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Supplemental Information

Chemically recyclable polyesters

from CO₂, H₂, and 1,3-butadiene

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Materials and reagents

All reactions and manipulations of air- and moisture-sensitive materials were carried out in oven-dried glassware on a dual-manifold Schlenk line, or in a nitrogen-filled glovebox. Tetrahydrofuran (THF) was degassed and dried over CaH₂ for one day, followed by vacuum distillation, then dried over activated 4 Å molecular sieves for three times. Toluene was degassed and dried over Na for two days with benzophenone indicator, then vacuum distilled, followed by drying over activated 4 Å molecular sieves for three times. Other organic solvents employed were degassed and dried before use.

3,6-diethyltetrahydro-2H-pyran-2-one (**HL**) was dried over CaH₂ overnight, vacuum distilled and dried over activated 4 Å molecular sieves for three times for further use. Palladium on activated charcoal (Pd/C), Tris(dibenzylideneacetone)dipalladium [Pd₂(dba)₃] and tris(2-methoxyphenyl)phosphine (TOMPP) were purchased from Aladdin Reagent Co., Ltd., J&K Scientific Ltd., J&K Scientific Ltd. respectively, and used as received. 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylide-*namino*]-2λ⁵,4λ⁵-catenadi(phosphazene) (*t*Bu-P₄, 0.8 M in hexane), *tert*-Butylimino-tris(dimethylamino)phosphorane (*t*Bu-P₁) and 1-*tert*-butyl-2,2,4,4,4-pentakis-(dimethylamino)-2λ⁵,4λ⁵-catenadi(phosphazene) (*t*Bu-P₂, 2.0 M in THF) were purchased from Sigma Aldrich Co. Ltd., and the solvent were removed under vacuum prior to use. tri[*N,N*-bis(trimethylsilyl)amide] lanthanum(III) La[N(SiMe₃)₂]₃ (**La**) was purchased from Aldrich Chemical Co. and used as received. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), stannous octoate [Sn(Oct)₂], dibutyltin dilaurate (DBTDL) were purchased from TCI Co., Ltd., Aladdin Reagent Co., Ltd., Aladdin Reagent Co., Ltd., respectively, which were dried over activated 4 Å molecular sieves for further use. Diphenyl phosphate (DPP) was purchased from J&K Scientific Ltd., and used as received. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from TCI Co., Ltd., and used as received. Sodium methoxide (NaOMe), sodium ethoxide (NaOEt), sodium *tert*-butoxide (NaO*t*Bu) were purchased from TCI Co., Ltd.; potassium *tert*-butoxide (KO*t*Bu), lithium *tert*-butoxide (LiO*t*Bu) were purchased from J&K Scientific Ltd.; potassium methoxide (KOMe), potassium ethoxide(KOEt) and lithium methoxide (LiOMe) were purchased from Aladdin Reagent Co., Ltd., Shanghai Macklin Biochemical Technology Co. Ltd. and Adamas Reagent, Ltd., respectively, and all the alkali metal alkoxides were stored in a nitrogen-filled glovebox without further purification process.

General polymerization procedures

Polymerizations were performed in 10 mL oven-dried Schlenk tubes linked to a dual-manifold Schlenk line utilizing an external cooling bath. The Schlenk tube was charged with a predetermined amount of catalyst (and/or initiator) and solvent in a glovebox. The Schlenk tube was sealed with a septum, taken out of the glovebox, and the reaction started when immersing into the cooling bath. After equilibration at the desired polymerization temperature, the polymerization reaction was initiated by rapid addition of predetermined monomer solution via a gastight syringe. After a desired period of reaction time, the polymerization was quenched by addition of an excess methanol acidified with HCl (5%), a 0.05 mL of aliquot was taken from the reaction mixture and prepared for ¹H NMR analysis to obtain the monomer conversion data. The quenched mixture was then precipitated into 50 mL of cold methanol, and washed with methanol for several times to remove unreacted monomer and irrespective components, then dried in a vacuum oven at 80°C to a constant weight.

Thermodynamic studies

In a glovebox filled with nitrogen, an oven-dried 25 mL Schlenk tube was charged with **HL** monomer (50 equiv. to BnOH, 104.1 mg, 0.667 mmol). The Schlenk tube was sealed with rubber plug, taken out of the glovebox and immersed in the predetermined cooling/oil bath. After equilibration at the desired polymerization temperature, the polymerization was initiated by rapid addition of BnOH/*t*Bu-P₄ in THF at a ratio of 0.1/1 via a gastight syringe. After a desired period of polymerization time, the

mixture was quenched for ^1H NMR analysis. such parallel polymerization reactions at different temperatures gave respective $[\text{HL}]_{\text{eq}}$.

