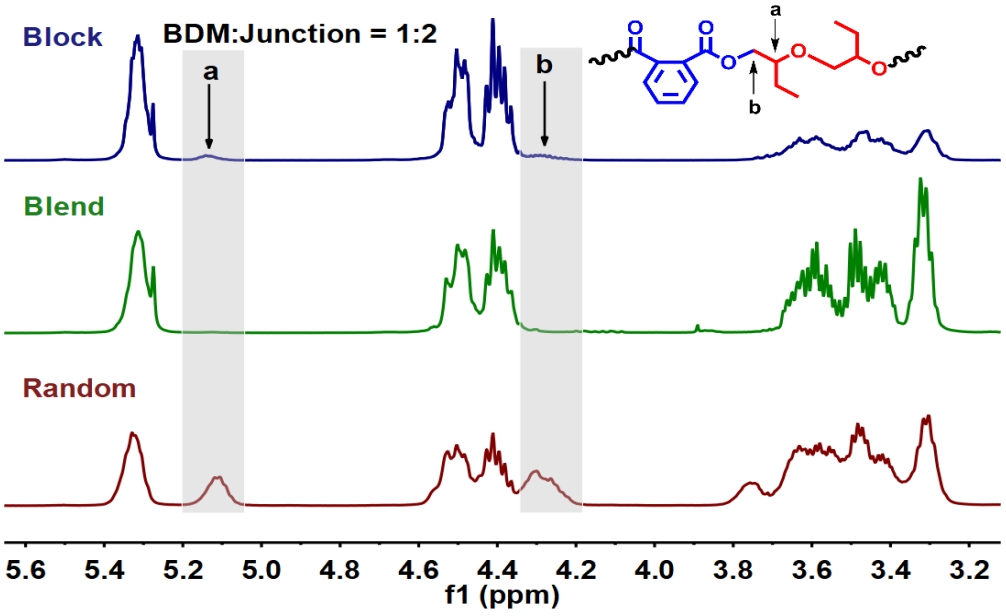


Figure S29. Analyzing the junctions in the resultant PBO-*b*-PBOPA-*b*-PBO by ^{1}H NMR spectrum. The precise junctions of polyester and polyether in the block copolymer excluded the formation of gradient and random copolymer. While high intensity of junctions in the random copolymer indicated irregular ester and ether sequences (30%).

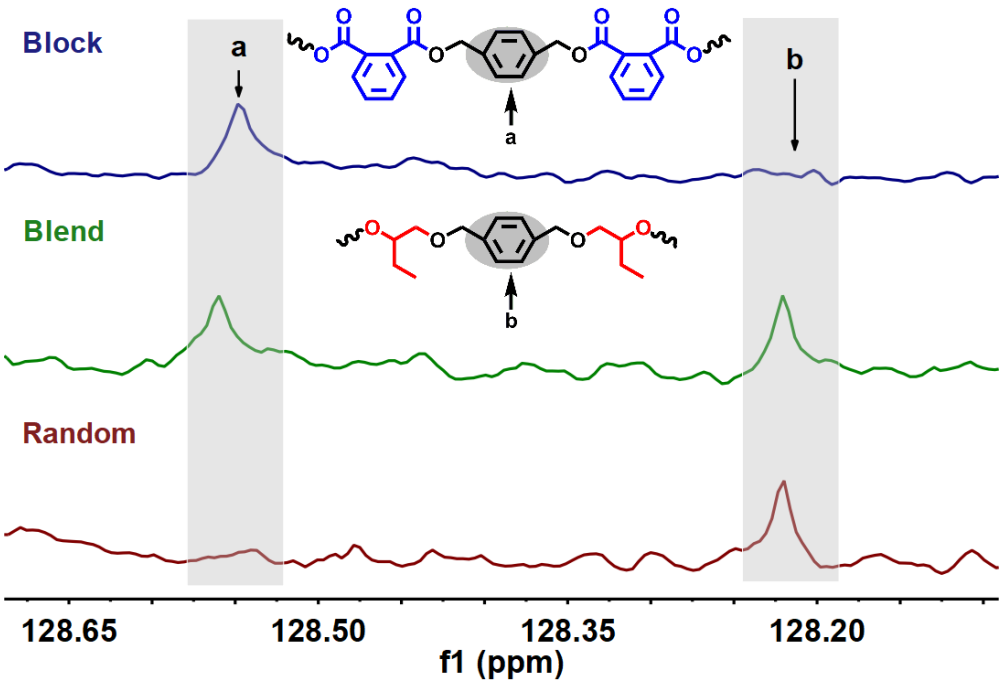


Figure S30. Comparison of ^{13}C NMR spectra in the region of initiators. BO was competitively initiated by BDM in random copolymerization under bulk condition since its insertion rate (k_3) strikingly increased.

5.6. DOSY spectrum

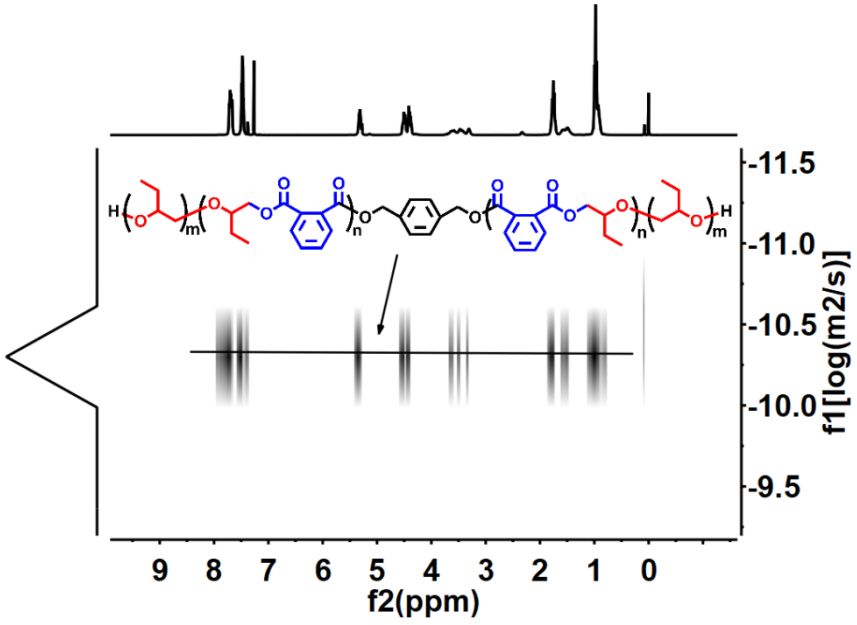


Figure S31. The DOSY NMR spectrum of the PBO-*b*-PBOPA-*b*-PBO triblock copolymer (D = 5.01 × 10^{-11} m^2/s).

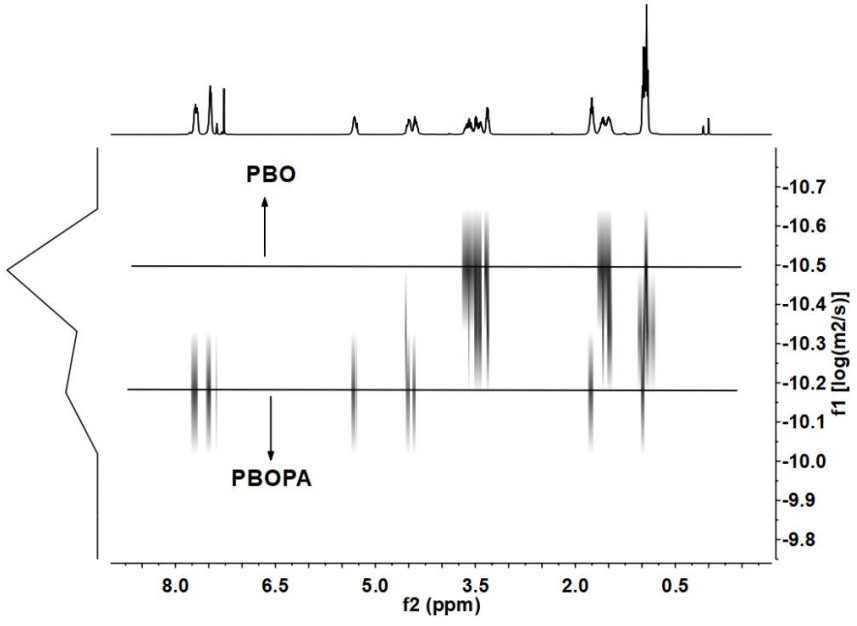


Figure S32. The DOSY NMR spectrum of the mixtures of PBOPA (D = 7.08 × 10^{-11} m^2/s) and PBO (D = 3.16 × 10^{-11} m^2/s).

5.7. End group Assays[5]

Scheme S2. Derivatization reaction of polyols and model chemicals with 1,3,2-dioxaphospholanyl chloride.

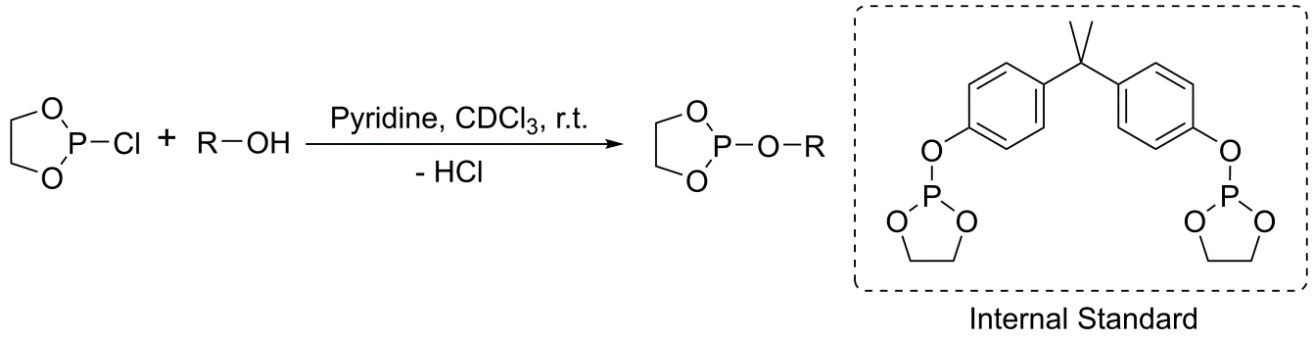


Table S4. The chemical shifts in ^{31}P NMR spectra after treating the copolymers and model chemicals with 2-chloro-1,3,2-dioxaphospholane agent. Internal standard: bisphenol A (BPA).

Sample	Chemical shifts after reaction with phosphorus reagent (ppm)
Benzoic acid	127.60
1,2-Butanediol	136.04; 134.97
Products A, B & C in Figure 1A	135.75; 127.52
PBO	135.72
PBO-*b*-PBOPA-*b*-PBO	135.71

6. Monomer scope

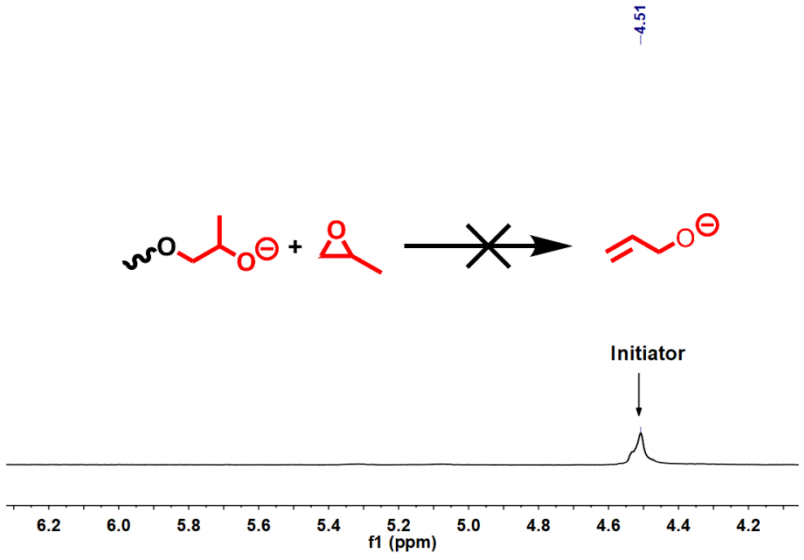


Figure S33. ^{1}H NMR spectrum of P*S*PO. Chain transfer to monomer was precluded, because no α–allyl-ω-hydroxyl P*S*PO was detected in the system.

