

Supporting Information

Ring-Opening Polymerization of Tri-Substituted Six- Membered Lactone Derived from CO₂/Butadiene

Jialin Xu, Yuxuan Niu, Bo-lin Lin

Experimental Section

Materials and reagents

All reactions using air and moisture sensitive materials were conducted or sealed in a nitrogen glove-box. Glassware used was dried in a 120°C oven overnight or subjected to flame drying before being transferred into the glove box. Tetrahydrofuran (THF), toluene (Tol), monomers and other ROP-related solutions were refluxed and reacted with CaH₂ for at least 24 hours, followed by distillation, transferring to glove box and soaking in activated 3Å molecular sieves to maintain a water content below 30 ppm. Mesitylene and benzyl alcohol (BnOH) super dry solvent were purchased from J&K Scientific and used as received. Lithium bis(trimethylsilyl)amide (LiHMDS) and iodoethane (EtI) were purchased from Adamas and used as received. 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylide-namino]-2λ5,4λ5-catenadi-(phosphazene) (^tBu-P₄, 0.8 m in hexane) was purchased from Sigma Aldrich, solvent was removed completely before use. Tri[*N,N*-bis(trimethylsilyl)amide] lanthanum(III) La[N(SiMe₃)₂]₃ (La) was purchased from Aldrich Chemical Co., Ltd., sodium methoxide (NaOMe) and triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from TCI Co., Ltd., respectively. All these compounds were stored in a nitrogen glove-box and used as received without further purification.

General polymerization procedures

Most polymerizations were performed in 5 mL Schlenk tubes pre-sealed in glove-box and reacted in an external cooling bath. Predetermined amount of catalyst (and/or initiator) and solvent were charged in a glovebox in sequence. The reaction tube was sealed with a septum, taken out of the glovebox and equilibrated to the desired temperature. The polymerization reaction was initiated by rapid addition of monomer solution via a gastight syringe. After a desired period of reaction time, the polymerization was quenched by addition of an excess THF acidified with PhCOOH (5%), a minor amount was taken and prepared for ¹H NMR analysis to obtain the monomer conversion. The quenched mixture was then precipitated into 50 mL of cold methanol, and washed with methanol for three times to remove remained monomer and catalysts, then dried in a vacuum oven at 80°C to a constant weight.

Special quenching method was referred in Table 1 using pure dehydrated hexane as quenching reagent. The resulting product was also washed three times with dehydrated hexane and characterized as others. For kinetic studies, several parallel polymerization reactions were conducted at the feeding ratio of [Et-HL]/[^tBu-P₄]/[BnOH] = 200/1/1, [Et-HL] = 4.5 M in THF at -25°C, to avoid conversion systematic error induced by aliquot extraction. The thermodynamic studies were carried out in the same procedures with different temperature.

Reaction procedures for mechanism studies

To enhance the signals of the intermediates in NMR spectra, the feeding ratio of the reactions in Figure 5b were [Et-HL]/[^tBu-P₄]/[BnOH] = 10/1/1, the others in Figure 5 were [monomer]/[^tBu-P₄] = 2/1 without any solvent. The feeding ratio of the reactions in Figures S20-25 were [monomer]/[^tBu-P₄] = 10/1 to lower the relative intensity of ^tBu-P₄ signals. The reaction time was controlled to be 10 mins for Figures 5, S22 and S23 and 30 mins for Figures S24, 25. In Figure 5, 1 equiv. of CF₃COOD to ^tBu-P₄ was added to the system after the designed reaction time and stirred for 10 mins, then extra toluene-*H*₈ was added and ²H NMR tests were taken at 298K. In Figures S20-25, similar procedure without CF₃COOD were conducted and toluene-*d*₈ was used as

solvent for ^1H NMR and DOSY NMR tests. All these NMR tests were conducted using J-Young tube to preserve the sample from air and moisture.

Instruments

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ADVANCE III HD500 MHz (FT 500 MHz, ^1H ; 126 MHz, ^{13}C ; 77 MHz, ^2H NMR) spectrometer, calibrated using internal solvent reference signals and reported as parts per million (ppm) relative to SiMe_4 . Molecular weight in DOSY were estimated based on Stokes-Einstein Gierer-Wirtz Estimation (SEGWE) method, using a spreadsheet for SEGWE calculations (developed at the University of Manchester) according to diffusion coefficient ($\text{m}^2 \text{S}^{-1}$)¹.

The number-average molecular weight (M_n) and molecular weight distribution ($D = M_w/M_n$) of the polymer were measured using a Malvern TDA305 multi-detector gel permeation chromatography (GPC) instrument equipped with two comprehensive mixed organic columns (light scattering, refractive index, and ultraviolet detection). Tests were conducted at 40 °C with a flow rate of 1.0 mL min^{-1} using THF as eluent. The instrument was calibrated using seven narrow PMMA standards, and chromatograms were calculated using Malvern OmniSEC software (version 12.1).

The Mark-Houwink plot and the dn/dc values of polymers were measured using a Malvern Viscotek TDMax Multiple Detector (light scattering, refractive index, viscometer and ultra violet) GPC instrument. Experiments were conducted in a similar way as before using PS standards. To measure the dn/dc values, a series of tests were taken from the same sample (10.0 mg mL^{-1}) using different injecting volumes from 20 – 100 μL . A plot of change in refractive index versus change in injecting volume was obtained. The slope from a linear fitting of the data was the dn/dc value of the polymer.

End-group fidelity of the polymer samples was analyzed using MALDI-TOF-MS and experiments were conducted in positive ion mode on a Bruker Autoflex Speed MALDI-TOF mass spectrometer. A layer of 1.0 μL mixed sample and matrix (2,5-dihydroxybenzoic acid, DHB, 20 mg/mL in 50% THF, 0.1% TFA) was first deposited on the target plate. External calibration was done using a peptide calibration mixture on a spot next to the sample spot. Raw data were processed using flexAnalysis version 3.4, and plotted using Origin Pro 2019b.

Glass transition temperature (T_g) was carried out by differential scanning calorimetry (DSC) on a DSC 250, TA instruments. T_g were obtained from a second scan after the thermal history was removed from the first scan. The second heating rate and the first cooling rate were controlled at 5°C/min. Decomposition onset temperatures ($T_d,5\%$) and maximum rate decomposition temperatures (T_{max}) of the polymers were measured by thermal gravimetric analysis (TGA) on a TGA/DSC3+ Synchronous thermal analyzer, Mettler Toledo. Samples were heated from 30°C to 600°C at a rate of 10°C/min.

Preparation of DEtP

DEtP was prepared according to previously reported procedures². The obtained monomer was purified and stored in a refrigerator in glove box for further use.

Procedure for the synthesis of 3,3,6-Triethyltetrahydro-2H-pyran-2-one (Et-HL)

The synthesis of Et-HL was derived from former study³. LiHMDS solution (29 mL, 29 mmol, 1.0 M in THF) was added dropwise to a solution of DEtP (2 g, 13 mmol) and iodoethane (2.08 mL,

26 mmol) in THF (30 mL) equilibrated to -78°C in advance. After the complete adding of LiHMDS solution, the system was slowly warmed to room temperature and reacted overnight. The reaction mixture was quenched with saturated NH_4Cl aqueous solution (60 mL), the aqueous layer was extracted with EtOAc three times (3 x 60 mL). The organic layers were combined, dried over anhydrous NaSO_4 , filtered, and concentrated in vacuo. The residue was purified by chromatography using 8% EtOAc/petroleum ether as eluent. The obtained Et-HL was a colorless oil-like liquid (isolated yield ~96%). ^1H NMR (500 MHz, CDCl_3) δ 4.25 – 4.07 (m, 1H), 1.89 – 1.67 (m, 6H), 1.59 (td, $J = 13.4, 6.8$ Hz, 3H), 1.47 (dd, $J = 14.0, 7.1$ Hz, 1H), 0.98 (t, $J = 7.5$ Hz, 3H), 0.89 (t, $J = 7.5$ Hz, 6H). ^{13}C NMR (126 MHz, Chloroform- d) δ 176.41, 82.13, 45.78, 32.19, 31.34, 28.94, 27.95, 26.08, 9.18, 8.76, 8.72.

General chemical recycling procedures

50 mg of purified polymer and predetermined amount of catalyst solution were added in a round bottom flask containing magnetic stirring bar. The flask was taken out of the glovebox and immersed in an metal bath with a reflux device on top and nitrogen protection. After a period of reaction time, the mixture was cooled to room temperature and the solvent was completely removed in vacuo. The Et-HL monomer recovery data was determined by crude ^1H NMR spectrum.

Supporting Figures

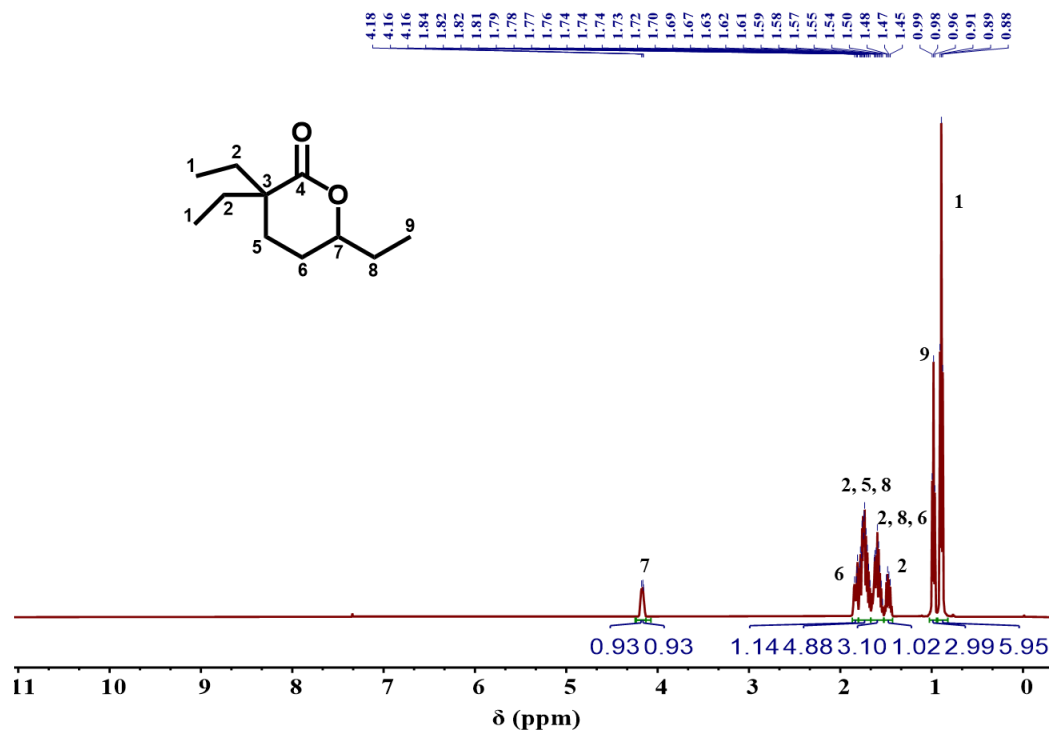


Figure S1. ¹H NMR spectrum of Et-HL monomer (CDCl₃, 500 MHz).