Kinetic studies

For kinetic studies, the dependence of monomer conversion at -25°C on polymerization time was determined by ^1H NMR. Several parallel polymerization reactions were conducted to avoid conversion systematic error induced by aliquot extraction. The ROP reactions with different $[\text{HL}]/[\text{tBu-P}_4]/[\text{BnOH}]$ ratios of 50/0.1/1 and 50/1/0 were carried out. $[\text{HL}]/[\text{tBu-P}_4]/[\text{BnOH}] = 50/0.1/1$: $\text{HL} = 104$ mg, $[\text{HL}]_0 = 5.3$ M in THF; $[\text{HL}]/[\text{tBu-P}_4]/[\text{BnOH}] = 50/1/0$: $\text{HL} = 104$ mg, $[\text{HL}]_0 = 4.0$ M in THF (See in Table S2 and S3).

Measurements of molecular weight and intrinsic viscosity

Polymer number-average molecular weights (M_n) and molecular weight distributions ($D = M_w/M_n$) were measured by gel permeation chromatography (GPC) analyses carried out at 40°C and a flow rate of 1.0 mL/min with THF as the eluent on a Malvern GPC TDA305 instrument with D6000M general mixed org columns. The instrument was calibrated with seven PMMA standards, and the calculation of chromatograms were processed with Malvern OmniSEC software (administrator, version 12.1).

Analysis of the selected *linear*- and *cyclic*-poly HL for the Mark-Houwink plot was performed on a Malvern Viscotek TDMax Multiple Detector (light scattering, refractive index, viscometer and ultra violet) GPC instrument. The test was carried out at 40°C and the flow rate was set 1.0 mL min^{-1} , the eluent was THF, and related calculations and chromatograms was processed with Malvern OmniSEC software (administrator, version 12.1).

Spectroscopic characterizations

The isolated low molecular weight sample was analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). The experiment was performed on a Bruker Autoflex Speed MALDI-TOF mass spectrometer (Bruker Daltonics) operated in positive ion, reflector mode. A thin layer of a 1% NaI solution was first deposited on the target plate, followed by an aliquot of 1.0 μL mixed sample and matrix solution (2,5-dihydroxybenzoic acid, DHB, 20 mg/mL in 50% THF, 0.1% TFA) before air dry. External calibration was done using a peptide calibration mixture on a spot next to the sample spot. The raw data was processed in the flexAnalysis software (version 3.4, Bruker Daltonics) and the figure was depicted in Origin Pro 2019b software.

NMR spectra were recorded on a Bruker ADVANCE III HD500 500 MHz (FT 500 MHz, H; 125 MHz, ^{13}C) or a Bruker ADVANCE III HD500 400MHz (FT 400 MHz, H; 100 MHz, ^{13}C) spectrometer. Chemical shifts for all spectra were referenced to internal solvent resonances and were reported as parts per million (ppm) relative to SiMe_4 .

Thermal analysis

The probing of Melting transition temperature (T_m) and glass transition temperature (T_g) were carried out by differential scanning calorimetry (DSC) on a DSC 8500 instrument, Perk Elmer. T_g values 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 $5^\circ\text{C}/\text{min}$. 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 8000 instrument, Perk Elmer. Polymer samples were heated from 30°C to 600°C at a rate of $10^\circ\text{C}/\text{min}$.

180° peel test

180° peel test was performed using an Instron 5966 universal testing instrument at a peeling rate of 10 mm/min. The high MW poly \mathbf{HL} sample was evenly coated on a smooth glass slide (2.5 cm width) and adhered to a slip of A4 paper (15 cm \times 2.5 cm) with a constant pressure provided by the same person. After incubation for 24h under constant temperature and humidity, the average peel force was collected and reported from three parallel samples. The poly \mathbf{HL} samples with different MW employed in the test were synthesized by $t\text{-Bu-P}_4$ alone at a ratio of $[\mathbf{HL}]/[t\text{-Bu-P}_4] = 100/1$ at -25°C in varied reaction time ($[\mathbf{HL}]_0 = 5.3 \text{ M}$).

The commercial 3M[®] 665, 810 and 1600 tapes employed in the control group were also adhered to the glass slides of the identical specification with a constant pressure provided by the same person. The average peel force was also collected and reported from three parallel samples made after incubation under the identical conditions.

General chemical recycling procedures

A sealed tube containing 500 mg of the purified poly \mathbf{HL} under a nitrogen atmosphere dissolved in predetermined solvents was subsequently sealed, taken out of the glovebox, and immersed in an oil bath. Then an aliquot of predetermined amount of catalyst solution was added into the tube via a gastight syringe. After a required period of time, the reaction mixture was rapidly cooled to room temperature and then the solvent was completely removed in vacuo. A colorless oil was formed and the \mathbf{HL} monomer recovery data was subsequently determined by crude ^1H NMR probing. Finally, the chemically recycled \mathbf{HL} monomer was further purified by column chromatography.