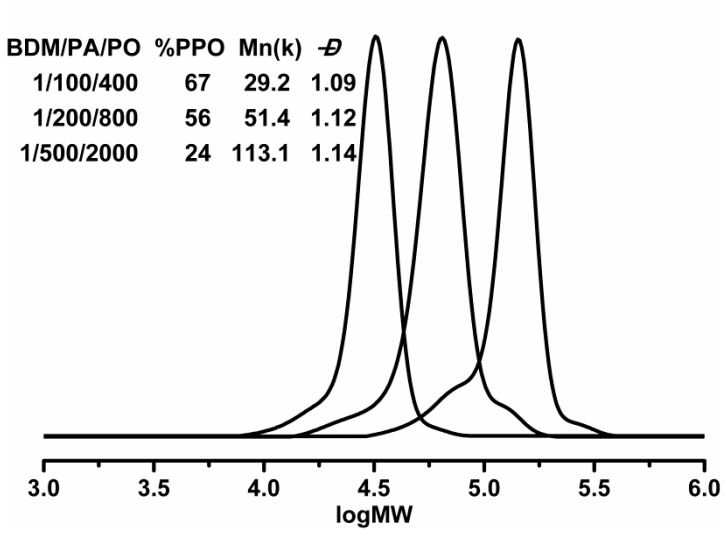


Figure S34. Synthesis of high-molecular-weight PSPO-*b*-PSPOPA-*b*-P*S*PO triblock copolymers by lowering the loading of catalyst and initiator.

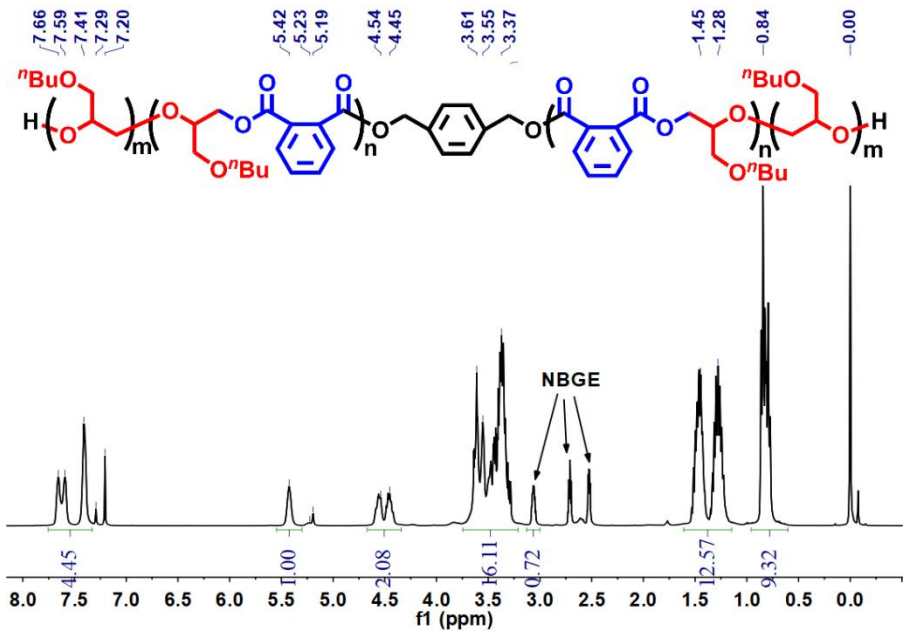


Figure S35. The ^{1}H NMR spectrum of the resultant PNBGE-*b*-PNBGEPA-*b*-PNBGE.

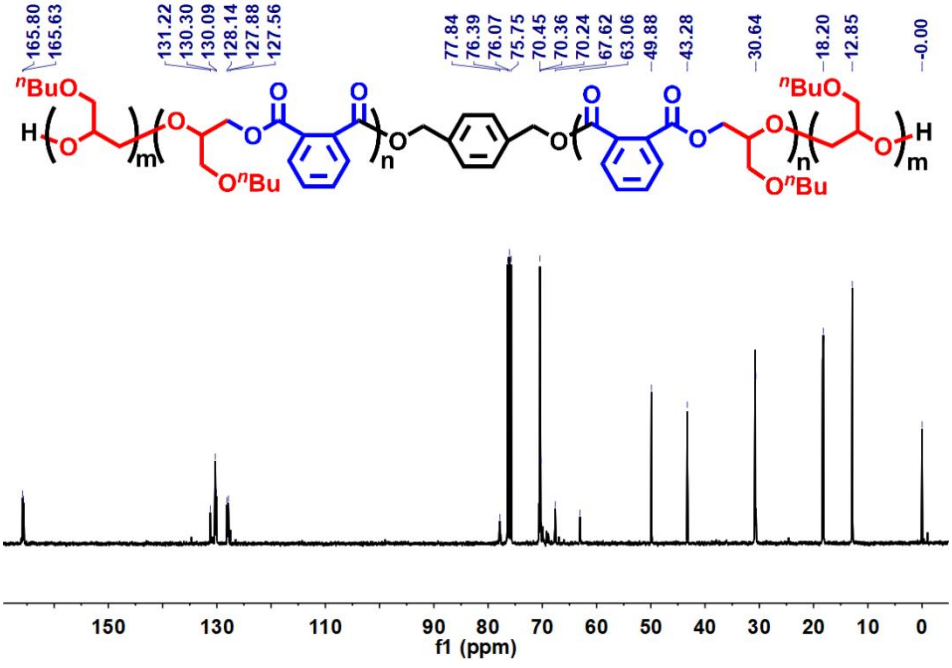


Figure S36. The ^{13}C NMR spectrum of the resultant PNBGE-*b*-PNBGEPA-*b*-PNBGE.

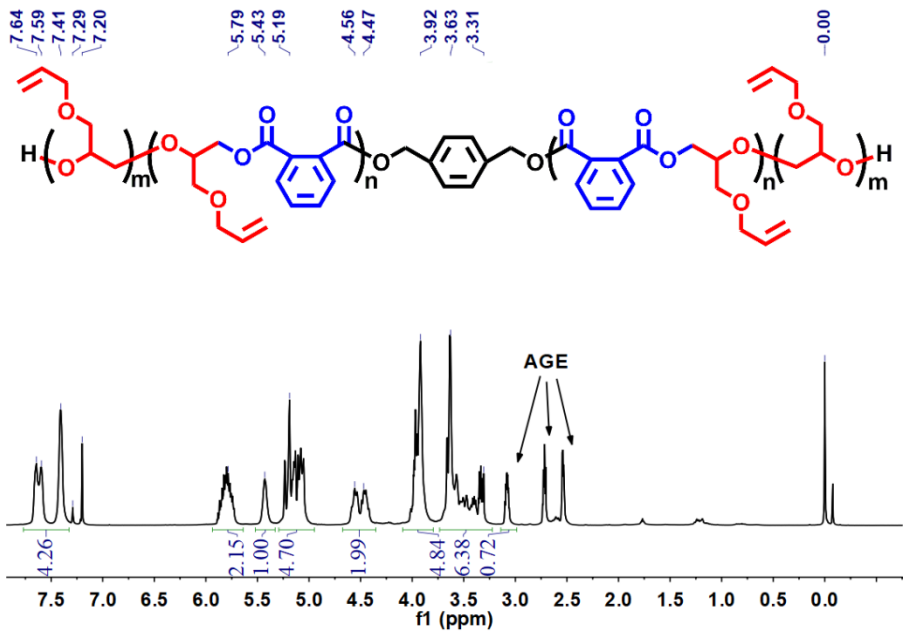


Figure S37. The ^{1}H NMR spectrum of the resultant PAGE-*b*-PAGEPA-*b*-PAGE.

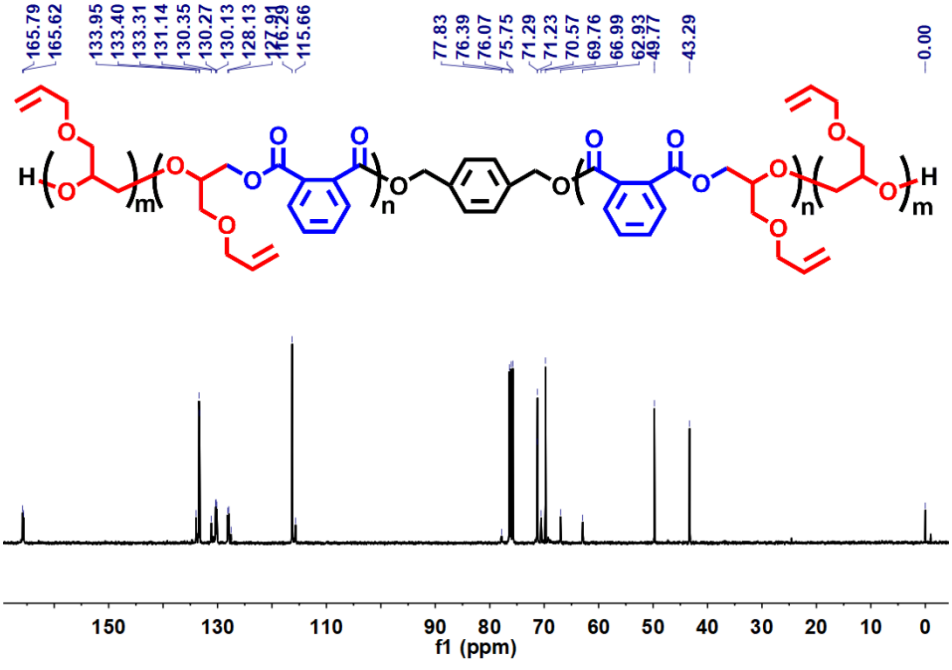


Figure S38. The ^{13}C NMR spectrum of the resultant PAGE-*b*-PAGEPA-*b*-PAGE.

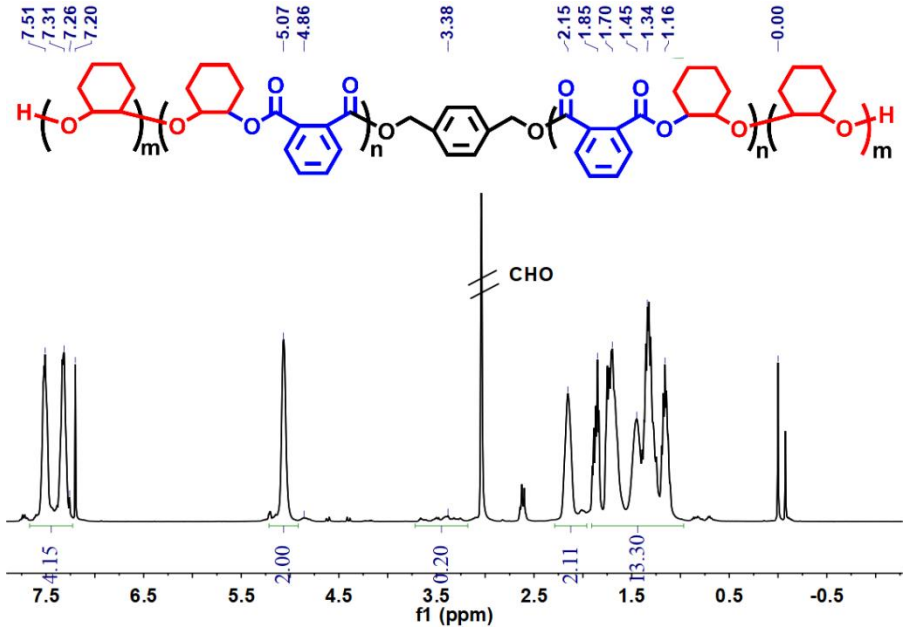


Figure S39. The ^{1}H NMR spectrum of the resultant PCHO-*b*-PCHOPA-*b*-PCHO.