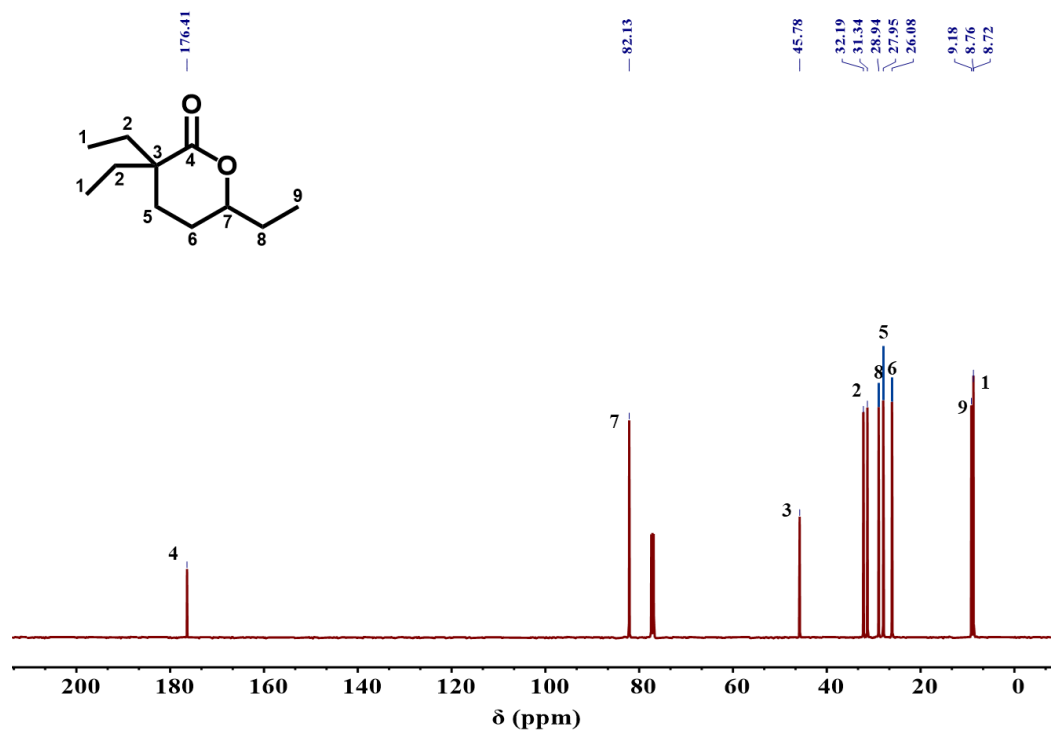


Figure S2. ¹³C NMR spectrum of Et-HL monomer (CDCl₃, 126 MHz).

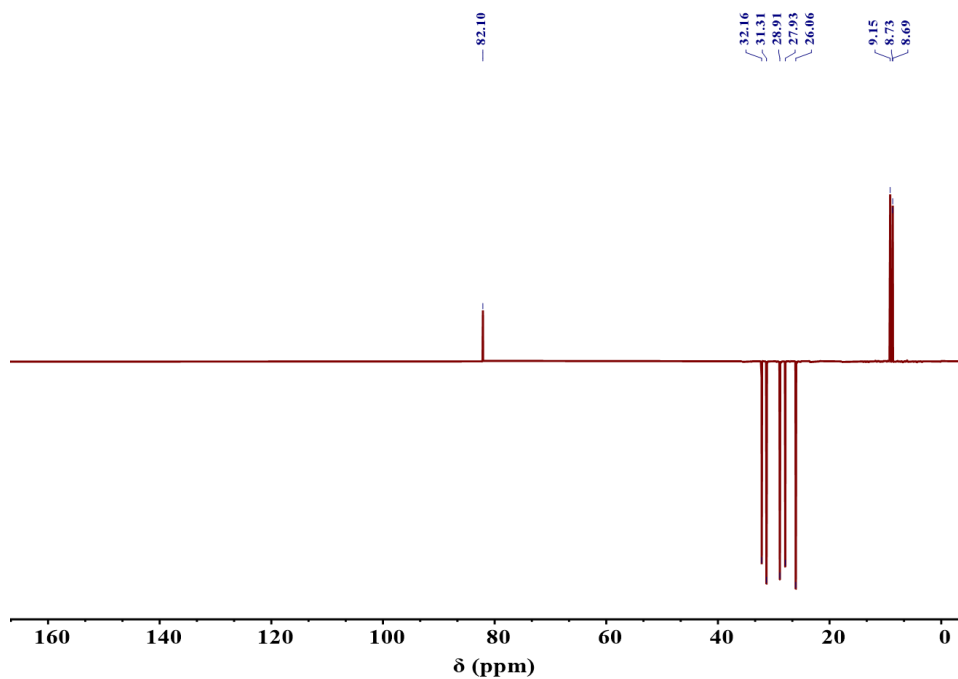


Figure S3. DEPT-135 spectrum of Et-HL monomer (CDCl_3 , 126 MHz). The inverted peaks are assigned to methylene carbon signals.

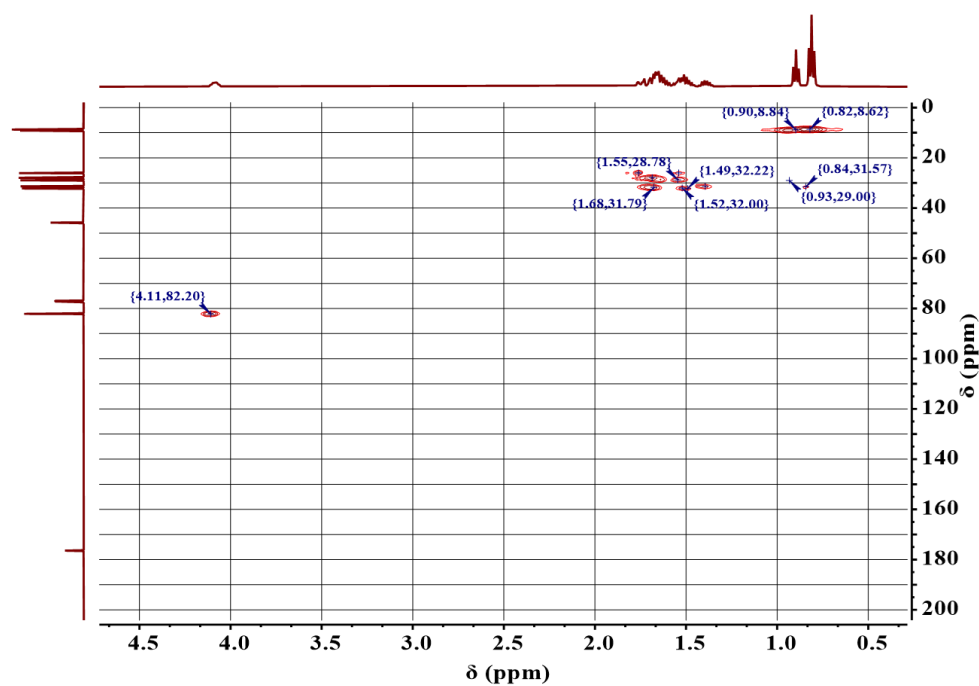


Figure S4. ^1H - ^{13}C HSQC spectrum of Et-HL monomer (CDCl_3).

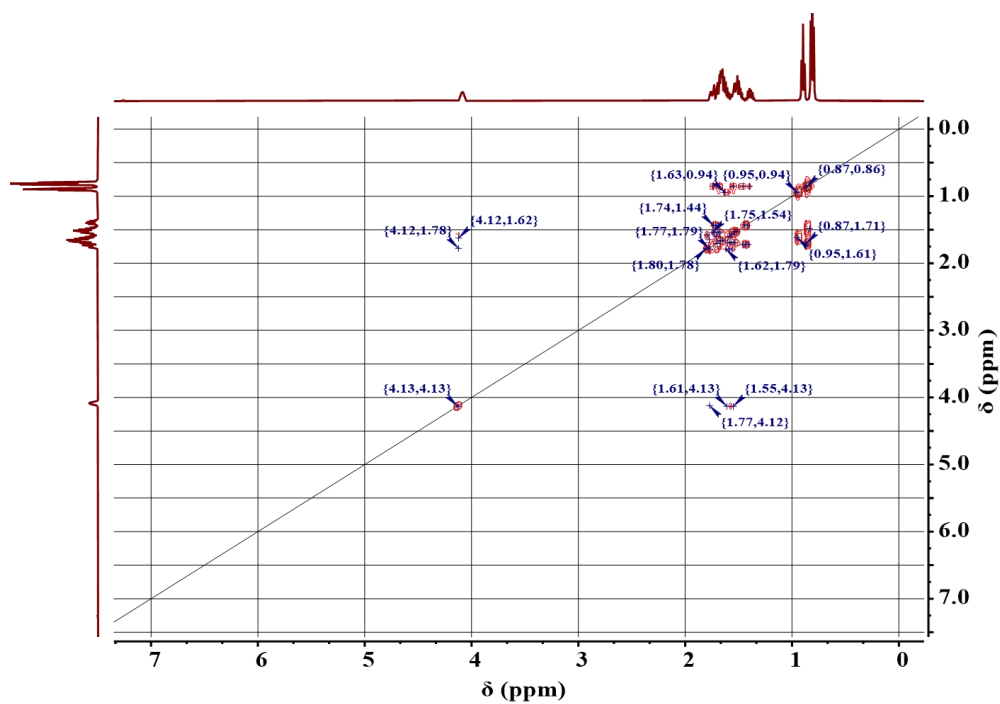


Figure S5. ^1H - ^1H COSY spectrum of Et-HL monomer (CDCl_3).

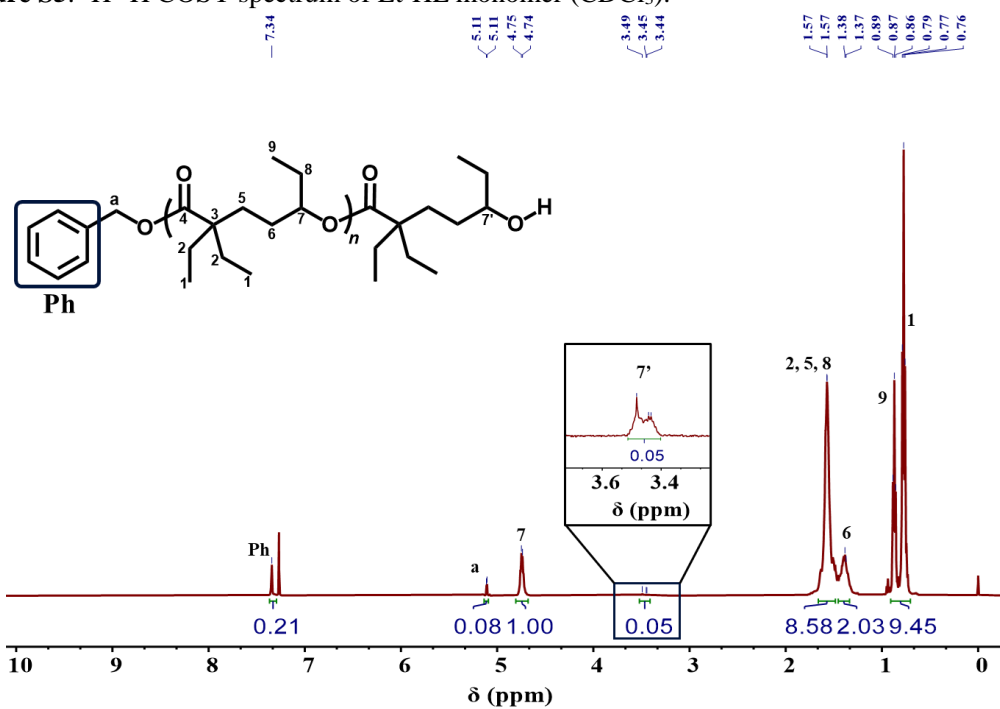


Figure S6. ^1H NMR spectrum of poly(Et-HL) initiated by BnOH (CDCl_3 , 500 MHz).