Procedure for the synthesis of 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one ($\delta\text{-L}$) from CO_2 and 1,3-butadiene

$\delta\text{-L}$ was synthesized according to the literature¹. To a 100 ml stainless steel autoclave with a magnetic stirring bar, $\text{Pd}_2(\text{dba})_3$ (156.7mg, 0.03 mol%), tris(2-methoxyphenyl)phosphine (TOMPP) (361.5 mg, 0.18 mol%) and 20 ml anhydrous acetonitrile were added into the vessel to form a clear solution. 1,3-butadiene (49 ml, 0.57 mol) was cooled into a pressure flask in advance, followed by added dropwise into the clear solution. The reaction mixture was subsequently stirred at -25°C under N_2 atmosphere, then 50 bar of CO_2 (99.99% purity) was inflated into the autoclave and heated at 80°C for 20 h. The obtained mixture was purified through column chromatography on silica gel with hexane/EtOAc ($v/v = 5/1$). Yellow oil was obtained after column chromatography, subsequently the product was further purified by vacuum distillation. ^1H NMR (500 MHz, Chloroform- d) δ 7.13 (qt, $J = 7.1, 2.3 \text{ Hz}$, 1H), 5.88 (ddd, $J = 16.8, 10.6, 5.4 \text{ Hz}$, 1H), 5.34 (dt, $J = 17.2 \text{ Hz}$, 1H), 5.23 (d, $J = 10.6 \text{ Hz}$, 1H), 4.77 (m, 1H), 2.59 (m, 1H), 2.43 (s, 1H), 2.05 (m, 1H), 1.82 – 1.70 (m, 4H). ^{13}C NMR (125 MHz, Chloroform- d) δ 166.28, 141.19, 135.78, 125.88, 116.85, 78.91, 27.55, 21.91, 14.10

Procedure for the synthesis of 3,6-diethyltetrahydro-2H-pyran-2-one (\mathbf{HL}).

$\delta\text{-L}$ (3.11 g, 20.4 mmol), THF (25 ml) and Pd/C (28.8 mg, 5 wt% of Pd) were added into a 100 ml stainless steel autoclave with a magnetic stirring bar, under N_2 atmosphere. 30 bar of H_2 was inflated into the autoclave and the suspension was stirred at 60°C for 2 h. After removal of the solvent, the obtained mixture was purified by chromatography and vacuum distillation. The obtained \mathbf{HL} was a colorless liquid (isolated yield $\sim 80\%$). ^1H NMR (500 MHz, Chloroform- d) δ 4.20 – 4.07 (m, 1H), 2.39 – 2.20 (m, 1H), 2.09 – 1.75 (m, 3H), 1.60 – 1.33 (m, 5H), 0.98 – 0.86 (m, 6H). ^{13}C NMR (125 MHz, Chloroform- d , data in parentheses refer to the diastereomer signal with relatively low chemical shift) δ 175.70 (173.82), 85.52 (79.24), 42.06 (39.63), 29.10 (28.24), 28.27 (26.21), 24.84 (23.81), 24.81 (22.84), 11.54 (11.00), 9.53 (9.19).

Computational Methods

The quantum-mechanical calculations (Gaussian 09, Revision E.01) were performed at the level of b3lyp/AUG-cc-pVTZ to gain the stability property of four deprotonated-HL structures. Solvent effects (tetrahydrofuran (THF)) were further calculated by SMD method. The results were summarized in Table S12. The reactions in Figure S20 were calculated with 6-31+g* basis set followed by solvation corrections in THF at the level of b3lyp/6-311+g**.

Table S1. Results of ROP of **HL** catalyzed by varied common ROP catalytic systems.

Run	HL/Cat. /BnOH	Cat.	[M] ₀ (mol/L)	Temp. (°C)	Time (h)	Solvent	Conv. ^b (%)	M _n ^c (g mol ⁻¹)	Đ ^c
1	40/1/1	Sn(oct) ₂	neat	60	48	-	-	-	-
2	80/1/2	Sn(oct) ₂	neat	100	24	-	-	-	-
3	40/1/1	DBTDL	5.0	-25	48	TOL	-	-	-
4	80/1/2	DBTDL	neat	100	24	-	-	-	-
5	30/1/1	DPP	neat	-25	24	-	4	-	-
6	30/1/1	DPP	neat	25	24	-	7	-	-
7	30/1/1	DPP	neat	80	24	-	11	-	-
8	40/1/1	DBU	neat	30	96	-	3	-	-
9	40/1/1	TBD	neat	30	96	-	54	6010	1.14
10	40/1/1	TBD	5.0	30	96	THF	37	5596	1.18
11	40/1/1	TBD	4.0	30	96	THF	19	-	-
12	40/1/1	TBD	3.0	30	96	THF	9	-	-
13	40/1/1	TBD	2.0	30	96	THF	4	-	-

^aConditions: **HL** = 0.10 g (0.67 mmol), the catalyst amount varied according to **[HL]/[Cat.]** ratios; ^bConversion determined by ¹H NMR spectroscopy. ^cM_n and Đ determined by GPC at 40°C in THF relative to PMMA standards.

Table S2. Kinetic studies of ROP results of **HL** catalyzed by ^tBu-P₄/BnOH system^a.

