Supporting Information

Lewis Pair Catalyzed Highly Selective Polymerization for One-Step Synthesis of $A_zC_y(AB)_xC_yA_z$ Pentablock Terpolymers

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1. Materials

Propylene oxide (PO, Alfa, 99%) and toluene (Alfa, 99%)were distilled from calcium hydride (CaH_2) under argon atmosphere. Ethylene oxide (EO, Alfa, 99%) was distilled from sodium hydride and stored in an inert gas(Ar)-filled glove box under -30 ^oC. Racemic lactide (*rac*-LA, Acros, 99%), phthalic anhydride (PA, TCI, 99%), cis-1,2,3,6-tetrahydrophthalic anhydride (THPA, Adamas, 99%), succinic anhydride (SA, Aladdin, 99%) and cis-5-norbornene-endo-2,3-dicarboxylic anhydride (NBA, Alfa, 97%) were recrystallized in anhydrous toluene and sublimed under high vacuum two times. 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU, Alfa, 99%) was purified by distillation over CaH_2 and stored in an inert gas (Ar)-filled glove box. Triethylborane (Et_3B, 1.0 M in THF) was purchased from Alfa and used as received.

2. Characterization

NMR: ^1H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^1H, 400 MHz and ^{13}C, 100 MHz) spectrometer. Chemical shifts were reported in ppm from the internal standard, tetramethylsilane (0 ppm) for ^1H, data were presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. DOSY experiments were performed at a steady temperature of 298K 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.[1]

GPC: The molecular weight and its distribution of the products were determined by gel permeation chromatography at 40 ^oC in polystyrene standard on Waters 410 GPC instrument with THF as eluent, where the flow rate was set at 1.0 mL/min.

MALDI-TOF-MS: MALDI-TOF-MS spectra were carried out on LDI-1700 mass spectrometer by matrix-assisted laser desorption/ionization-time-of-flight method. The polymer samples were dissolved in THF at a concentration of 1mg·mL^{-1}. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix at a concentration of 10 mg·mL^{-1} in THF. Potassium trifluoroacetate (KTFA) was used as the cationizing agent at a concentration of 1 mg·mL^{-1}. The solutions of polymer, matrix and salt were mixed in a ratio of 1/1/1 (v/v/v), respectively. The mixed solution was spotted on a stainless steel MALDI plate repeatedly (5 times) and left to dry in the fume hood, overnight. The spectrum was recorded using reflectron mode.

IR Spectroscopy: IR spertra were obtained by directly casting the reaction mixture onto a KBr disk with a Bruker Vertex 80 FTIR spectrometer.

DSC : The thermogram were measured using DSC Q20 (DuPont TA Instruments). A sealed empty crucible was used as a reference, and the DSC was calibrated using indium. Samples were heated from room temperature to 150 °C, at a rate of

10 °C·min^{-1}, under helium flow, and were kept at 150 °C for 2 mins to erase the thermal history. Subsequently, the samples were cooled to -80 °C, at a rate of 10 °C·min^{-1}, and kept at -80 °C for further 2 mins, followed by a heating procedure from -80 °C to 150 °C, at a rate of 10 °C·min^{-1}.

3. Experimental Section

Typical procedure for ROCOP of PO/PA

In a glovebox, PA (1.48 g, 10 mmol) were measured into a 10 mL autoclave equipped with a stir bar. PO (3.5 mL, 50 mmol), H_2O (9 μL, 0.5 mmol) Et_3B (1 mmol/mL in THF, 100 μL, 0.1 mmol) and DBU (14 μL, 0.1 mmol) was then carefully added to the reactor via syringe. The autoclave was then taken out of the glove box and allowed to stirred at 60 ^oC for periods of time before it was cooled down to room temperature. A small aliquot of the polymerization mixture was taken out for ^1H NMR spectroscopy. The remained crude mixture was precipitated into an excess of cold methanol to yield a white powder, which was dried in vacuum at 40 °C until a constant weight.

Typical procedure for ROP of *rac*-LA

In a glovebox, *rac*-LA (1.44 g, 10 mmol) were measured into a 10 mL autoclave equipped with a stir bar. PO (3.5 mL, 50 mmol), H_2O (9 μL, 0.5 mmol) Et_3B (1 mmol/mL in THF, 100 μL, 0.1 mmol) and DBU (14 μL, 0.1 mmol) was then carefully added to the reactor via syringe. The autoclave was then taken out of the glove box and allowed to stirred at 25 ^oC for periods of time before it was cooled down to room temperature. A small aliquot of the polymerization mixture was taken out for ^1H NMR spectroscopy. The remained crude mixture was precipitated into an excess of cold methanol to yield a white powder, which was dried in vacuum at 40 °C until a constant weight.

Typical procedure for ROP of PO

In a glovebox, PO (3.5 mL, 50 mmol), H_2O (9 μL, 0.5 mmol) Et_3B (1 mmol/mL in THF, 100 μL, 0.1 mmol) and DBU (14 μL, 0.1 mmol) was carefully added to a 10 mL autoclave equipped with a stir bar via syringe. The autoclave was then taken out of the glove box and allowed to stirred at 60 ^oC for periods of time before it was cooled down to room temperature. A small aliquot of the polymerization mixture was taken out for ^1H NMR spectroscopy. Solvent was removed by rotary evaporation, and the product (viscous liquid) was substantially dried in vacuum at 40 °C until a constant weight.

Typical procedure for selective terpolymerization from PO, PA and *rac*-LA mixtures

In a glovebox, *rac*-LA (1.44g, 10 mmol) and PA (1.48 g, 10 mmol) were measured into a 10 mL autoclave equipped with a stir bar. PO (3.5 mL, 50 mmol), H_2O (9 μL, 0.5 mmol) Et_3B (1 mmol/mL in THF, 300 μL, 0.3 mmol) and DBU (14 μL, 0.1 mmol) was then carefully added to the reactor via syringe. The autoclave was then taken out of the glove box and allowed to stirred at 60 ^oC for periods of time before it was cooled down to room temperature. A small aliquot of the polymerization mixture was taken out for ^1H NMR spectroscopy. The remained crude mixture was precipitated into an

excess of cold methanol to yield a white powder, which was dried in vacuum at 40 °C until a constant weight.

Typical procedure for transesterification of block copolymers:

In a glovebox, PLA-*b*-PPE-*b*-PLA (0.1 mmol, $M_{n,GPC}$ = 12.6 kg/mol) and DBU (28 μL, 0.2 mmol) were dissolved in PO (3.5 mL, 50 mmol) in a 10 mL autoclave equipped with a stir bar. The autoclave was then taken out of the glove box and allowed to stirred at 80 °C for 24 h before it was cooled down to room temperature. A small aliquot of the polymerization mixture was taken out for ^{1}H NMR spectroscopy. The remained crude mixture precipitated into an excess of cold methanol to yield a white powder, which was dried in vacuum at 40 °C until a constant weight.

Typical proedure for selective terpoymerization from EO, PA and rac-LA mixtures

A 10 mL autoclave equipped with a stir bar was cooled below 0 °C in a glovebox before *rac*-LA (1.44 g, 10 mmol) and PA (1.48 g, 10 mmol) were measured into the autoclave. EO (2.5 mL, 50 mmol), H_2O (5.4 μL, 0.3 mmol), Et_3B (1 mmol/mL in THF, 150 μL, 0.15 mmol) and DBU (14 μL, 0.1 mmol) was then carefully added to the reactor via syringe. The autoclave was then taken out of the glove box and allowed to stirred at 60 °C for periods of time before it was cooled down to 0 °C. A small aliquot of the polymerization mixture was taken out for ^{1}H NMR spectroscopy. The remained crude mixture precipitated into an excess of cold n-hexane and dried in vacuum at 40 °C until a constant weight.

Table S1 Et_3B/DBU pair catalyzed ring-opening copolymerization of PO and PA.[a]

Entry	PO/PA/Et_3B/ DBU/H_2O	T (^oC)	time (h)	PA Conv.[b] (%)	TOF[c] (h^{-1})	$M_{n,th}$[d] (kDa)	$M_{n,GPC}$[e] (kDa)	$Đ$[e]
1	500/100/1/1/0	25	10	52	5	-	8.4	1.15
2	500/100/1/1/0	60	3	80	27	-	13.2	1.14
3	500/100/1/0/0	60	10	0	0	-	-	-
4	500/100/0/1/0	60	10	0	0	-	-	-
5	500/100/1/1/3	25	11	60	5	4.1	3.2	1.09
6	500/100/1/1/3	40	6	78	13	5.3	3.7	1.07
7	500/100/1/1/3	50	2.5	68	27	4.6	3.6	1.10
8	500/100/1/1/3	60	2	56	28	3.8	2.8	1.08
9	500/100/1/1/3	80	1	90	90	6.2	4.7	1.09
10	500/100/2/1/3	60	1	46	46	3.1	2.1	1.11
11	500/100/3/1/3	60	1	49	49	3.4	2.5	1.08
12	500/100/1/1/5	60	2.5	51	20	2.1	1.9	1.06
13	500/100/2/1/5	60	1	54	54	2.2	2.0	1.07
14	500/100/2/1/10	60	3	57	19	1.1	1.1	1.07
15	500/100/3/1/5	60	1	92	92	3.7	3.4	1.08
16	500/100/3/1/10	60	3	86	29	1.7	1.6	1.08

[a]Reaction condition: PO (3.5 mL, 50 mmol), [PO]:[PA] = 500:100, in a 10 mL autoclave. [b]Determined by using ^1H NMR spectroscopy. [c]Turnover frequency calculated as (mol PA consumed)/(mol DBU)/time. [d] Theoretical number-average molar mass calculated from feed ratio and monomer conversion. [e]Determined by using gel permeation chromatography in THF, calibrated with polystyrene standards.

Table S2 Et_3B /DBU pair (2/1) catalyzed ring-opening polymerization of PO.[a]

Entry	time (h)	PO Conv.[b] (%)	TOF[c] (h^{-1})	$In[M]_0/[M]_t$
1	0.5	0	0	0
2	1	7	34	0.07
3	1.5	39	128	0.48
4	2	60	149	0.91
5	2.5	75	150	1.38
6	3	78	129	1.50
7	3.5	83	118	1.75
8	4	87	108	2.01
9	4.5	90	99	2.29
10	5	91	91	2.38

[a]Reaction condition: PO (3.5 mL, 50 mmol), [PO]:[Et_3B]:[DBU] = 500:2:1, under Ar at 25 ^oC. [b]Determined by using ^1H NMR spectroscopy. [c]Turnover frequency calculated as (mol PO consumed)/(mol DBU)/time.

Table S3 Et_3B/DBU pair (3/1) catalyzed ring-opening polymerization of PO.[a]

Entry	time (h)	PO Conv.[b] (%)	TOF[c] (h^{-1})	$In[M]_0/[M]_t$
1	0.5	0	0	0
2	1	54	272	0.78
3	1.5	86	287	1.99
4	2	96	238	3.10
5	2.5	97	192	3.26

[a]Reaction condition: PO (3.5 mL, 50 mmol), [PO]:[Et_3B]:[DBU] = 500:3:1, under Ar at 25 °C. [b]Determined by using ^1H NMR spectroscopy. [c]Turnover frequency calculated as (mol PO consumed)/(mol DBU)/time.

Table S4 Et_3B/DBU pair catalyzed ring-opening polymerization of PO with H_2O as the initiator.[a]

Entry	PO/Et_3B/ DBU/H_2O	time (h)	PO Conv.[b] (%)	TOF[c] (h^{-1})	$M_{n,th}$[d] (kDa)	$M_{n,GPC}$[e] (kDa)	$Đ$[e]
1	500/1/1/5	24	<1	-	-	-	-
2	500/2/1/5	24	55	12	3.2	3.1	1.05
3	500/2/1/10	48	92	10	2.7	2.6	1.06
4	500/3/1/5	24	95	20	5.5	5.5	1.05
5	500/3/1/10	24	97	20	2.9	3.2	1.06
6	500/3/1/15	24	63	13	1.2	1.0	1.05

[a]Reaction condition: PO (3.5 mL, 50 mmol), in a 10 mL autoclave at 60 °C. [b]Determined by using ^1H NMR spectroscopy. [c]Turnover frequency calculated as (mol PO consumed)/(mol DBU)/time. [d] Theoretical number-average molar mass calculated from feed ratio and monomer conversion. [e]Determined by using gel permeation chromatography in THF, calibrated with polystyrene standards.

Table S5 DBU catalyzed ring-opening polymerization of *rac*-LA in PO.[a]

Entry	time (min)	*rac*-LA Conv.[b] (%)	TOF[c] (h^{-1})	$In[M]_0/[M]_t$
1	20	90	271	2.34
2	40	95	142	2.97
3	60	97	97	3.84
4	80	98	74	4.02

[a]Reaction condition: PO (3.5 mL, 50 mmol), [PO]:[*rac*-LA]:[DBU] = 500:100:1, under Ar at 25 °C. [b]Determined by using ^{1}H NMR spectroscopy. [c]Turnover frequency calculated as (mol *rac*-LA consumed)/(mol DBU)/time.

Table S6 Et_3B/DBU pair (2/1) catalyzed copolymerization of *rac*-LA and PO with H_2O as the initiator.[a]

Entry	PO/PA/*rac*-LA / Et_3B/DBU//H_2O	time (min)	*rac*-LA Conv. (%)[b]	PO Conv. (%)[b]
1	500/100/100/2/1/3	30	75	0
2	500/100/100/2/1/3	40	94	0
3	500/100/100/2/1/3	50	97	0
4	500/100/100/2/1/3	60	98	2
5	500/100/100/2/1/3	120	>99	80
6	500/100/100/2/1/3	240	>99	92

[a]Reaction condition: PO (3.5 mL, 50 mmol), in a 10 mL autoclave at 60 °C. [b]Determined by using ^{1}H NMR spectroscopy.

Table S7 Et_3B/DBU pair (3/1) catalyzed copolymerization of *rac*-LA and PO with H_2O as the initiator.[a]

Entry	PO/PA/*rac*-LA / Et_3B/DBU//H_2O	time (min)	*rac*-LA Conv. (%)[b]	PO Conv. (%)[b]
1	500/100/100/3/1/3	15	25	0
2	500/100/100/3/1/3	30	65	0
3	500/100/100/3/1/3	45	73	8
4	500/100/100/3/1/3	60	92	20
5	500/100/100/3/1/3	90	>99	45
6	500/100/100/3/1/3	120	>99	75

[a]Reaction condition: PO (3.5 mL, 50 mmol), in a 10 mL autoclave at 60 °C.

[b]Determined by using ^{1}H NMR spectroscopy.

Table S8 Et_3B/DBU pair (1/1) catalyzed selective terpolymerization from PO, PA and *rac*-LA with H_2O as the initiator.[a]

Entry	PO/PA/*rac*-LA / Et_3B/DBU//H_2O	time (h)	PA Conv. (%)[b]	*rac*-LA Conv. (%)[b]	$M_{n,th}$[c] (kDa)	$M_{n,GPC}$[d] (kDa)	$Đ$[d]
1	500/100/100/1/1/3	1	34	0	2.3	1.5	1.10
2	500/100/100/1/1/3	1.5	45	0	3.1	2.5	1.09
3	500/100/100/1/1/3	2	74	0	5.1	4.1	1.09
4	500/100/100/1/1/3	3	85	0	6.5	6.3	1.12
5	500/100/100/1/1/3	3.5	91	0	6.2	6.7	1.14
6	500/100/100/1/1/3	4	>99	46	9.1	8.5	1.14
7	500/100/100/1/1/3	5	>99	>99	11.7	9.7	1.15

[a]Reaction condition: PO (3.5 mL, 50 mmol), in a 10 mL autoclave at 60 °C. [b]Determined by using ^{1}H NMR spectroscopy. [c]Theoretical number-average molar mass calculated from feed ratio and monomer conversion. [d]Determined by using gel permeation chromatography in THF, calibrated with polystyrene standards.

Table S9 Et_3B/DBU pair (2/1) catalyzed selective terpolymerization from PO, PA and *rac*-LA with H_2O as the initiator.[a]

Entry	PO/PA/*rac*-LA / Et_3B/DBU//H_2O	time (h)	PA Conv. (%)[b]	*rac*-LA Conv. (%)[b]	PO Conv. (%)[b]	$M_{n,th}$[c] (kDa)	$M_{n,GPC}$[d] (kDa)	$Đ$[d]
1	500/100/100/2/1/3	2	31	0	6	2.1	1.7	1.15
2	500/100/100/2/1/3	4	80	0	16	5.2	4.1	1.14
3	500/100/100/2/1/3	5	>99	70	20	10.2	7.9	1.12
4	500/100/100/2/1/3	6	>99	97	22	11.7	8.6	1.13
5	500/100/100/2/1/3	7	>99	>99	26	12.2	9.1	1.12
6	500/100/100/2/1/3	8	>99	>99	37	13.3	11.1	1.12
7	500/100/100/2/1/3	12	>99	>99	44	13.9	12.6	1.12

[a]Reaction condition: PO (3.5 mL, 50 mmol), in a 10 mL autoclave at 60 °C. [b]Determined by using ^{1}H NMR spectroscopy. [c] Theoretical number-average molar mass calculated from feed ratio and monomer conversion. [d]Determined by using gel permeation chromatography in THF, calibrated with polystyrene standards.

Table S10 Et_3B/DBU pair (3/1) catalyzed selective terpolymerization from PO, PA and *rac*-LA with H_2O as the initiator.[a]

Entry	PO/PA/*rac*-LA / Et_3B/DBU//H_2O	time (h)	PA Conv. (%)[b]	*rac*-LA Conv. (%)[b]	PO Conv. (%)[b]
1	500/100/100/3/1/3	1	55	0	11
2	500/100/100/3/1/3	1.5	91	0	18
3	500/100/100/3/1/3	1.75	>99	13	20
4	500/100/100/3/1/3	2	>99	73	20
5	500/100/100/3/1/3	2.5	>99	94	29
6	500/100/100/3/1/3	3	>99	>99	32
7	500/100/100/3/1/3	4	>99	>99	46

[a]Reaction condition: PO (3.5 mL, 50 mmol), in a 10 mL autoclave at 60 °C. [b]Determined by using ^{1}H NMR spectroscopy.

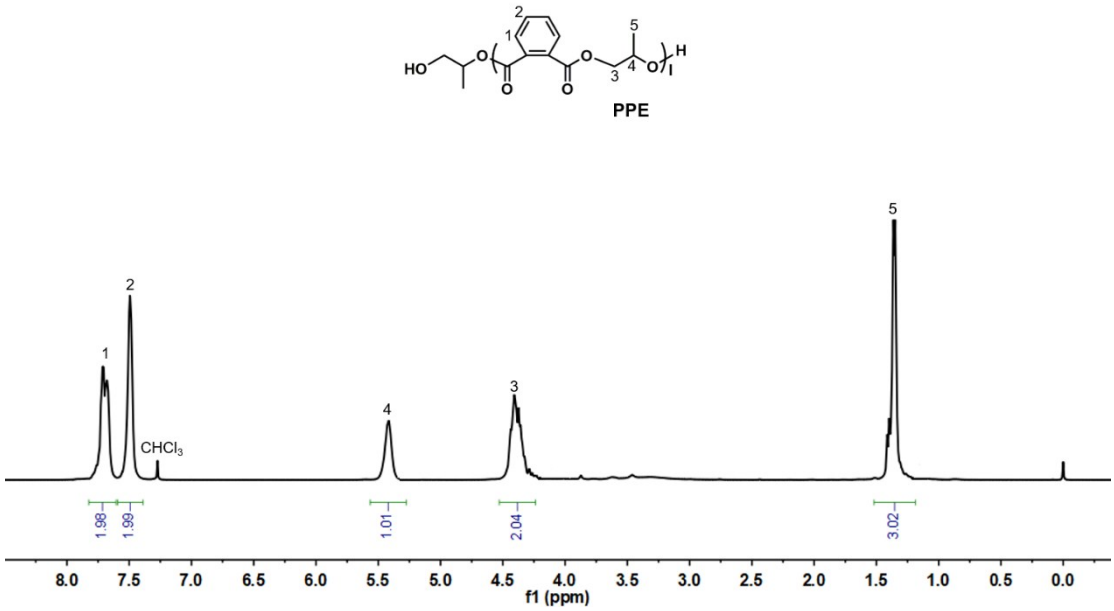


Figure S1. ^{1}H NMR spectrum of PPE obtained from Et_3B/DBU pair (1/1) catalyzed PO/PA ROCOP (Table S1, entry 1).

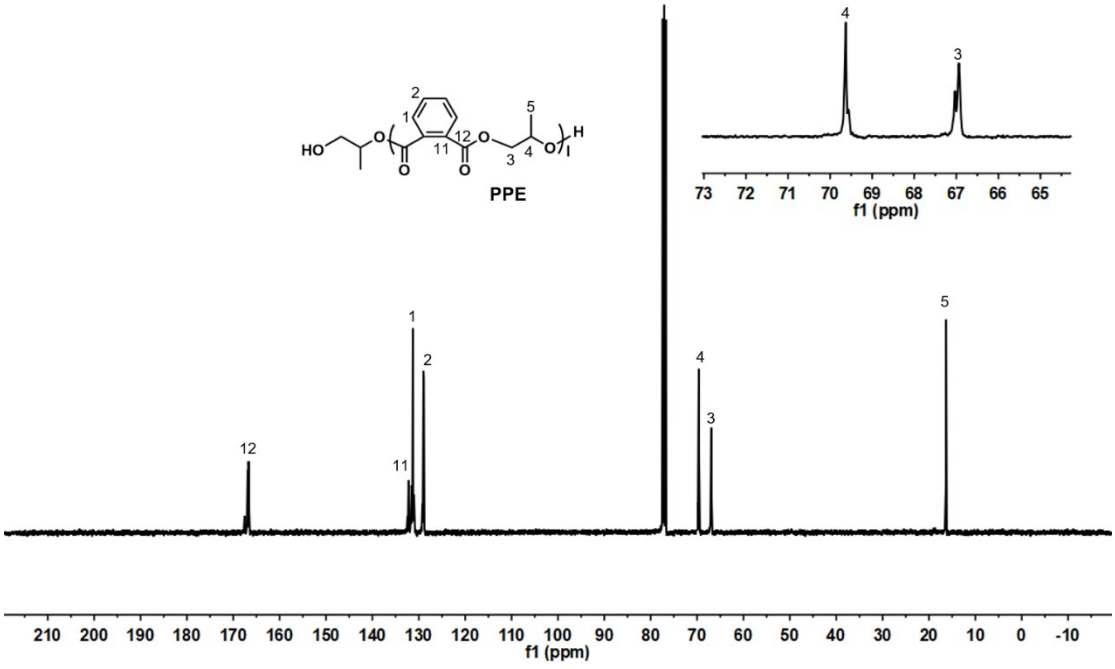


Figure S2. ^{13}C NMR spectrum of PPE obtained from Et_3B/DBU pair (1/1) catalyzed PO/PA ROCOP (Table S1, entry 1).

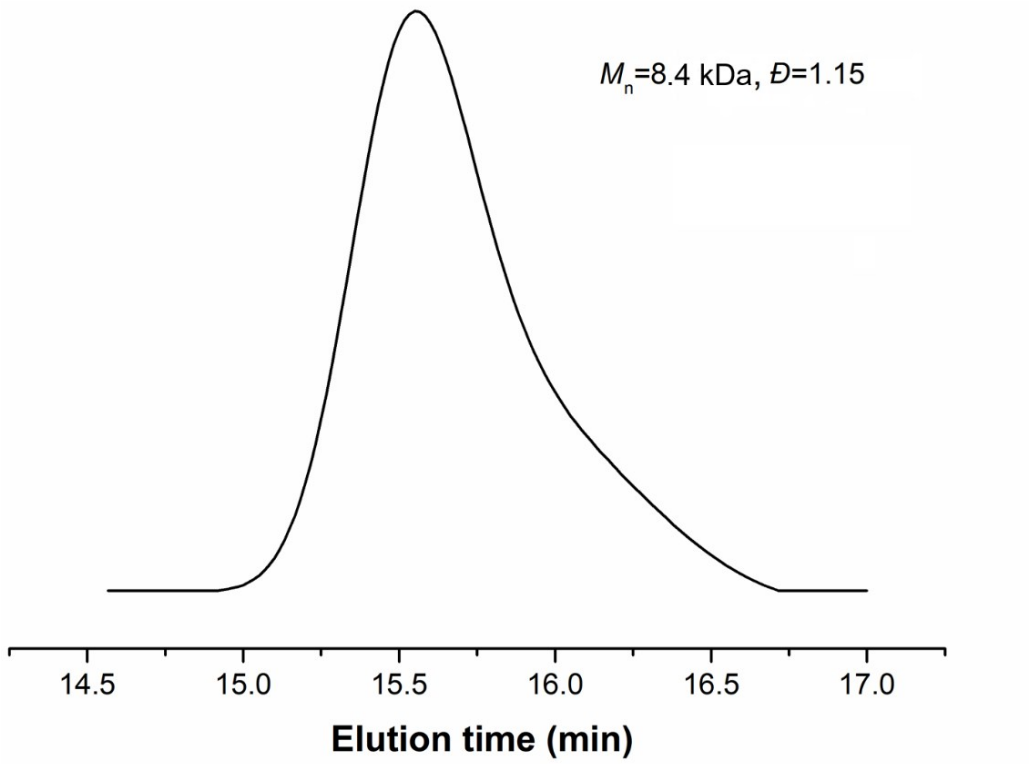


Figure S3. GPC curve of PPE obtained from Et_3B/DBU pair (1/1) catalyzed PO/PA ROCOP (Table S1, entry 1).