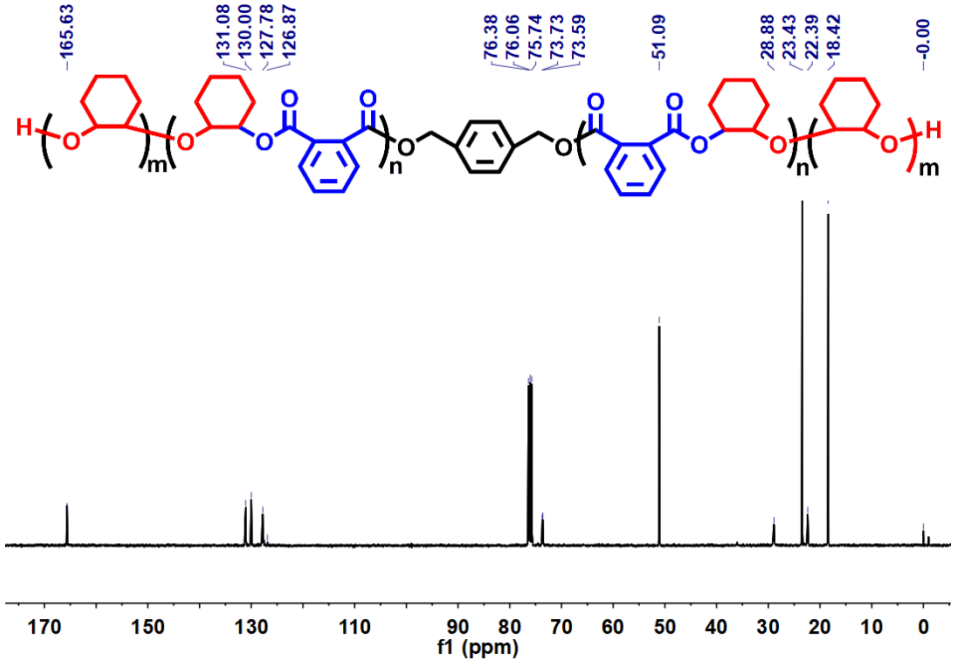


Figure S40. The ^{13}C NMR spectrum of the resultant PCHO-*b*-PCHOPA-*b*-PCHO.

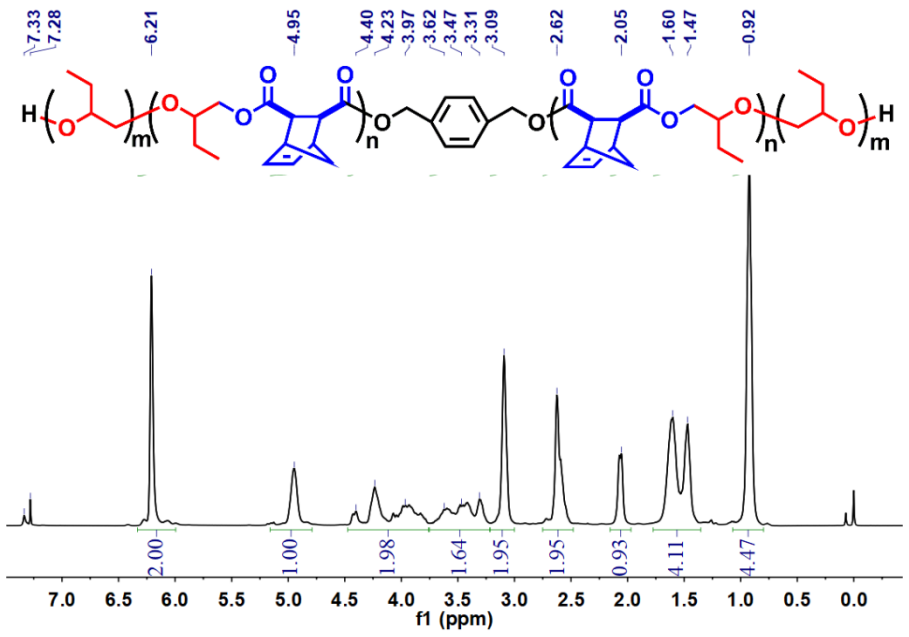


Figure S41. The ^{1}H NMR spectrum of the resultant PBO-*b*-PBONA-*b*-PBO.

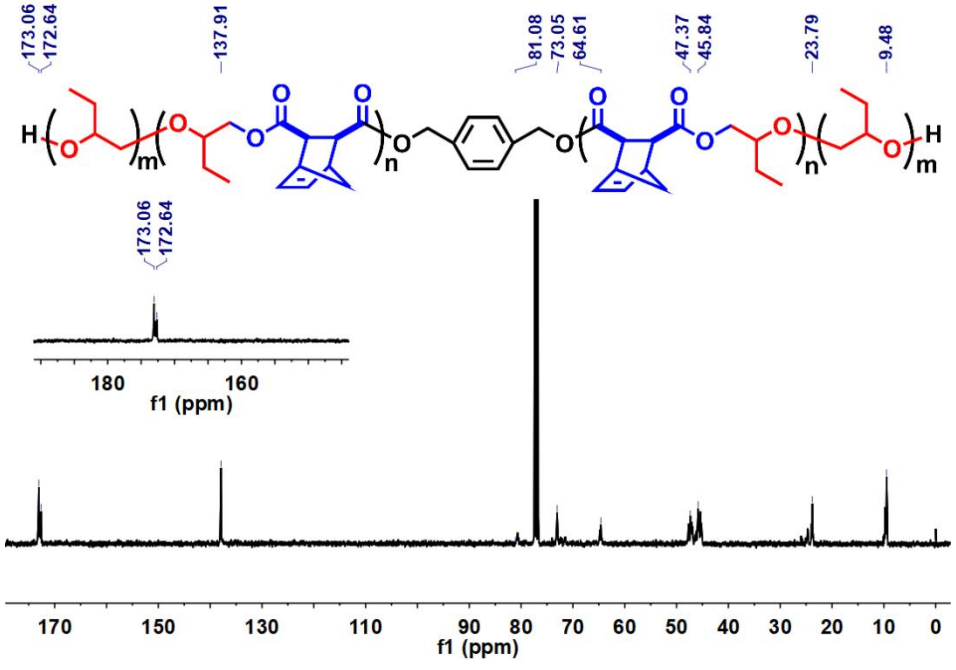


Figure S42. The ^{13}C NMR spectrum of the resultant PBO-*b*-PBONA-*b*-PBO. Inset: the expanded region of carbonyl.

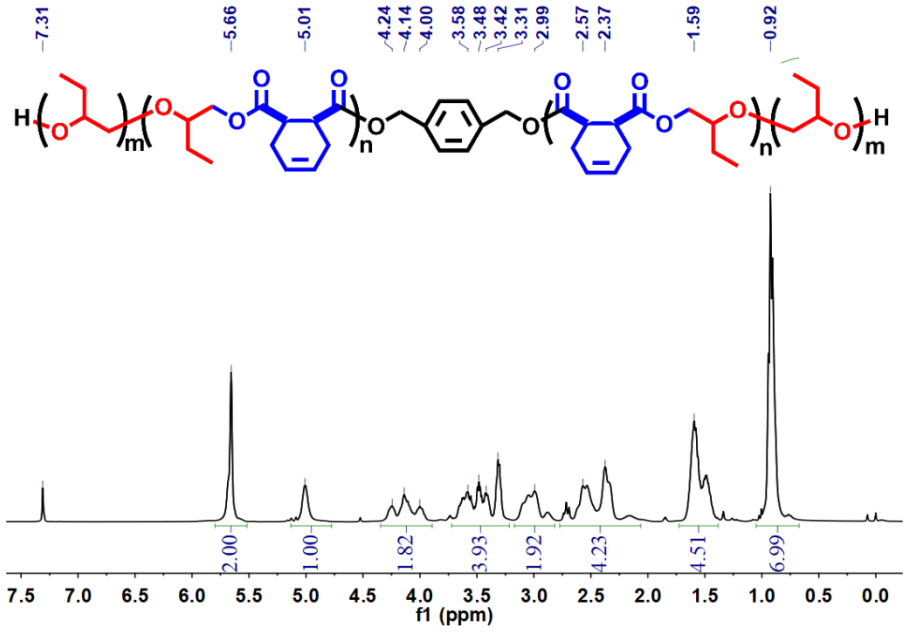


Figure S43. The ^{1}H NMR spectrum of the resultant PBO-*b*-PBOTHPA-*b*-PBO.

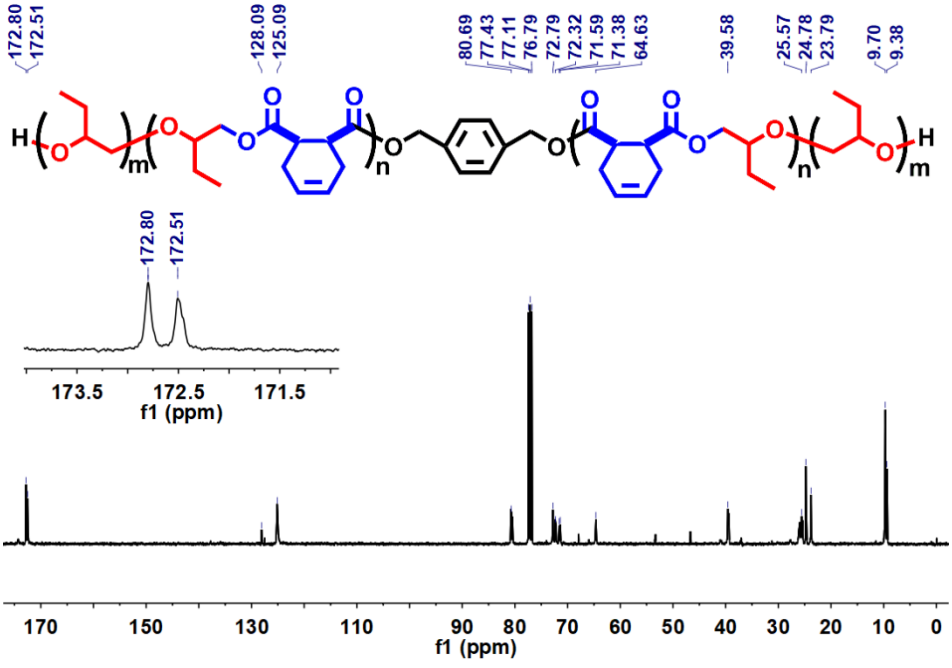


Figure S44. The ^{13}C NMR spectrum of the resultant PBO-*b*-PBOTHPA-*b*-PBO. Inset: the expanded region of carbonyl.

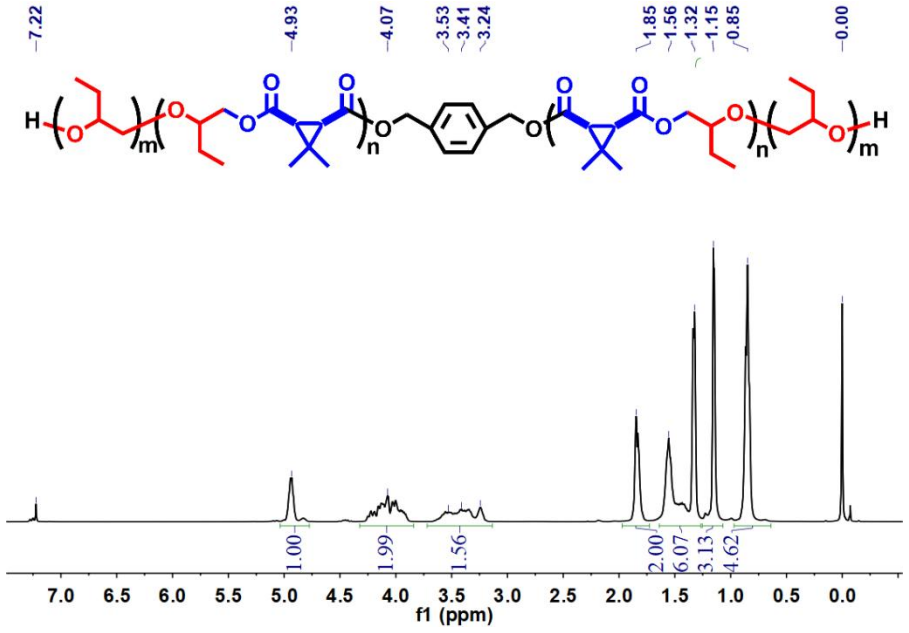


Figure S45. The ^{1}H NMR spectrum of the resultant PBO-*b*-PBOCA-*b*-PBO.