Time (h)	Conv. (%)	M _n (g mol ⁻¹)	Đ	[M] _t (mol/L)	ln([M] ₀ /[M] _t)	[M] ₀ /[M] _t
0	0	0	0.00	5.26	0	1
0.083	8	546	1.10	4.84	0.083382	1.086957
0.167	10	763	1.12	4.74	0.105361	1.111111
0.3	21	2114	1.11	4.16	0.235722	1.265823
0.467	41	4201	1.09	3.11	0.527633	1.694915
0.667	57	6984	1.08	2.26	0.84397	2.325581
0.833	65	7856	1.09	1.84	1.049822	2.857143
0.917	68	8360	1.08	1.68	1.139434	3.125
1	72	7717	1.08	1.47	1.272966	3.571429
2	79	9064	1.08	1.11	1.560648	4.761905
4	84	9134	1.08	0.84	1.832581	6.25
8	88	9154	1.09	0.63	2.120264	8.333333

^aConditions: **[HL]/[^tBu-P₄]/[BnOH]** = 50/0.1/1, **[HL]₀** = 5.3 M in THF, T = -25°C. Parallel polymerization reactions were conducted to avoid conversion systematic error induced by aliquot extraction.

Table S3. Results of ROP of **HL** by PBs alone^[a].

Run	HL/Cat.	Cat.	Conv ^[b] . (%)	M_n ^[c] (kg mol ⁻¹)	\mathcal{D} ^[c]
1	50/1	^t Bu-P ₁	n.d.	-	-
2	50/1	^t Bu-P ₂	n.d.	-	-
3	50/1	^t Bu-P ₄	88	613.8	1.45
4	100/1	^t Bu-P ₄	87	571.5	1.40
5	150/1	^t Bu-P ₄	87	543.4	1.40
6	200/1	^t Bu-P ₄	72	598.8	1.35

[a] Conditions: **HL** = 0.104 g, (0.67 mmol) in THF ($[\mathbf{HL}]_0 = 5.3$ M) at -25°C; **HL** was dissolved in THF first, followed by addition of PBs; reaction time = 12 h. [b] Monomer conversion were measured by ¹H NMR. [c] M_n and \mathcal{D} were determined by GPC at 40°C in THF relative to PMMA standards.

Table S4. Kinetic studies of ROP results of **HL** catalyzed by ^tBu-P₄ alone^a.

Time (h)	Conv. (%)	M_n (kg mol ⁻¹)	\mathcal{D}	$[\mathbf{M}]_t$ (mol/L)	$\ln([\mathbf{M}]_0/[\mathbf{M}]_t)$	$[\mathbf{M}]_0/[\mathbf{M}]_t$
0.183	9	36.5	1.11	3.64	0.094311	1.098901
0.267	10	39.2	1.15	3.60	0.105361	1.111111
0.5	11	55.5	1.17	3.56	0.116534	1.123596
1	14	80.8	1.19	3.44	0.150823	1.162791
2	26	166.3	1.26	2.96	0.301105	1.351351
2.5	33	199.6	1.31	2.68	0.400478	1.492537
3	39	254.5	1.32	2.44	0.494296	1.639344
4	63	396.2	1.35	1.48	0.994252	2.702703
7	75	502.2	1.45	1.00	1.386294	4
10	84	507.8	1.54	0.64	1.832581	6.25
12	84	495.7	1.59	0.64	1.832581	6.25

^aConditions: $[\mathbf{HL}]/[\sup{t}\text{Bu-P}_4] = 50/1$, $[\mathbf{HL}]_0 = 4.0$ M in THF, $T = -25^\circ\text{C}$. Parallel polymerization reactions were conducted to avoid conversion systematic error induced by aliquot extraction.

Table S5. Results of ROP of **HL** initiated by varied alkali metal alkoxides^a.

Run	Initiator	HL/Initiator	Time (h)	Conv. ^b (%)	M_n ^c (kg mol ⁻¹)	\mathcal{D} ^c
1	KOMe	50/1	48	88	330.0	1.17
2	NaOMe	50/1	48	89	174.9	1.18
3	KOEt	50/1	48	88	98.3	1.07
4	NaOEt	50/1	48	87	180.1	1.15
5	KO ^t Bu	50/1	48	83	27.8	1.39
6	NaO ^t Bu	50/1	48	87	25.8	1.33
7	LiO ^t Bu	50/1	48	16	-	-
8	LiOMe	50/1	48	-	-	-
9	KOMe	20/1	48	89	258.8	1.30
10	KOMe	100/1	48	89	423.6	1.28
11	KOMe	200/1	48	87	475.7	1.24

^aConditions: all polymerizations were conducted in THF at -25°C, **HL** = 0.104 g (0.67 mmol), $[\mathbf{HL}]_0 = 5.0$ M. ^bmonomer conversion, determined by ¹H NMR. ^c M_n and dispersity were determined by GPC equipped with RI and MALLS detector at 40°C in THF relative to PMMA standards.