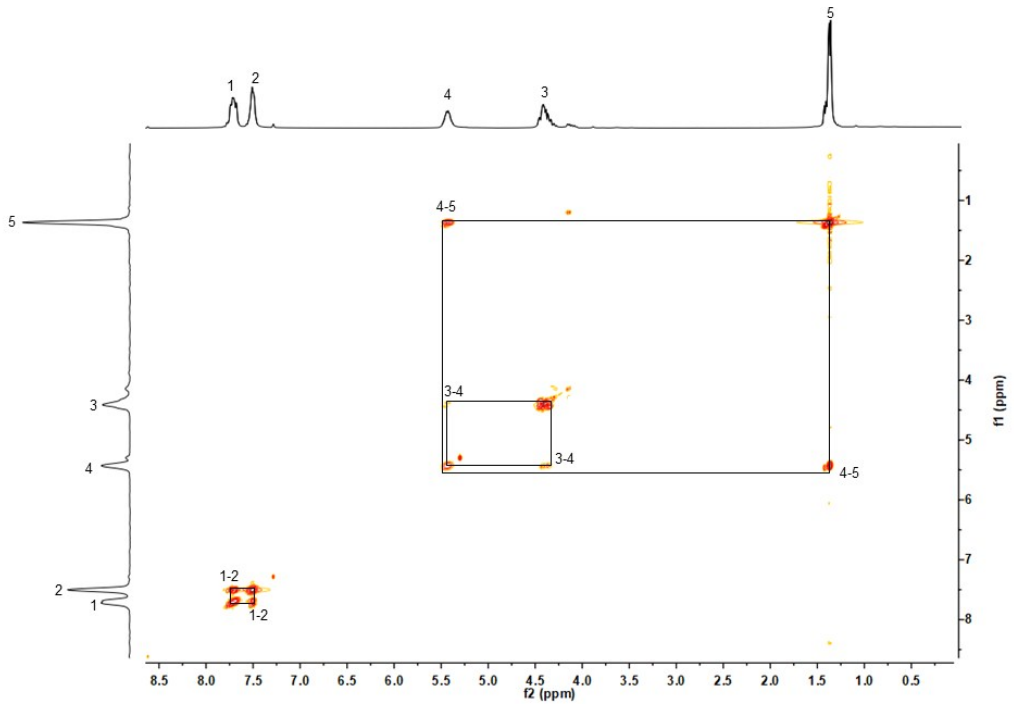


Figure S4. COSY NMR spectrum of PPE obtained from Et_3B/DBU pair (1/1) catalyzed PO/PA ROCOP (Table S1, entry 1).

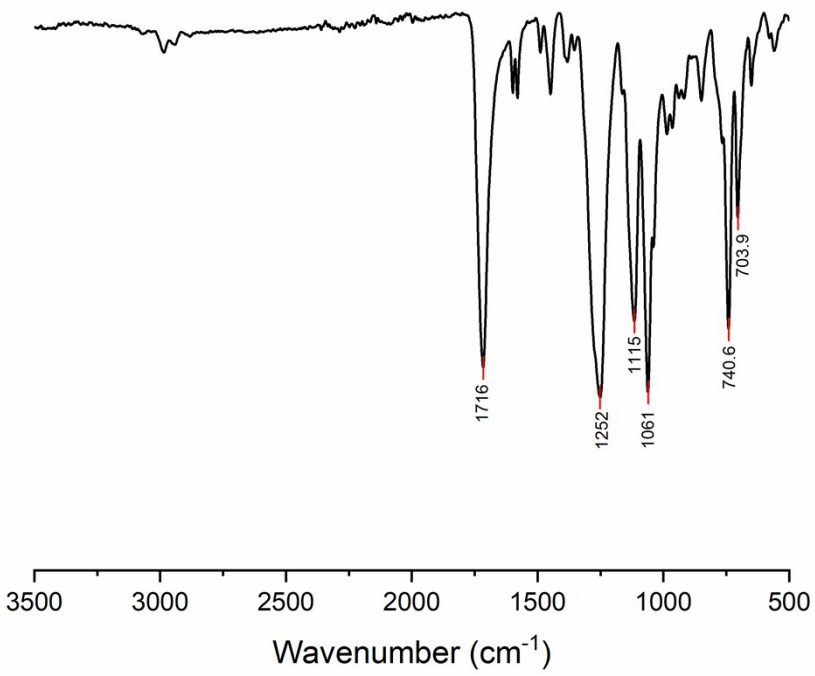


Figure S5. IR spectrum of PPE obtained from Et_3B/DBU pair (1/1) catalyzed PO/PA ROCOP (Table S1, entry 1).

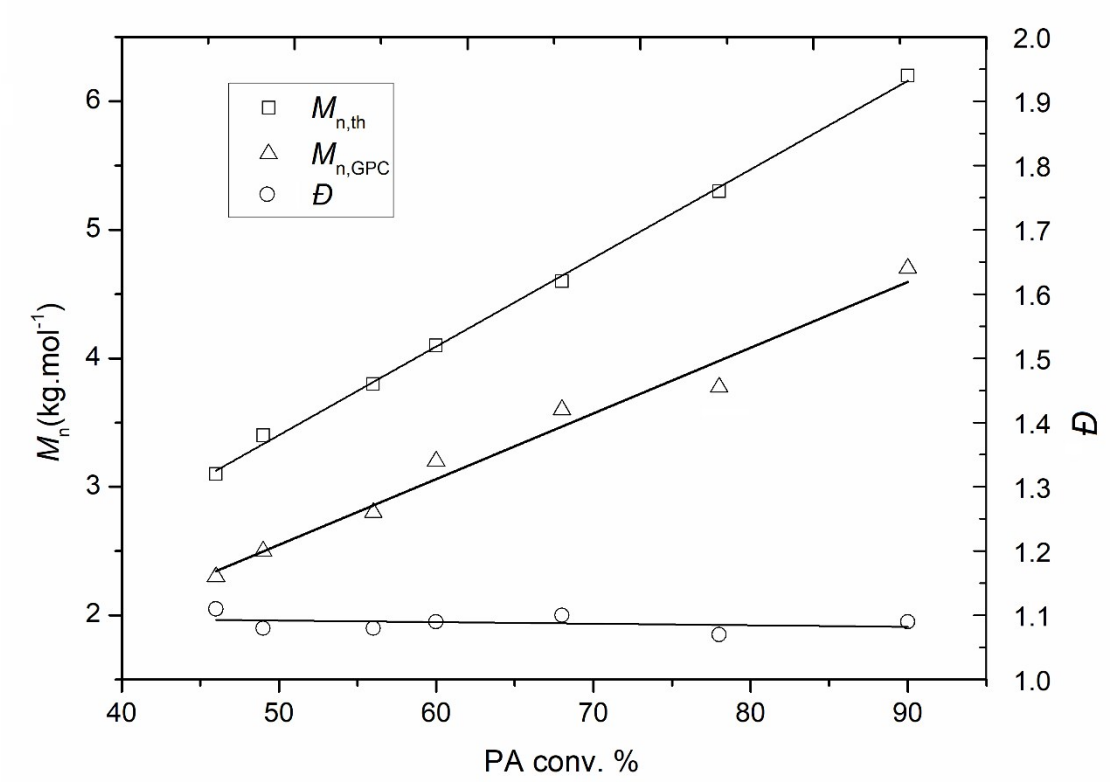


Figure S6. Evolution of $M_{n.GPC}$, $M_{n.theo}$ and $Đ$ in PO/PA ROCOP catalyzed by Et_3B/DBU pair with 3 eq H_2O as the initiator (Table S1, entry 5-11).

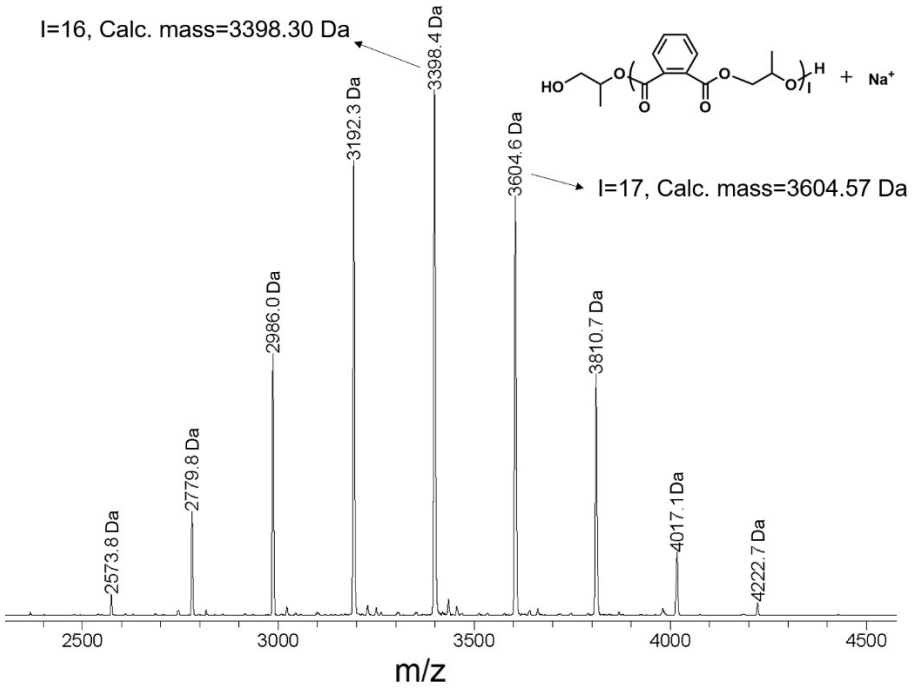


Figure S7. MALDI-TOF-MS spectrum of the PPE obtained from PO/PA ROCOP with H_2O as the initiator (Table S1, entry 15).

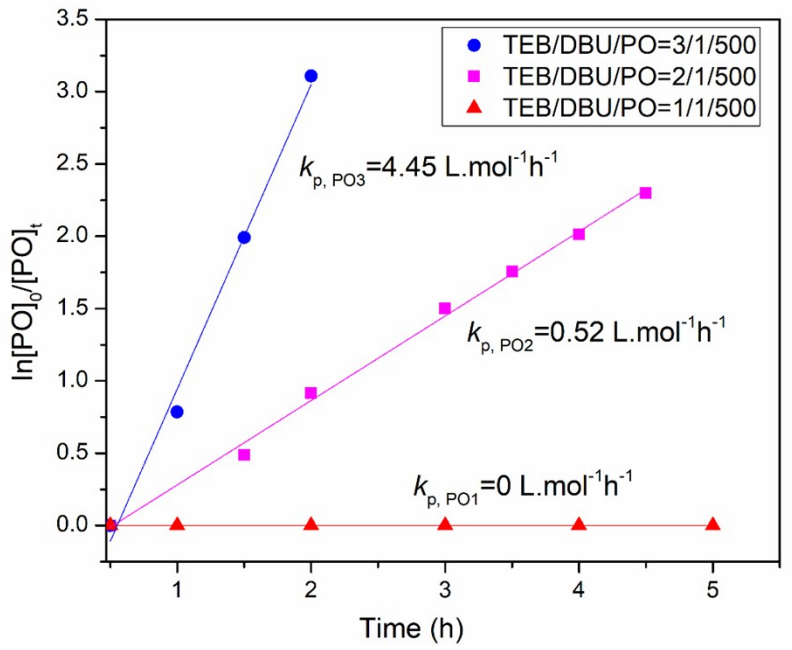


Figure S8. First-order plot of PO conversion vs time for the ring-opening polymerization process at 25 °C, PO (3.5 mL, 50 mmol), [PO]:[DBU]=500:1. Red dot, [Et_3B]:[DBU]=1:1; Purple dot, [Et_3B]:[DBU]=2:1; Blue dot, [Et_3B]:[DBU]=3:1. Rate constants (k_p) can be calculated by the following equation: $\ln([PO]_0/[PO]_t)=k_p[C]t$, where [PO] is the concentration of PO, [C] the concentration of the initiator, and t the reaction time.

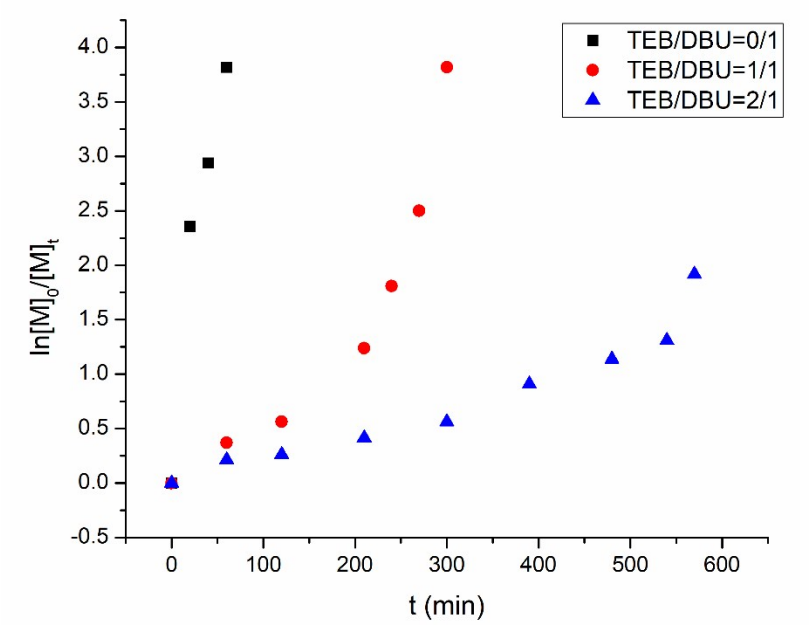


Figure S9. Kinetic plot of *rac*-LA conversion vs time for the ring-opening polymerization process at 25 °C, PO (3.5 mL, 50 mmol), [PO]:[*rac*-LA]:[DBU]=500:100:1. Dark dot, sole catalysis of [DBU]; Red dot, [Et_3B]:[DBU]=1:1; Blue dot, [Et_3B]:[DBU]=2:1.

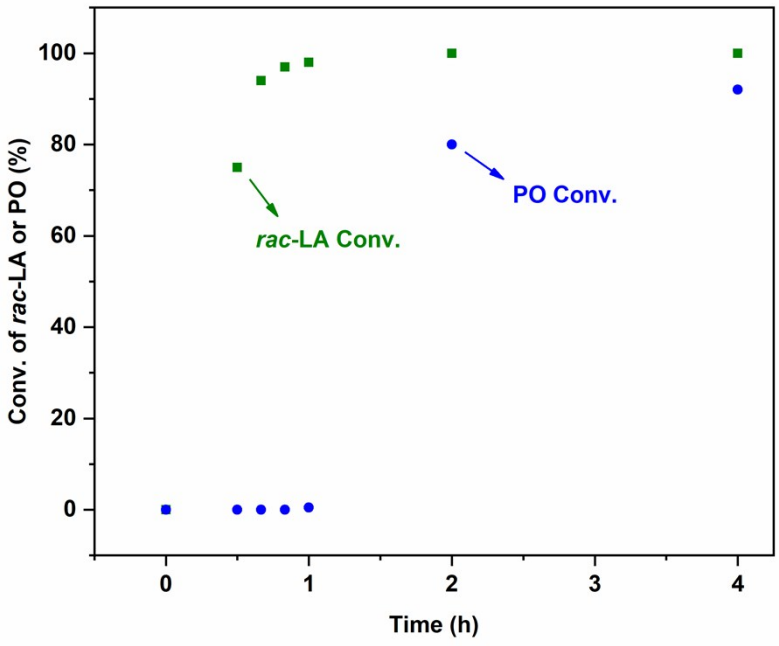


Figure S10. The plots of monomer conversion versus time for Et_3B/DBU pair (2/1) catalyzed copolymerization of *rac*-LA and PO with 3 eq H_2O as the initiator at 60 °C. (Table S6).

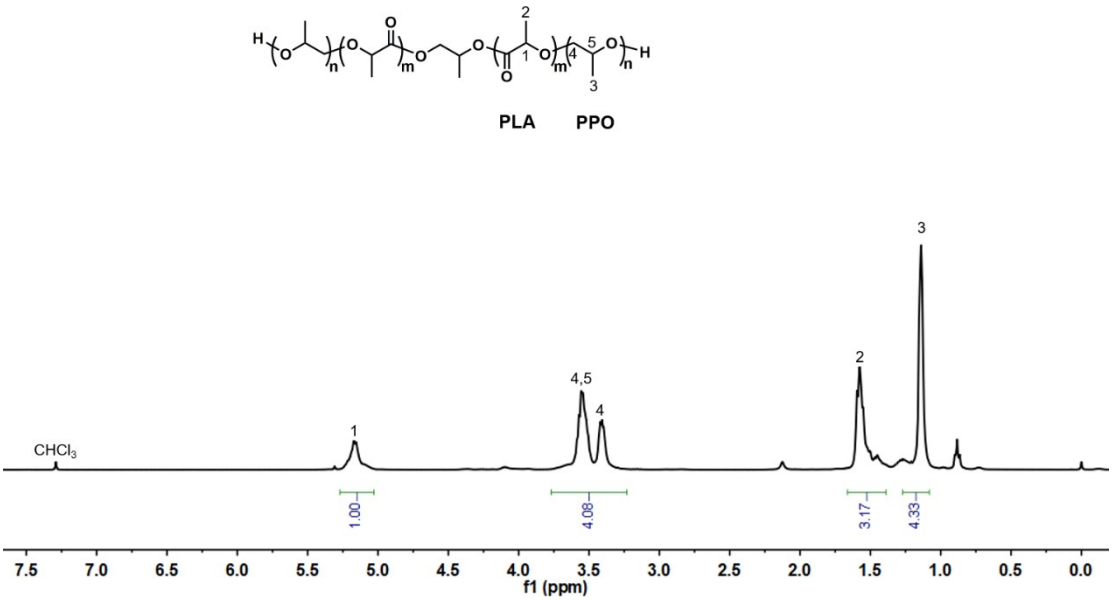


Figure S11. ^{1}H NMR spectrum of the product obtained from copolymerization of *rac*-LA and PO catalyzed by Et_3B/DBU pair (2/1) at 60 °C (Table S6, entry 6).

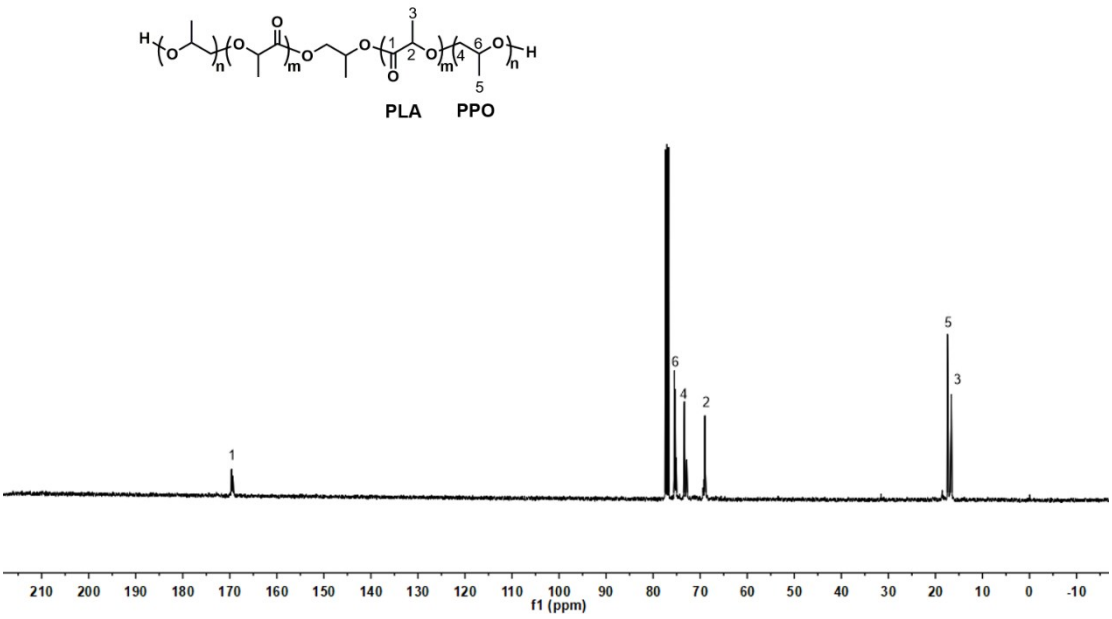


Figure S12. ^{13}C NMR spectrum of the product obtained from copolymerization of *rac*-LA and PO catalyzed by Et_3B/DBU pair (2/1) at 60 °C (Table S6, entry 6).

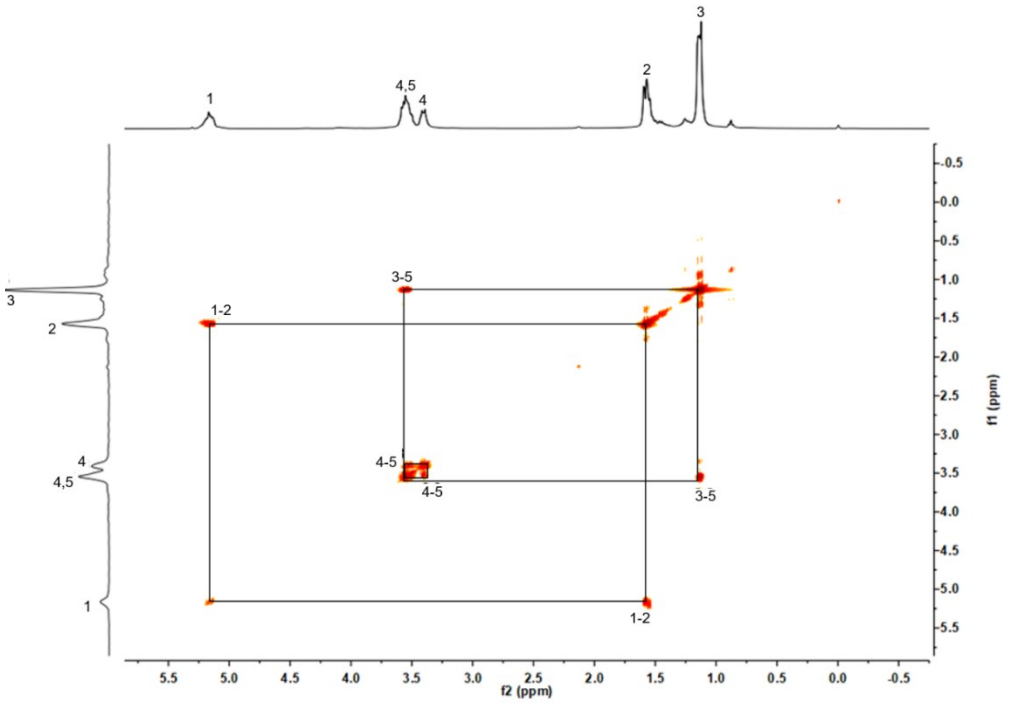


Figure S13. COSY NMR spectrum of the product obtained from copolymerization of *rac*-LA and PO catalyzed by Et_3B/DBU pair (2/1) at 60 °C (Table S6, entry 6).

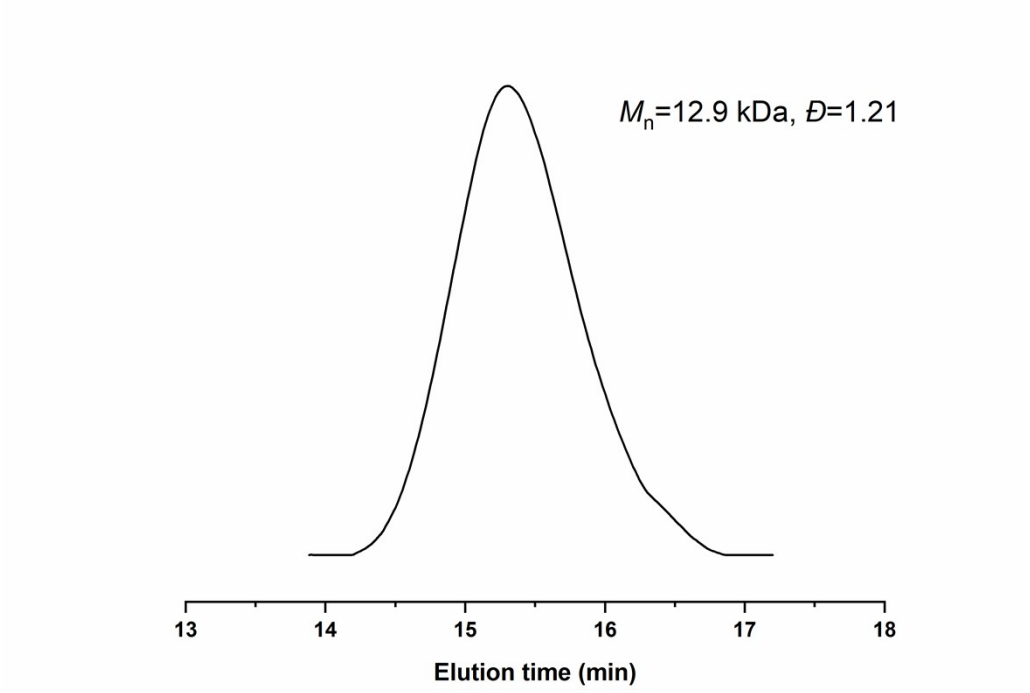


Figure S14. GPC curve of the product obtained from copolymerization of *rac*-LA and PO catalyzed by Et_3B/DBU pair (2/1) at 60 °C (Table S6, entry 6).

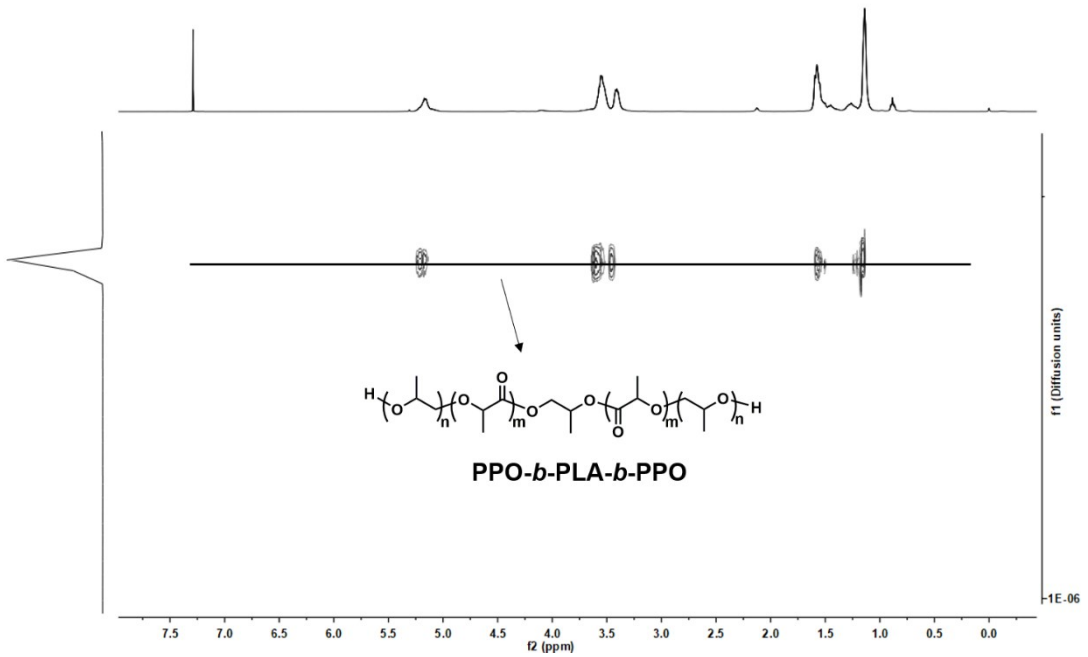


Figure S15. DOSY NMR spectrum of the product obtained from copolymerization of *rac*-LA and PO catalyzed by Et_3B/DBU pair (2/1) at 60 °C (Table S6, entry 6), and the $M_{n,th}$ of PLA and PPO was calculated as 4.7 kDa and 8.7 kDa, respectively.