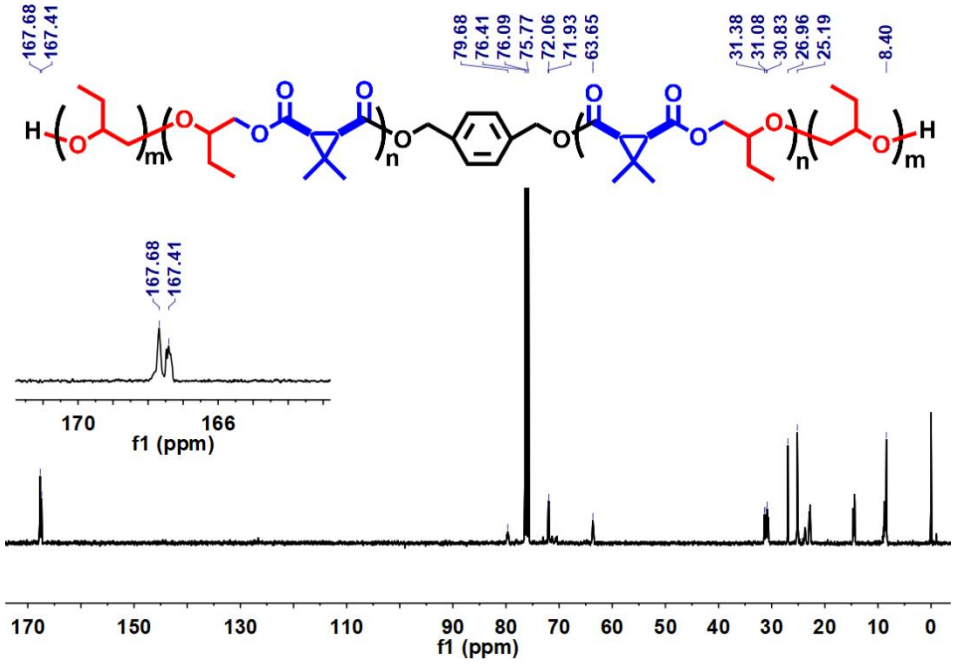


Figure S46. The ^{13}C NMR spectrum of the resultant PBO-*b*-PBOCA-*b*-PBO. Inset: the expanded region of carbonyl.

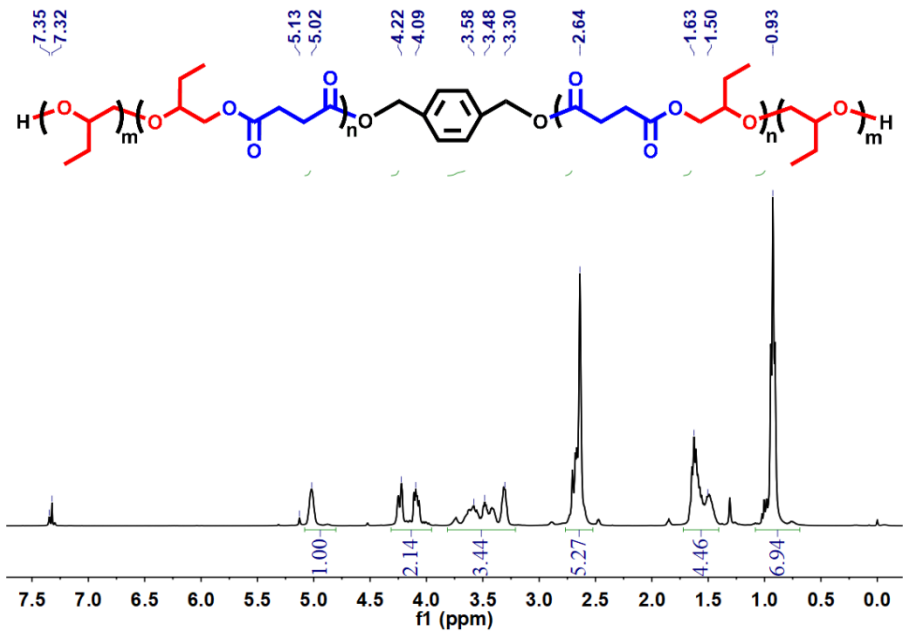


Figure S47. The ^{1}H NMR spectrum of the resultant PBO-*b*-PBOSA-*b*-PBO.

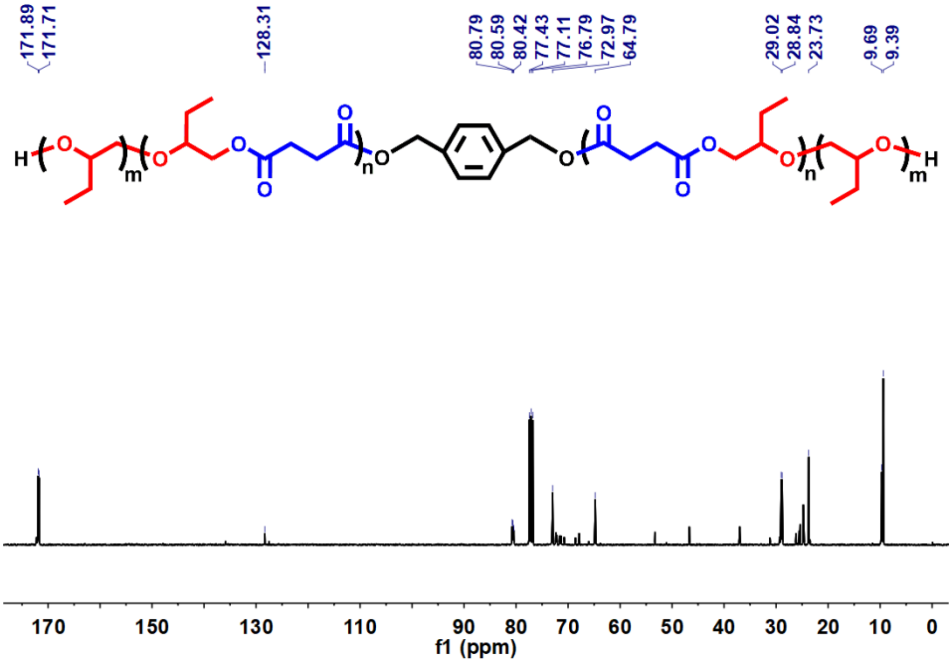


Figure S48. The ^{13}C NMR spectrum of the resultant PBO-*b*-PBOSA-*b*-PBO.

7. Regioselective homopolymerization of *S*-PO

The regioselective ROP of *S*-PO was investigated in this section. Living/controlled and highly regioselective nature was observed in the ROP of *S*-PO. Meanwhile, the chain transfer to PO monomer was totally suppressed since the nucleophilicity of alkoxide active species was reduced by binding to BEt_3.

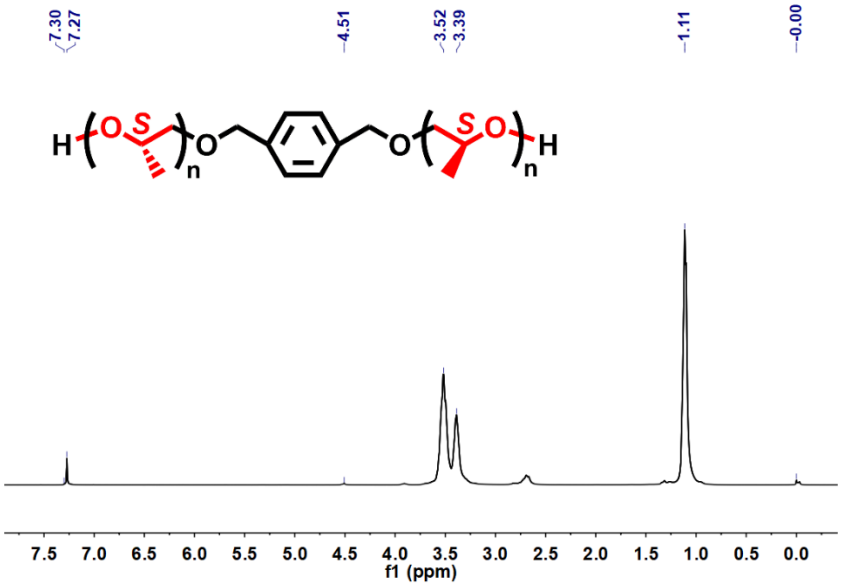


Figure S49. The ^{1}H NMR spectrum of the resultant P*S*PO isolated from the mixture.

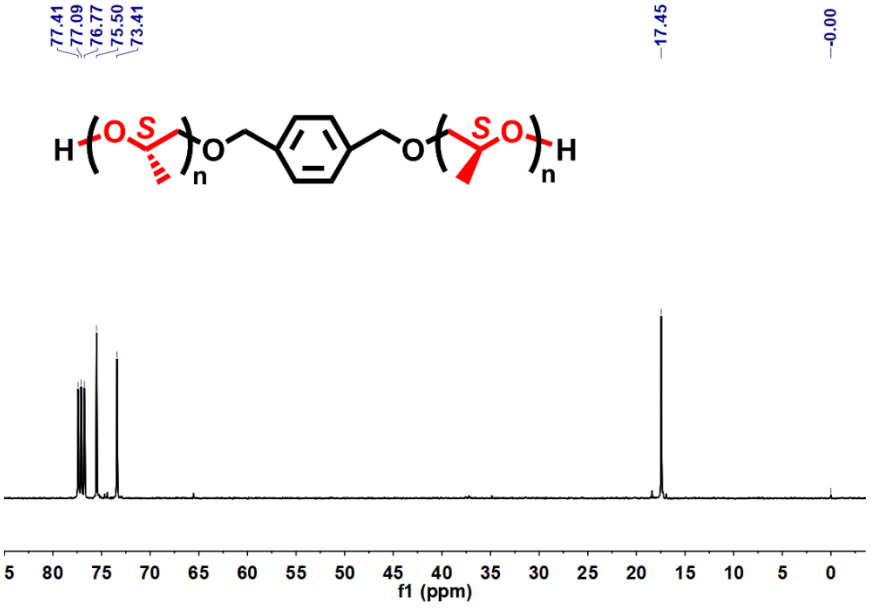


Figure S50. The ^{13}C NMR spectrum of the resultant P*S*PO isolated from the mixture.

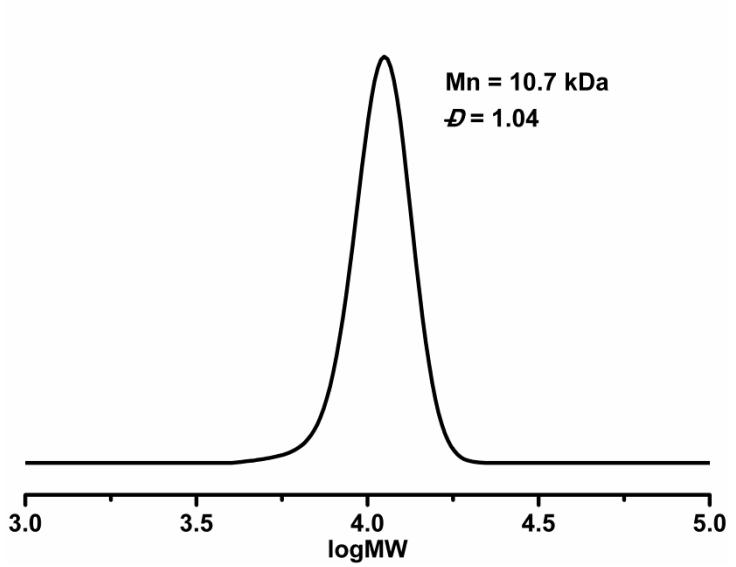


Figure S51. The GPC trace of the P*S*PO.

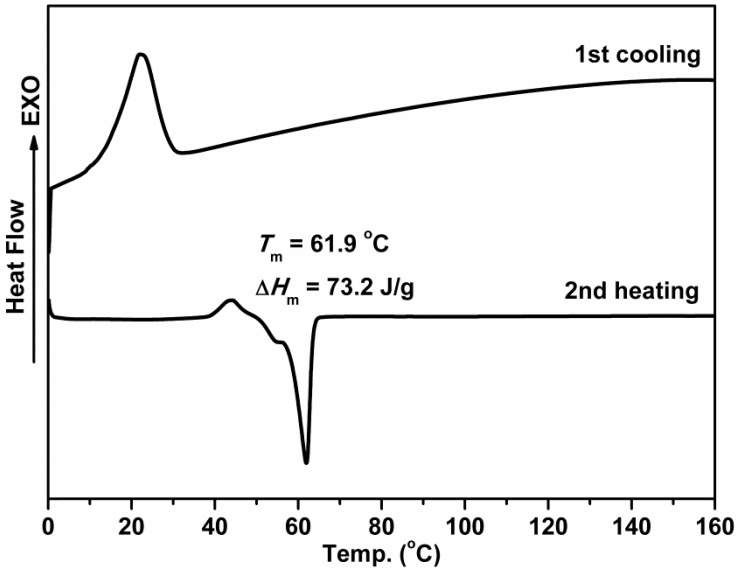


Figure S52. The DSC profiles of P*S*PO (T_m = 62 ℃, ΔH_m = 73.2 J/g).