Table S6. Results of the 180° peel test for polyHL with different MW and commercial 3M® tapes^a.

	polyHL_562	polyHL319	polyHL_160	3M® 665	3M® 810	3M® 1600
Peel strength_1 ^b (N/cm)	3.280	3.926	1.217	2.544	1.547	0.6220
Peel strength_2 ^b (N/cm)	3.667	3.694	2.241	2.746	1.853	0.8250
Peel strength_3 ^b (N/cm)	3.586	3.756	1.025	1.976	2.175	0.9572
Avg. peel strength (N/cm)	3.51	3.79	1.49	2.42	1.86	0.80
Standard deviation	0.20	0.12	0.65	0.40	0.31	0.17

Note: ^aProcedures of 180° peel test can be seen above. ^bThree parallel experiments were carried out to calculate the average peel strength and standard deviation.

Table S7. Monomer concentration as a function of time at different temperature^a.

Time (h)	-25°C		Time (h)	-16°C		Time (h)	-9°C	
	Conv.(%)	[HL] _t		Conv.(%)	[HL] _t		Conv.(%)	[HL] _t
1	72	1.47	1	71	1.53	1	78	1.16
4	74	0.84	4	83	0.89	4	82	0.95
8	88	0.63	8	86	0.74	8	82	0.95
12	88	0.63	12	86	0.74	12	82	0.95

^aConditions: HL = 0.104 g, [HL]/[^tBu-P₄]/[BnOH] = 50/0.1/1, [HL]₀ = 5.3 M in THF.

Table S7 continued. Monomer concentration as a function of time at different temperature^a.

Time (h)	28°C		Time (h)	41°C	
	Conv.(%)	[HL] _t		Conv.(%)	[HL] _t
1	64	1.89	1	53	2.47
4	64	1.89	4	53	2.47
8	64	1.89	8	52	2.53
12	65	1.84	12	52	2.53

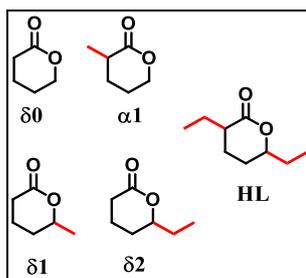
^aConditions: HL = 0.104 g, [HL]/[^tBu-P₄]/[BnOH] = 50/0.1/1, [HL]₀ = 5.3 M in THF.

Table S8. Monomer concentration as a function of time at different temperature.

Temp (°C)	Conv. _{eq} (%)	[HL] ₀	[HL] _{eq}	ln[HL] _{eq}
-25	88	5.26	0.63	-0.46
-16	86	5.26	0.74	-0.05
-9	82	5.26	0.95	0.61
28	65	5.26	1.84	0.93
41	52	5.26	2.53	-0.31

Table S9. Summary of the change of enthalpy, change of entropy and T_c of the ROP of 6-membered alkyl-substituted lactones.

Monomer	ΔH_p° (kJ/mol)	ΔS_p° (J mol ⁻¹ K ⁻¹)	$[M]_0$	T_c (°C)	Reference
HL	-13.1	-49.1	1.0 M	-5.9	This work
$\delta 0$	-8.4	-14.7	1.0 M	158	2
$\alpha 1$	-13.0	-34	1.0 M	109	3
$\delta 1$	-19.3	-62	1.0 M	38	3
$\delta 2$	-16.4	-55	1.0 M	25	3



Note: the thermodynamic parameters for **HL** and **$\delta 0$** were acquired in solution polymerization, whereas those of **$\alpha 1$** , **$\delta 1$** and **$\delta 2$** were calculated in bulk polymerization, which cannot be compared directly, because of the effect of solvation. Furthermore, the ceiling temperature of varied monomers calculated were merely a result of linear extrapolation according to Dainton's equation. However, we suppose that the results can provide theoretical guidance to better understand the trend how alkyl substituents effect the ROP thermodynamics for different monomers.

Table S10. Results of chemical recycling of **polyHL**^a.

Run	Cat.	Temp. (°C)	Time (h)	Solvent	HL Recovery ^b (%)
1	AgCF ₃ SO ₃	120	24	TOL	-
2	Cu(CF ₃ SO ₃) ₂	120	24	TOL	-
3	Fe(CF ₃ SO ₃) ₃	120	24	TOL	53
4	Sc(CF ₃ SO ₃) ₃	120	24	TOL	27
5	Y(CF ₃ SO ₃) ₃	120	24	TOL	-
6	FeCl ₂	150	12	mesitylene	21
7	Fe(acac) ₂	150	12	mesitylene	-
8	Sn(Oct) ₂	150	12	mesitylene	5
9	DBTDL	150	12	mesitylene	-
10	^t Bu-P ₄	150	12	mesitylene	-
11	ZnCl ₂	130	12	TOL	31
12	ZnCl ₂	140	12	TOL	39
13	ZnCl ₂	150	12	TOL	54
14	ZnCl ₂	150	12	<i>o</i> -DCB ^c	91
15	ZnCl ₂	160	12	<i>o</i> -DCB ^c	100

^aConditions: the chemical recycling procedures were performed in the presence of a catalyst (5.0 mol%) under nitrogen atmosphere. $[HL]_0 = 0.5$ M; polyHL samples employed were cyclic polymers with M_n in a range of 300-400 kg mol⁻¹. ^bHL recovery was determined by ¹H NMR; ^c*o*-DCB = 1,2-dichlorobenzene.