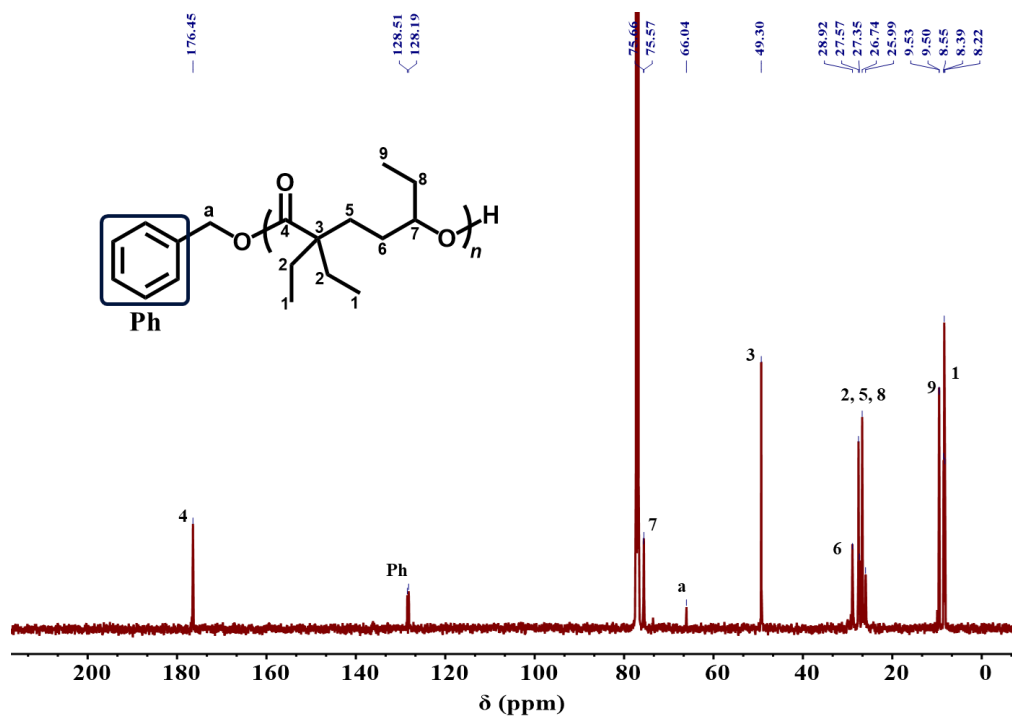


Figure S7. ^{13}C NMR spectrum of poly(Et-HL) initiated by BnOH (CDCl_3 , 126 MHz.).

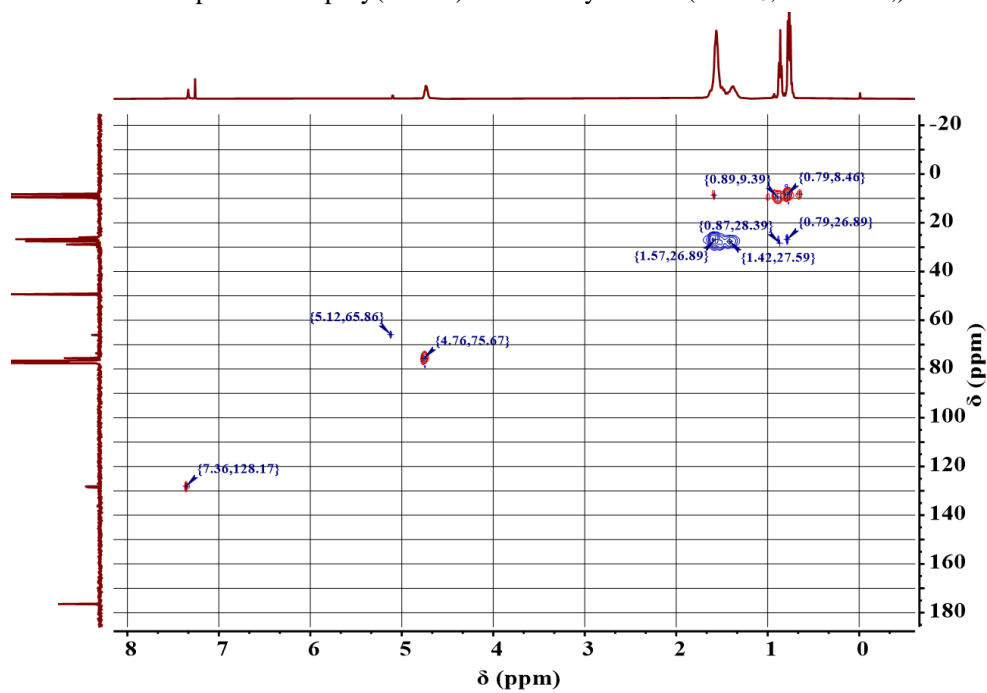


Figure S8. ^1H - ^{13}C HSQC spectrum of poly(Et-HL) initiated by BnOH (CDCl_3).

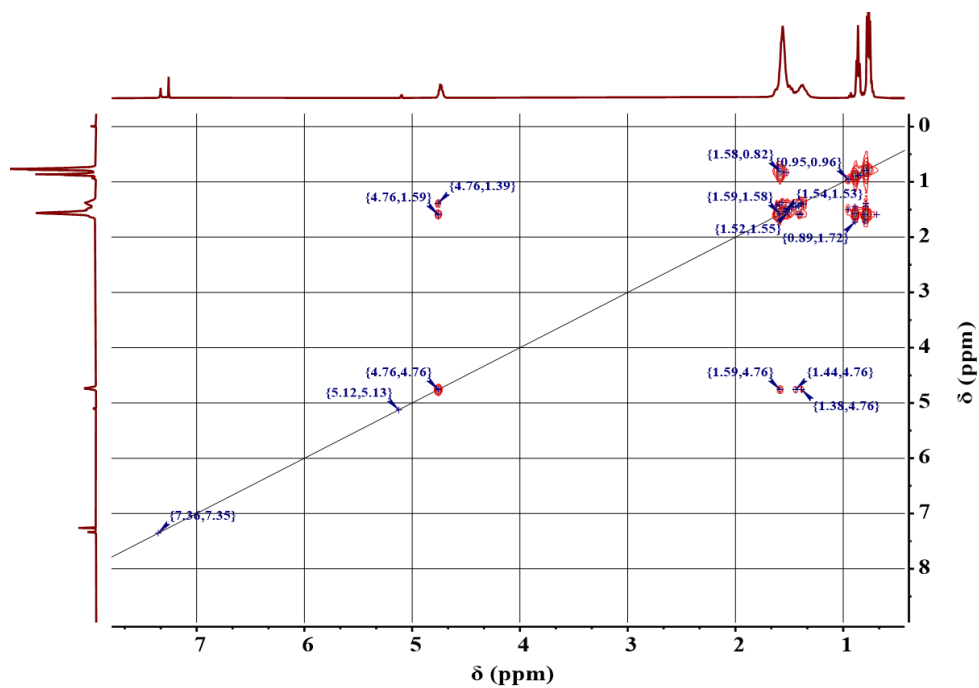


Figure S9. ^1H - ^1H COSY spectrum of poly(Et-HL) initiated by BnOH (CDCl_3).

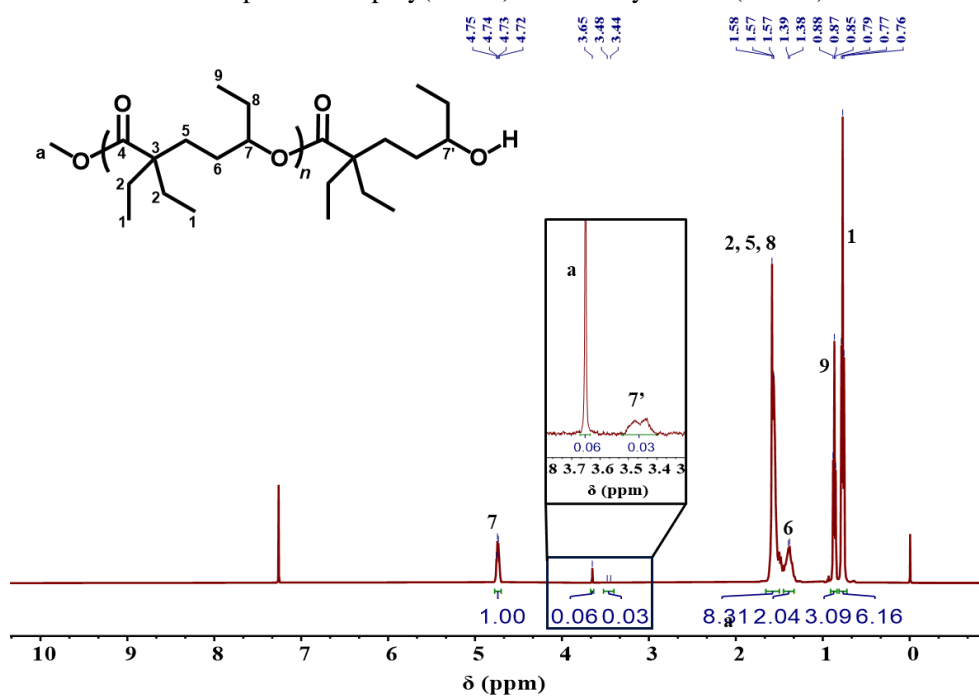


Figure S10. ^1H NMR spectrum of poly(Et-HL) initiated by NaOMe (CDCl_3 , 500 MHz).

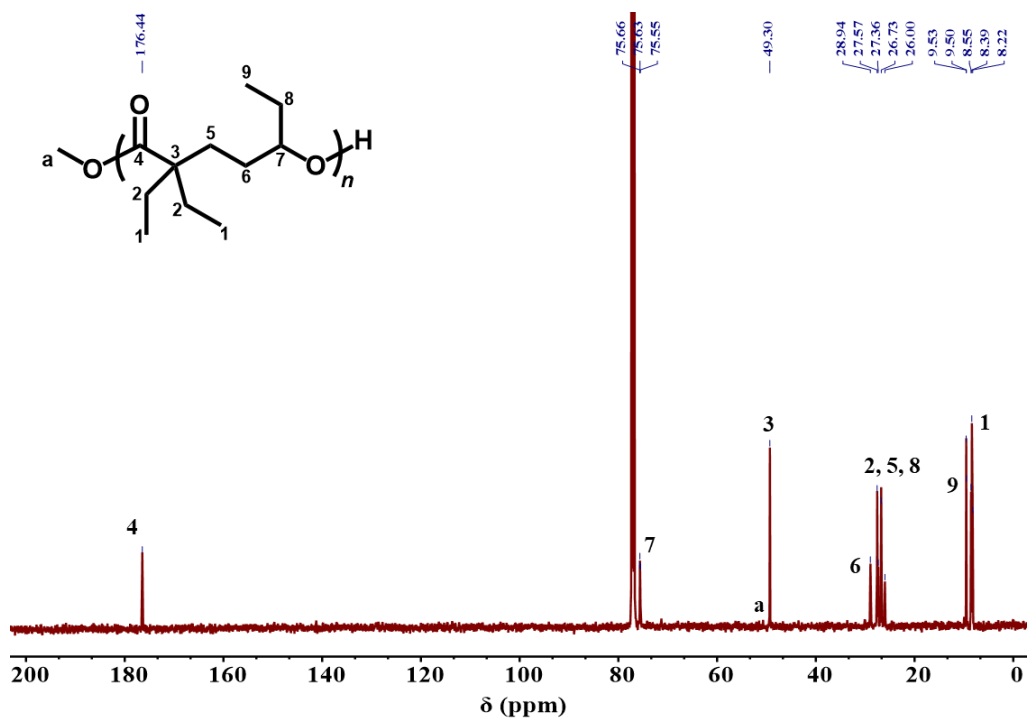


Figure S11. ^{13}C NMR spectrum of poly(Et-HL) initiated by NaOMe (CDCl_3 , 126 MHz.).