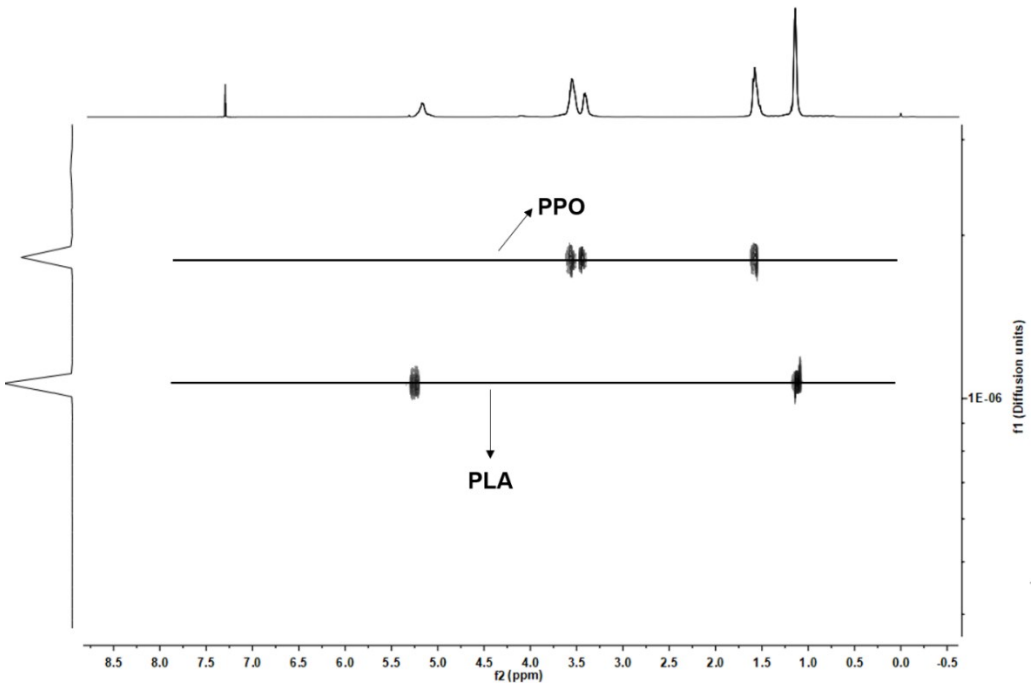


Figure S16. DOSY NMR spectrum of blend of PLA ($M_{n,GPC}$ = 5.1 kDa, $Đ$ = 1.07) and PPO ($M_{n,GPC}$ = 8.5 kDa, $Đ$ = 1.04).

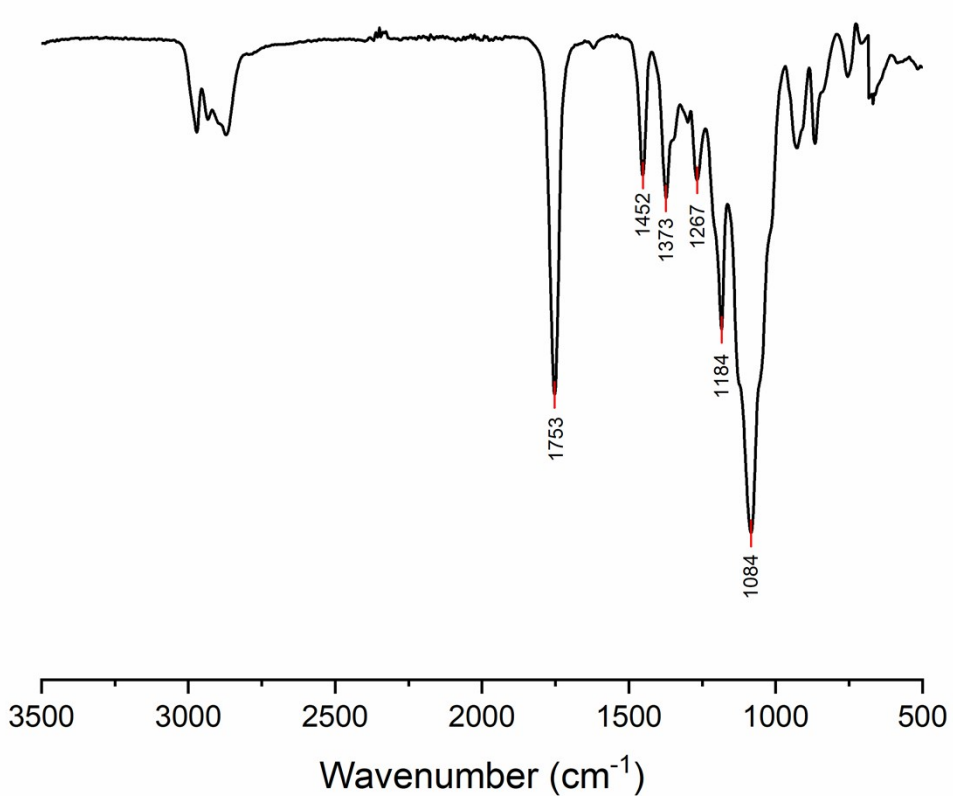


Figure S17. IR spectrum of PPO-*b*-PLA-*b*-PPO obtained from copolymerization of *rac*-LA and PO catalyzed by Et_3B/DBU pair (2/1) at 60 °C (Table S6, entry 6).

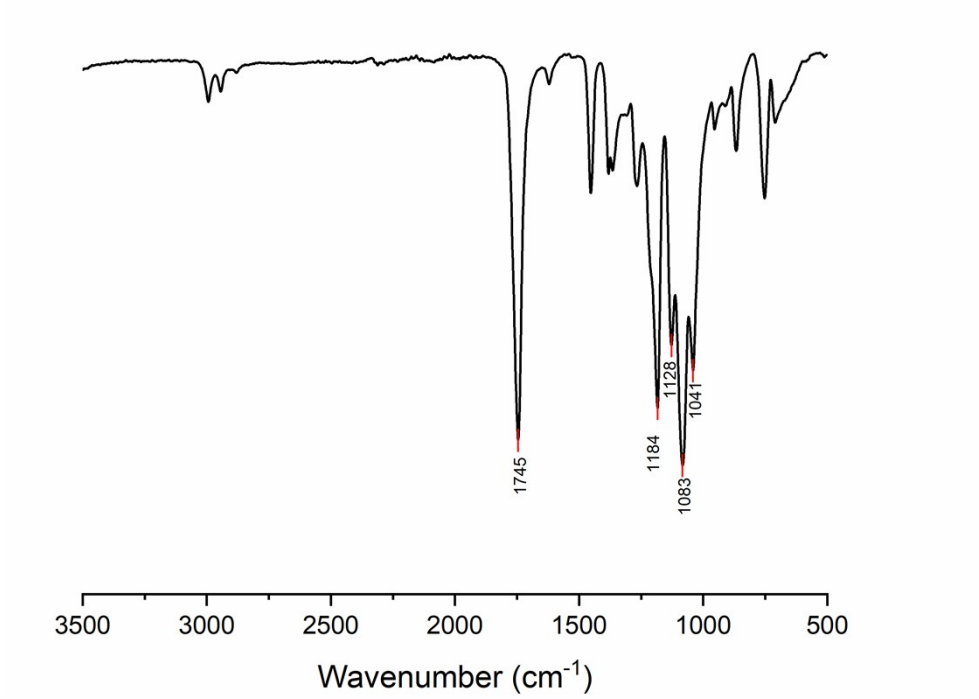


Figure S18. IR spectrum of PLA obtained from DBU catalyzed ring-opening polymerization of *rac*-LA in PO (Table S5, entry 3).

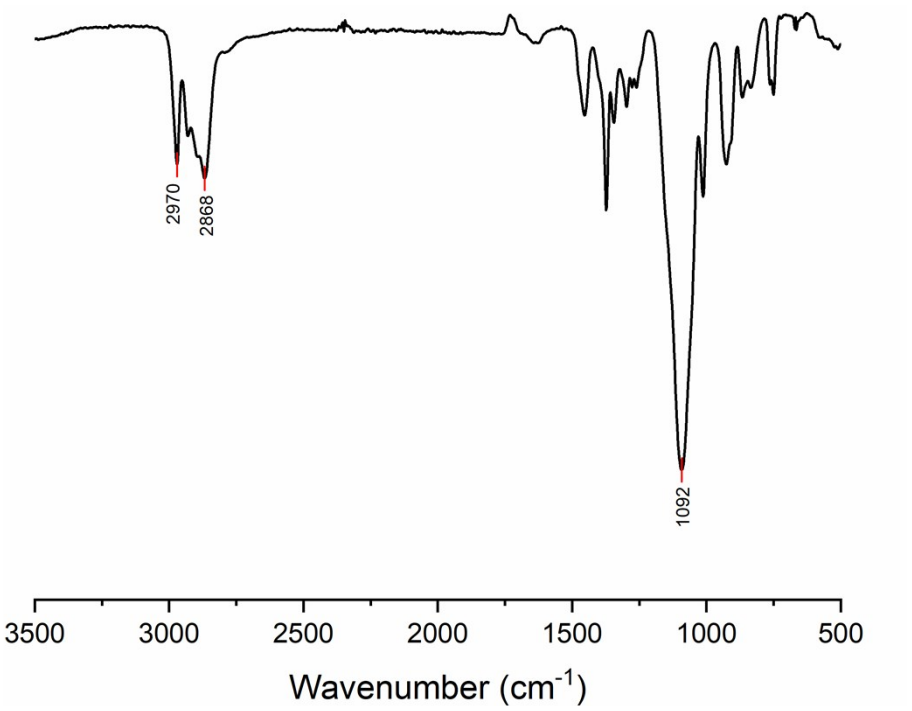


Figure S19. IR spectrum of PPO obtained from Et_3B/DBU pair (3/1) catalyzed ring-opening polymerization of PO. (Table S4, entry 5).

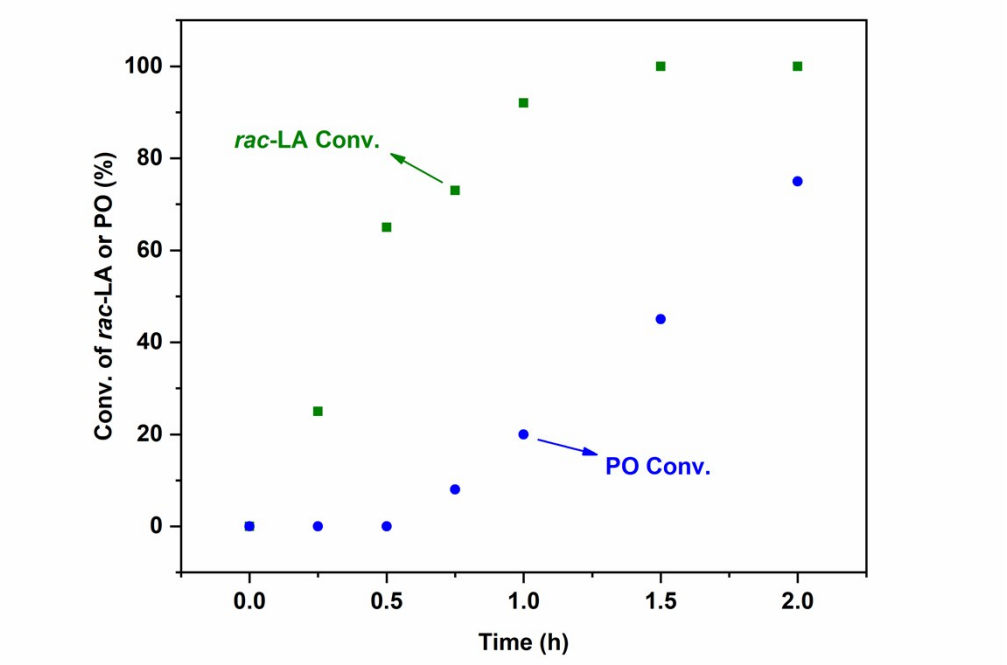


Figure S20. The plots of monomer conversion versus time for Et_3B/DBU pair (3/1) catalyzed copolymerization of *rac*-LA and PO with 3 eq H_2O as the initiator at 60 °C. (Table S7).

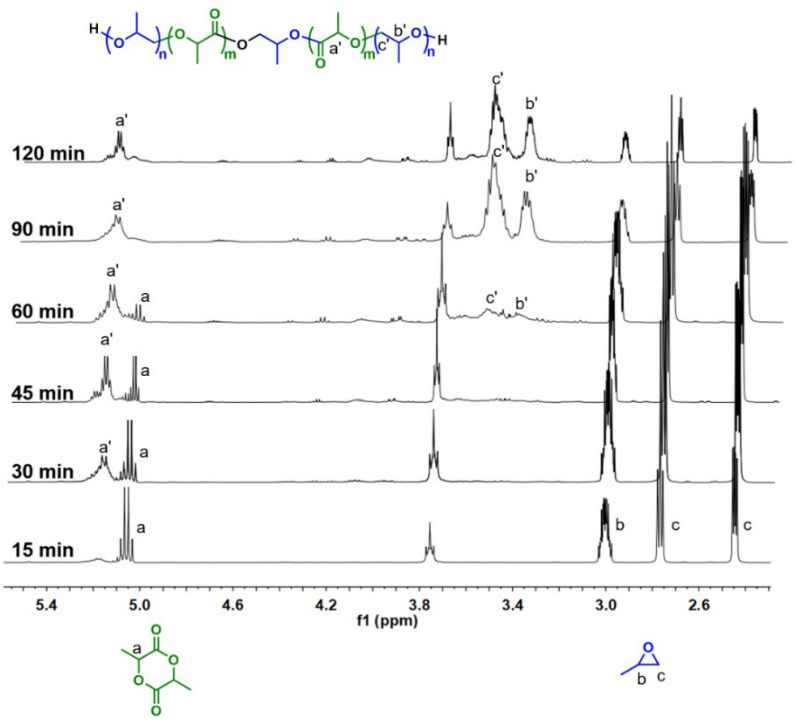


Figure S21. Evolution of ^{1}H NMR spectra for Et_3B/DBU pair (3/1) catalyzed copolymerization of *rac*-LA and PO with 3 eq H_2O as the initiator at 60 °C.

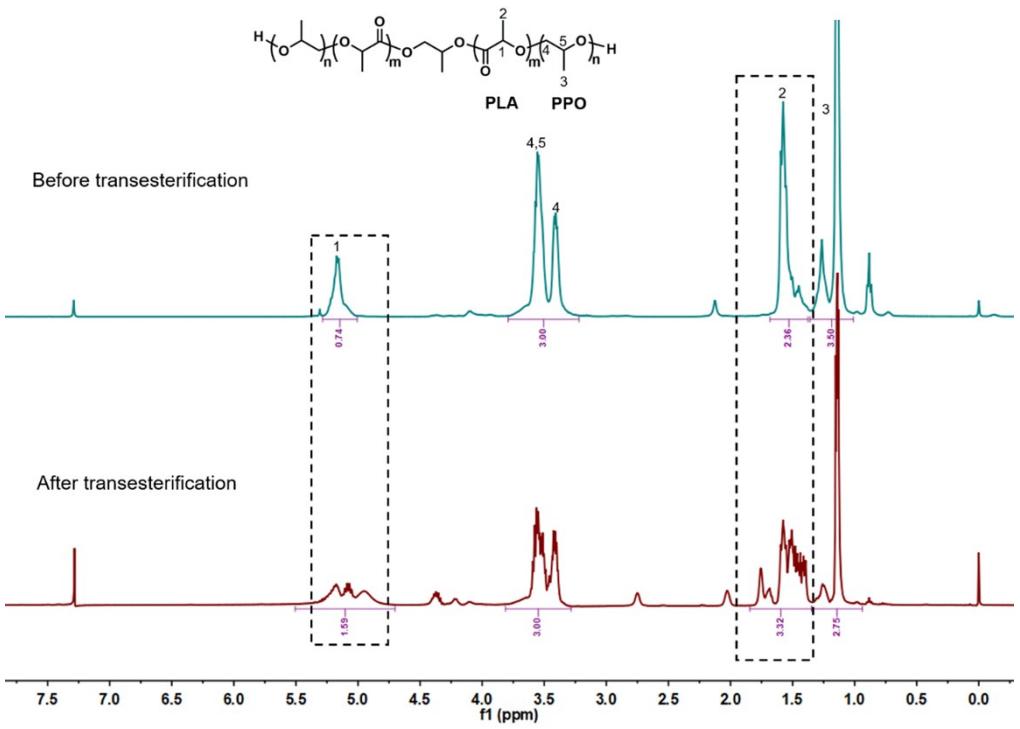


Figure S22. The comparison about ^{1}H NMR spectra of the resultant PPO-*b*-PLA-*b*-PPO and random copolymer by transesterification using DBU.

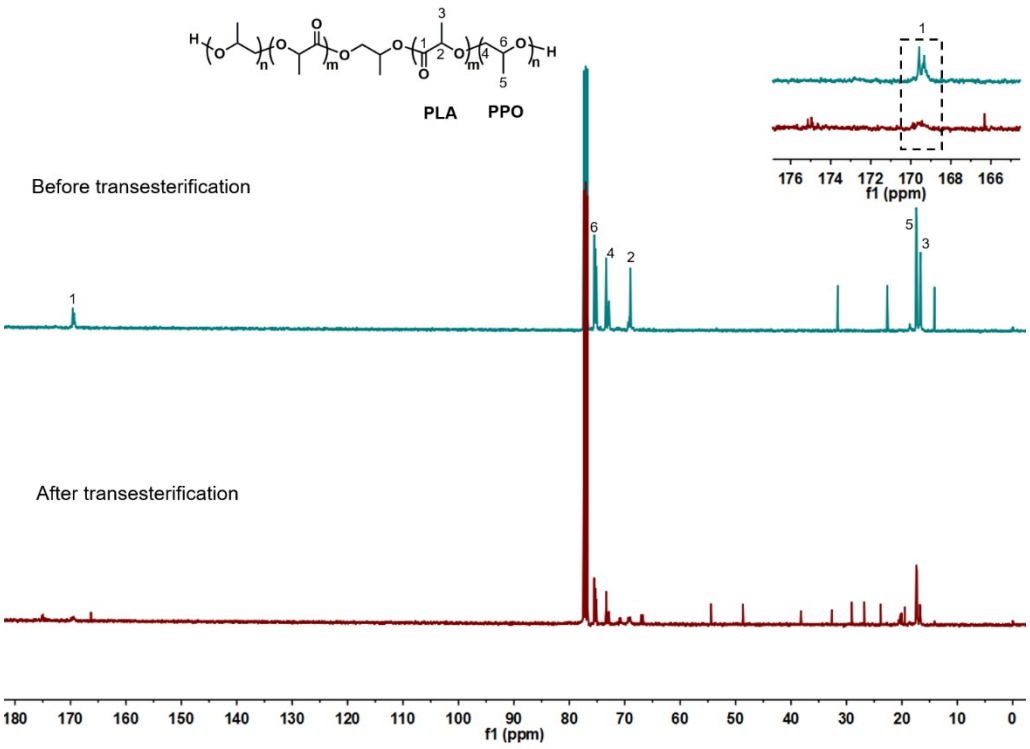


Figure S23. The comparison about ^{13}C NMR spectra of the resultant PPO-*b*-PLA-*b*-PPO and random copolymer by transesterification using DBU.

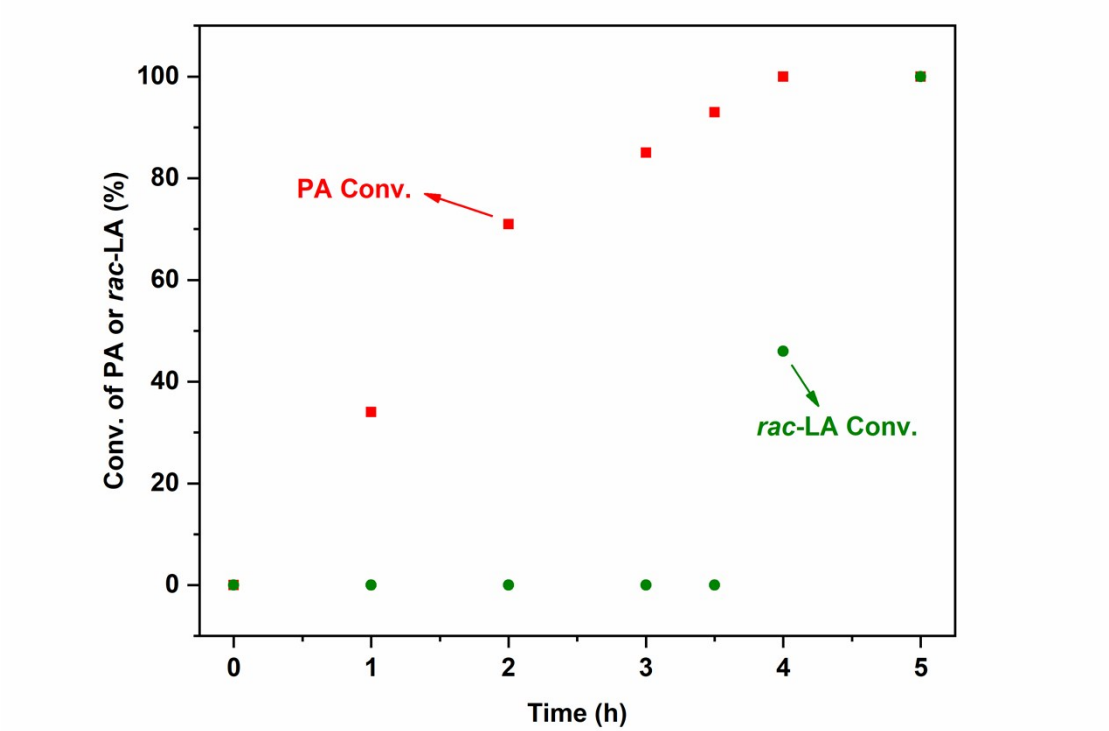


Figure S24. The plots of monomer conversion versus time for Et_3B/DBU pair (1/1) catalyzed terpolymerization of PO, PA and *rac*-LA with 3 eq H_2O as the initiator at 80 °C.(Table S8).

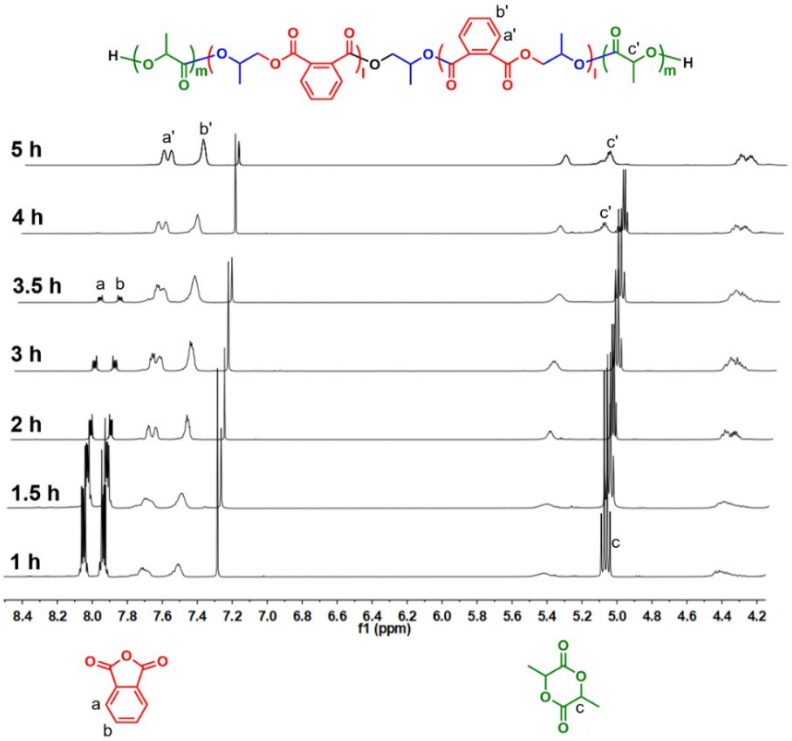


Figure S25. Evolution of ^{1}H NMR spectra for Et_3B/DBU pair (1/1) catalyzed terpolymerization of PO, PA and *rac*-LA with 3 eq H_2O as the initiator at 80 °C.

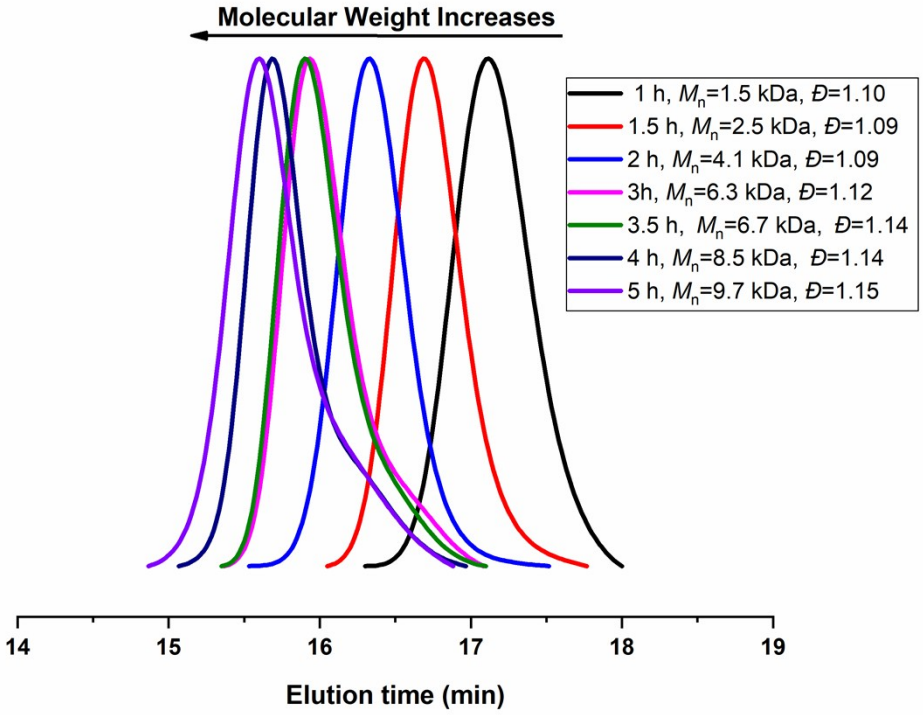


Figure S26. Evolution of GPC traces for Et_3B/DBU pair (1/1) catalyzed terpolymerization of PO, PA and *rac*-LA with 3 eq H_2O as the initiator at 80 °C.