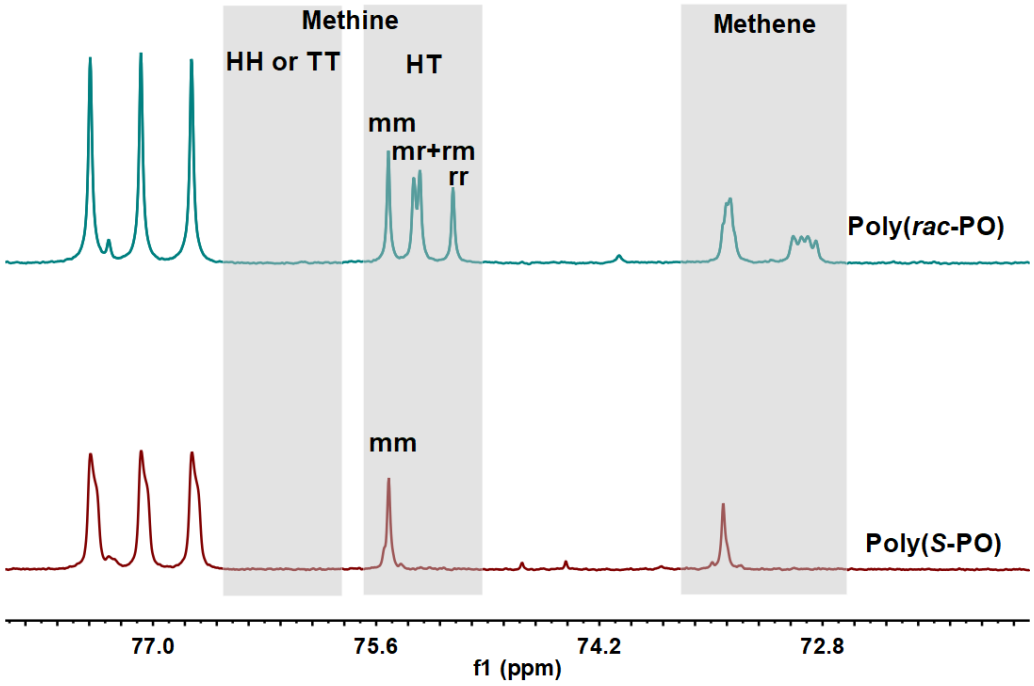


Figure S53. Analyzing isotacticity of PSPO by comparing ^{13}C NMR of PPOs generated by using *rac*-PO and *S*-PO respectively.

8. Regioselective alternating copolymerization of *S*-PO and PA

The copolymerization of PO with PA was investigated in this section, because of its low cost, ease of handling, high reactivity, and improved industrial synthesis. The selective copolymerization of PA with PO was not monitored by ^{1}H NMR and GPC duo to the low boiling point of PO (34 ℃).

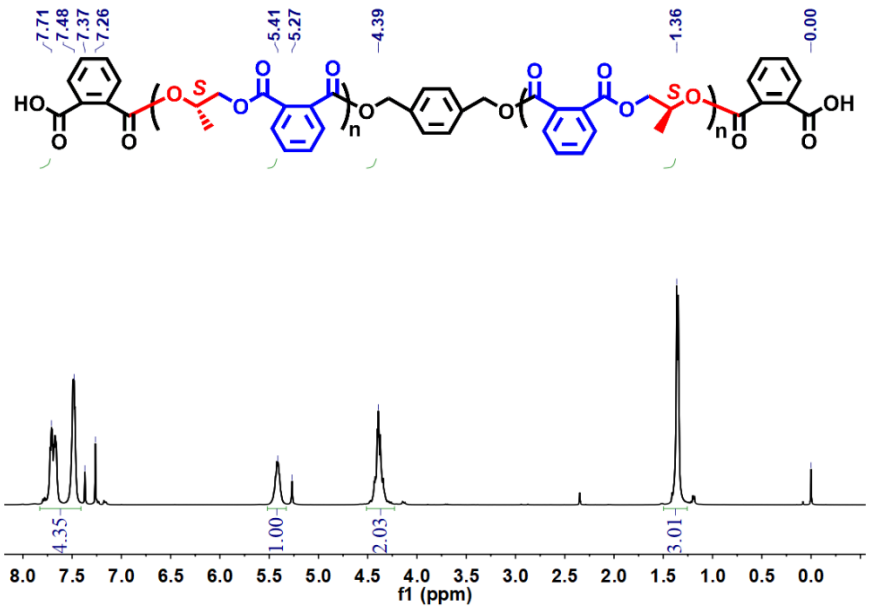


Figure S54. The ^{1}H NMR spectrum of the resultant PSPOPA isolated from the mixture.

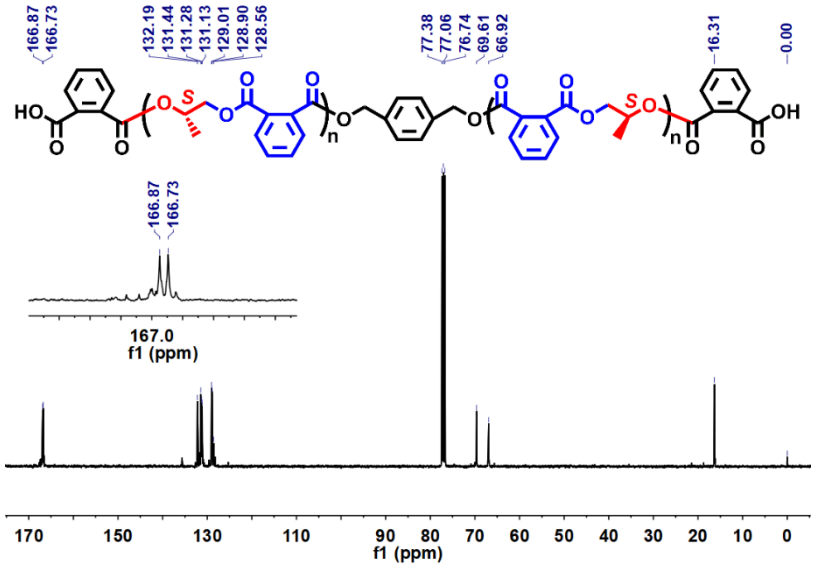


Figure S55. The ^{13}C NMR spectrum of the resultant PSPOPA precipitated from the mixture. Inset: expanded region of carbonyl.

9. Selective copolymerization of *S*-PO and PA

Selective copolymerization of S-PO/PA initiated by BDM was performed. Notably, the selective copolymerization of PA with PO was not monitored by ^{1}H NMR and GPC duo to the low boiling point of PO.

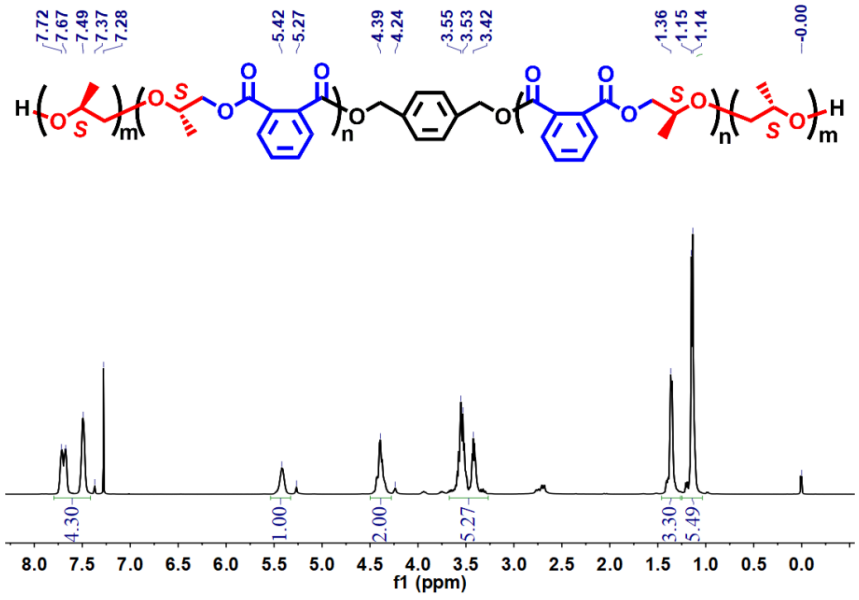


Figure S56. The ^{1}H NMR spectrum of the resultant P*S*PO-*b*-P*S*POPA-*b*-P*S*PO isolated from the mixture.

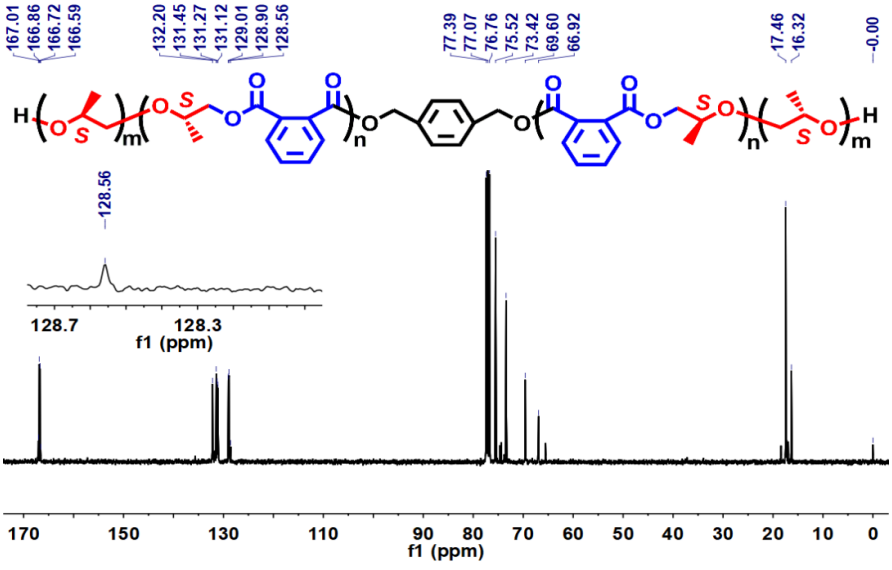
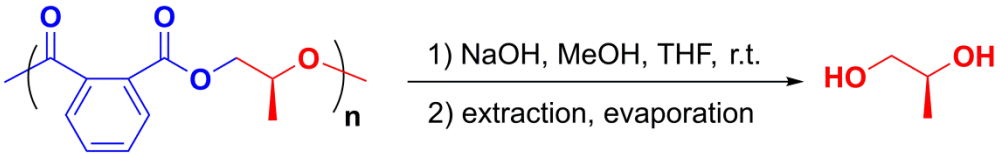


Figure S57. The ^{13}C NMR spectrum of the resultant P*S*PO-*b*-P*S*POPA-*b*-P*S*PO isolated from the mixture. Inset: the expanded ^{13}C chemical shifts of initiator.

Scheme S3. Determination of regioselective ring-opening of *S*-PO



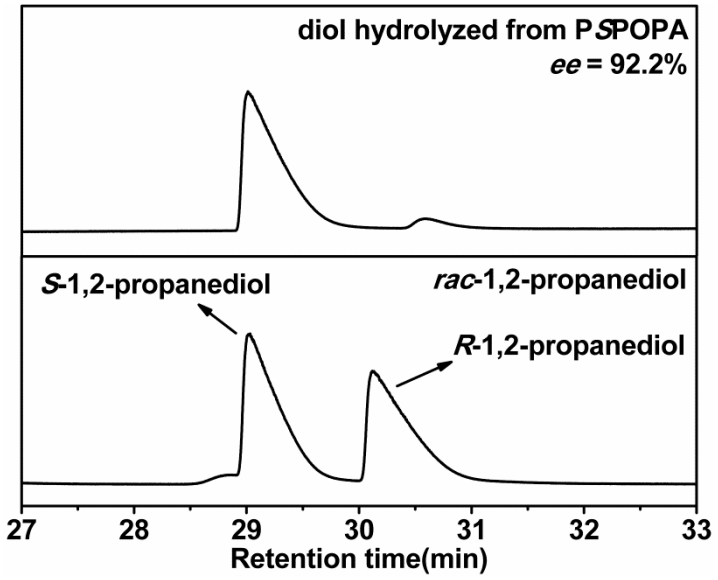


Figure S58. Chiral GC analyses of diols hydrolyzed from the resultant PSPOPA. Top: the *S*-enriched 1,2-propanediol (*ee* = 92.2%). Bottom: the *racemic* 1,2-propanediol.