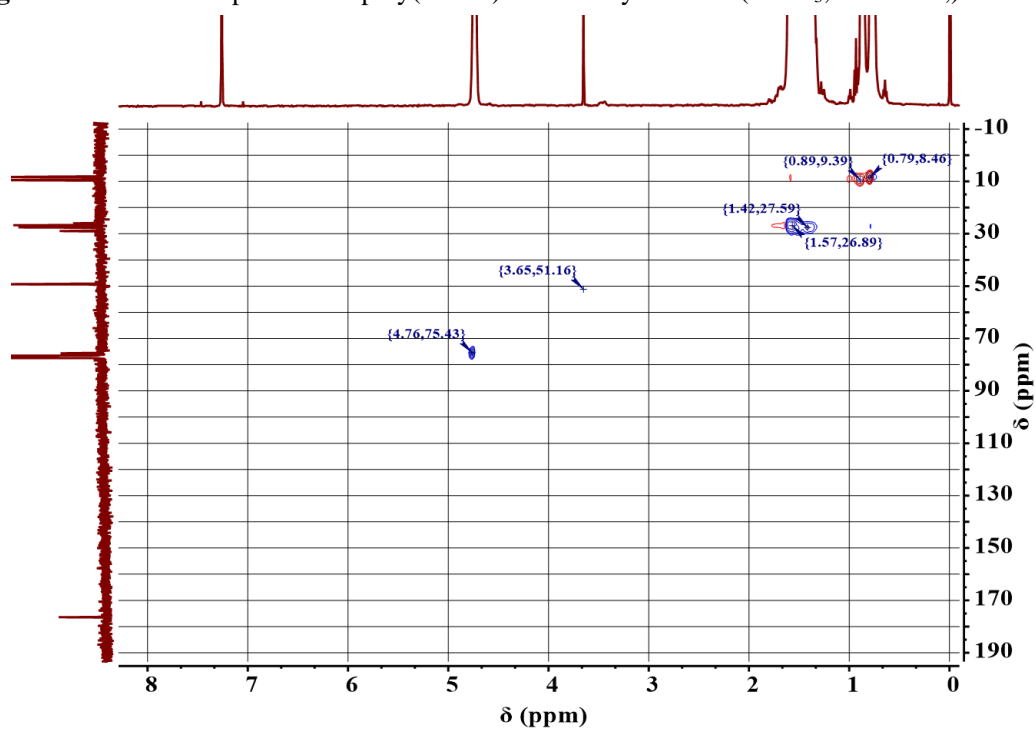


Figure S12. ^1H - ^{13}C HSQC spectrum of poly(Et-HL) initiated by NaOMe (CDCl_3).

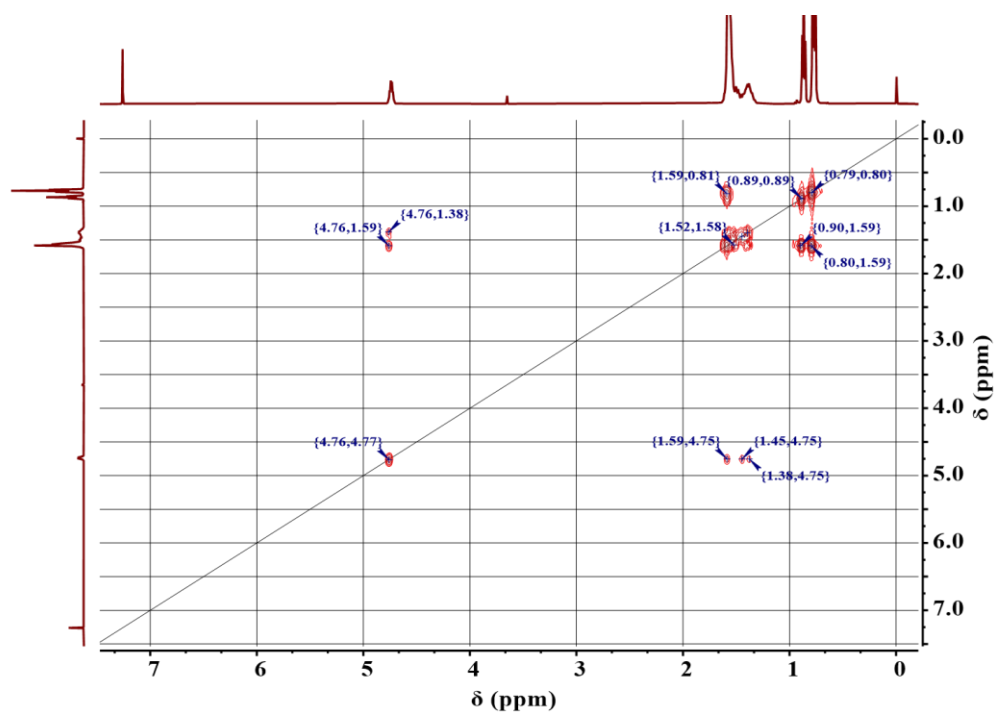


Figure S13. ^1H - ^1H COSY spectrum of poly(Et-HL) initiated by NaOMe (CDCl_3).

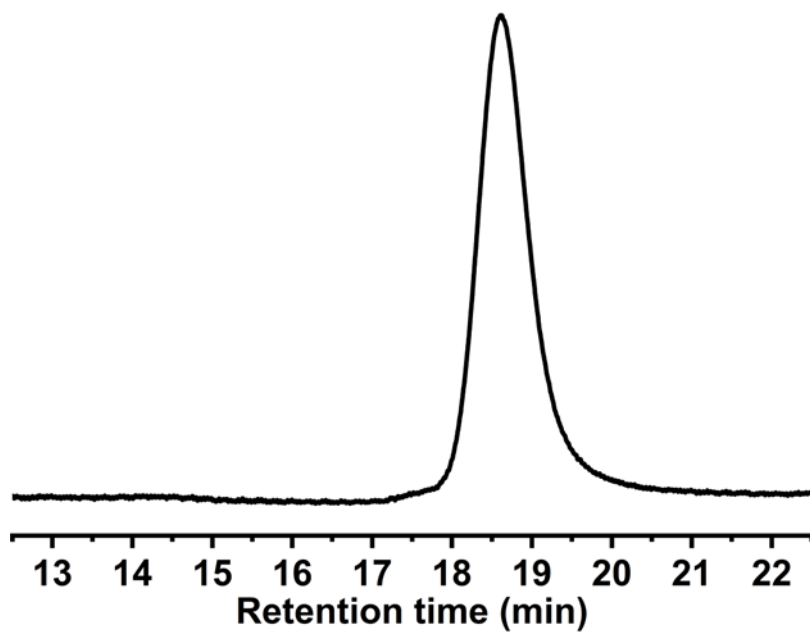


Figure S14. GPC spectrum of linear poly(Et-HL) initiated by NaOMe with $M_n = 31829 \text{ g mol}^{-1}$ $D = 1.05$ (Tabel 1, run 10).

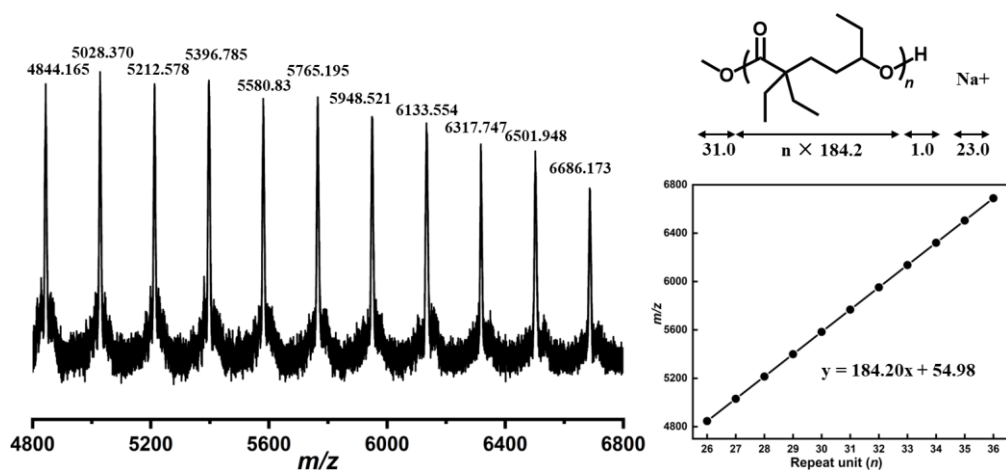


Figure S15. MALDI-TOF mass spectrum of linear poly(Et-HL) initiated by NaOMe.

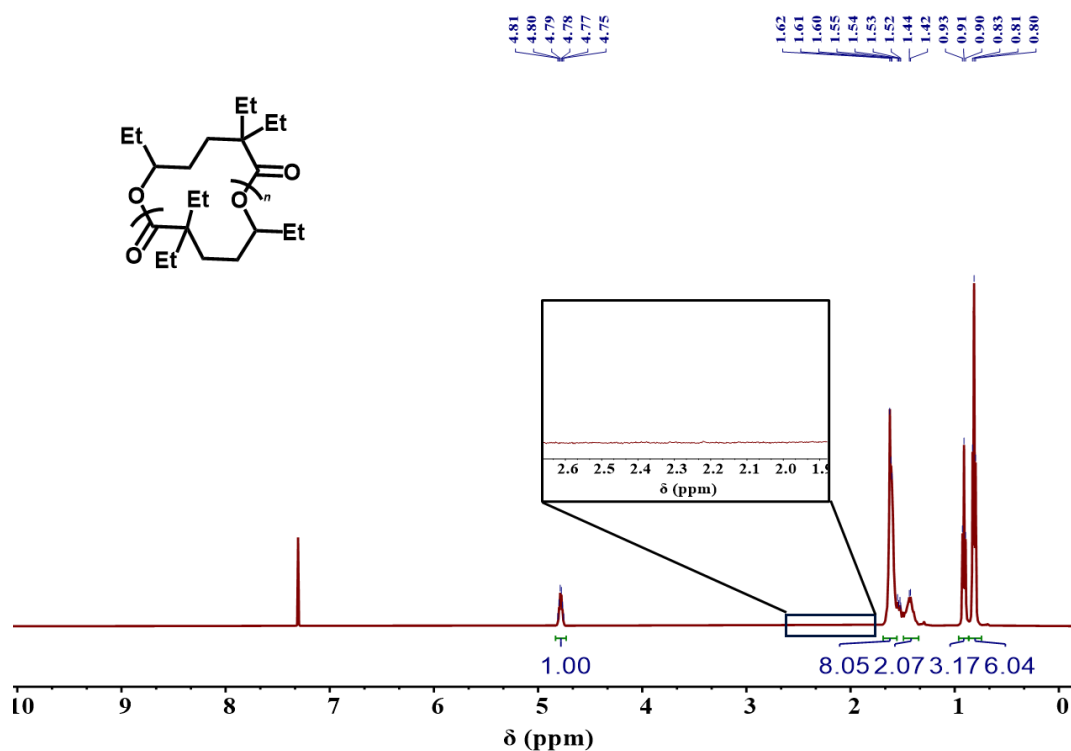


Figure S16. ^1H NMR spectrum of cyclic poly(Et-HL) (CDCl_3 , 500 MHz).