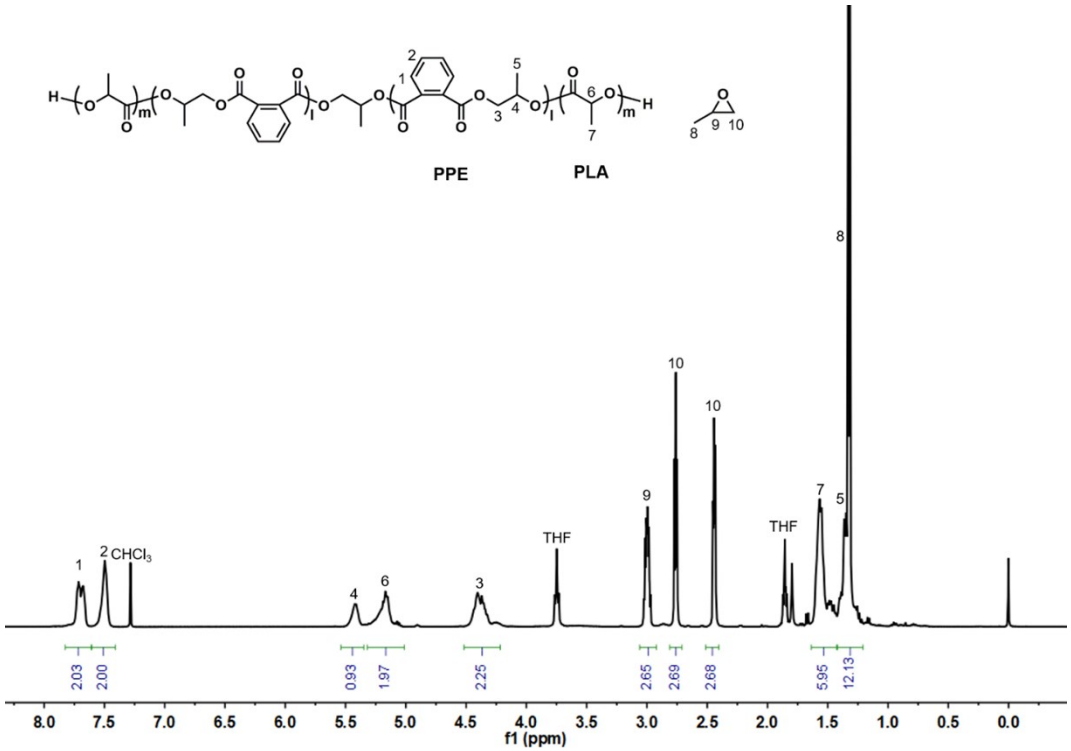


Figure S27. ^{1}H NMR spectrum of the reaction mixture from the terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1/1) (Table S8, entry 7).

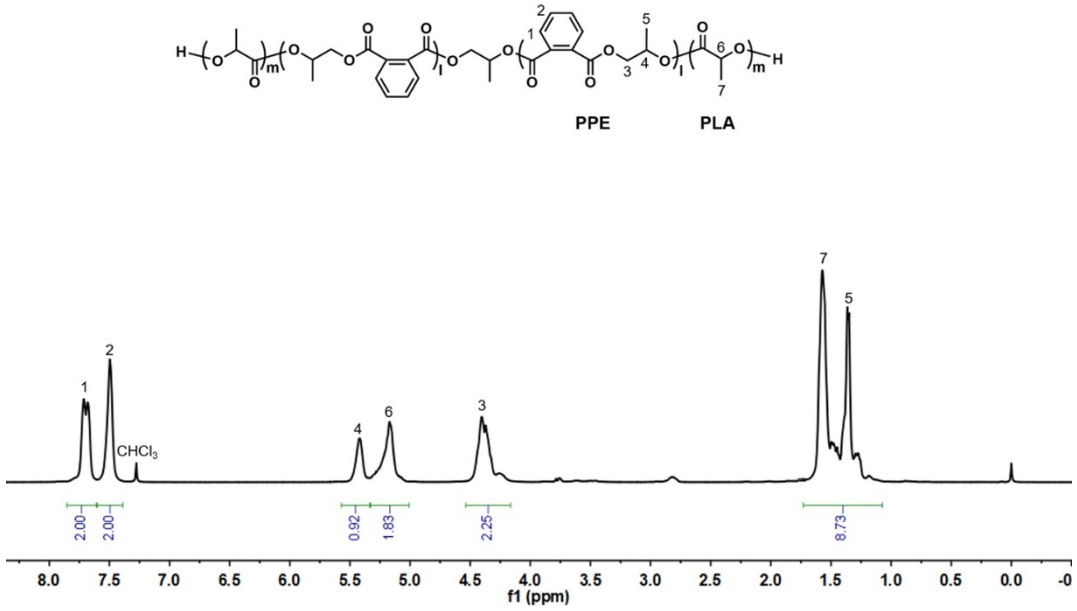


Figure S28. ^{1}H NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1/1) (Table S8, entry 7)[2].

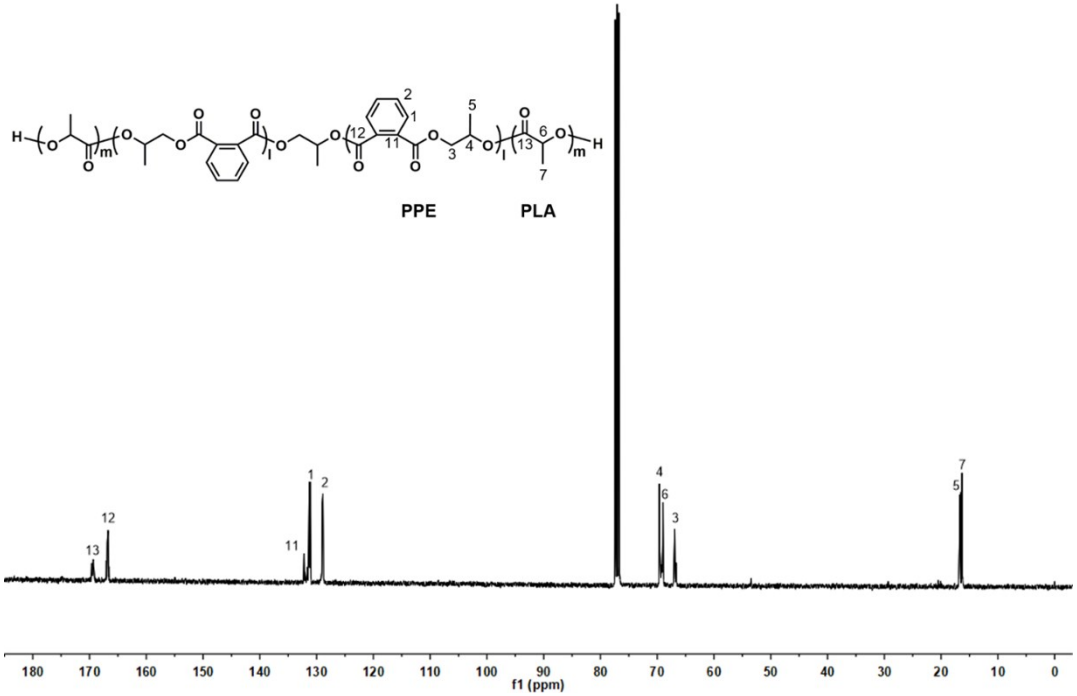


Figure S29. ^{13}C NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1/1). (Table S8, entry 7).

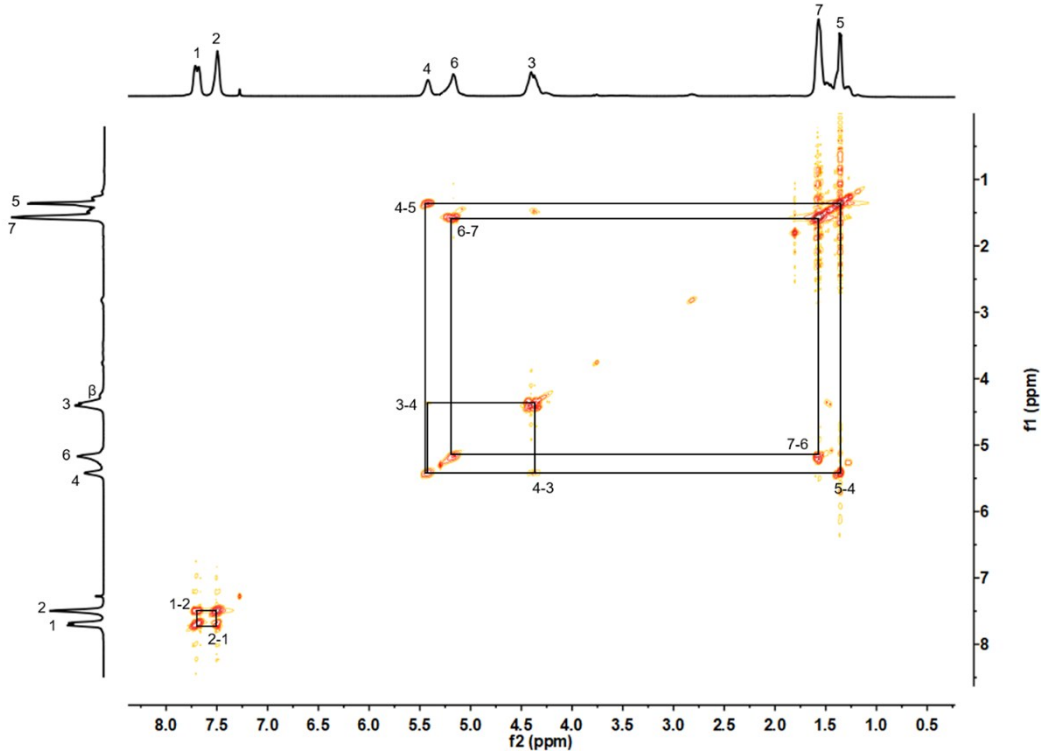


Figure S30. COSY NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1/1). (Table S8, entry 7).

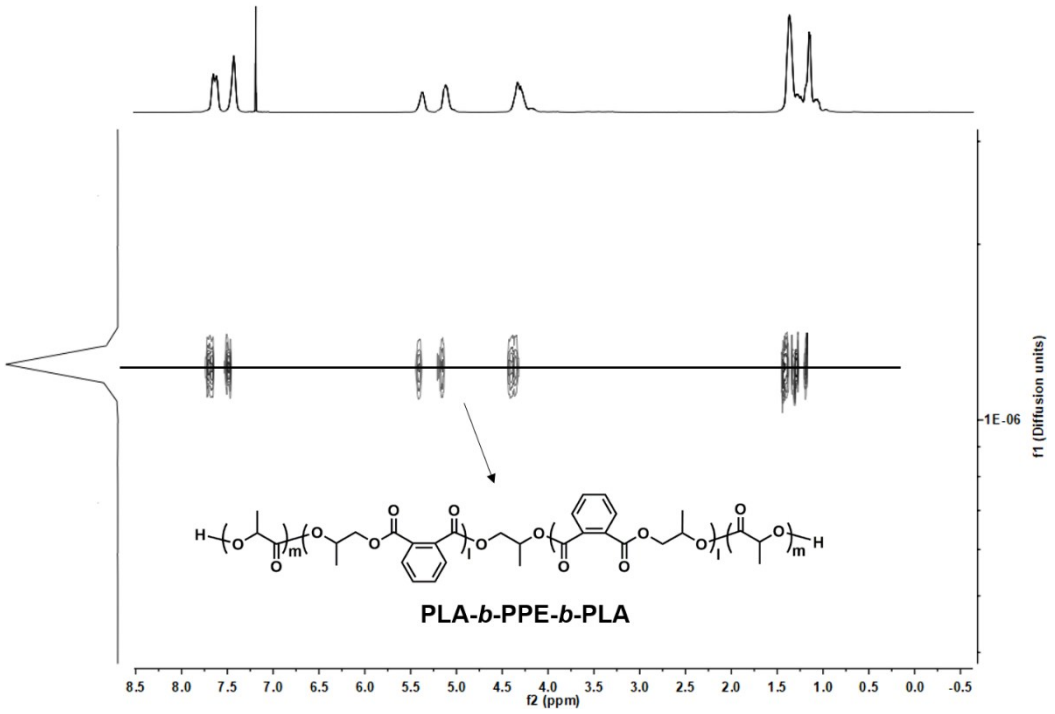


Figure S31. DOSY NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1/1) (Table S8, entry 7), and the $M_{n,th}$ of PPE and PLA was calculated as 6.8 kDa and 4.8 kDa, respectively.

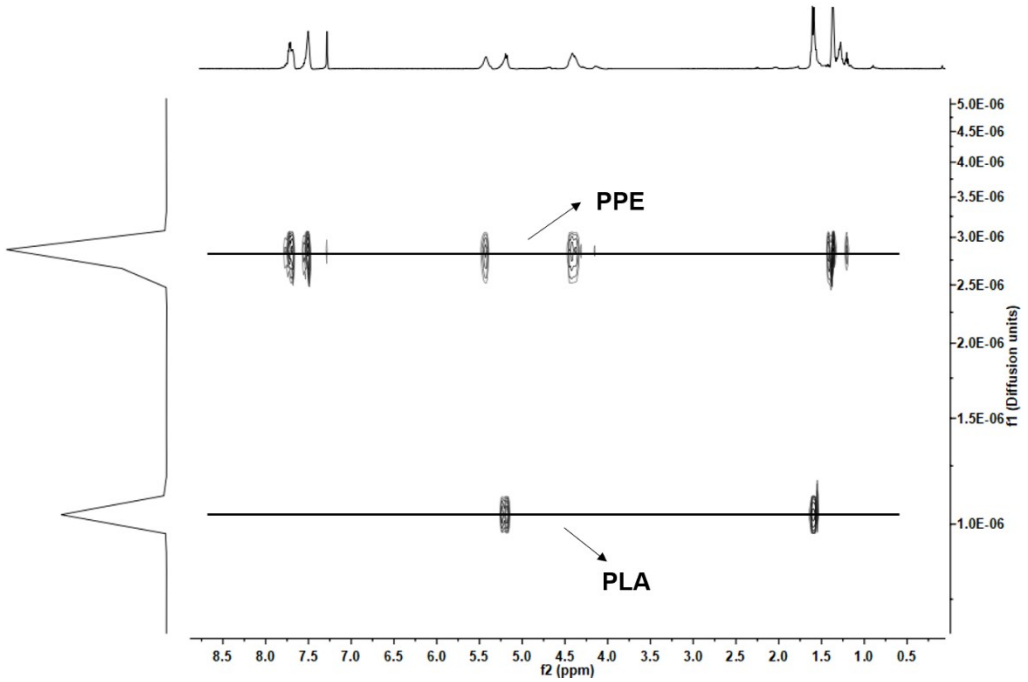


Figure S32. DOSY NMR spectrum of blend of PPE ($M_{n,GPC}$ = 7.1 kDa, $Đ$ = 1.08) and PLA ($M_{n,GPC}$ = 5.1 kDa, $Đ$ = 1.07).

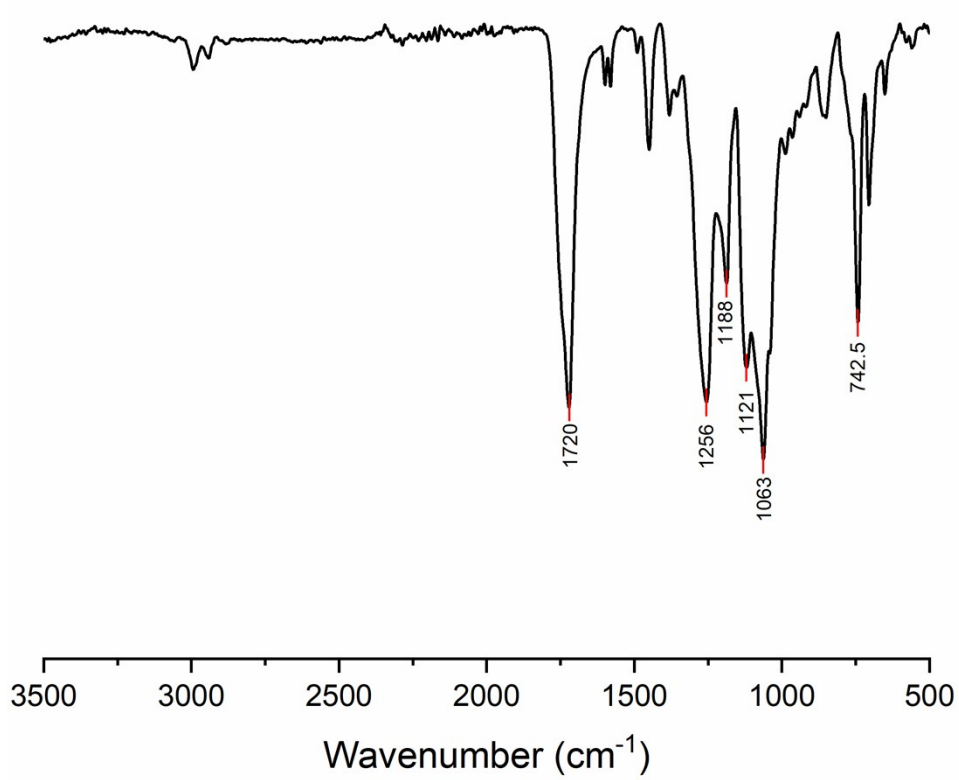


Figure S33. IR spectrum of PLA-*b*-PPE-*b*-PLA obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1/1) (Table S8, entry 7).

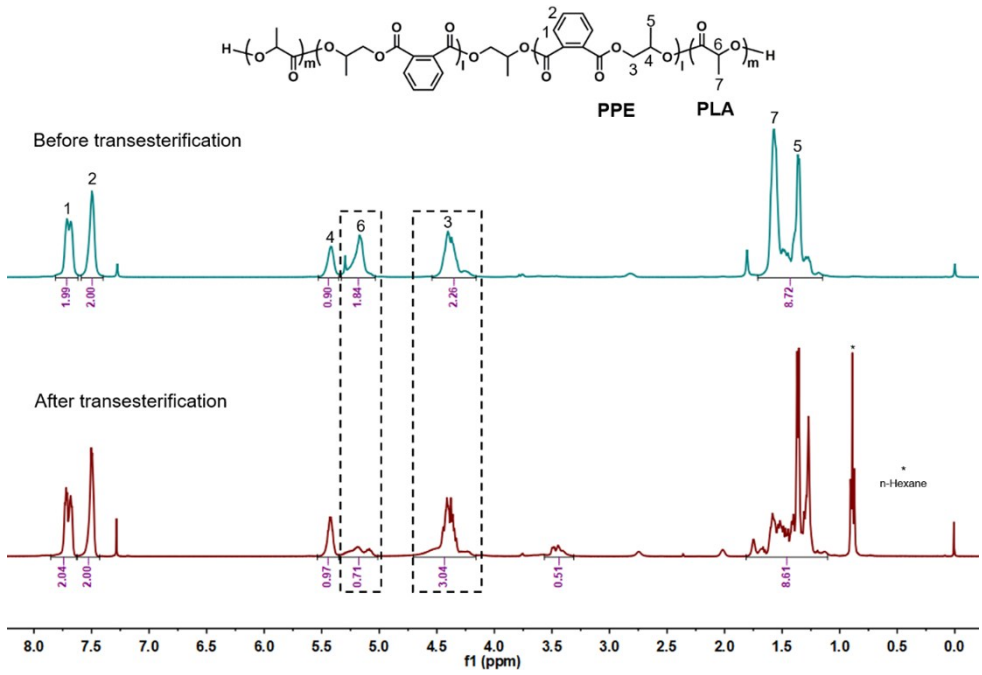


Figure S34. The comparison about ^{1}H NMR spectra of the resultant PLA-*b*-PPE-*b*-PLA and random copolymer by transesterification using DBU.

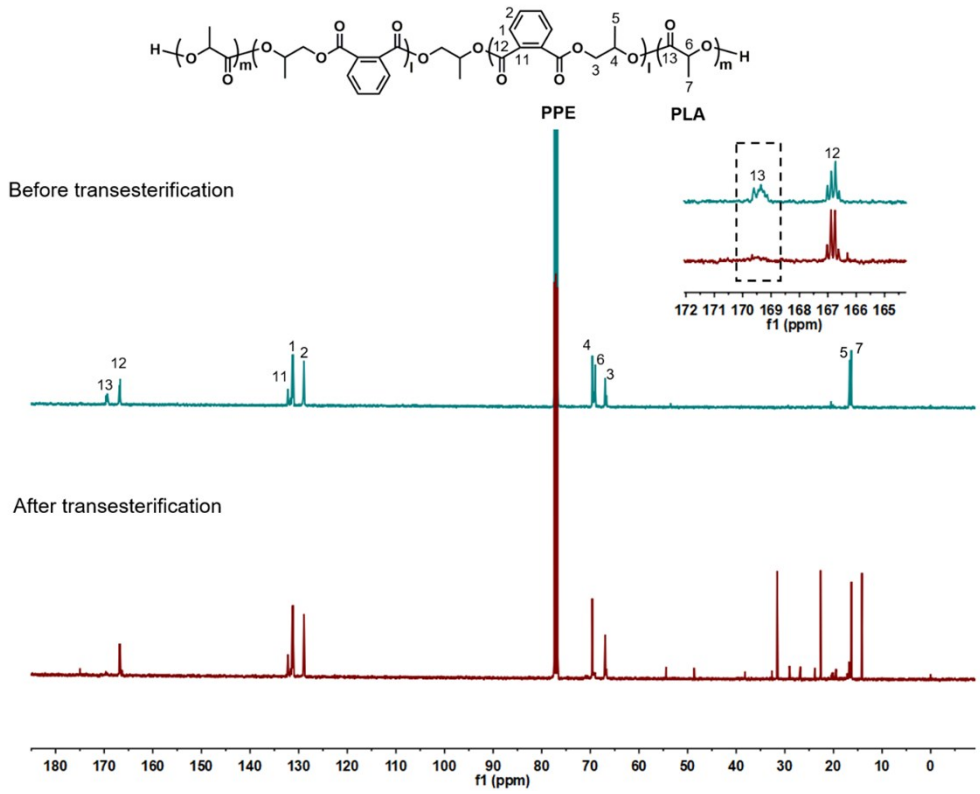


Figure S35. The comparison about ^{13}C NMR spectra of the resultant PLA-*b*-PPE-*b*-PLA and random copolymer by transesterification using DBU.

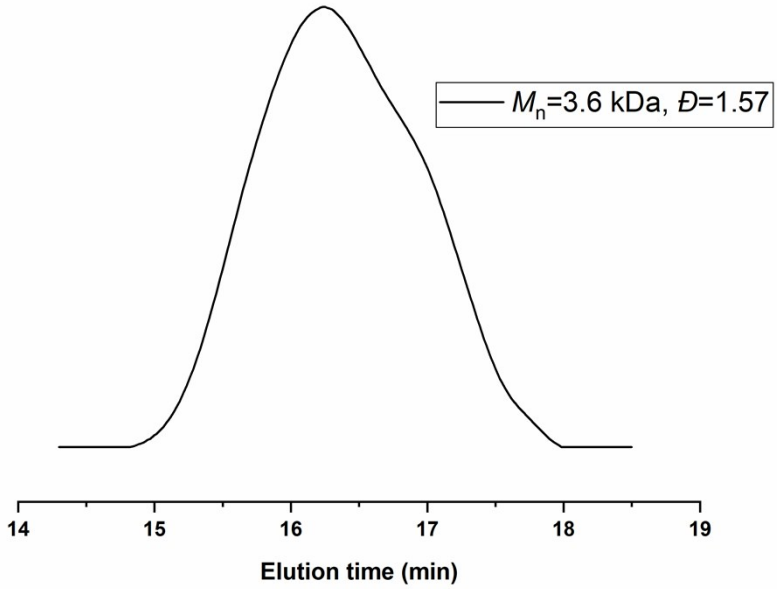


Figure S36. GPC curve of random copolymer by transesterification using DBU.

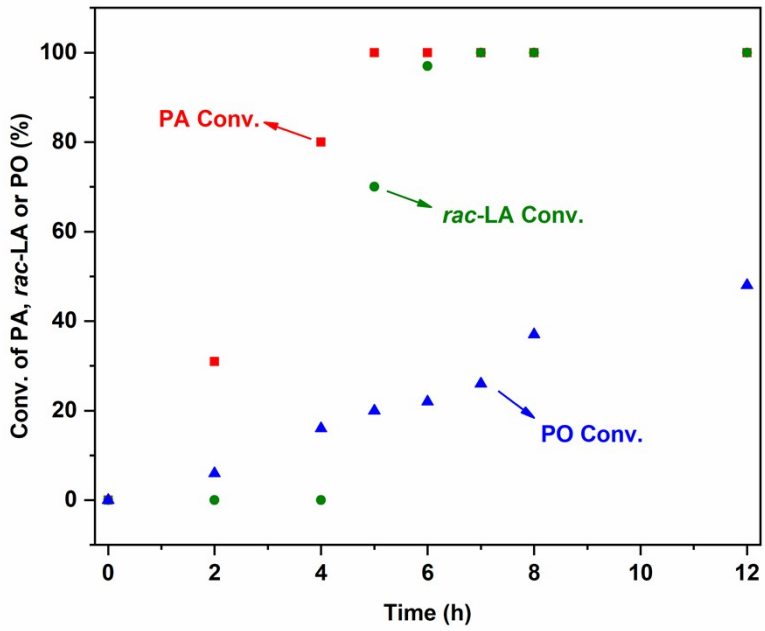


Figure S37. The plots of monomer conversion versus time for Et_3B/DBU pair (2/1) catalyzed terpolymerization of PO, PA and *rac*-LA with 3 eq H_2O as the initiator at 60 °C.