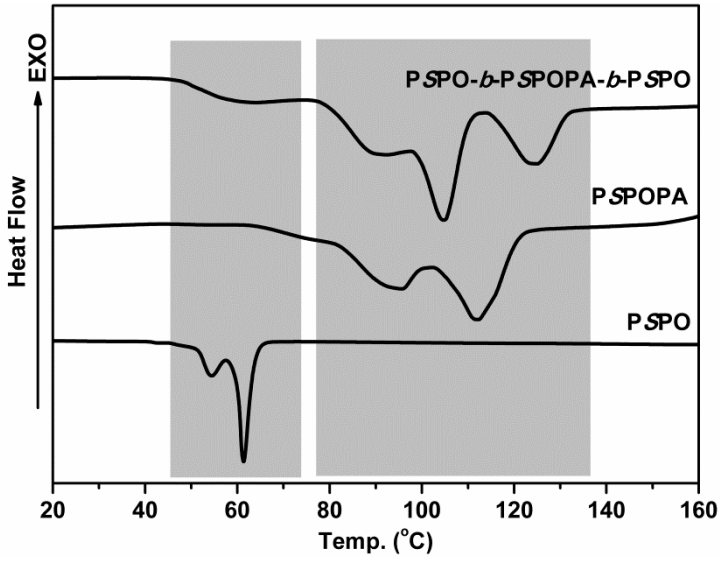


Figure S59. DSC curves of the block copolymer and homopolymers.

10.Homopolymerization of *L*-LA under BO and toluene

The selective ROP of *L*-LA was performed in the presence of BO and toluene ($[BO]_0$=4 mol/L). The *t*-BuP_2/BEt_3 (molar ratio = 1:2) catalytic system showed a high efficiency for the ROP of *L*-LA. Complete conversion of *L*-LA was achieved within 0.5 h. A slight of epimerization caused by active species or *t*-BuP_2 was detected with *mmm* tetrad content of *ca.* 80%.[6] The ROP of BO towards PBO kept unreacted regardless of the conversion of *L*-LA. The result gave a possibility to use *L*-LA as external modulation for turning the ROP of BO off.

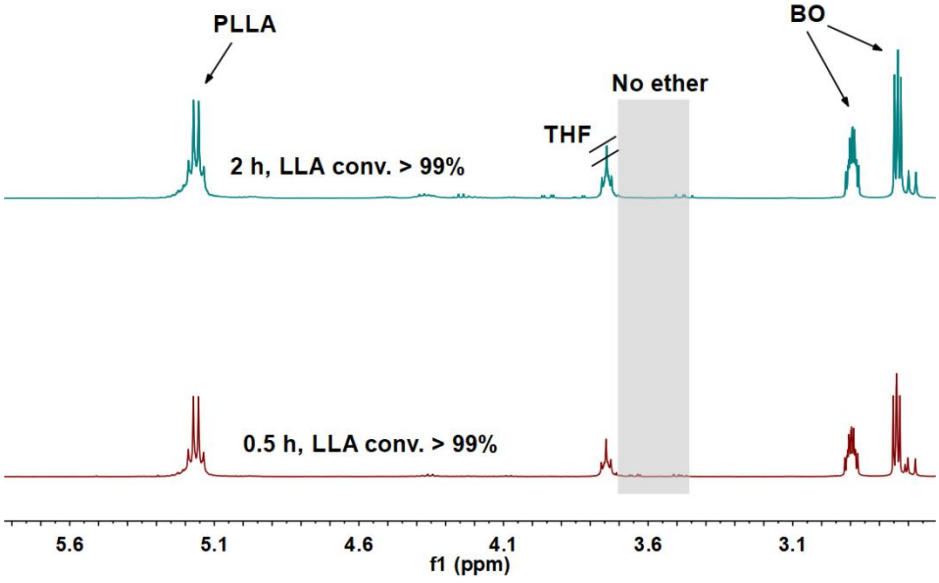


Figure S60. The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of *L*-LA and BO and the formation of PLLA.

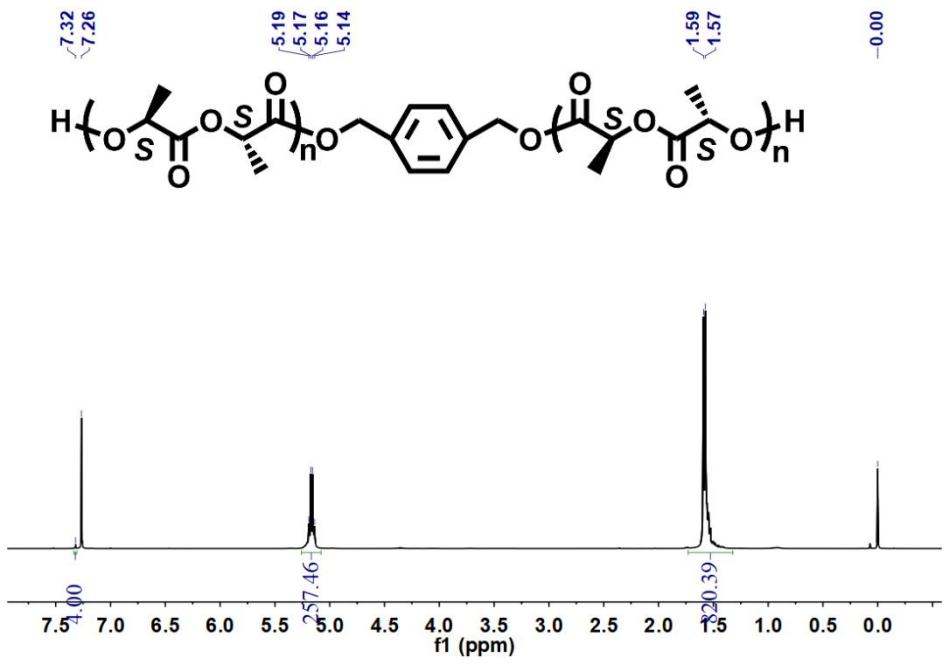


Figure S61. The ^{1}H NMR spectrum of the resultant PLLA isolated from the mixture.

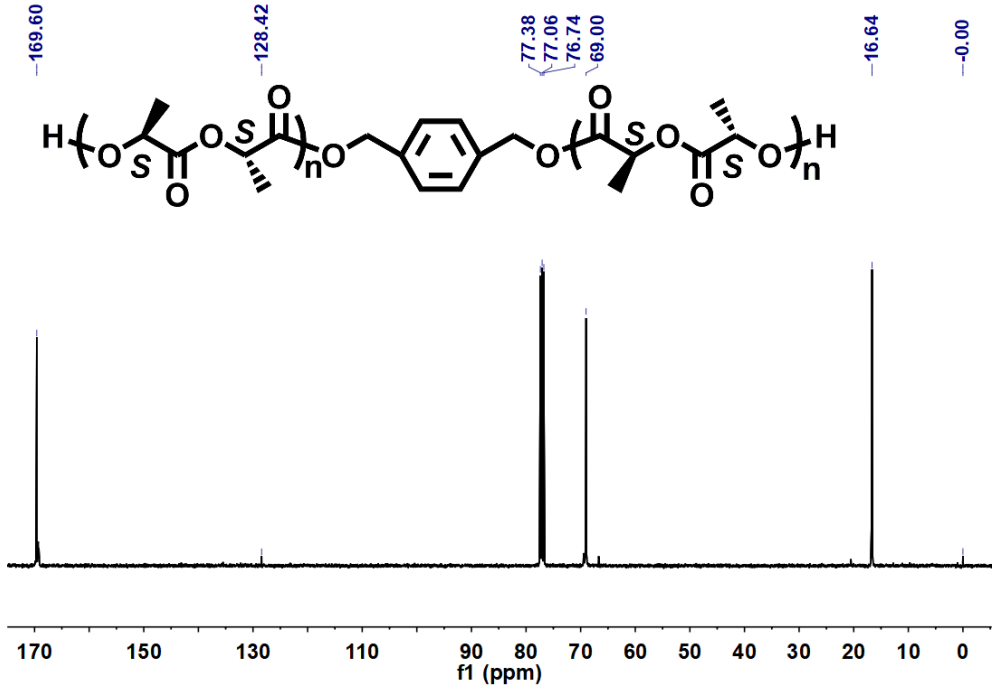


Figure S62. The ^{13}C NMR spectrum of the resultant PLLA isolated from the mixture.

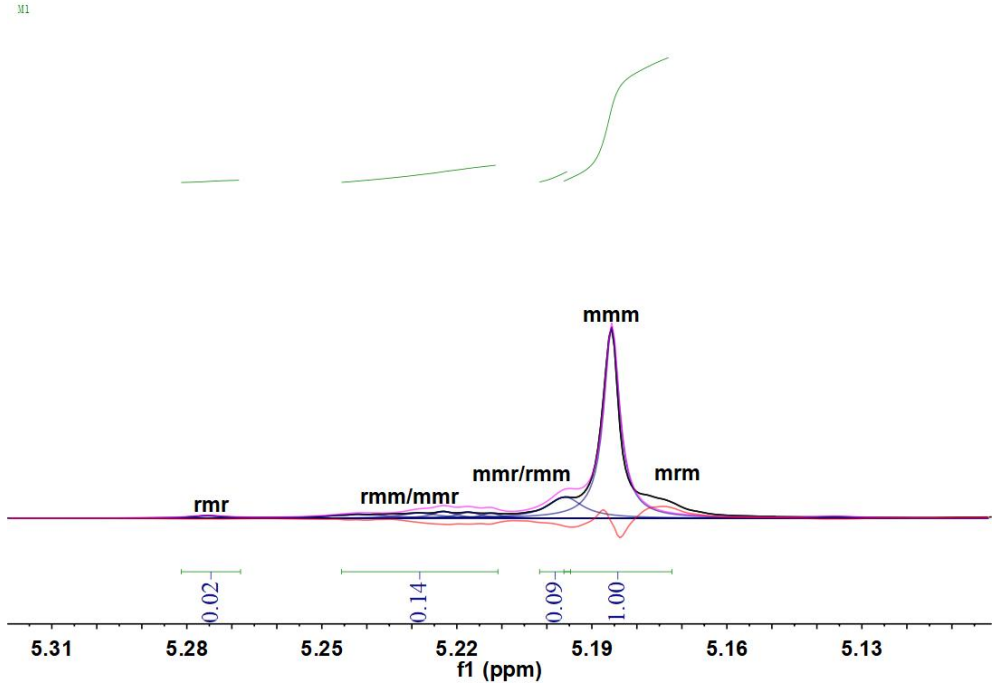


Figure S63. The homonuclear decoupled ^{1}H NMR spectrum of the methine region of PLLA (*mmm* tetrad = 80%).

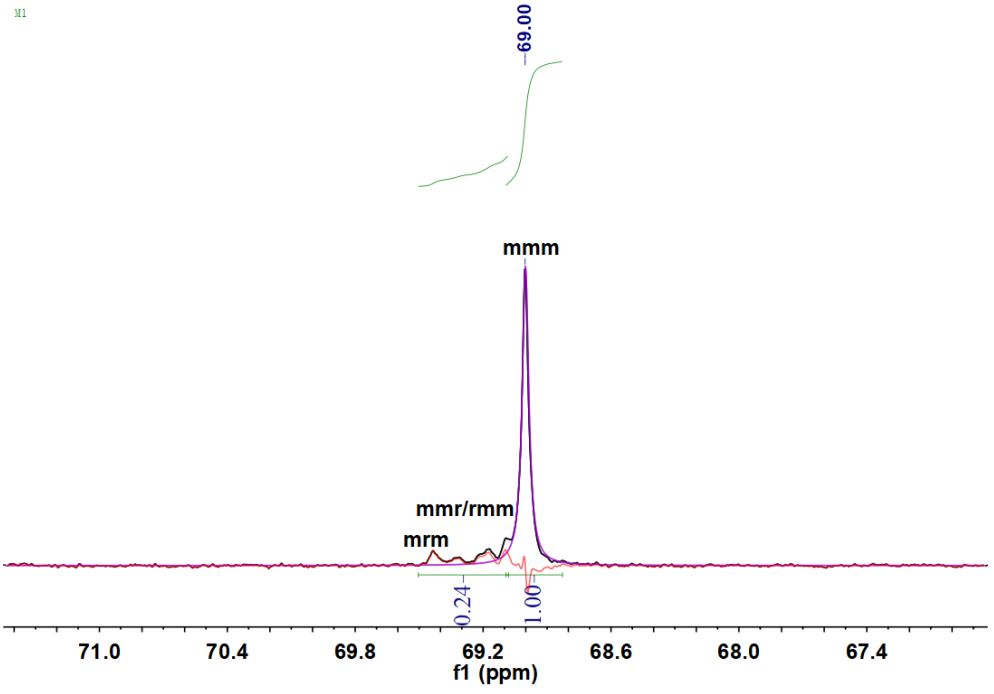


Figure S64. The ^{13}C NMR spectrum of the methine region of PLLA (*mmm* tetrad = 80%).