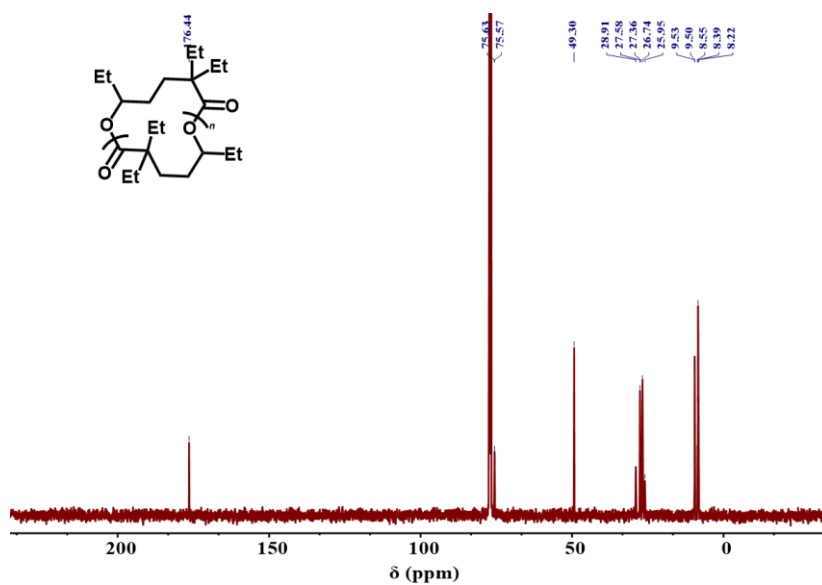


Figure S17. ^{13}C NMR spectrum of cyclic poly(Et-HL) (CDCl₃, 126 MHz).

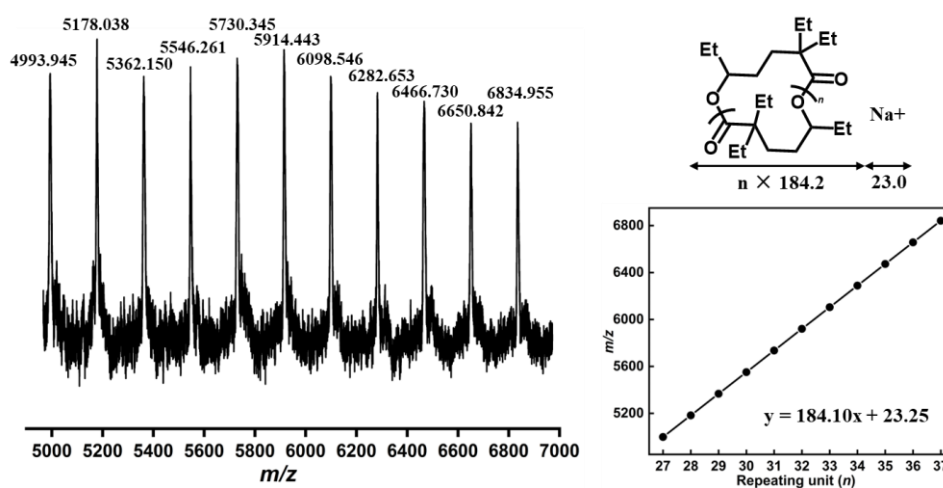


Figure S18. MALDI-TOF mass spectrum of cyclic poly(Et-HL).

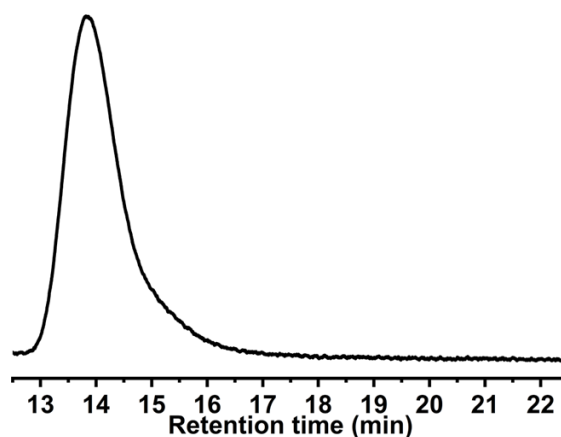


Figure S19. GPC spectrum of purified cyclic-poly(Et-HL) with $M_n = 1050 \text{ kg mol}^{-1}$ $D = 1.52$ (Tabel 1, run 15).

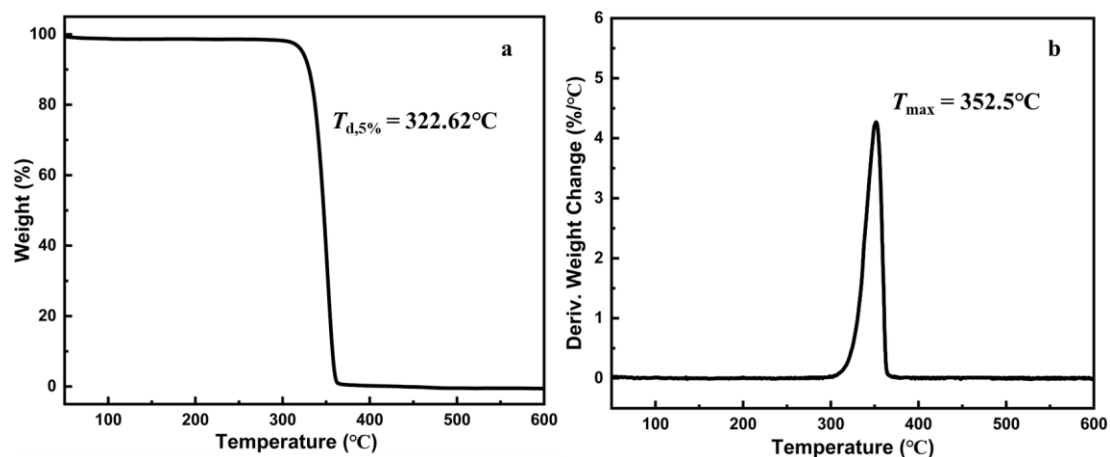


Figure S20. (a) TGA and (b) DTG of cyclic-poly(Et-HL).

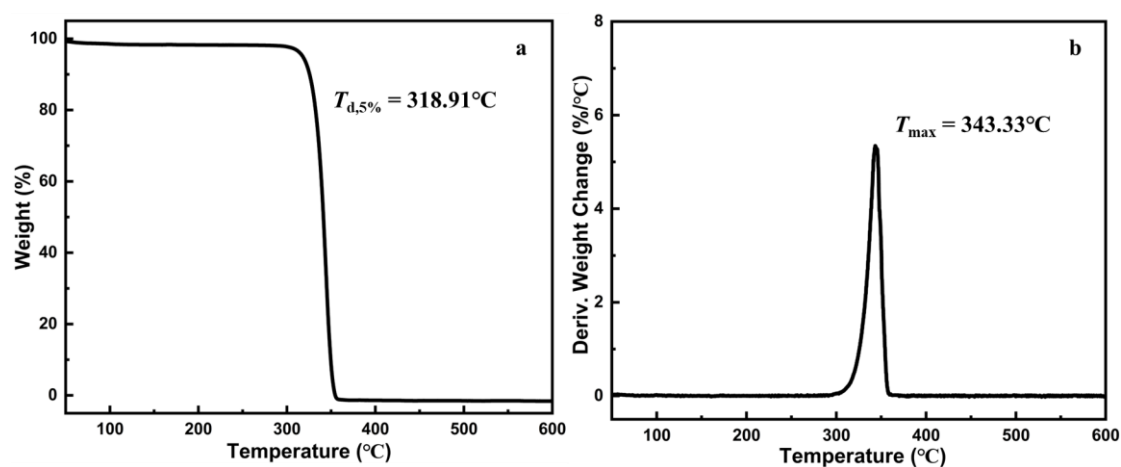


Figure S21. (a) TGA and (b) DTG of linear-poly(Et-HL).

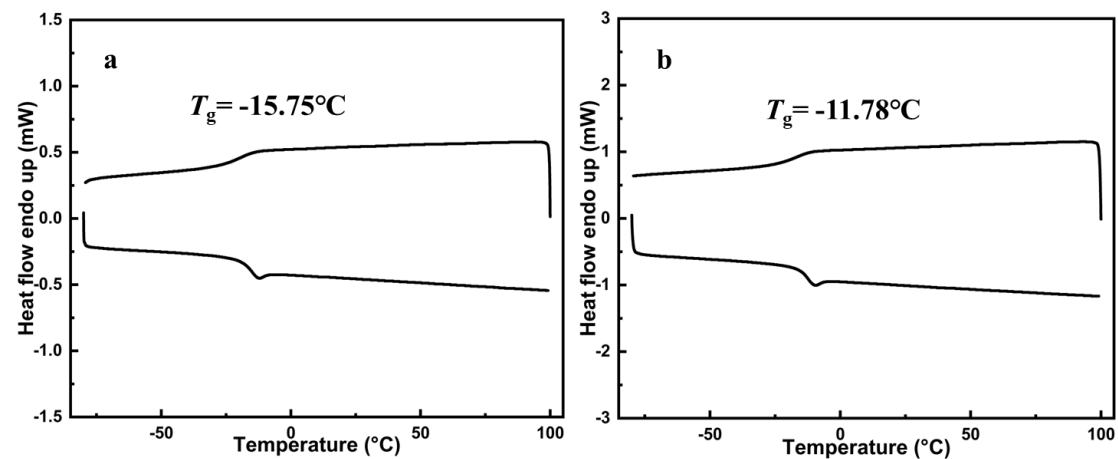


Figure S22. DSC curves of (a) linear-poly(Et-HL) and (b) cyclic-poly(Et-HL).

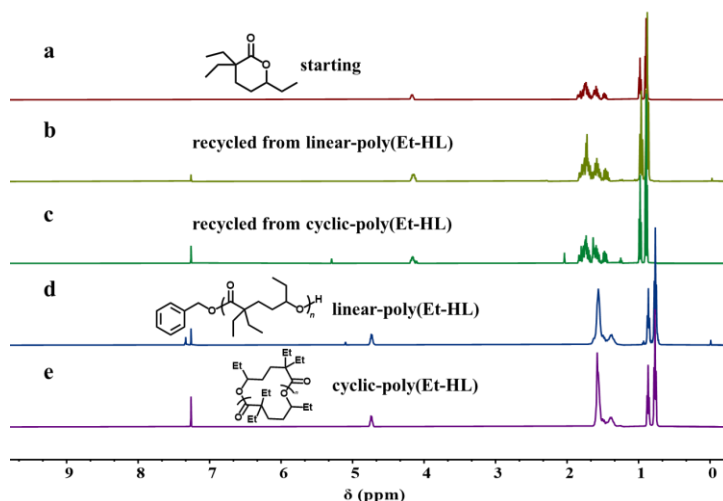


Figure S23. ^1H NMR spectrum of (a) Et-HL monomer; purified monomer from chemical recycling of (b) linear-poly(Et-HL) and (c) cyclic-poly(Et-HL) by 5 mol% $\text{Sc}(\text{CF}_3\text{SO}_3)_3$ at 120°C in toluene for 72 h; (d) linear-poly(Et-HL) synthesized by Et-HL/ $^t\text{Bu-P}_4$ /BnOH = 50/1/1 at -25°C in THF, $M_n = 9397 \text{ g mol}^{-1}$ and $D = 1.08$; (e) cyclic-poly(Et-HL) synthesized by Et-HL/ $^t\text{Bu-P}_4$ = 100/1/1 at -25°C in THF, $M_n = 166856 \text{ g mol}^{-1}$ and $D = 1.11$.