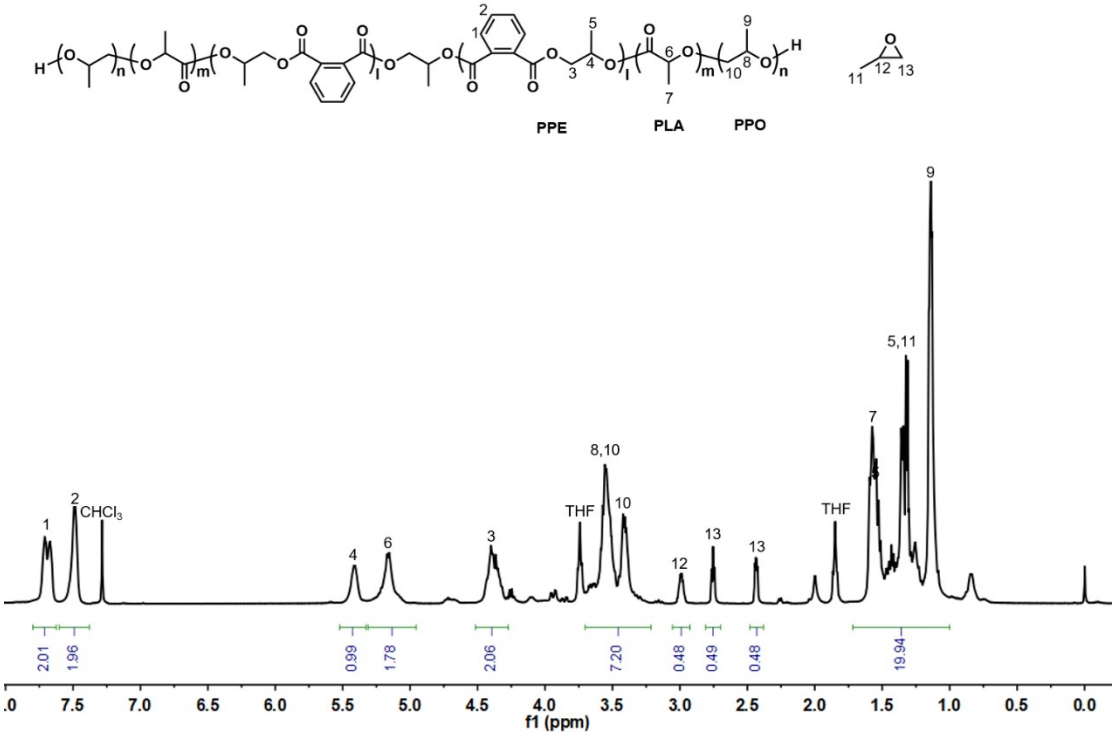


Figure S38. ^{1}H NMR spectrum of the reaction mixture from the terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table S9, entry 7).

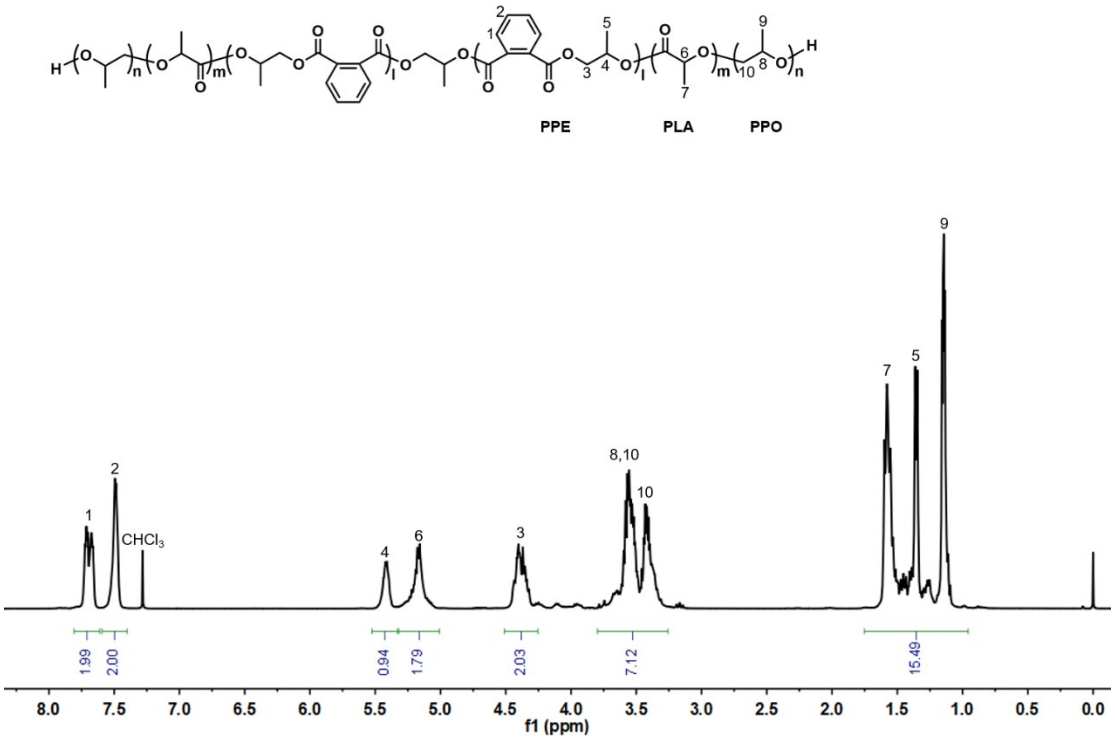


Figure S39. ^{1}H NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table S9, entry 7).

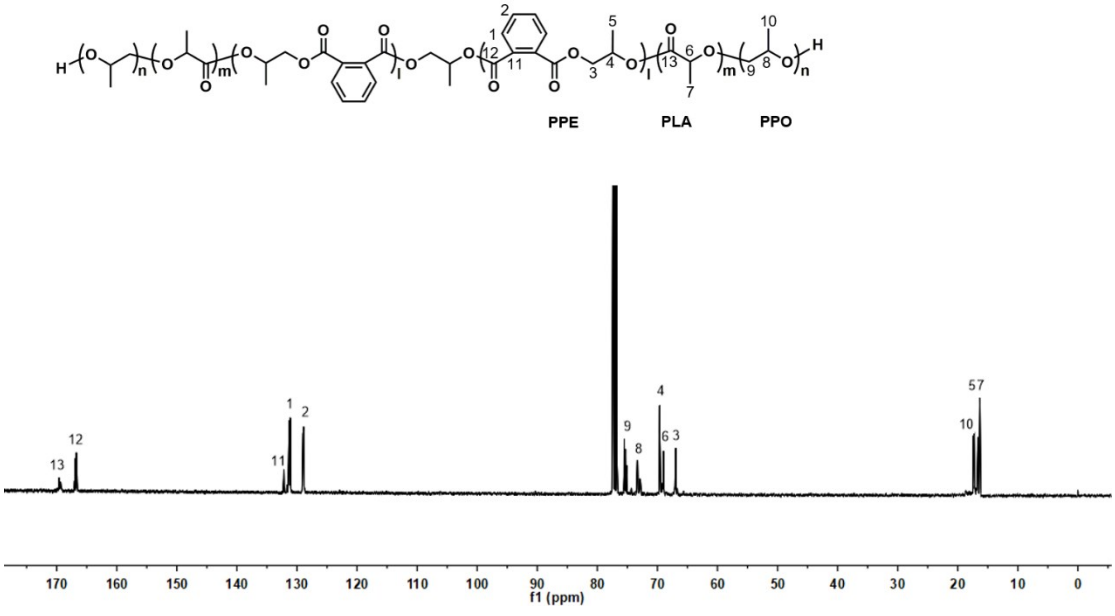


Figure S40. ^{13}C NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table S9, entry 7).

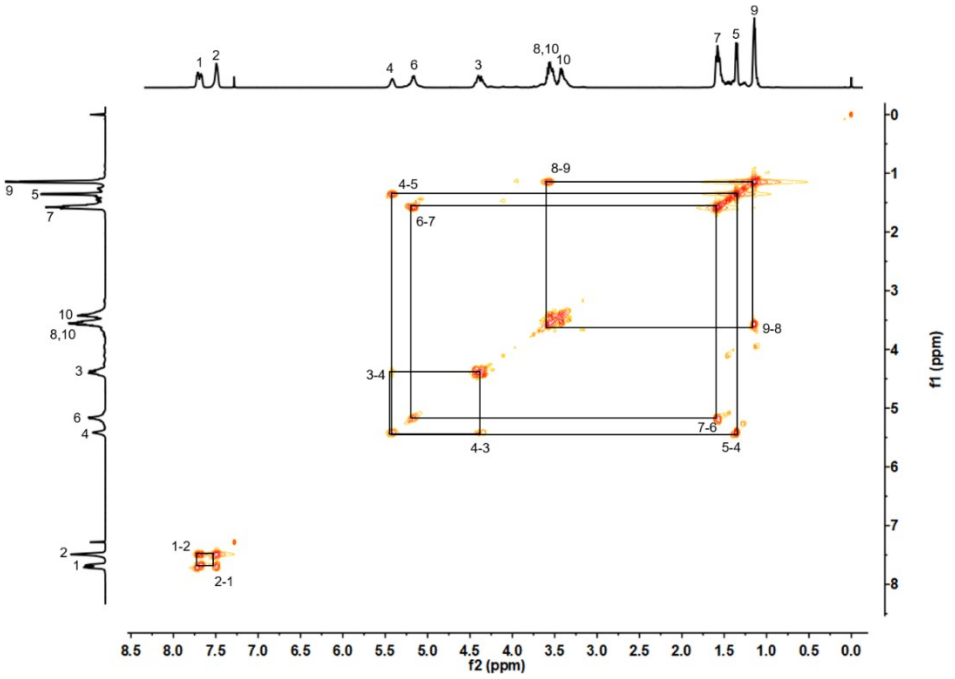


Figure S41. COSY NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table S9, entry 7).

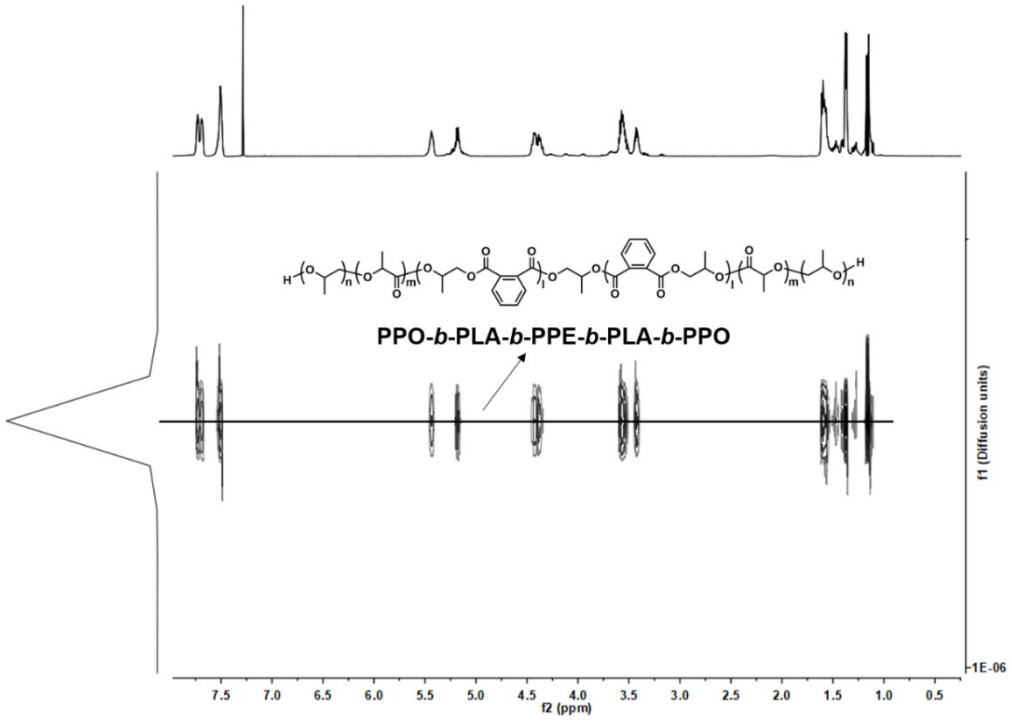


Figure S42. DOSY NMR spectrum of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table S9, entry 7), the $M_{n,th}$ of PPE, PLA and PPO was calculated as 6.8 kDa, 4.8 kDa and 2.5 kDa, respectively.

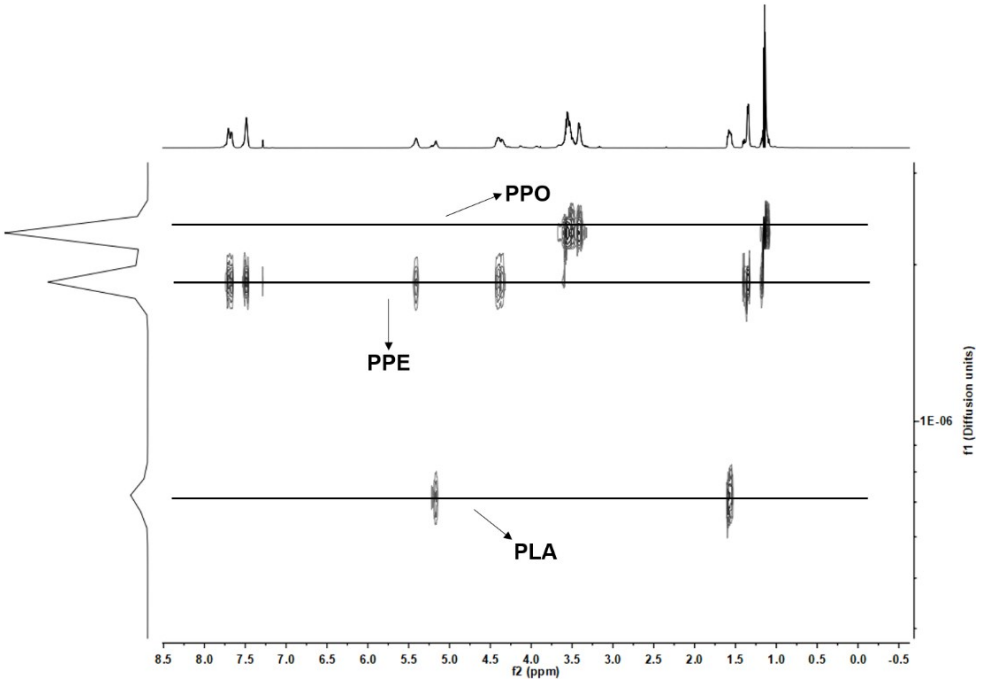


Figure S43. DOSY NMR spectrum of blend of PPE ($M_{n,GPC}$ = 7.1 kDa, $Đ$ = 1.08), PLA ($M_{n,GPC}$ = 5.1 kDa, $Đ$ = 1.07) and PPO ($M_{n,GPC}$ = 2.7 kDa, $Đ$ = 1.05).

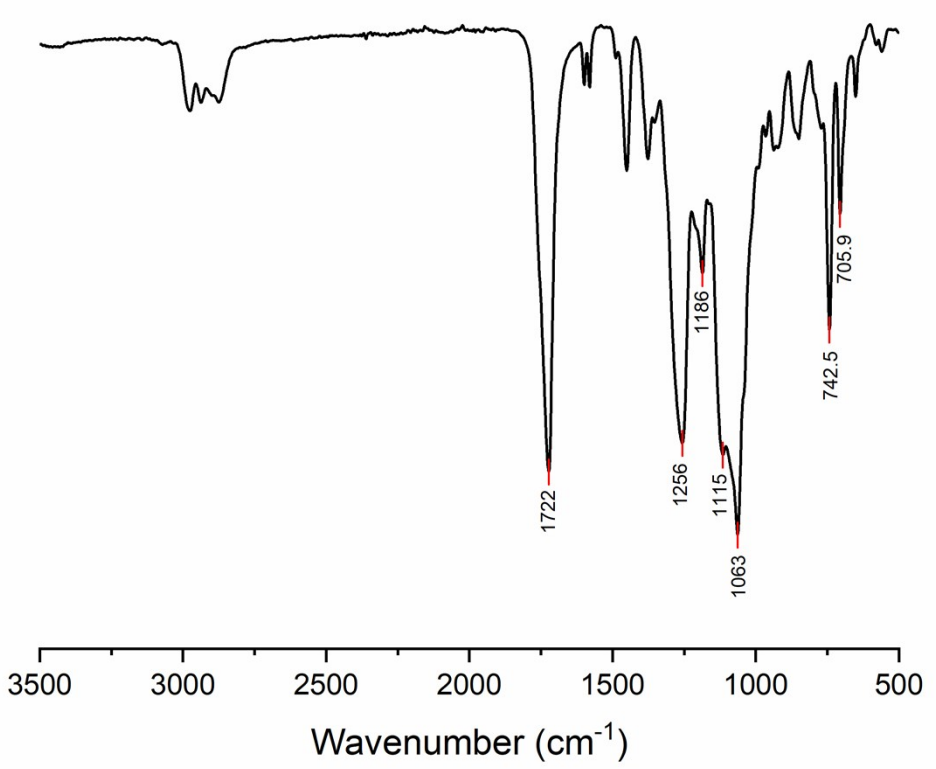


Figure S44. IR spectrum of PPO-*b*-PLA-*b*-PPE-*b*-PLA-*b*-PPO obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table S9, entry 7).

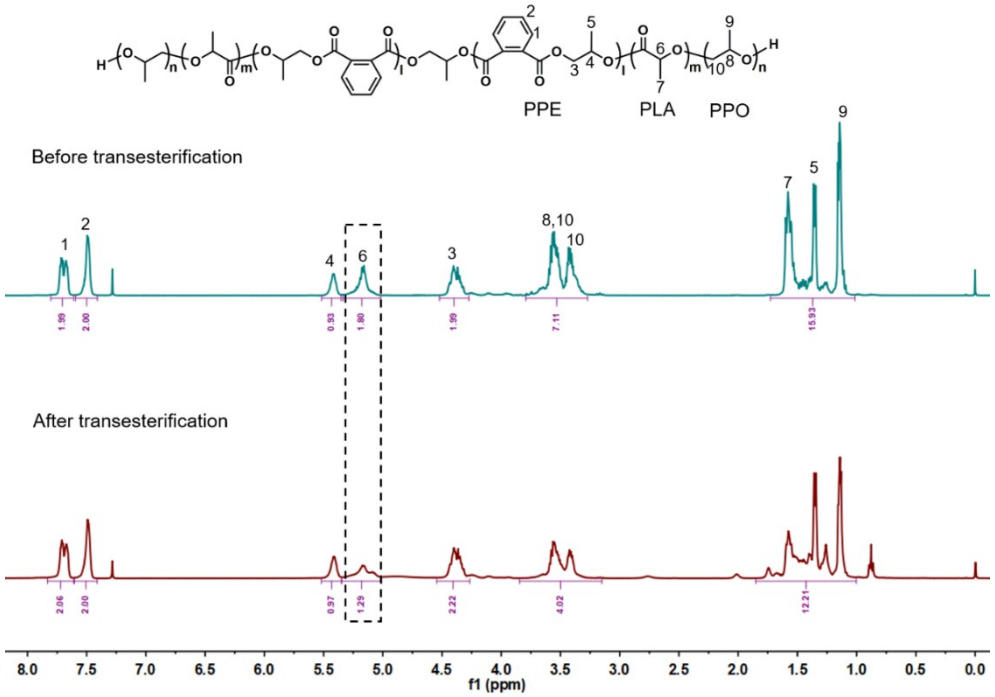


Figure S45. The comparison about ^{1}H NMR spectra of the resultant PPO-*b*-PLA-*b*-PPE-*b*-PLA-*b*-PPO and random copolymer by transesterification using DBU.

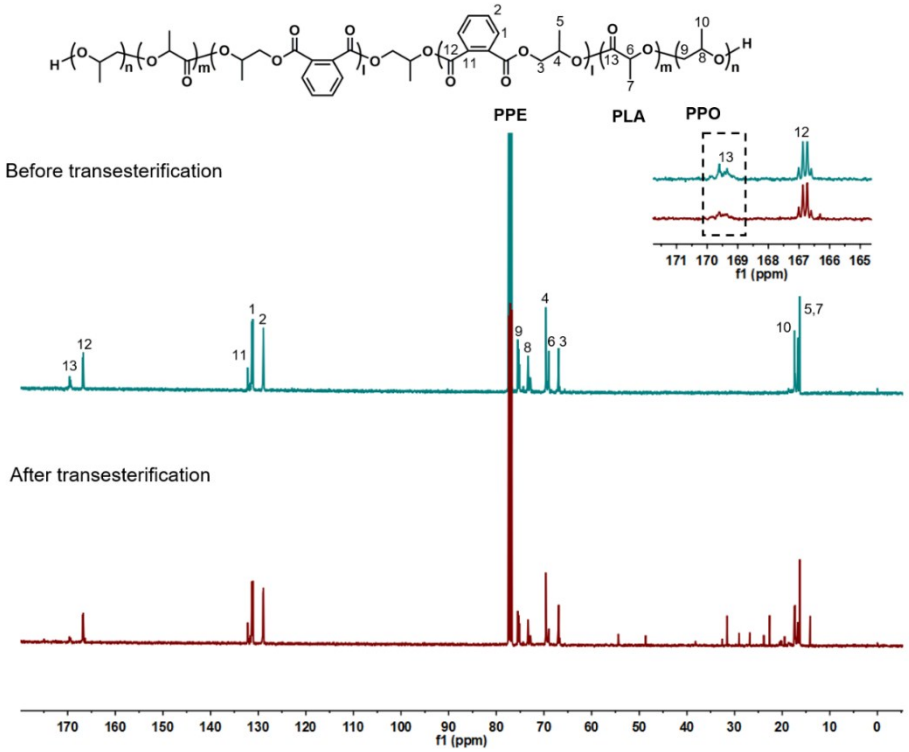


Figure S46. The comparison about ^{13}C NMR spectra of the resultant PPO-*b*-PLA-*b*-PPE-*b*-PLA-*b*-PPO and random copolymer by transesterification using DBU.

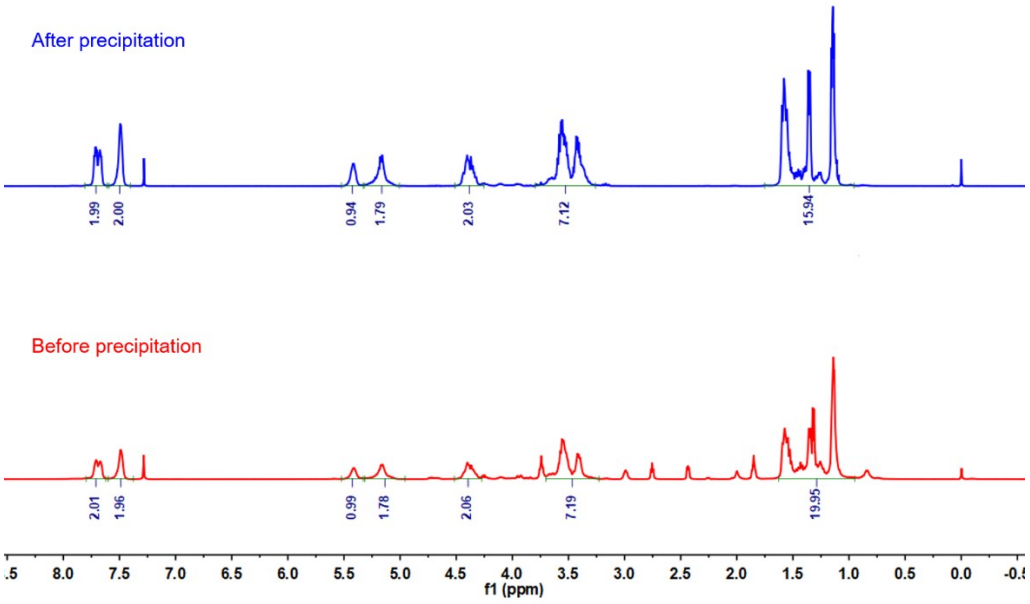


Figure S47. The comparison about ^{1}H NMR spectra of the resultant PPO-*b*-PLA-*b*-PPE-*b*-PLA-*b*-PPO (Table S9, entry 7) before and after precipitation in cold methanol.

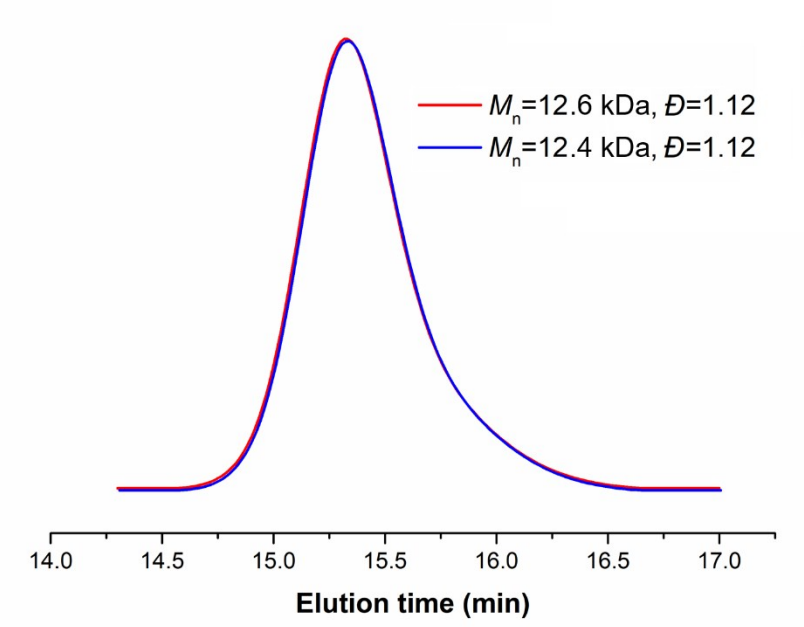


Figure S48. The comparison about GPC traces of the resultant PPO-*b*-PLA-*b*-PPE-*b*-PLA-*b*-PPO (Table S9, entry 7) before precipitation in cold methanol (Red) and after precipitation in cold methanol (Blue).

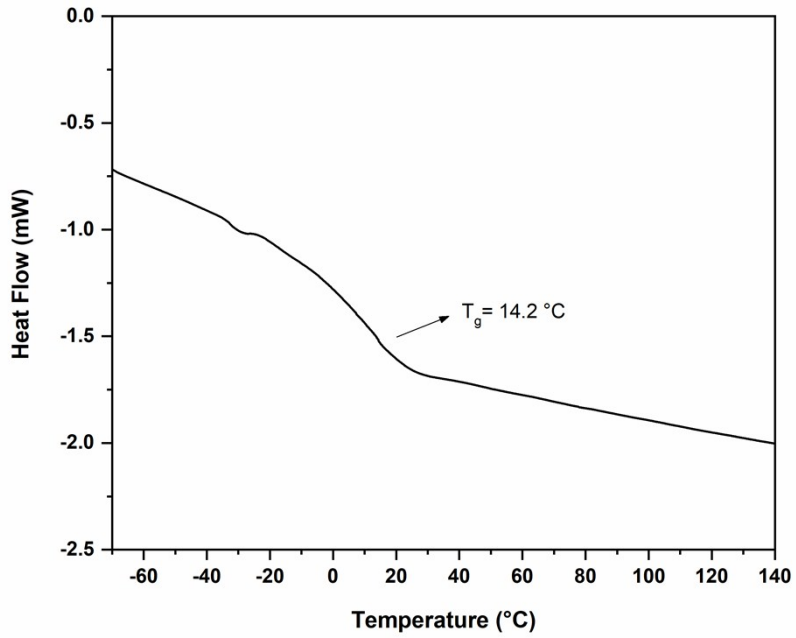


Figure S49. DSC thermogram of the product obtained from terpolymerization of PO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table S9, entry 7).