Table S11. Results of chemical recycling of **polyHL** by La catalyst^a.

Run	Cat.	Temp. (°C)	[HL] ₀ (mol/L)	Time (h)	Solvent	HL Recovery ^b (%)
1	La[N(SiMe ₃) ₂] ₃	50	0.5	3	TOL	47
2	La[N(SiMe ₃) ₂] ₃	50	0.5	12	TOL	81
3	La[N(SiMe ₃) ₂] ₃	50	0.5	24	TOL	88
4	La[N(SiMe ₃) ₂] ₃	50	0.1	3	TOL	34
5	La[N(SiMe ₃) ₂] ₃	50	0.1	24	TOL	87
6	La[N(SiMe ₃) ₂] ₃	80	0.5	3	TOL	85
7	La[N(SiMe ₃) ₂] ₃	80	0.5	12	TOL	85
8	La[N(SiMe ₃) ₂] ₃	80	0.1	3	TOL	93
9	La[N(SiMe ₃) ₂] ₃	80	0.1	12	TOL	100

^aConditions: the chemical recycling procedures were performed in the presence of **La** (3.0 mol%) under nitrogen atmosphere. **polyHL** samples employed were cyclic polymers with M_n in a range of 300-400 kg mol⁻¹. ^b**HL** recovery was determined by ¹H NMR.

Table S12. Verification of the effect of the water content and competitive initiation of the ROP system

Run	HL/Cat./Ini.	Catalyst	Initiator	Temp.(°C)	Time (h)	[HL] ₀ (M)	Conv. ^[d] (%)	M_n ^[e] (g mol ⁻¹)	\mathcal{D} ^[e]
1 ^[a]	40/1/0	^t Bu-P ₄	–	-25	12	5.3	0	–	–
2 ^[b]	80/1/1	^t Bu-P ₄	BnOH	-25	12	5.3	21	17938	2.26
3 ^[c]	50/0/1	–	PhCOOK	-25	24	5.0	0	–	–
4 ^[c]	50/0/1	–	HCOOCs	-25	24	5.0	0	–	–
5 ^[c]	50/0/1	–	KOAc	30	24	5.0	0	–	–
6 ^[c]	50/0/(1/1)	–	KOAc/BnOH	30	24	5.0	0	–	–

Conditions: ^[a] the **HL** utilized was directly used without any drying procedures. ^[b] The water content of **HL** was deliberately controlled at ~100 ppm. ^[c] The **HL** was rigorously dried prior to use. ^[d] Monomer conversion were measured by ¹H NMR. ^[e] M_n and \mathcal{D} were determined by GPC at 40°C in THF relative to PMMA standards.

Table S13. Calculated energy data of four deprotonated-HL structures (G: Sum of electronic and thermal Free Energies. H: Sum of electronic and thermal Enthalpies. HF: Sum of electronic and zero-point Energies).

Gas	CO-H-OR	CO-H-OS	O-H-COR	O-H-COS
G	-502.478557	-502.473909	-502.436561	-502.439019
H	-502.427549	-502.423121	-502.385515	-502.388633
HF	-502.663531	-502.659301	-502.620766	-502.623949
G-HF	0.184974	0.185392	0.184205	0.184930
H-HF	0.235982	0.236180	0.235251	0.235316
THF	CO-H-OR-thf	CO-H-OS-thf	O-H-COR-thf	O-H-COS-thf
HF	-502.737671	-502.733974	-502.694545	-502.696591
G	-502.552697	-502.548582	-502.510340	-502.511661
H	-502.501689	-502.497794	-502.459294	-502.461275