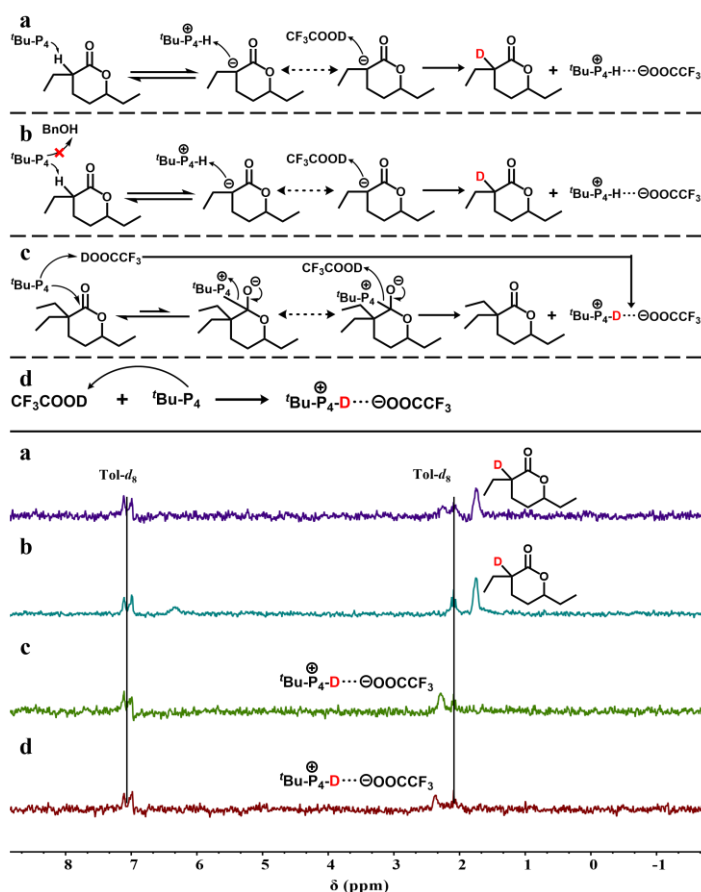


Figure S24. The reaction formula (left) and ^2H NMR spectra (right) of mechanism studies: (a) $\text{DEtP}/^t\text{Bu-P}_4 = 2/1$, quenched with 1 equiv. CF_3COOD ; (b) $\text{DEtP}/^t\text{Bu-P}_4/\text{BnOH} = 2/1/1$, quenched with 1 equiv. CF_3COOD ; (c) $\text{Et-HL}/^t\text{Bu-P}_4 = 2/1$, quenched with 1 equiv. CF_3COOD ; (d) $^t\text{Bu-P}_4/\text{CF}_3\text{COOD} = 1/1$. Reactions were conducted at -25°C and stirred for 10 mins. All four ^2H NMR spectra were obtained using toluene- H_8 as solvent and toluene- d_8 signals were detected and referenced at δ 2.09, 6.98, 7.00, 7.09 ppm in all ^2H NMR spectra.

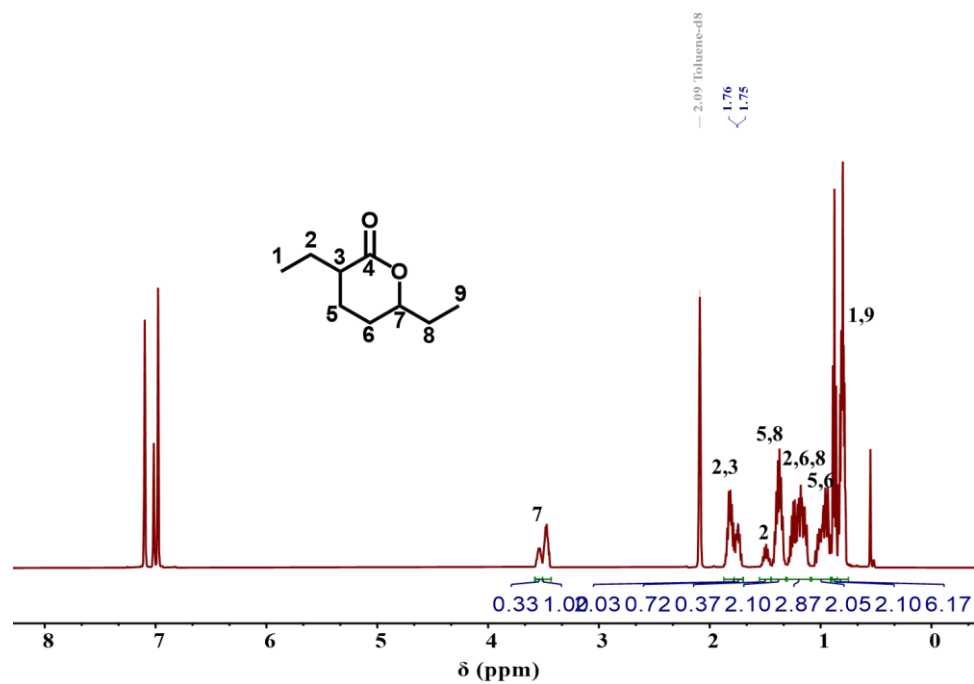


Figure S25. ^1H NMR spectrum of DETP in toluene- d_8 (CDCl_3 , 500 MHz).

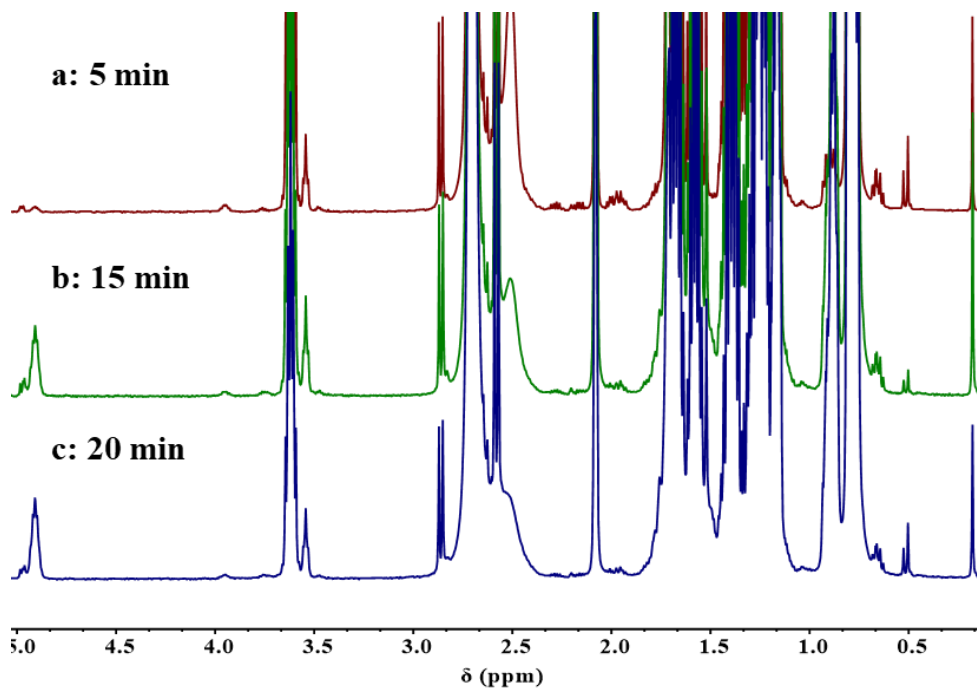


Figure S26. Full spectra of mechanism study at different reaction time (a) 5 mins; (b) 15 mins; (c) 20 mins under the feeding ratio of $[\text{Et-HL}]/[\text{Bu-P}_4] = 10/1$ without solution at -25°C .

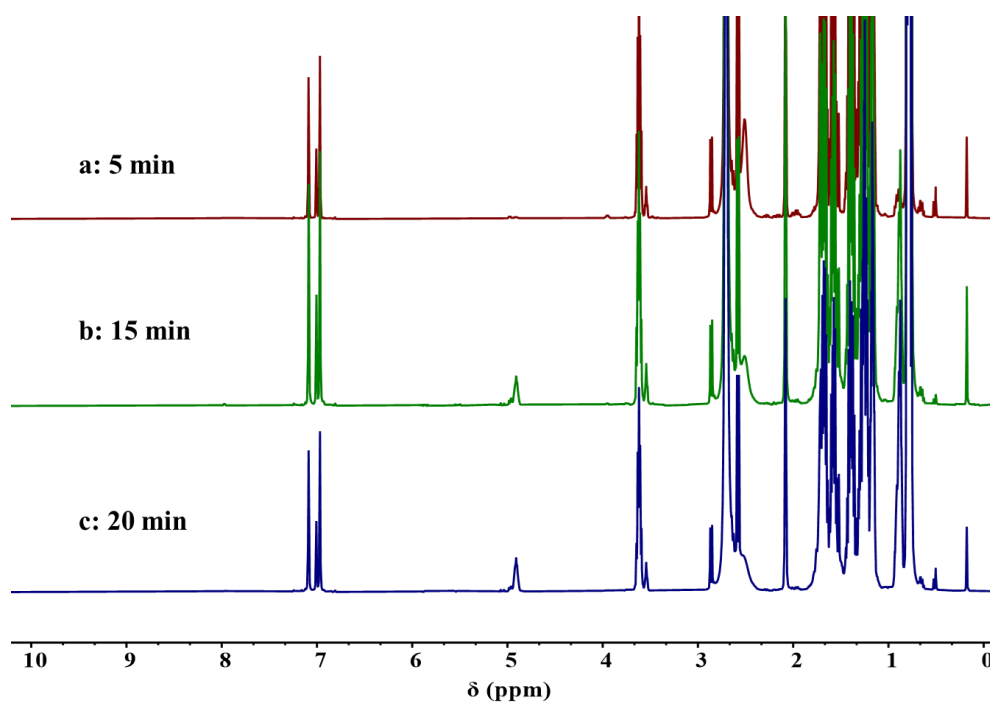


Figure S27. Enlarged spectrum of mechanism study at different reaction time (a) 5 mins; (b) 15 mins; (c) 20 mins at δ 0 – 5.0 ppm.