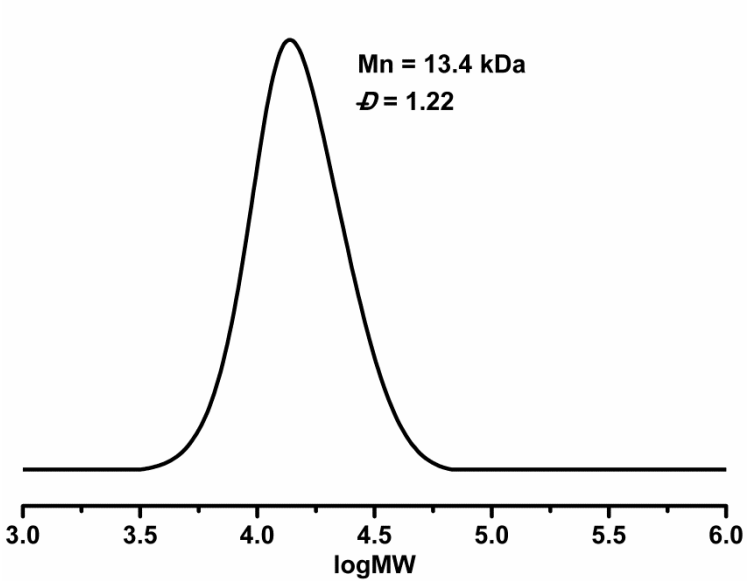
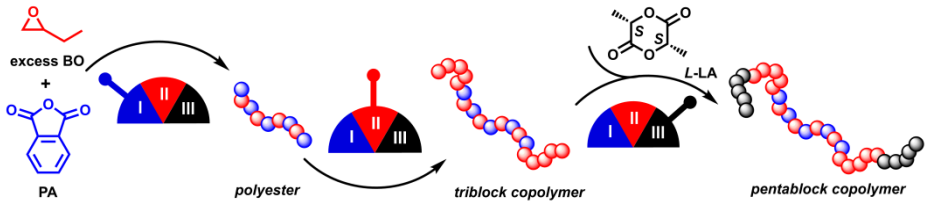


Figure S65. The GPC trace of the resultant PLLA.

Copolymerization of PA, BO and *L*-LA by a tandem polymerization strategy

The tandem copolymerization of PA/PO/*L*-LA was performed under the same conditions as entry 5, Table 1. When the copolymerization proceeds to 5 h, a batch of *L*-LA (100 equiv.) was added into the reaction mixture. The addition of *L*-LA as an external stimulus immediately terminate the ROP of BO and the ROP of *L*-LA was initiated by the triblock copolymer, yielding pentablock copolymer with PLLA as chain ends. The presence of BO in the reaction system has no influence on the ROP of *L*-LA.

Table S5. The tandem copolymerization of PA, BO and LLA by one-pot, two-step strategy.[a]



entry	Time (h)	%Conv. (PA)[b]	%Conv. (BO)[c]	%Conv. (*L*-LA)[d]	Ether forming[e]	M_n (kDa)[f]	$Đ$[f]
1	0.25	28	14	-	0	2.7	1.05
2	0.5	51	25	-	0	5.2	1.08
3	0.75	75	38	-	0	7.3	1.08
4	1	98	49	-	0	9.7	1.07
5	1.25	100	52	-	4	9.9	1.07
6	2	100	63	-	21	10.7	1.08
7	3	100	68	-	27	10.9	1.09
8	4	100	71	-	30	11.0	1.09
9	5	100	74	0	32	11.2	1.11
10	5.17	100	74	59	18	17.6	1.15
11	5.33	100	74	72	16	20.8	1.15
12	5.5	100	74	80	16	22.6	1.15
13	5.67	100	74	85	15	23.2	1.17
14	5.83	100	74	88	15	23.9	1.17
15	6	100	74	90	15	24.1	1.17
16	6.5	100	74	96	14	25.7	1.16

[a]The copolymerization reactions were conducted in toluene at 60 ℃, [*t*-BuP_2]:[BEt$_3$]:[BDM]:[PA]:[BO] = 1:2:1:50:100, $[BO]_0$ = 4 M. A batch of *L*-LA (100 equiv.) was added to the reaction mixture after 5 h of copolymerization. [b]The conversion of PA was determined by ^{1}H NMR spectroscopy. [c]The conversion of BO was determined by ^{1}H NMR spectroscopy. [d]The conversion of *L*-LA was determined by ^{1}H NMR spectroscopy. [e]The content of ether was determined by ^{1}H NMR spectroscopy. [f]M_n and $Đ$ were determined by GPC analysis in THF calibrated with polystyrene standards.

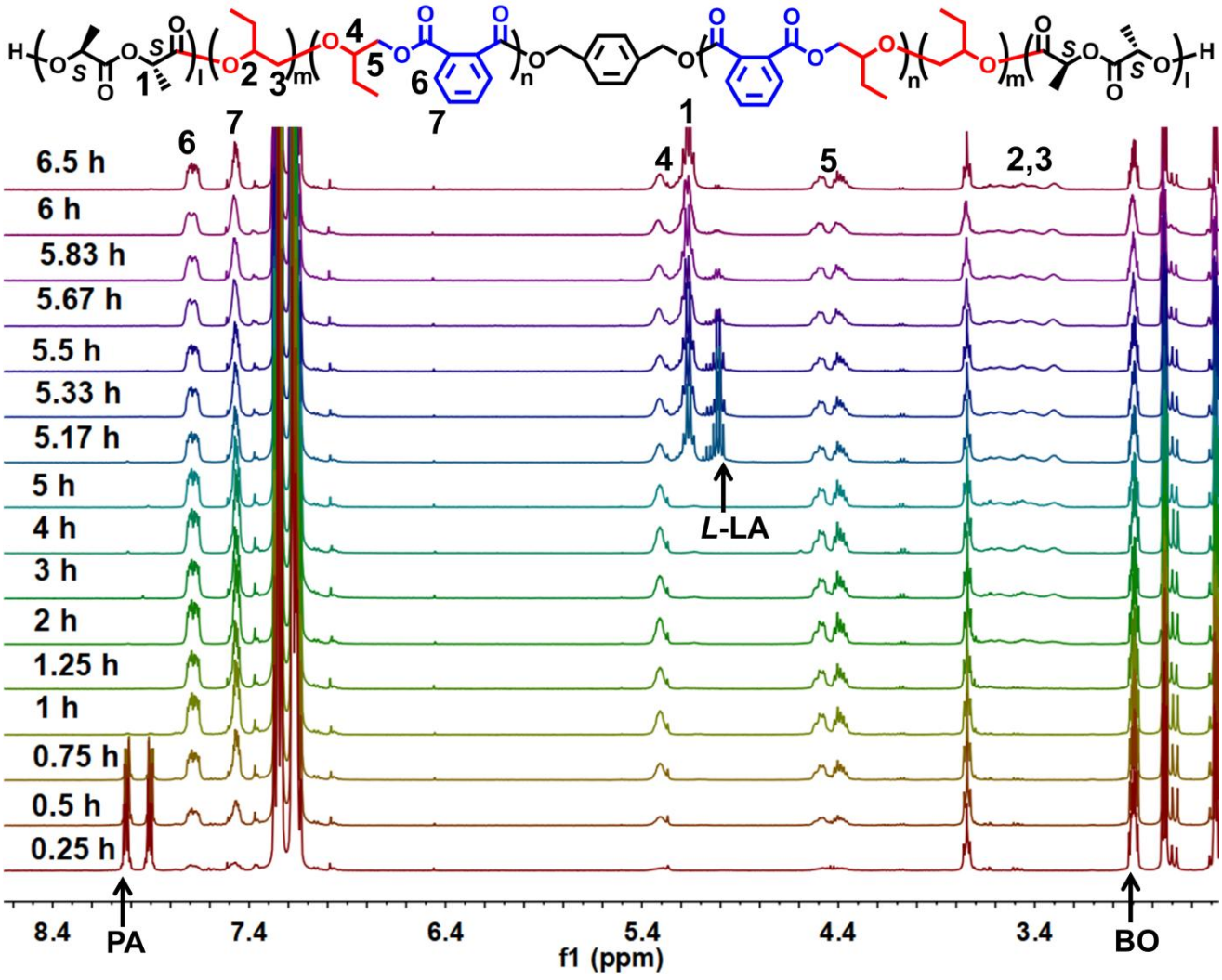


Figure S66. The ^{1}H NMR spectra of crude aliquots withdrawn from the reaction system for monitoring the conversion of *L*-LA, PA and BO and the formation of PLLA-*b*-PBO-*b*-PBOPA-*b*-PBO-*b*-PLLA.

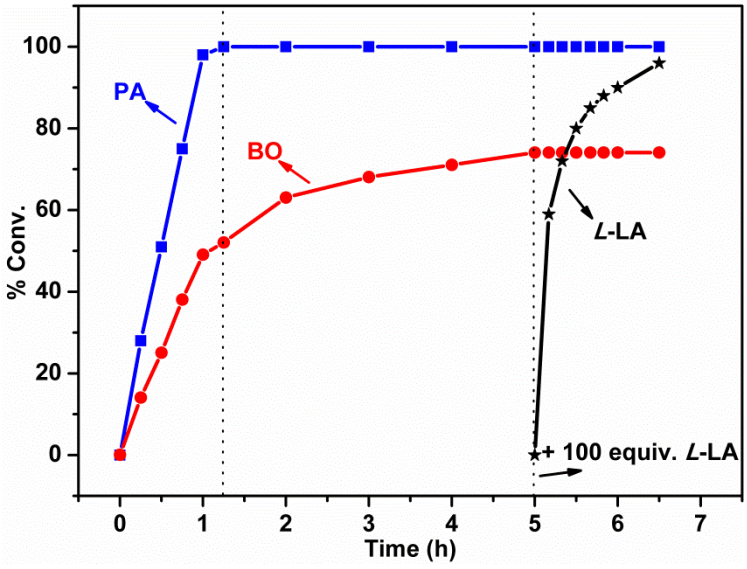


Figure S67. Plots of monomer conversion versus time as monitored by ^{1}H NMR spectroscopy.

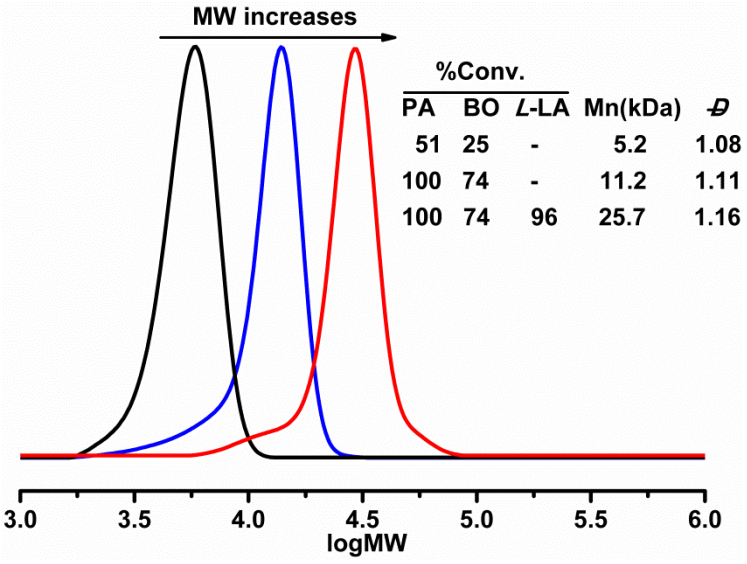


Figure S68. Evolution of GPC traces.