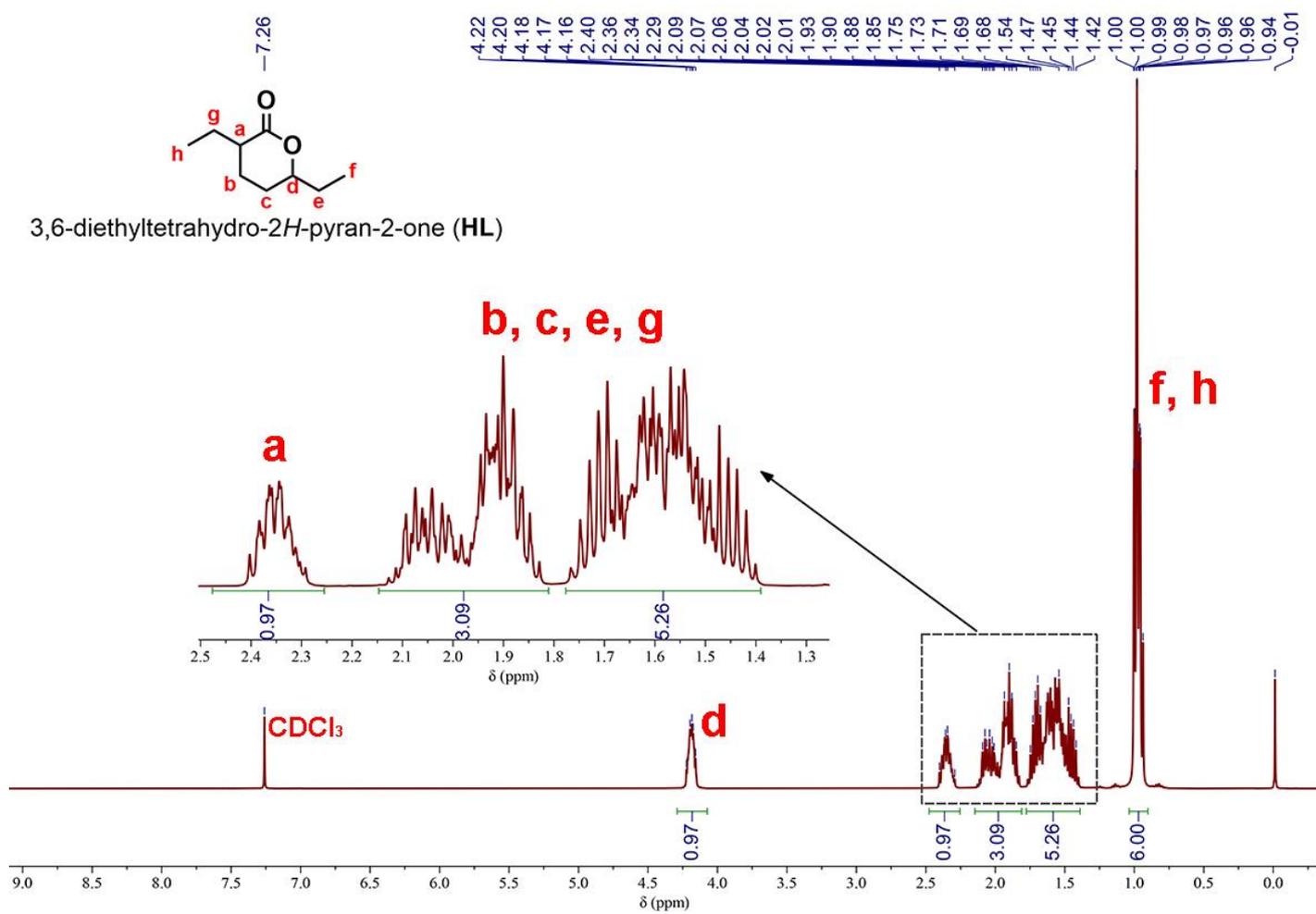


Figure S1. ¹H NMR spectrum of **HL** monomer (CDCl₃, 500 MHz, 25°C).