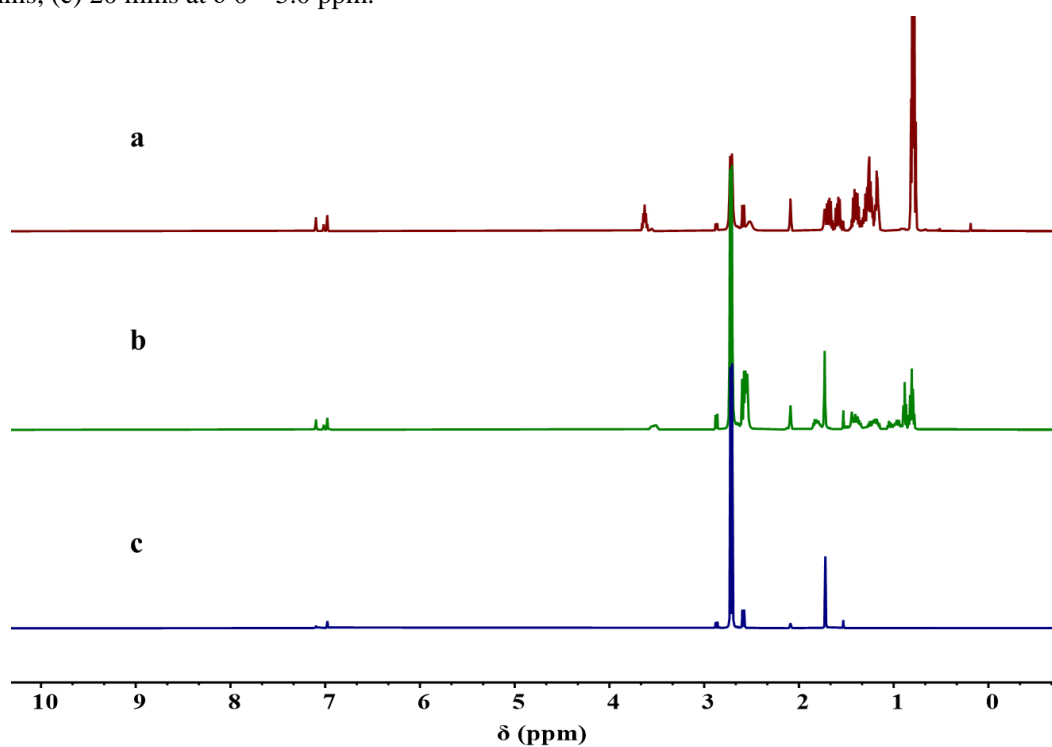


Figure S28. Full spectra of mechanism study at different reactions (a) $[\text{Et-HL}]/[\text{tBu-P}_4] = 10/1$, 10mins; (b) $[\text{DEtP}]/[\text{tBu-P}_4] = 10/1$, 10 mins; (c) tBu-P_4 alone in toluene- d_8 at -25°C .

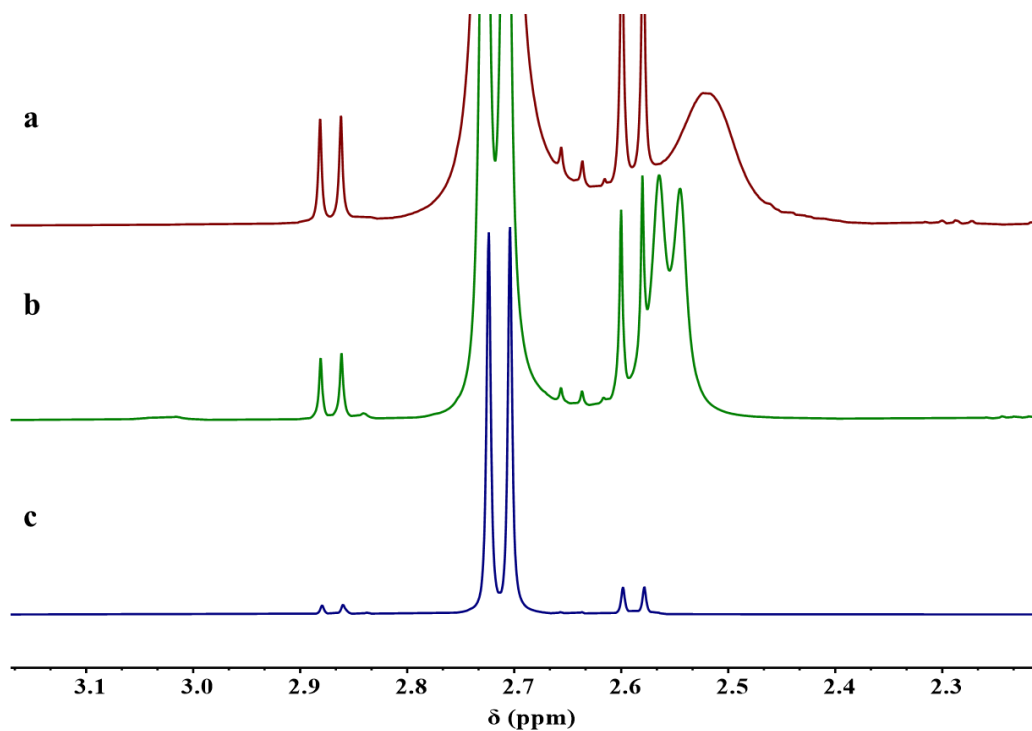


Figure S29. Enlarged spectra of mechanism study at different reactions (a) [Et-HL]/[^tBu-P₄] = 10/1, 10mins; (b) [DEtP]/[^tBu-P₄] = 10/1, 10 mins; (c) ^tBu-P₄ alone in toluene-*d*₈.

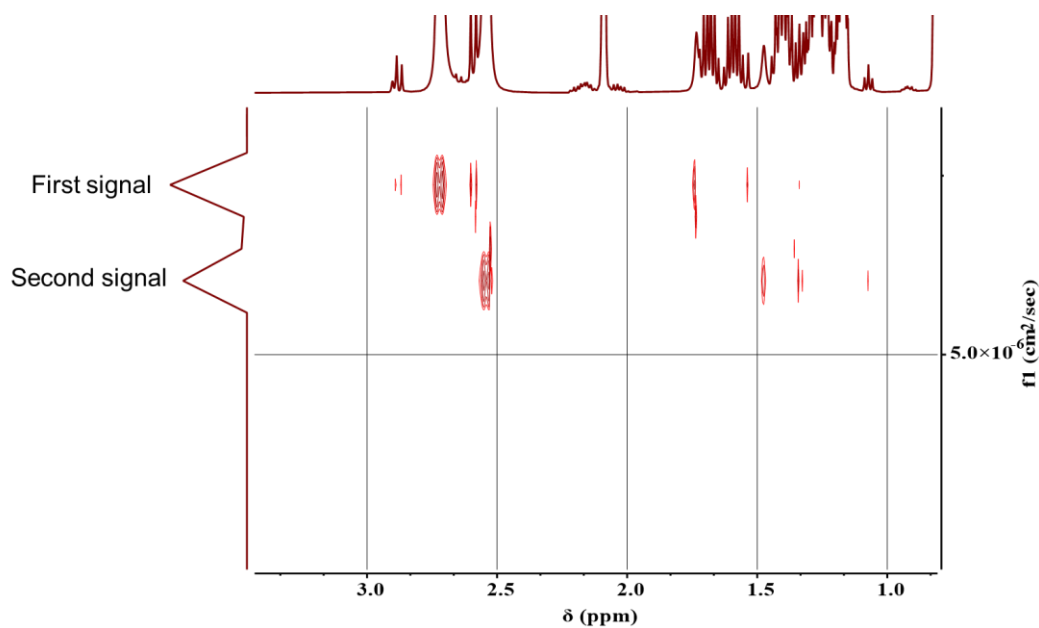


Figure S30. DOSY NMR spectrum of mechanism study under the feeding ratio of [Et-HL]/[^tBu-P₄] = 10/1, 10 mins, without solvent at -25°C. Toluene-*d*₈ was added after reaction. The first signal correlating to δ 2.70, 2.72 ppm, which was consistent with the ¹H NMR of the origin pure ^tBu-P₄. The second signal correlating to δ 2.52 ppm, which was excluded for monomer, BnOH or cyclic-poly(Et-HL), was considered as the novel catalytic species derived from ^tBu-P₄. The second signal was also correlating to δ 1.00 – 1.50 ppm along with δ 2.52 ppm.

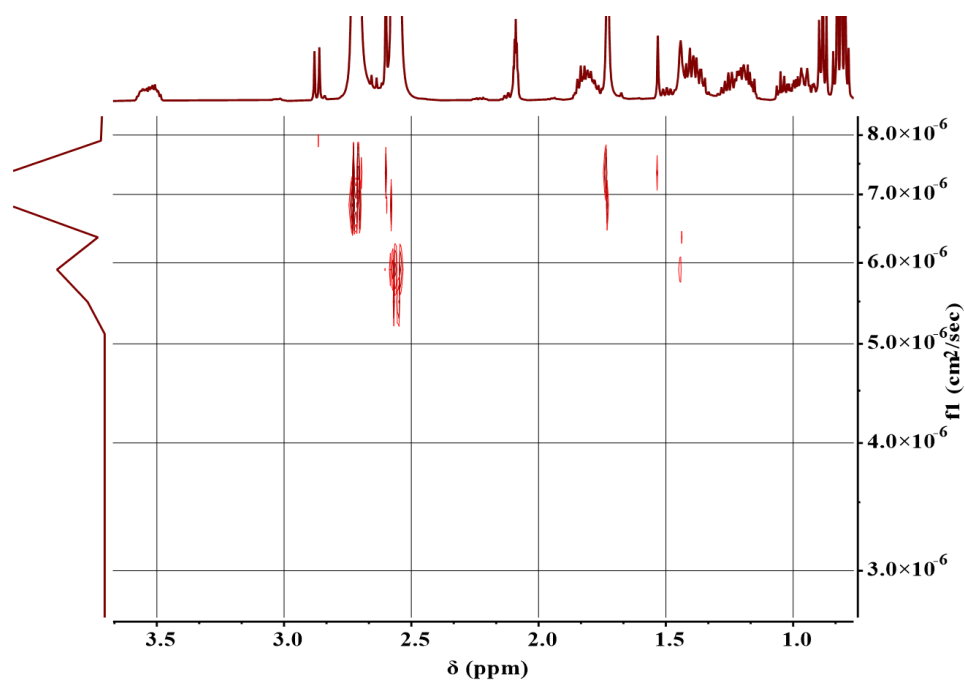


Figure S31. DOSY NMR spectrum of mechanism study under the feeding ratio of $[\text{DEtP}]/[\text{tBu-P}_4] = 10/1$, 10 mins, without solvent at -25°C . Toluene- d_8 was added after reaction.

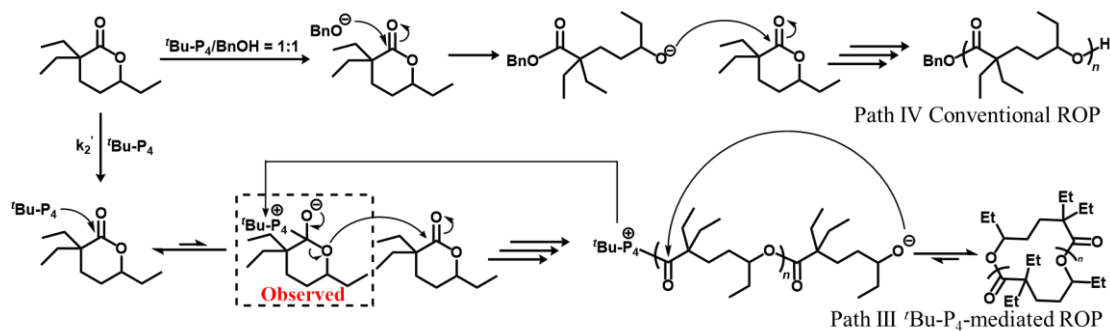


Figure S32. Proposed ROP mechanism of Et-HL using tBu-P_4 as the catalyst and BnOH as the initiator.