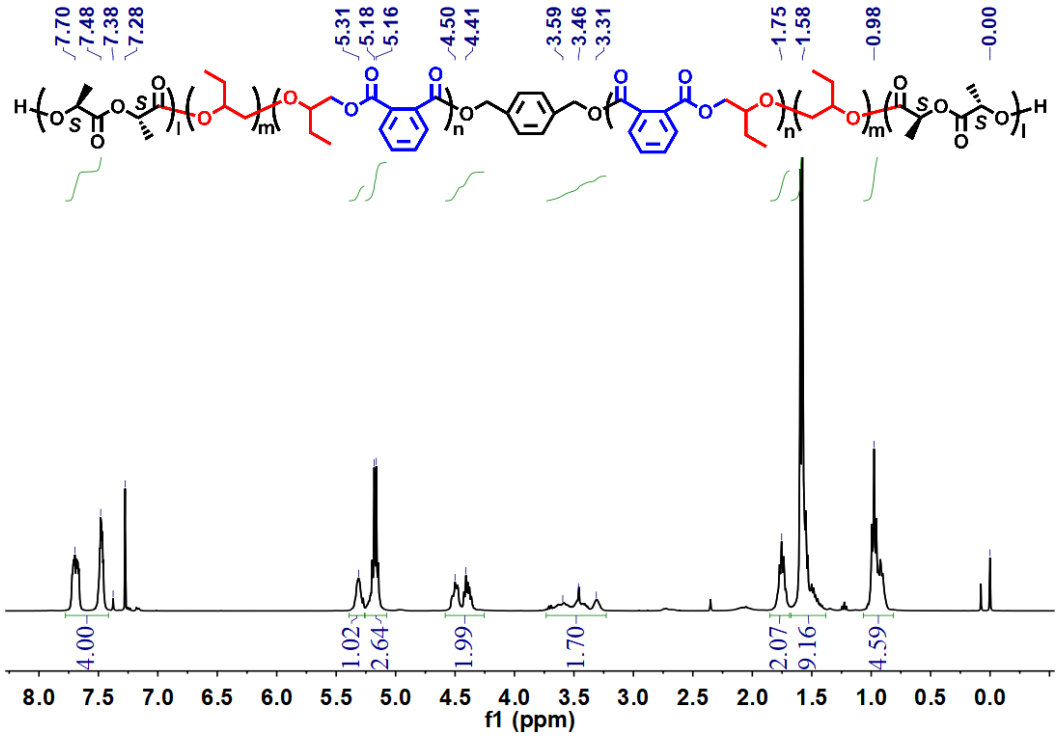


Figure S69. The ^{1}H NMR spectrum of the resultant pentablock copolymer containing PLLA isolated from the mixture.

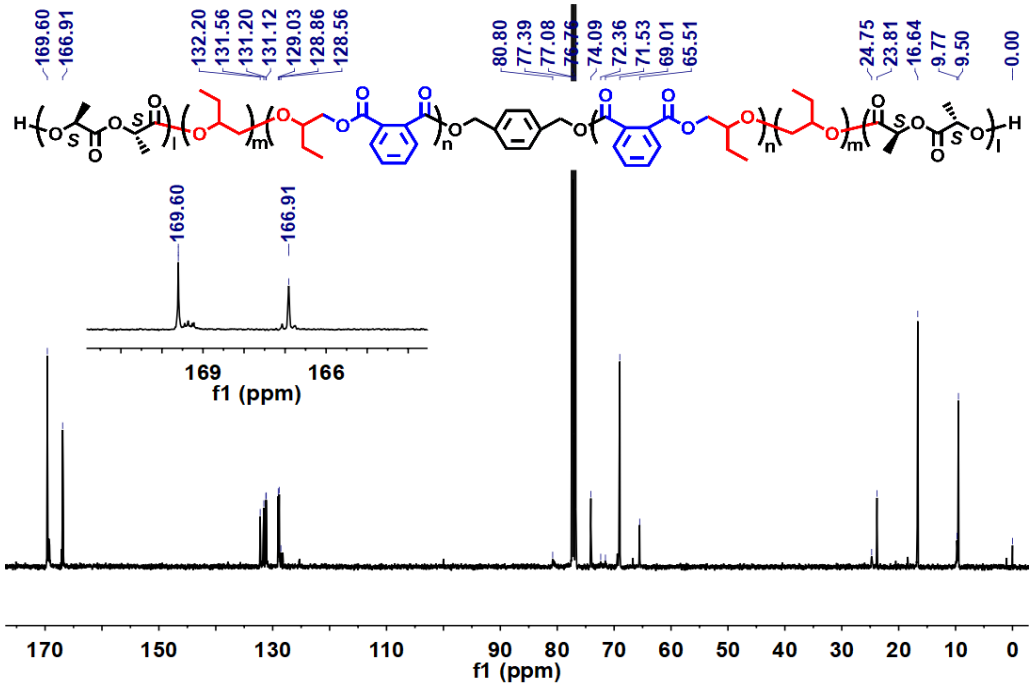


Figure S70. The ^{13}C NMR spectrum of the resultant pentablock copolymer containing PLLA isolated from the mixture. Inset: the expanded ^{13}C chemical shifts of the carbonyl region.

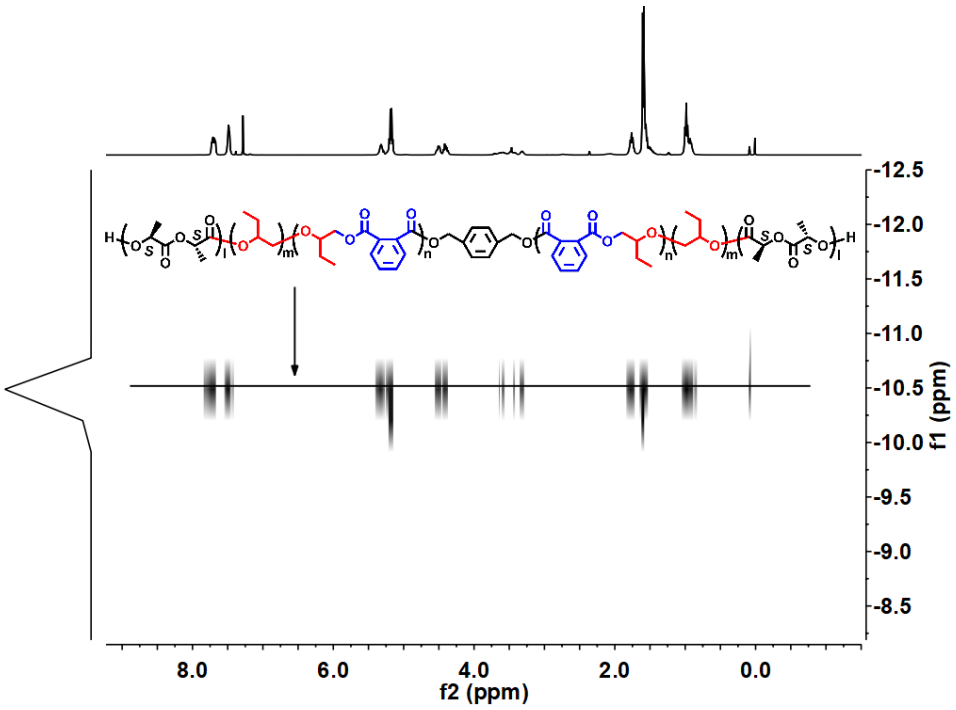


Figure S71. The DOSY NMR spectrum of the resultant pentablock copolymer containing PLLA isolated from the mixture (D = 3.55 × 10^{-11} m^2/s).

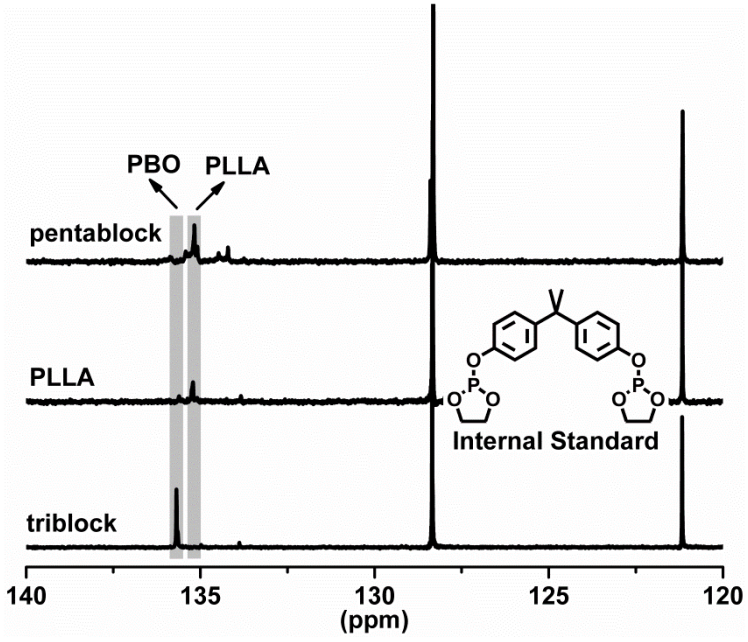


Figure S72. End group assay by ^{31}P NMR spectroscopy after treatment with phosphorus agent.

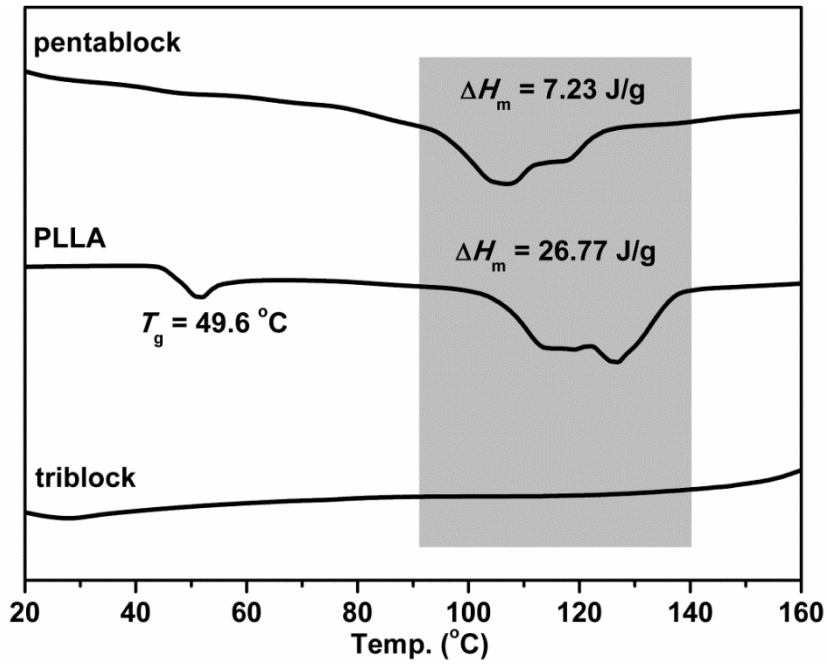


Figure S73. DSC curves of the pentablock copolymer, PLLA and triblock copolymers.

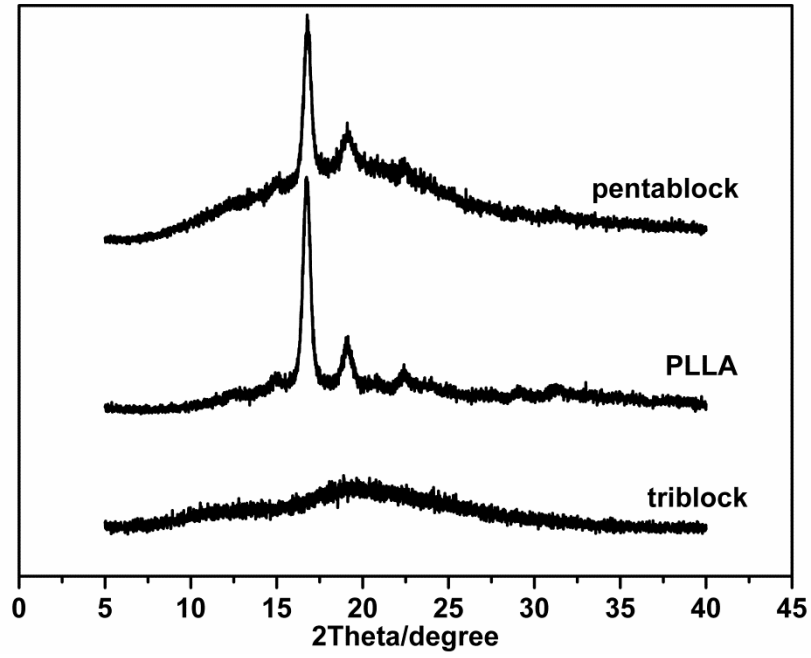


Figure S74. WAXD profiles of the block copolymer and homopolymers.

11.References

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