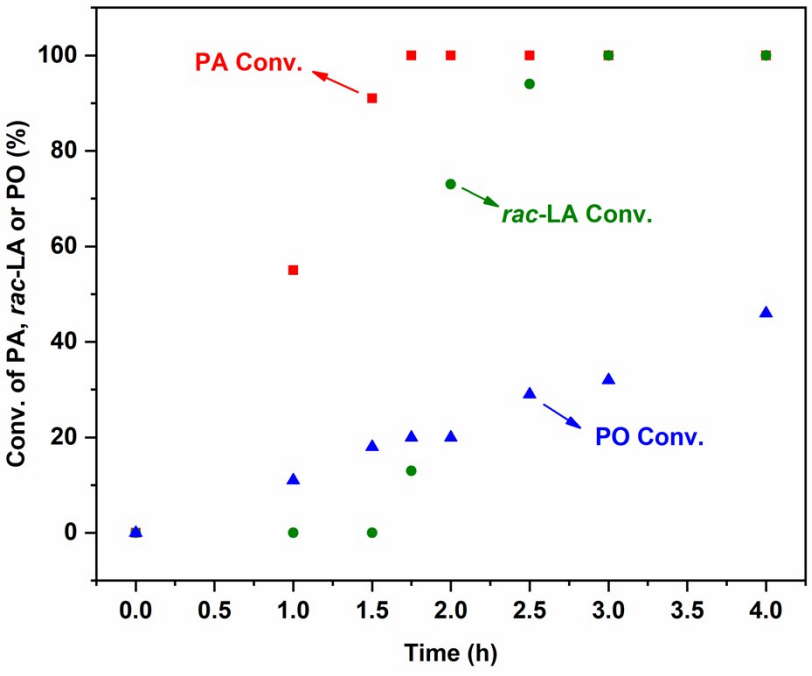


Figure S50. The plots of monomer conversion versus time for Et_3B/DBU pair (3/1) catalyzed terpolymerization of PO, PA and *rac*-LA with 3 eq H_2O as the initiator at 60 °C.

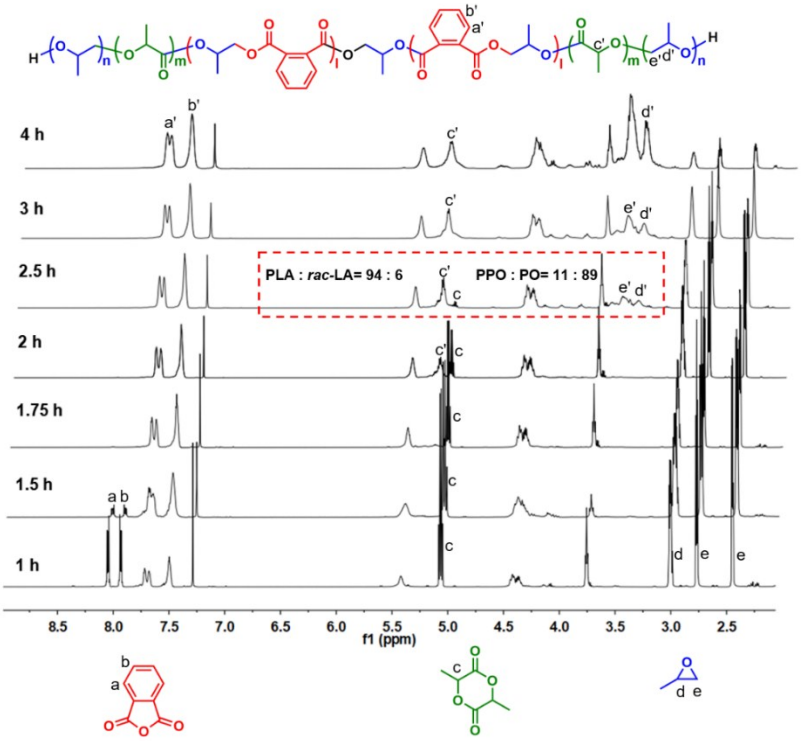


Figure S51. Evolution of ^{1}H NMR spectra for Et_3B/DBU pair (3/1) catalyzed terpolymerization of PO, PA and *rac*-LA with 3 eq H_2O as the initiator at 60 °C.

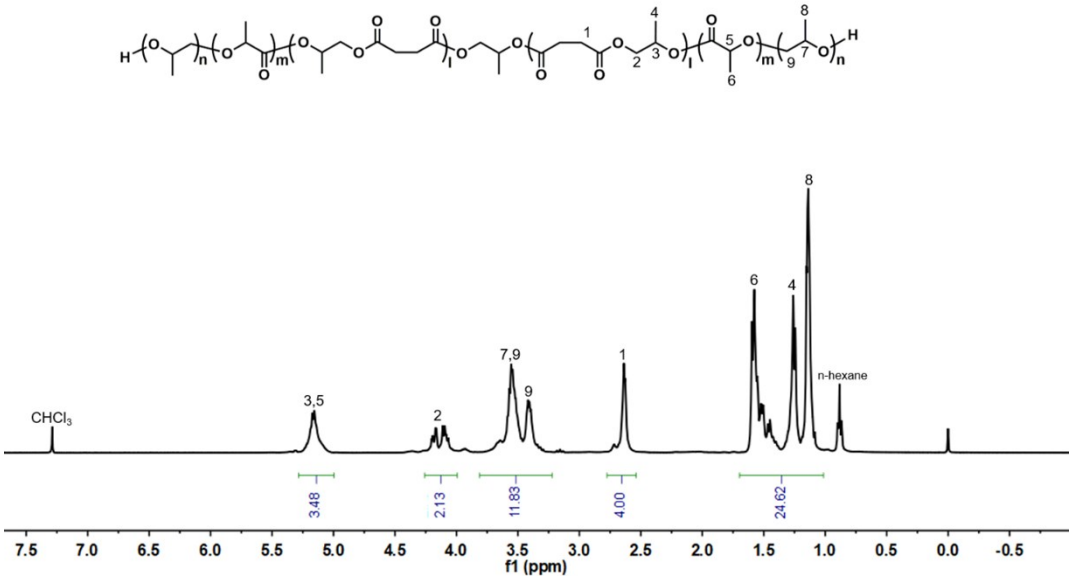


Figure S52. ^{1}H NMR spectrum of the product obtained from terpolymerization of PO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 2).

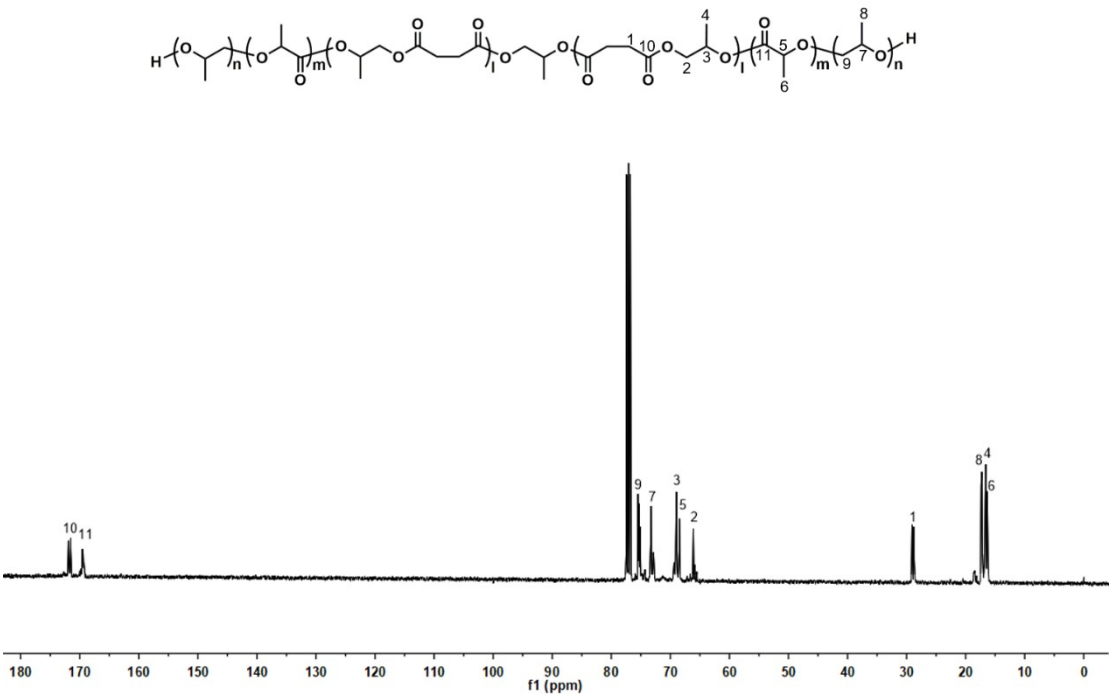


Figure S53. ^{13}C NMR spectrum of the product obtained from terpolymerization of PO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 2).

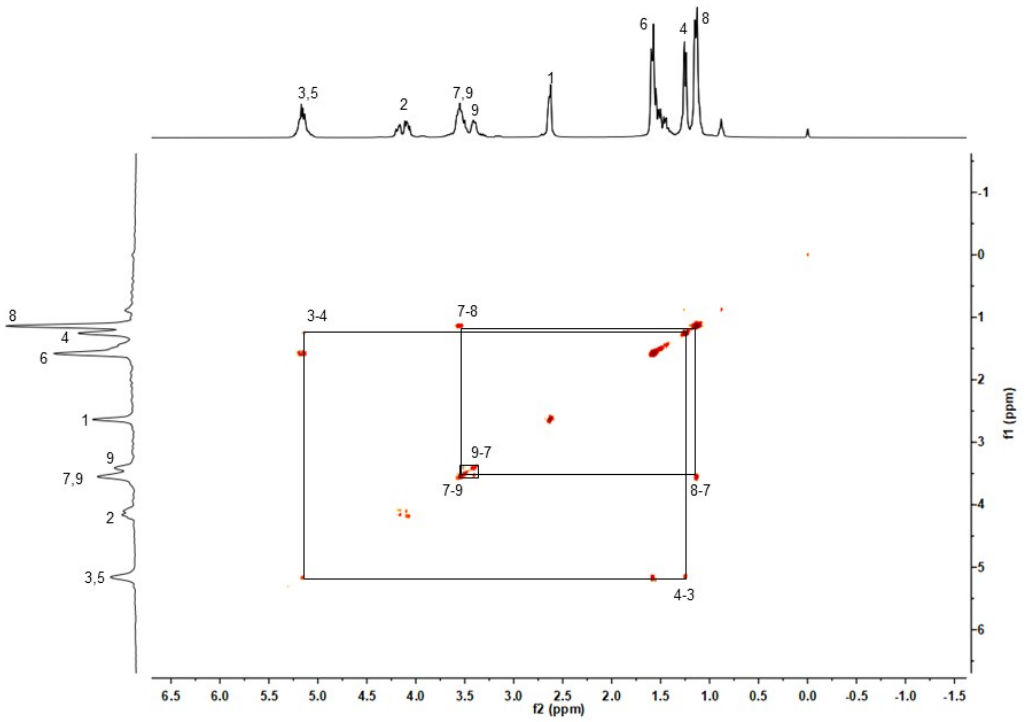


Figure S54. COSY NMR spectrum of the product obtained from terpolymerization of PO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 2).

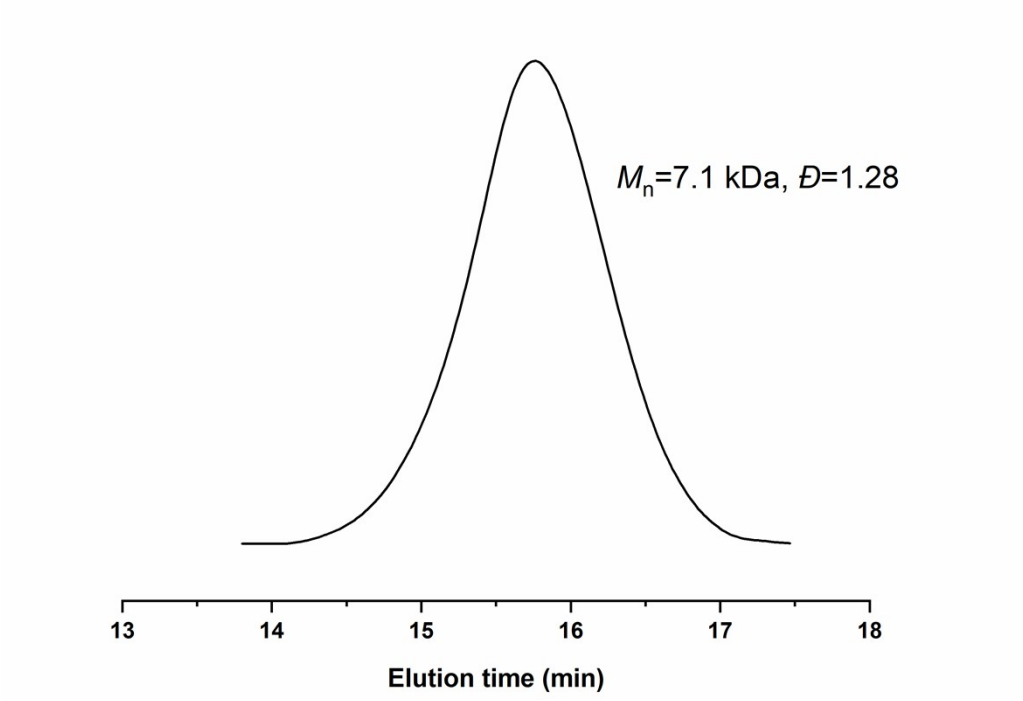


Figure S55. GPC curve of the product obtained from terpolymerization of PO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1)(Table 2, entry 2).

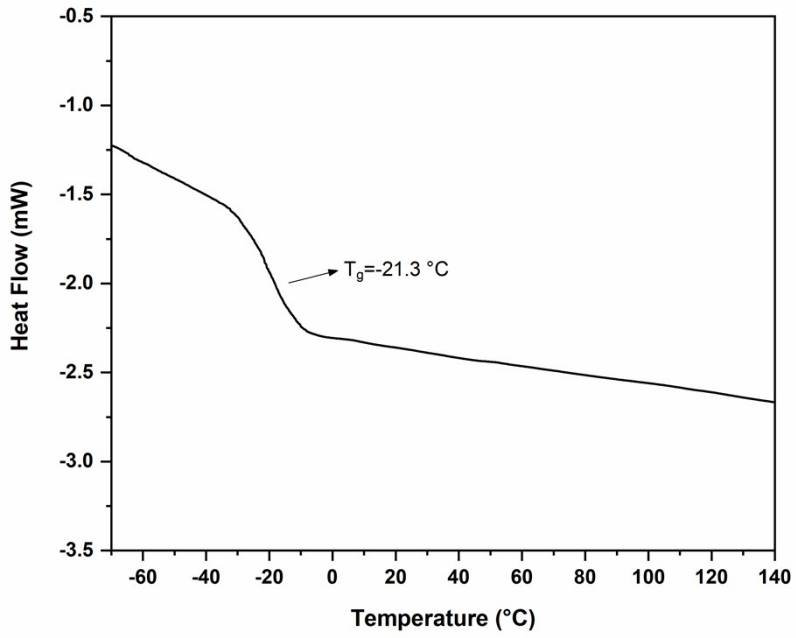


Figure S56. DSC thermogram of the product obtained from terpolymerization of PO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 2).

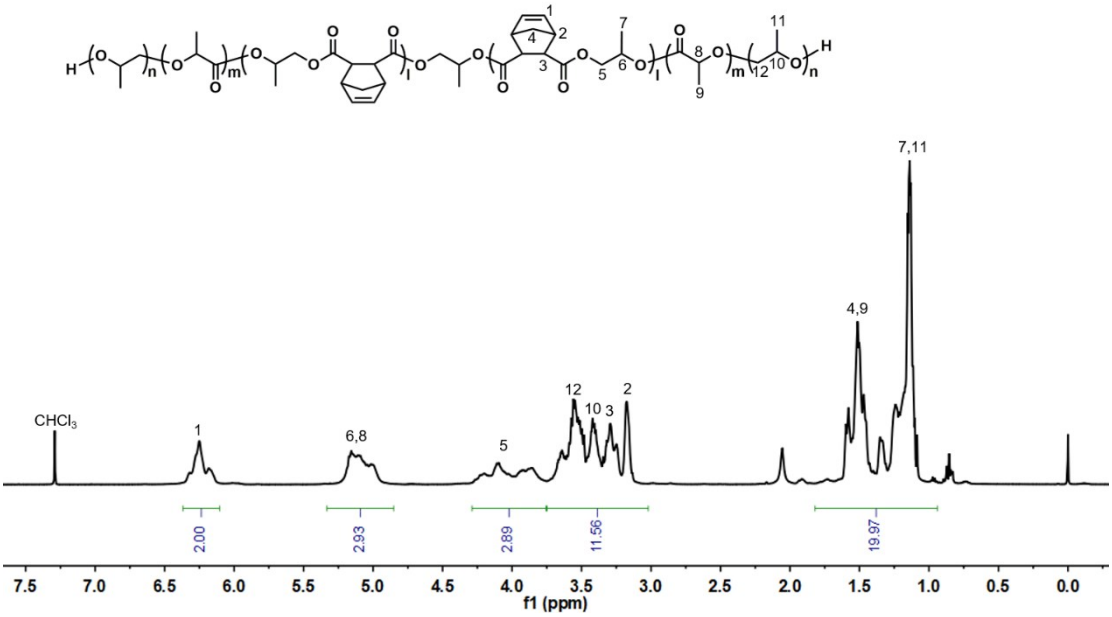


Figure S57. ^{1}H NMR spectrum of the product obtained from terpolymerization of PO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 1).

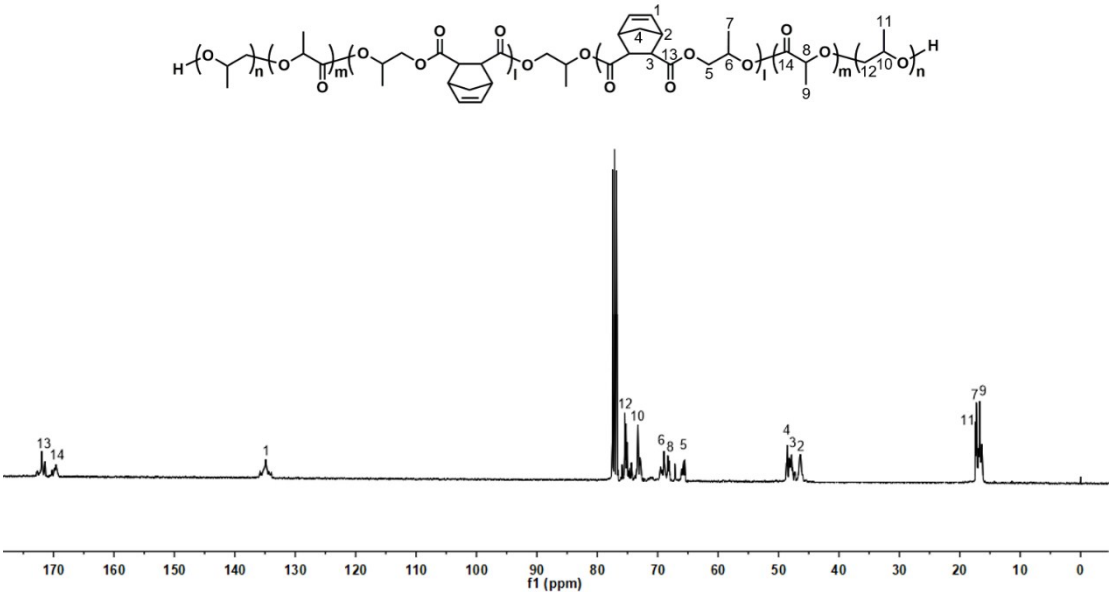


Figure S58. ^{13}C NMR spectrum of the product obtained from terpolymerization of PO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 1).

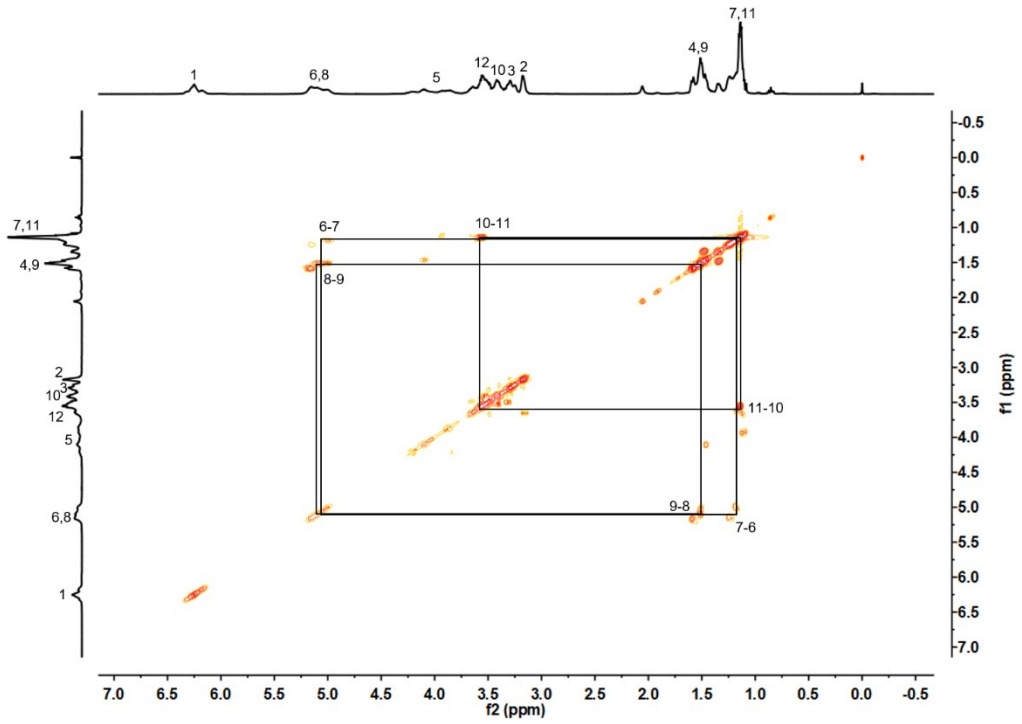


Figure S59. COSY NMR spectrum of the product obtained from terpolymerization of PO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 1).

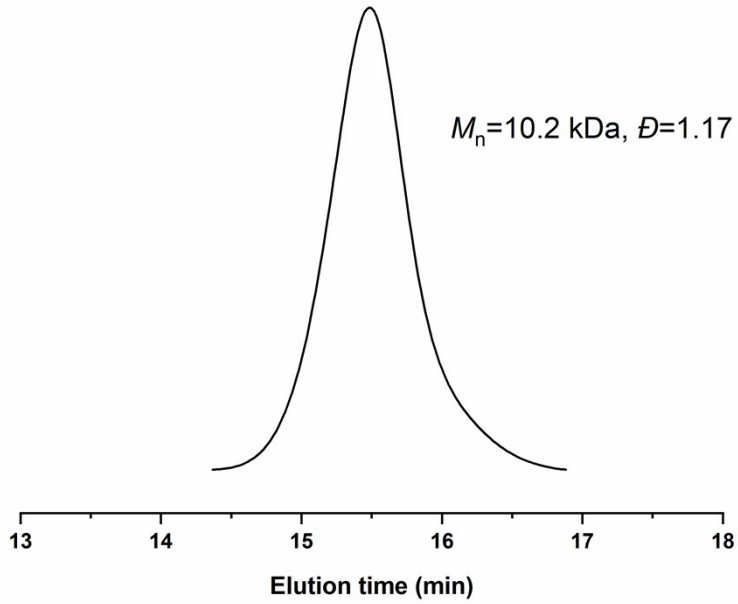


Figure S60. GPC curve of the product obtained from terpolymerization of PO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 1).

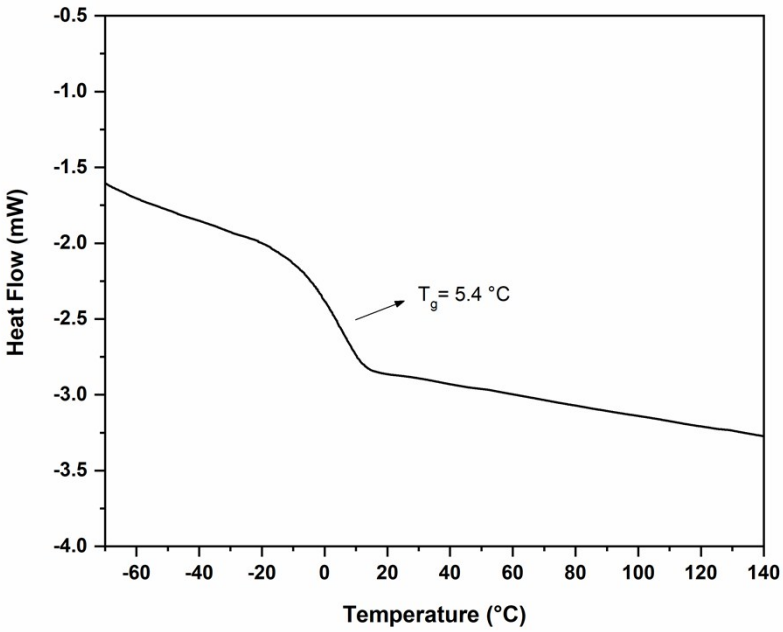
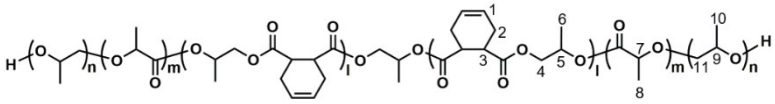


Figure S61. DSC thermogram of the product obtained from terpolymerization of PO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 1).