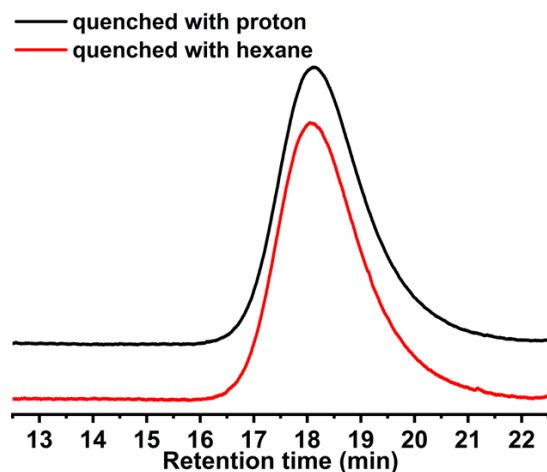


Figure S33. GPC spectrum comparison of cyclic polymers using active proton and hexane as quenching reagent (Table 1, runs 11, 12).

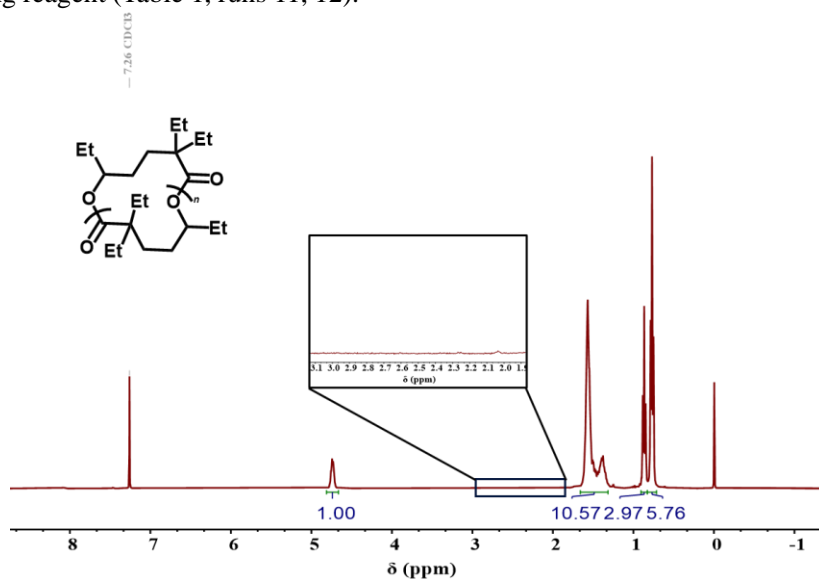


Figure 34. ^1H NMR spectrum of purified cyclic polymer using hexane as the quenching reagent (Table 1, run 12).

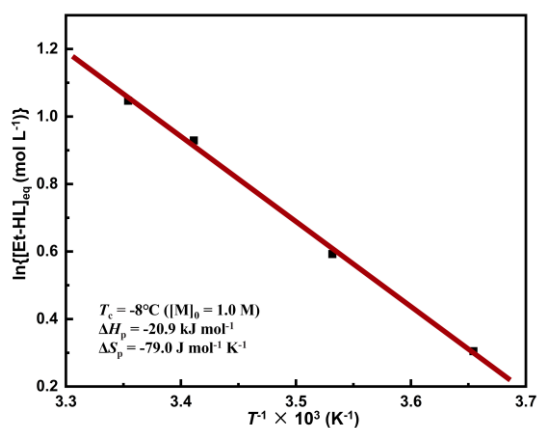


Figure S35. Van't Hoff plot of $\ln([\text{Et-HL}]_{\text{eq}})$ vs reciprocal of absolute temperature $T^{-1} \cdot 1000$ with $[\text{Et-HL}]/[\text{tBu-P}_4]/[\text{BnOH}] = 100/1/1$ at $[\text{Et-HL}]_0 = 4.5 \text{ mol L}^{-1}$ in THF. Detailed data was provided in Table S1.

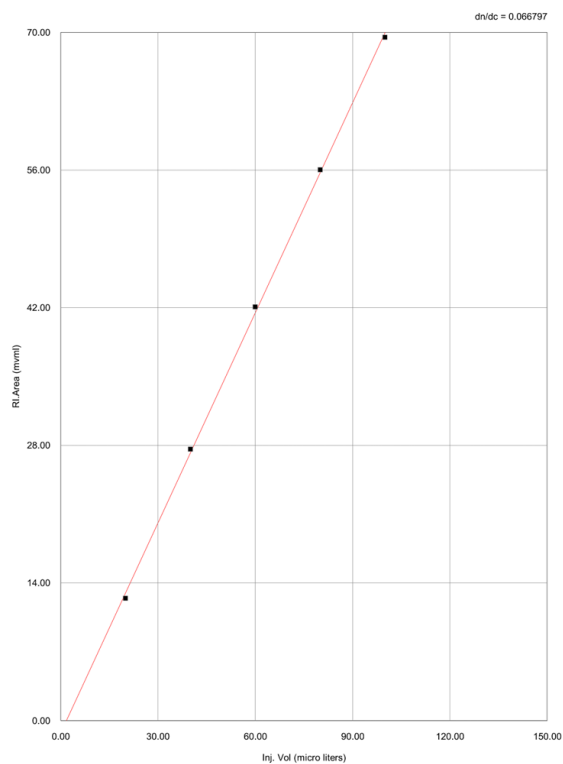


Figure S36. RI area vs injection volume plot used to measure dn/dc value for cyclic-poly(Et-HL) in THF. Calculated $dn/dc = 0.0668 \text{ mL g}^{-1}$.

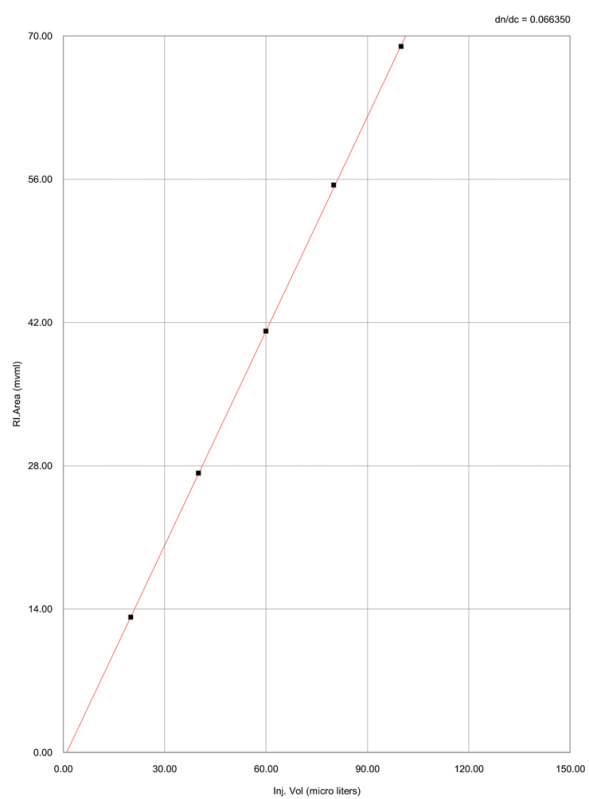


Figure S37. RI area vs injection volume plot used to measure dn/dc value for cyclic-poly(Et-HL) in THF. Calculated $dn/dc = 0.0664 \text{ mL g}^{-1}$.

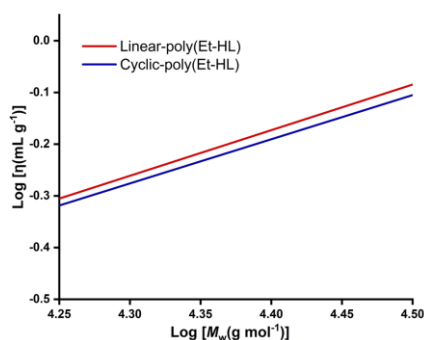


Figure S38. Mark–Houwink plot for linear- and cyclic-poly(Et-HL). Higher $[\eta]$ for the linear structure ($M_n = 20292 \text{ g mol}^{-1}$, $D = 1.12$, $\alpha = 0.88$) was observed (cyclic-poly(Et-HL), $M_n = 20614 \text{ g mol}^{-1}$, $D = 1.14$, $\alpha = 0.85$)

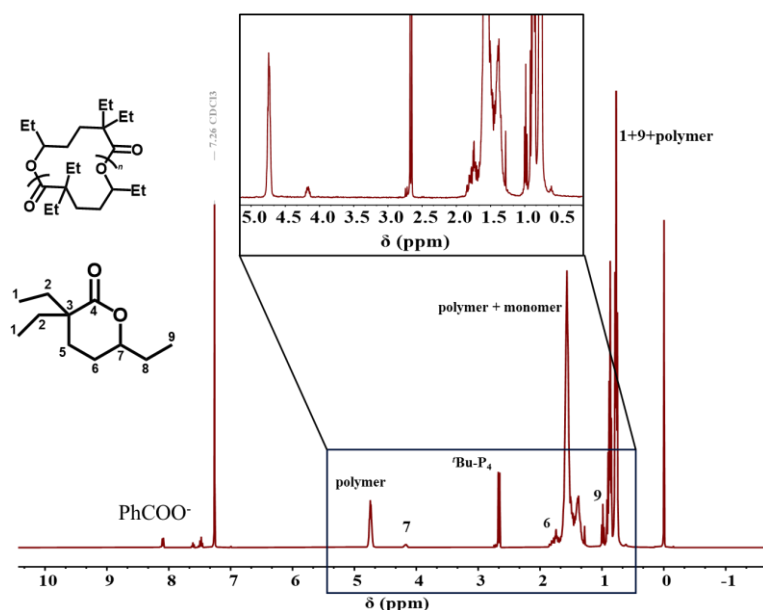


Figure S39. ^1H NMR spectrum of crude product using only $^t\text{Bu-P}_4$ as catalyst ($[\text{Et-HL}]/[^t\text{Bu-P}_4] = 100/1$ at $[\text{Et-HL}]_0 = 4.5 \text{ mol L}^{-1}$ in THF). All the signals in this spectrum can be corresponded to polymer, monomer or quenching agent. The enhanced figure provides a clearer view of this spectrum.

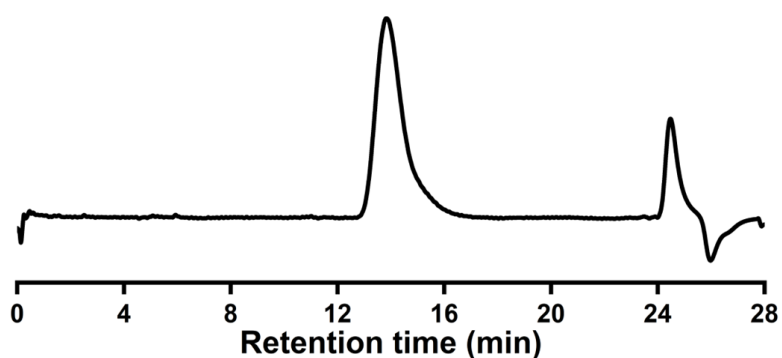


Figure S40. GPC spectrum of crude cyclic-poly(Et-HL) with $M_n = 1050 \text{ kg mol}^{-1}$ $D = 1.52$ (Tabel 1, run 15). The peak at 24.5 mins was the solvent signal from THF.

Table S1. Detailed plot data for Van't Hoff plot^a.

Temp. (K)	Conv. (%)	[Et-HL] ₀	[Et-HL] _{eq}	ln[Et-HL] _{eq}
273.65	70	4.52	1.36	0.30
283.15	60	4.52	1.81	0.59
293.15	44	4.52	2.53	0.93
298.15	37	4.52	2.85	1.04

a: Et-HL = 0.1000 g, (0.54 mmol). [Et-HL]/[^tBu-P₄]/[BnOH] = 100/1/1 in THF. The conversions in this table were confirmed repeatedly using ¹H NMR along the reaction time. The final conversions were determined when the conversion rate were identical for the last three times.

References

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