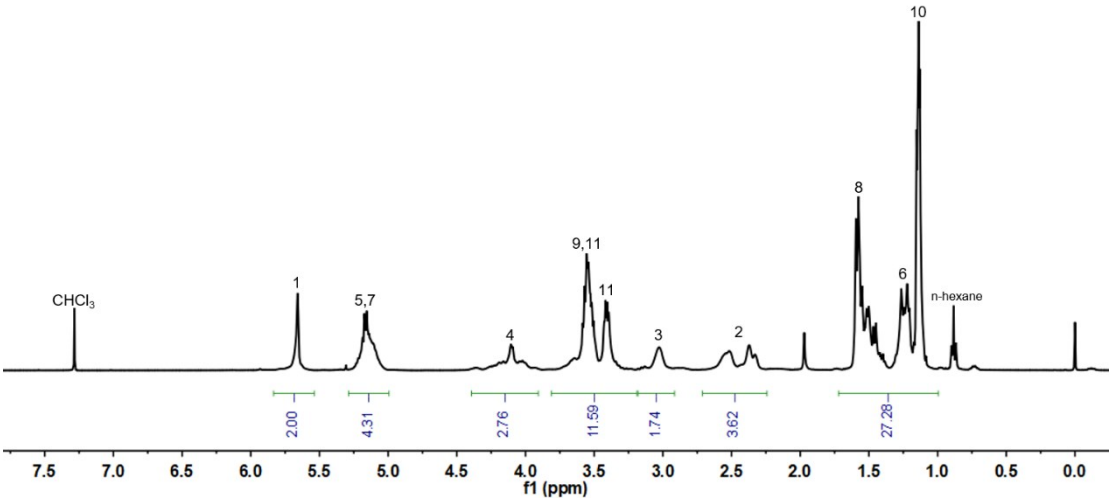


Figure S62. ^{1}H NMR spectrum of the product obtained from terpolymerization of PO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 3).

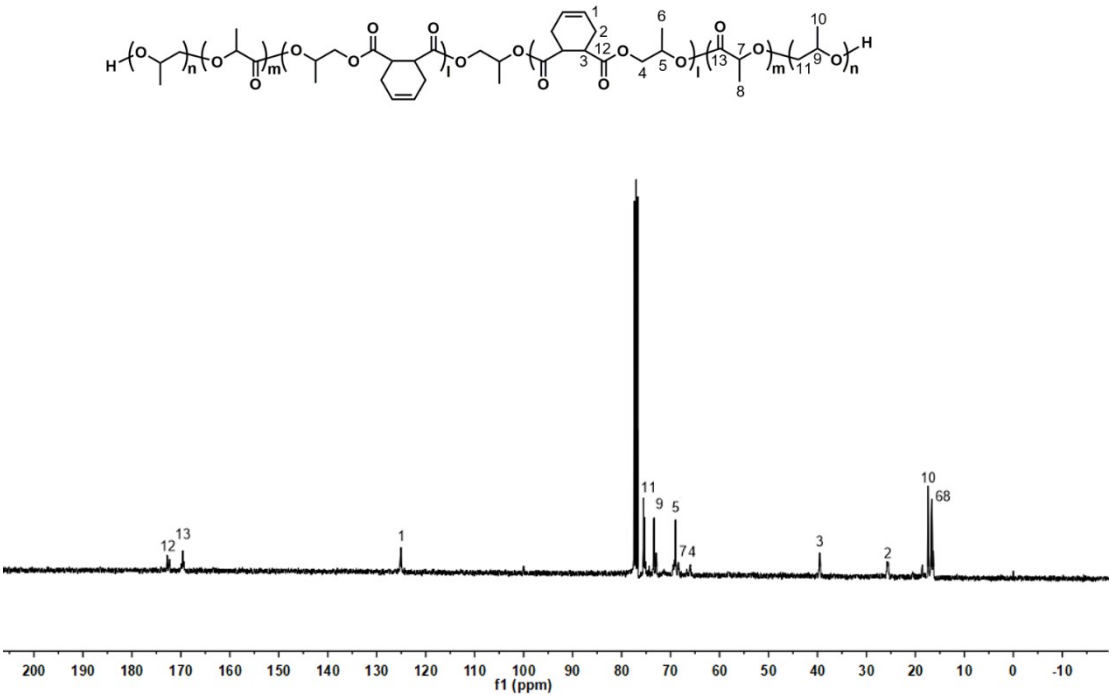


Figure S63. ^{13}C NMR spectrum of the product obtained from terpolymerization of PO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 3).

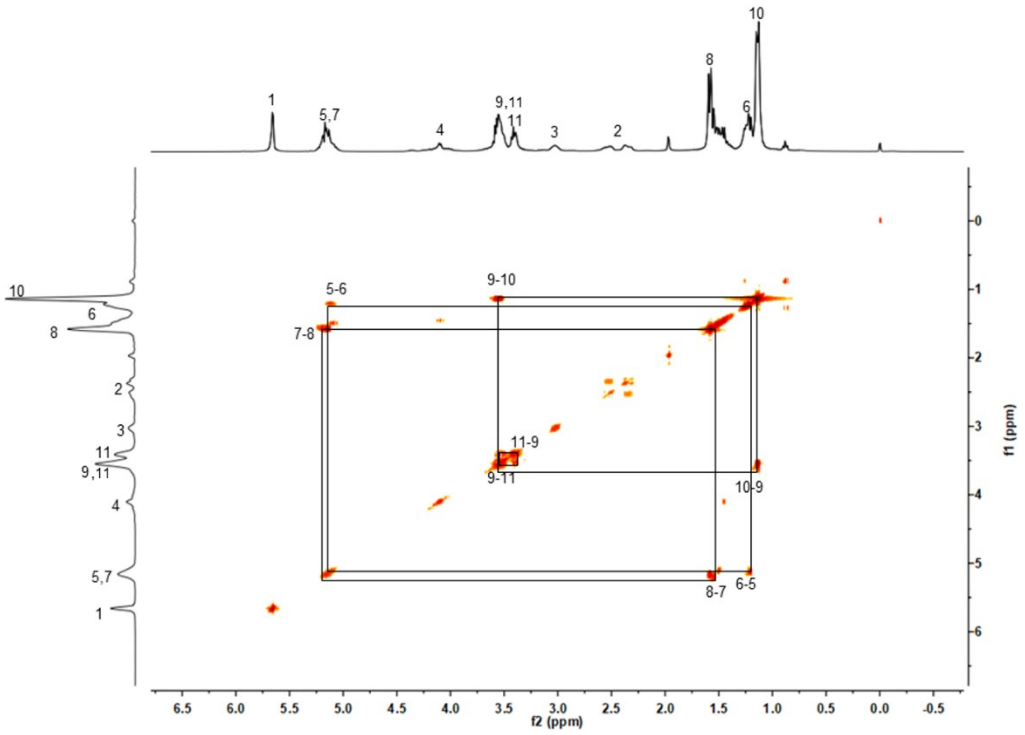


Figure S64. COSY NMR spectrum of the product obtained from terpolymerization of PO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 3).

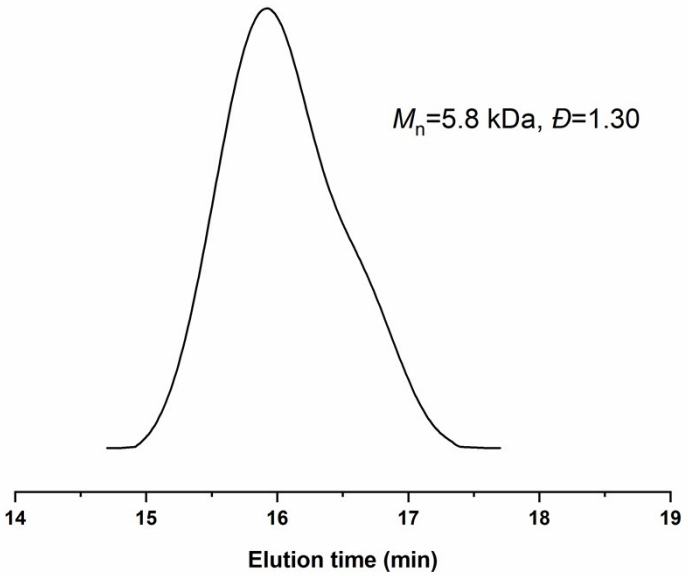


Figure S65. GPC curve of the product obtained from terpolymerization of PO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 3).

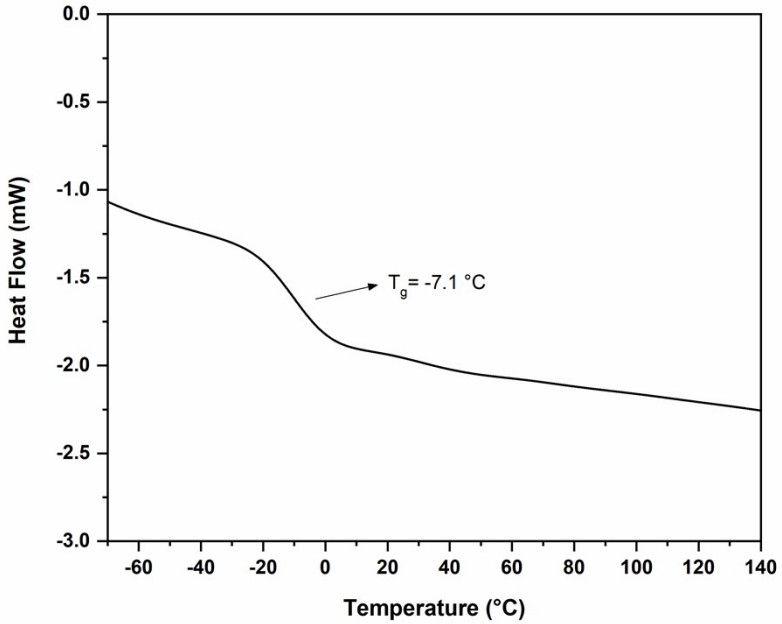


Figure S66. DSC thermogram of the product obtained from terpolymerization of PO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (2/1) (Table 2, entry 3).

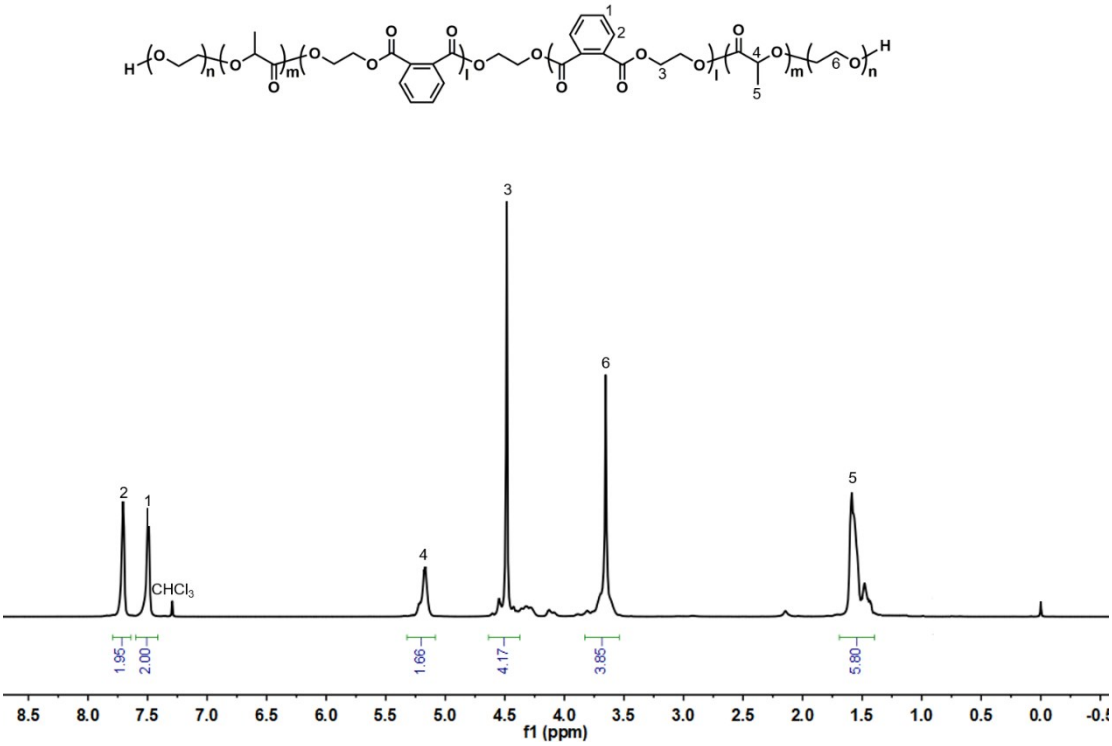


Figure S67. ^{1}H NMR spectrum of the product obtained from terpolymerization of EO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 4).

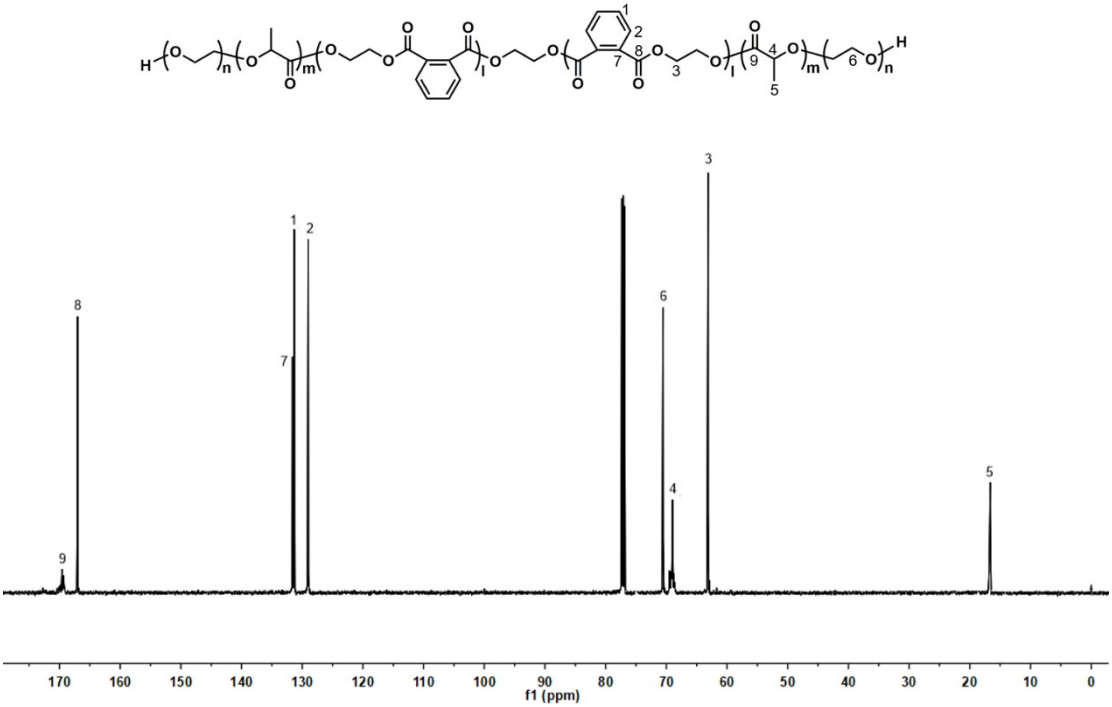


Figure S68. ^{13}C NMR spectrum of the product obtained from terpolymerization of EO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 4).

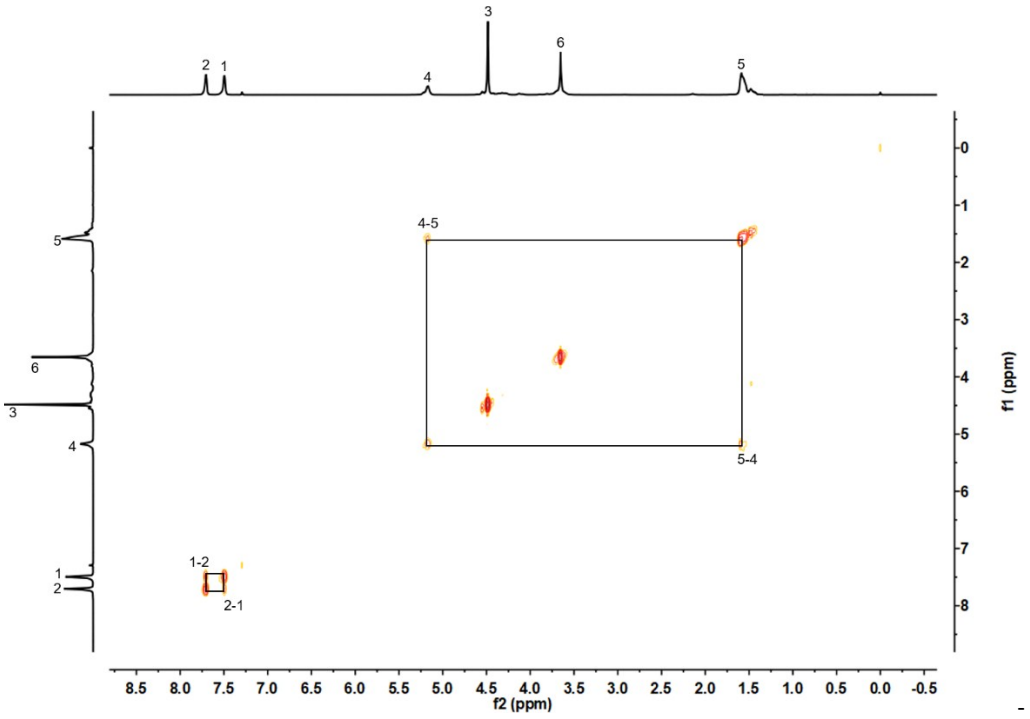


Figure S69. COSY NMR spectrum of the product obtained from terpolymerization of EO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 4).

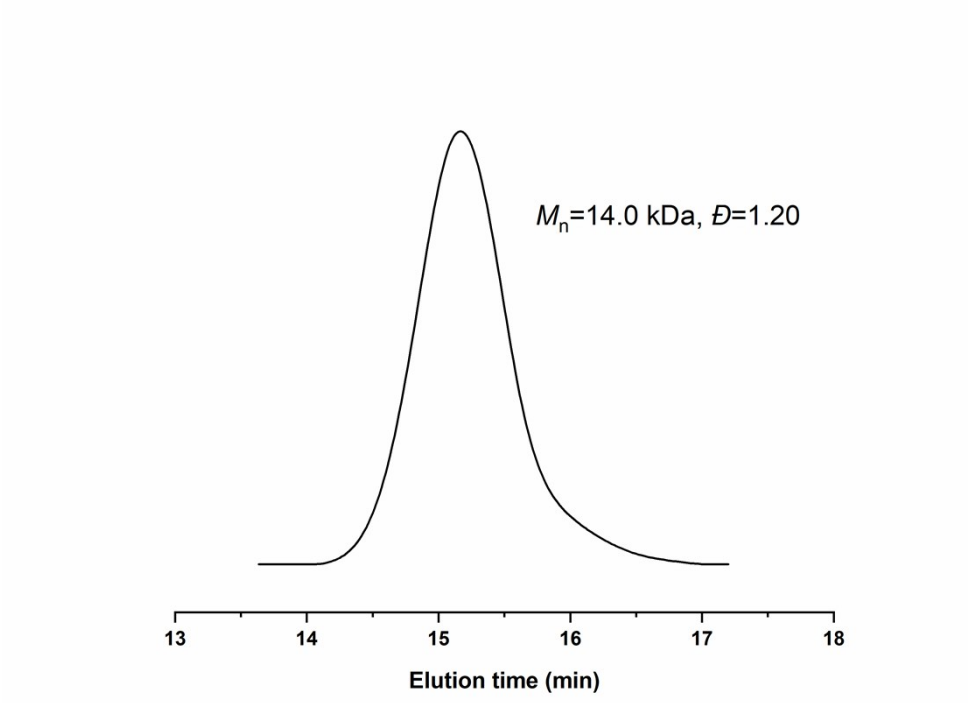


Figure S70. GPC curve of the product obtained from terpolymerization of EO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 4).

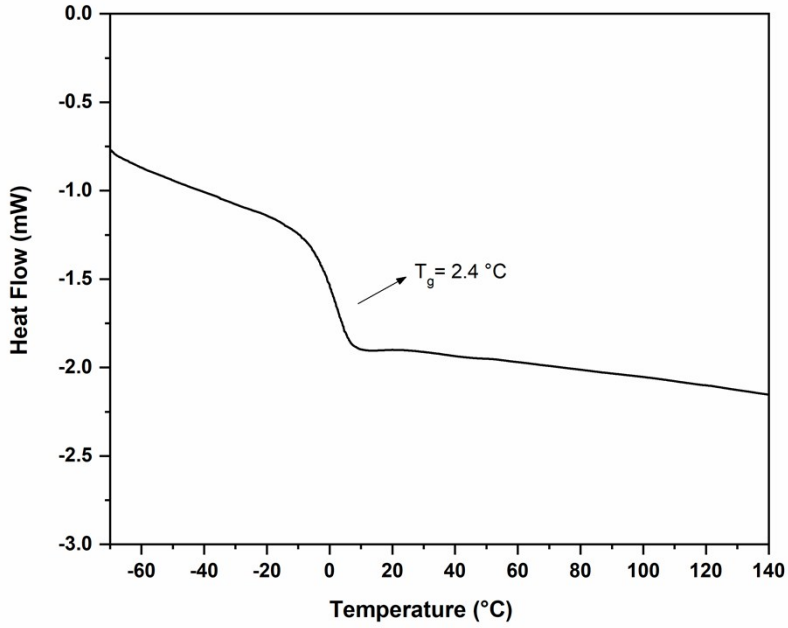


Figure S71. DSC thermogram of the product obtained from terpolymerization of EO, PA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 4).

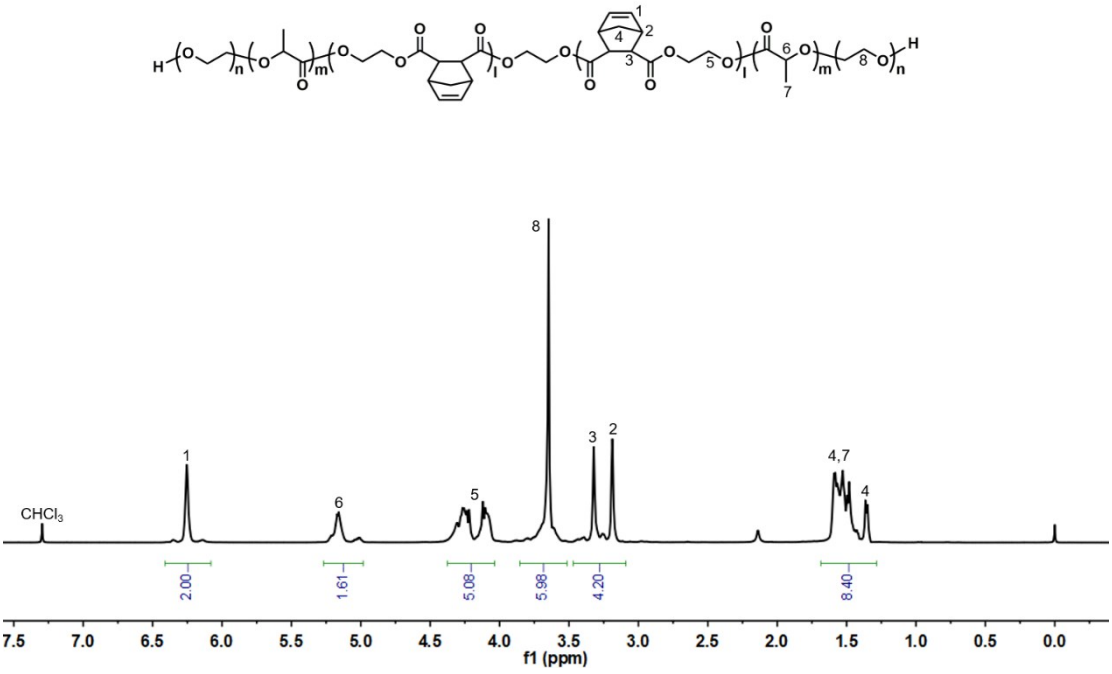


Figure S72. ^{1}H NMR spectrum of the product obtained from terpolymerization of EO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 5).

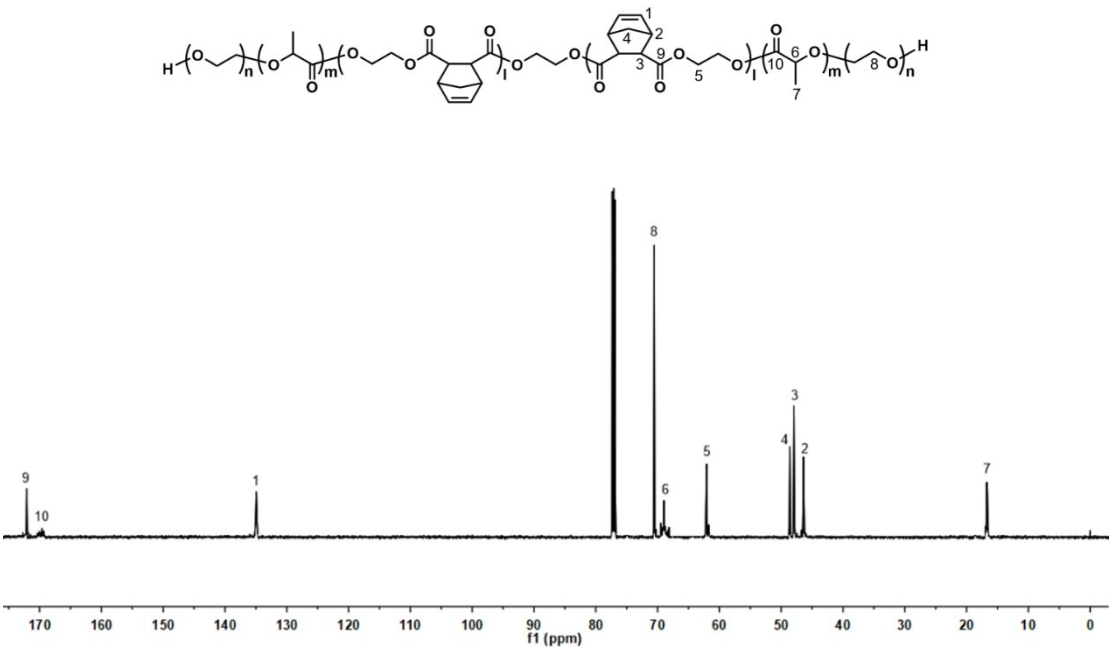


Figure S73. ^{13}C NMR spectrum of the product obtained from terpolymerization of EO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 5).

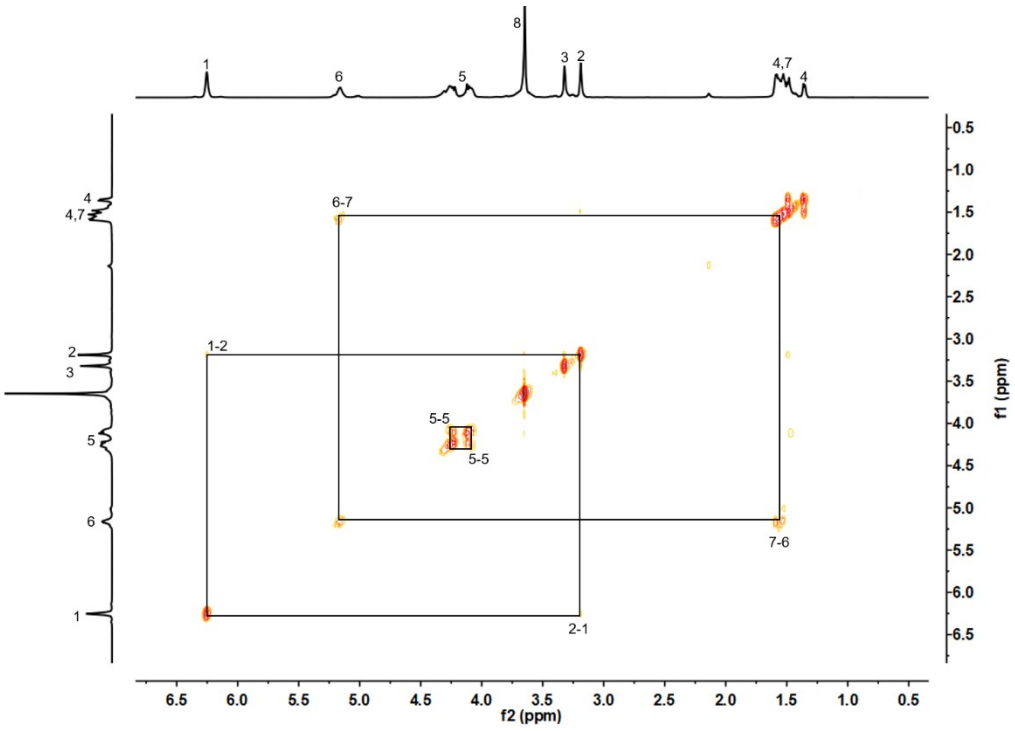


Figure S74. COSY NMR spectrum of the product obtained from terpolymerization of EO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 5).

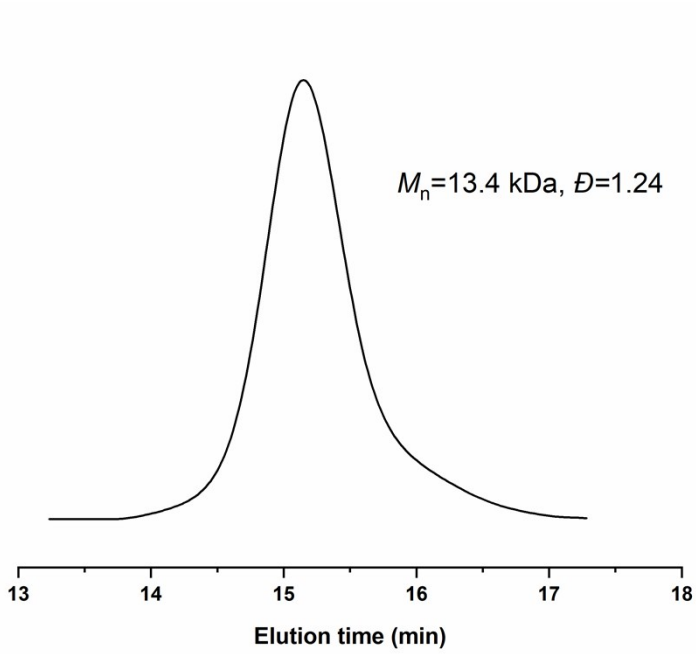


Figure S75. GPC curve of the product obtained from terpolymerization of EO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1). (Table 2, entry 5)

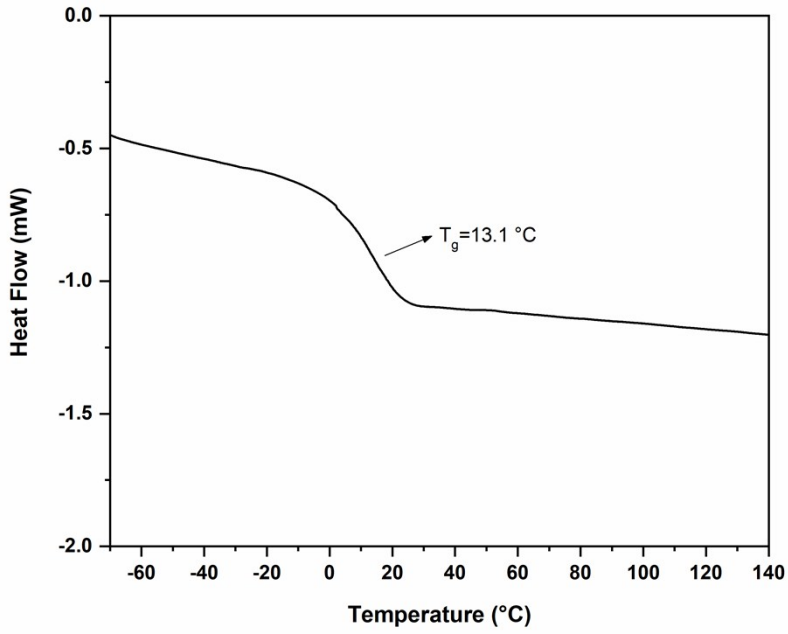


Figure S76. DSC thermogram of the product obtained from terpolymerization of EO, NBA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 5).

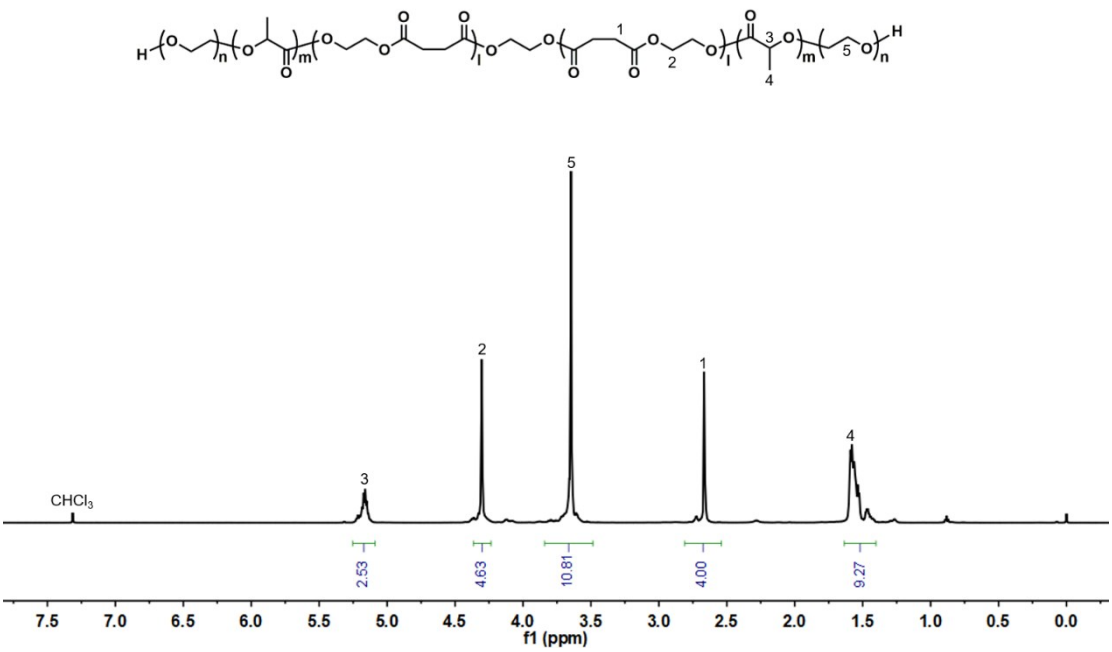


Figure S77. ^{1}H NMR spectrum of the product obtained from terpolymerization of EO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 6).

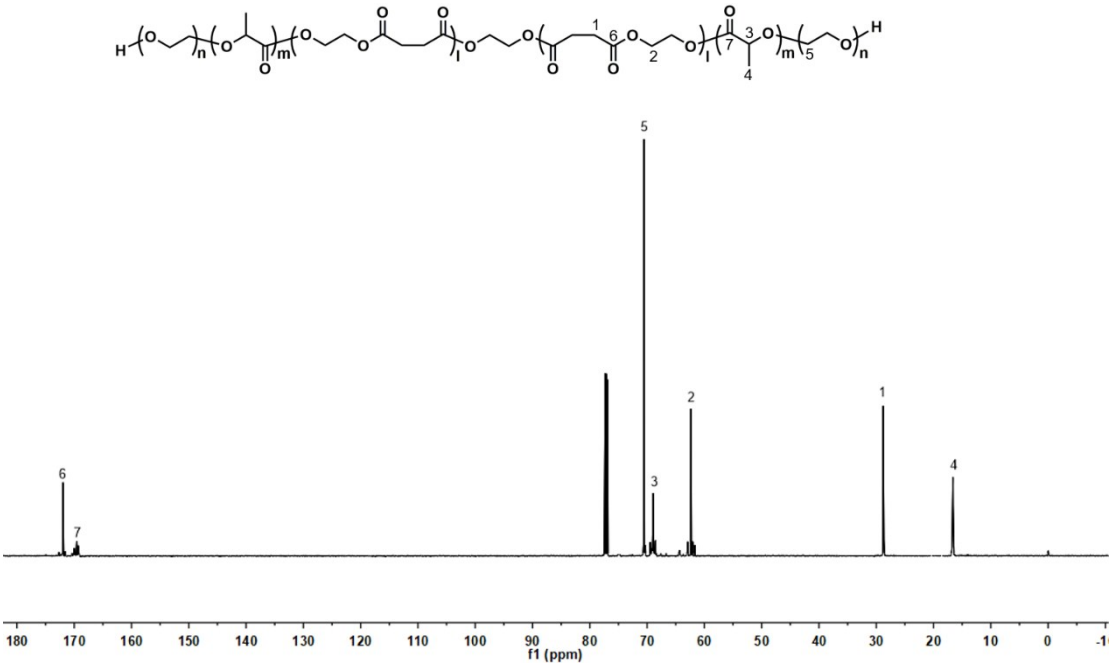


Figure S78. ^{13}C NMR spectrum of the product obtained from terpolymerization of EO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 6).

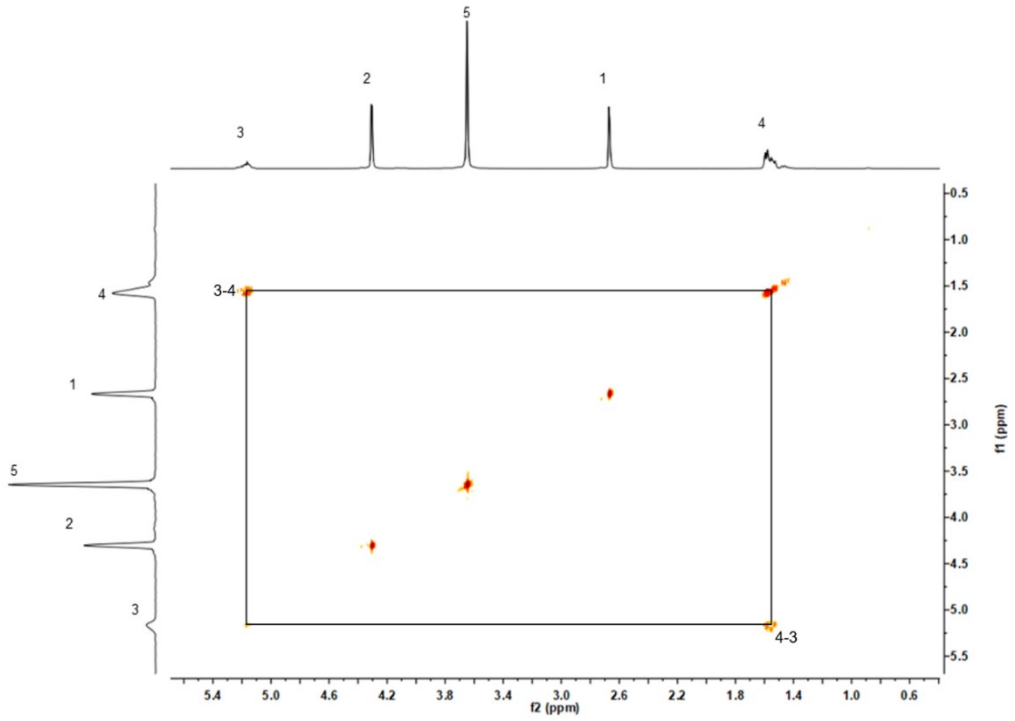


Figure S79. COSY NMR spectrum of the product obtained from terpolymerization of EO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 6).

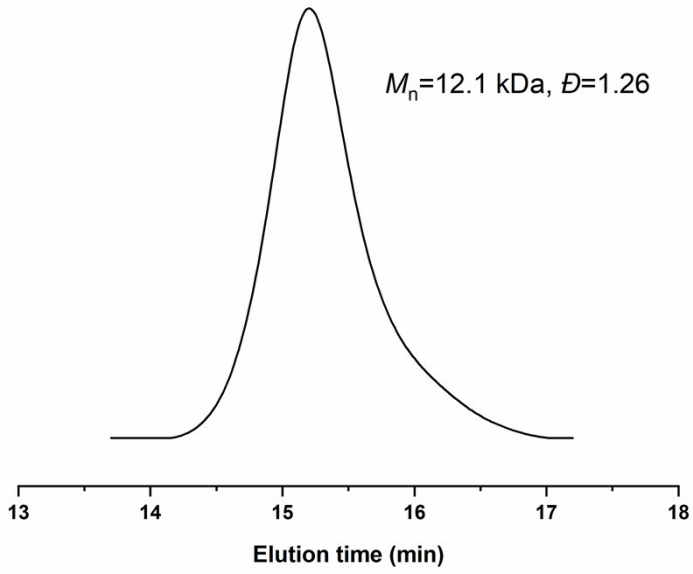


Figure S80. GPC curve of the product obtained from terpolymerization of EO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 6).

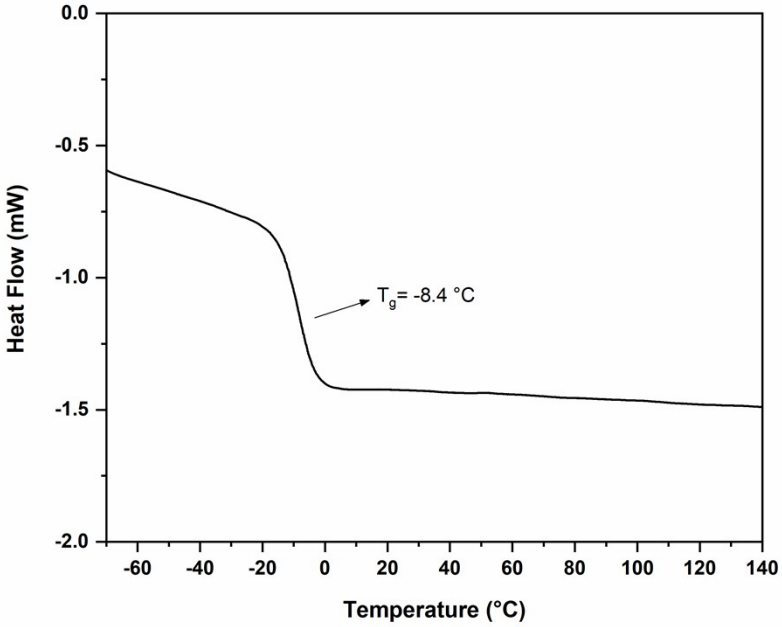
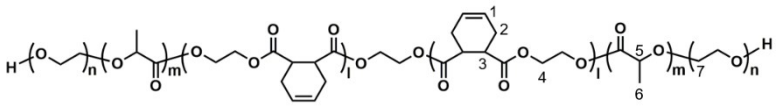


Figure S81. DSC thermogram of the product obtained from terpolymerization of EO, SA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 6).



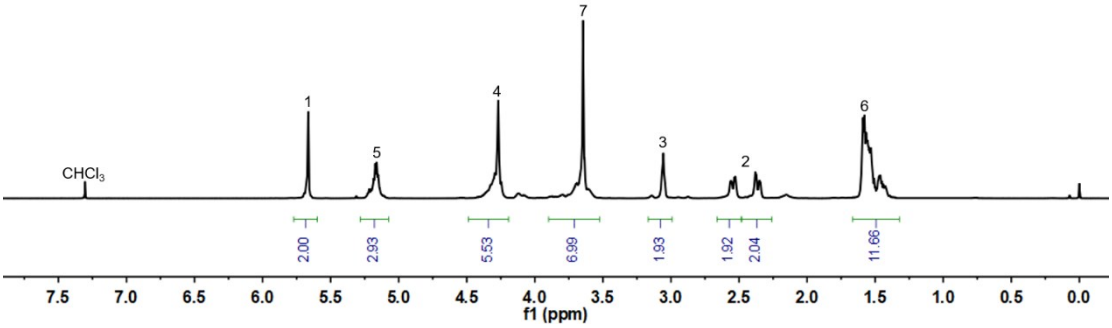


Figure S82. ^{1}H NMR spectrum of the product obtained from terpolymerization of EO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 7).

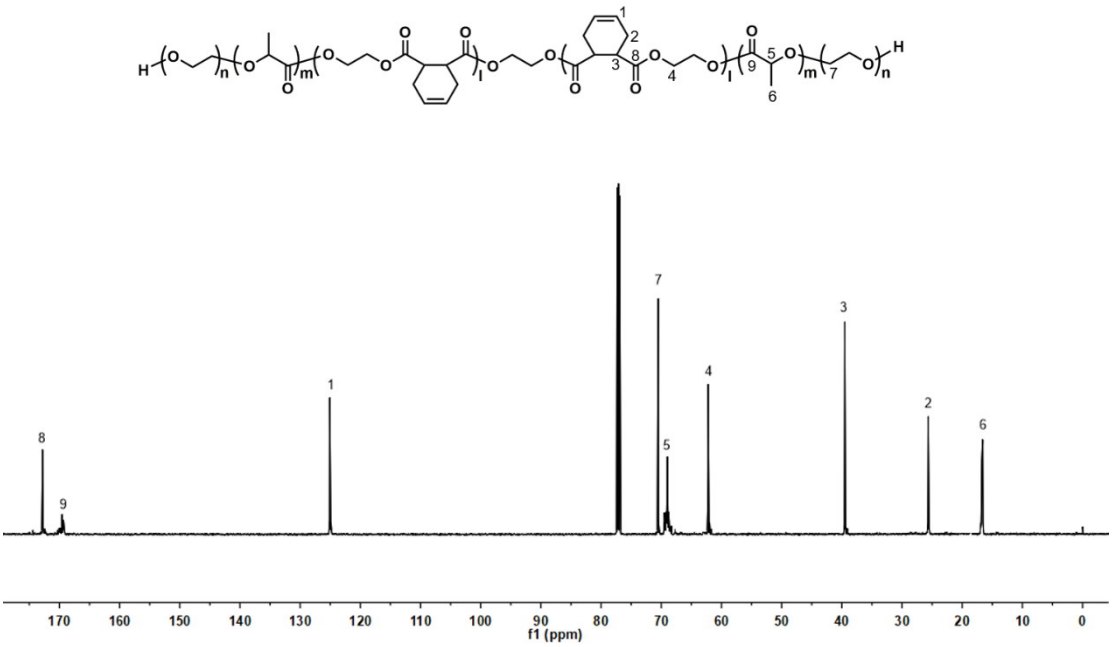


Figure S83. ^{13}C NMR spectrum of the product obtained from terpolymerization of EO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 7).

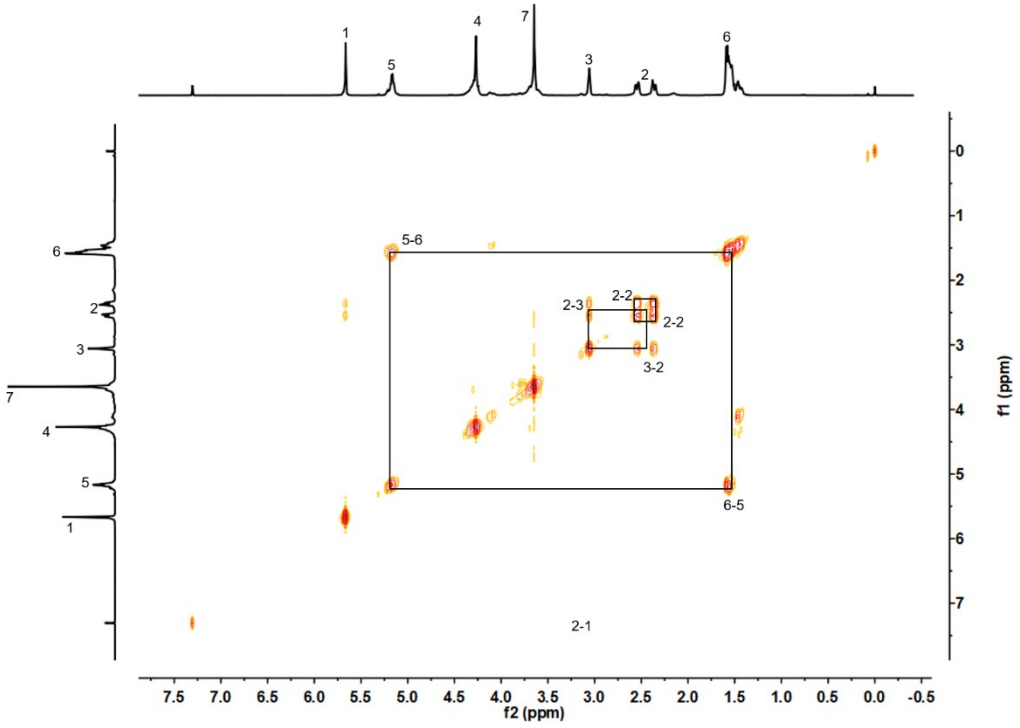


Figure S84. COSY NMR spectrum of the product obtained from terpolymerization of EO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 7).

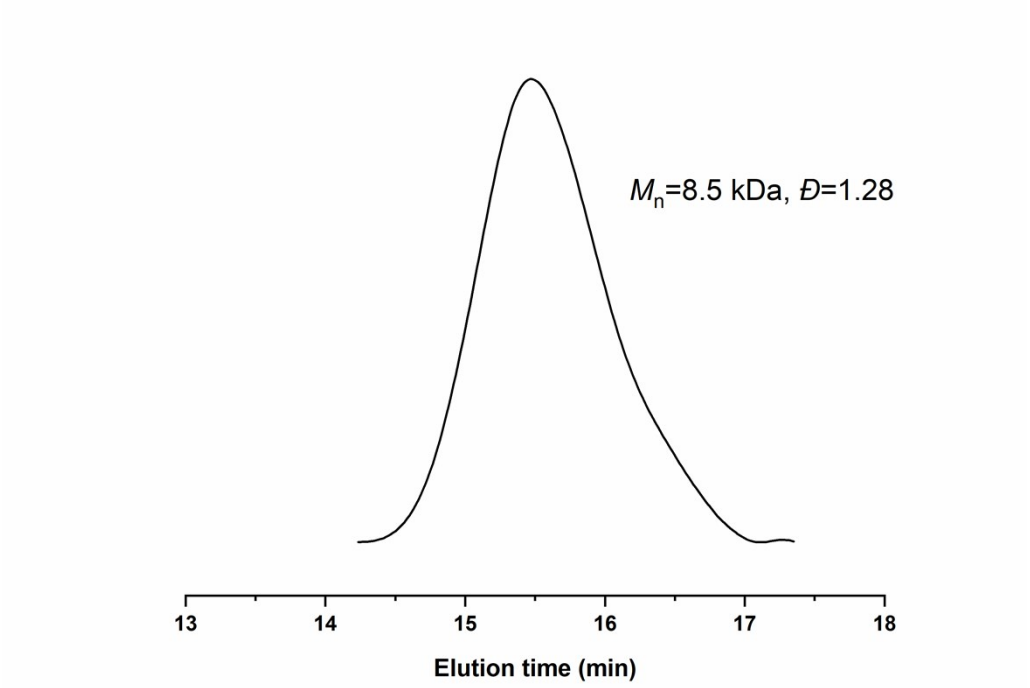


Figure S85. GPC curve of the product obtained from terpolymerization of EO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 7).

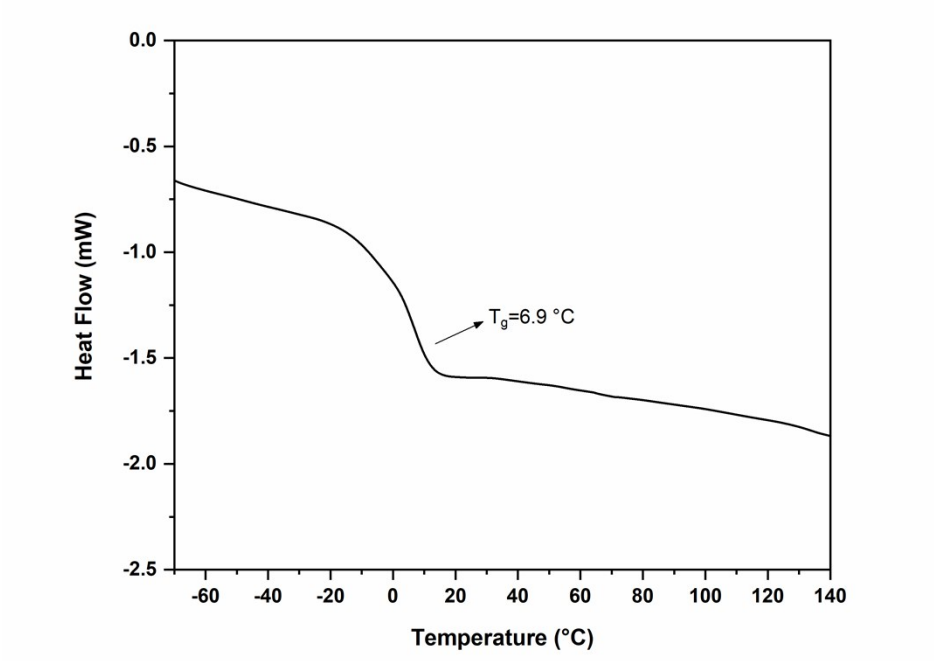


Figure S86. DSC thermogram of the product obtained from terpolymerization of EO, THPA and *rac*-LA catalyzed by Et_3B/DBU pair (1.5/1) (Table 2, entry 7).

4. References

1. Zhu, Y.; Romain, C.; Williams, C. K., Selective Polymerization Catalysis: Controlling the Metal Chain End Group to Prepare Block Copolyesters. *J. Am. Chem. Soc.* **2015**, *137* (38), 12179-12182.

2. Stosser, T.; Mulryan, D.; Williams, C. K., Switch Catalysis To Deliver Multi-Block Polyesters from Mixtures of Propene Oxide, Lactide, and Phthalic Anhydride. *Angew. Chem. Int. Ed.* **2018**, *57* (51), 16893-16897.