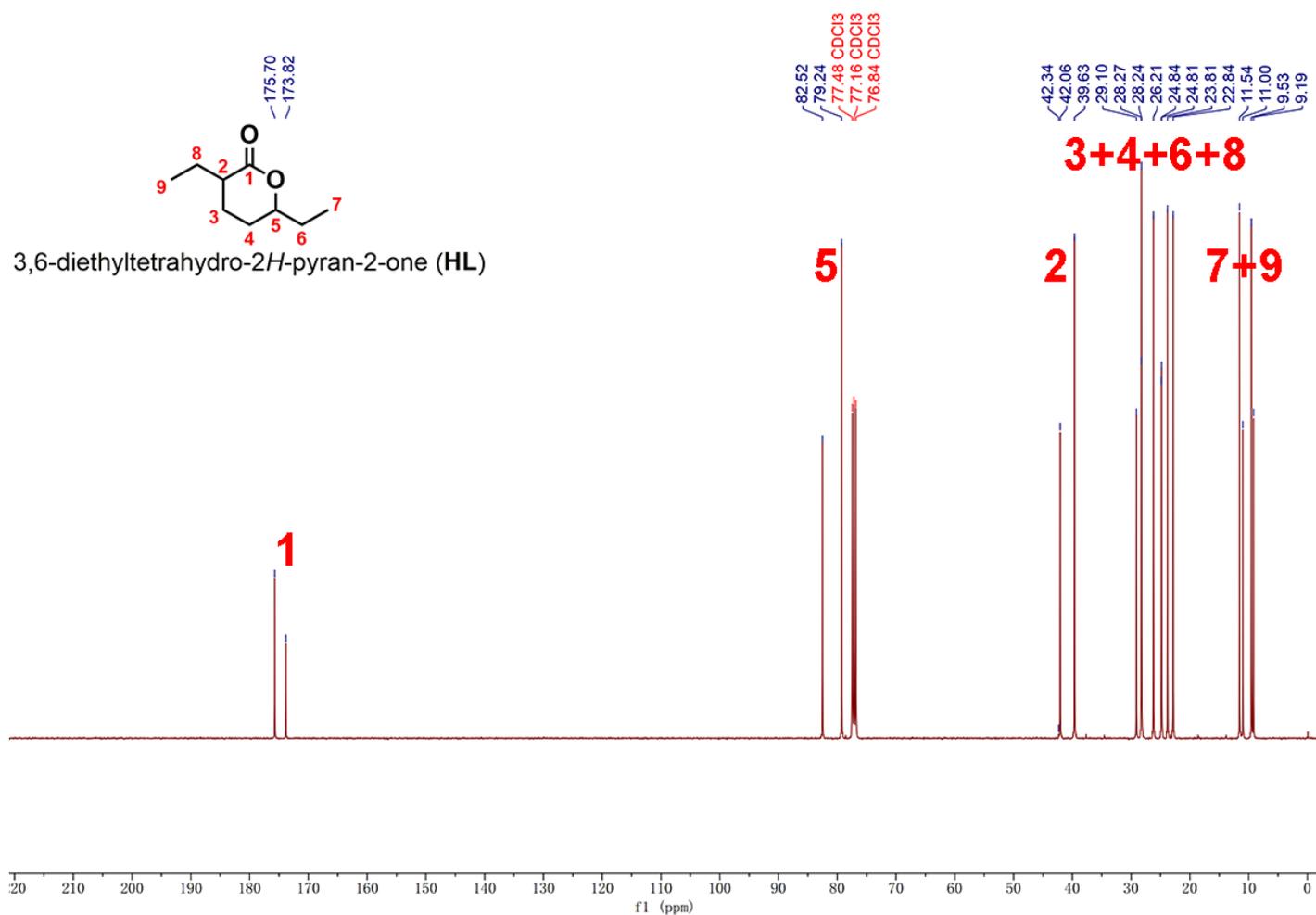


Figure S2. ¹³C NMR spectrum of **HL** monomer (CDCl₃, 125 MHz, 25°C). The **HL** obtained was a 63/37 diastereomeric mixture according to the ¹³C NMR spectrum.

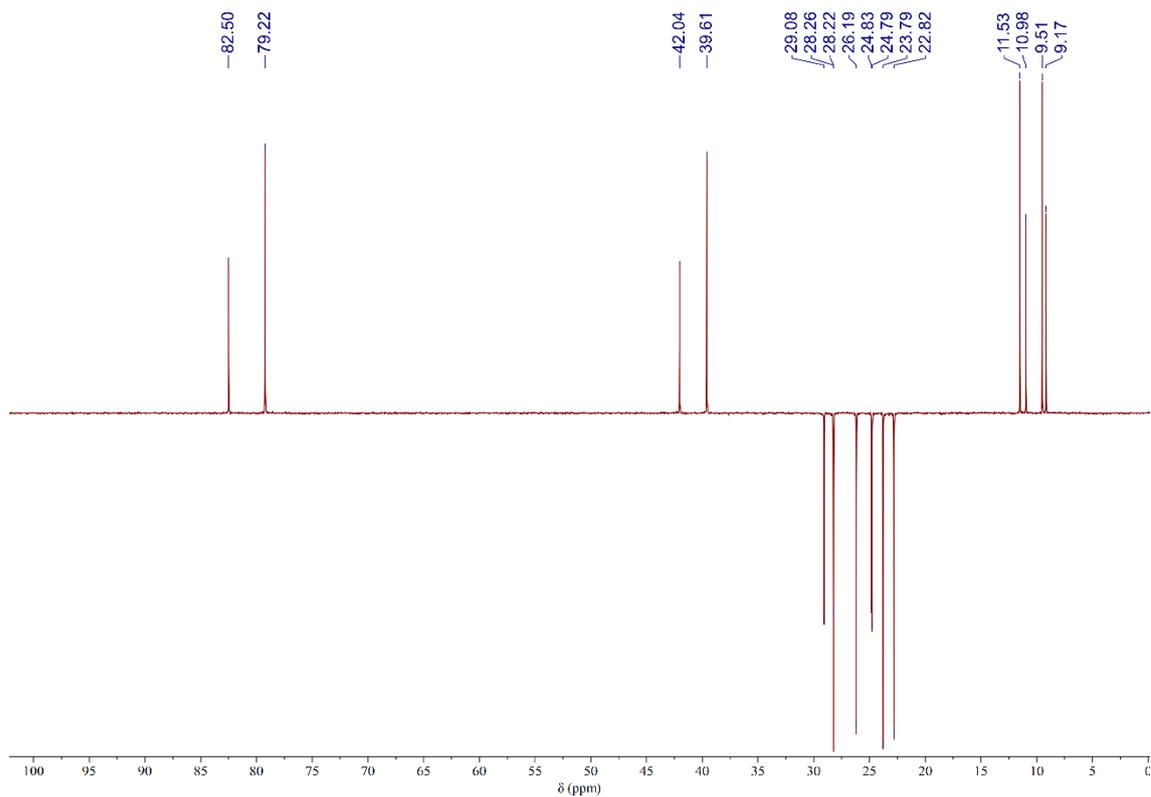


Figure S3. DEPT-135 spectrum of **HL** monomer (CDCl₃, 125 MHz, 25°C). The inverted peaks assign to methylene carbon signals.

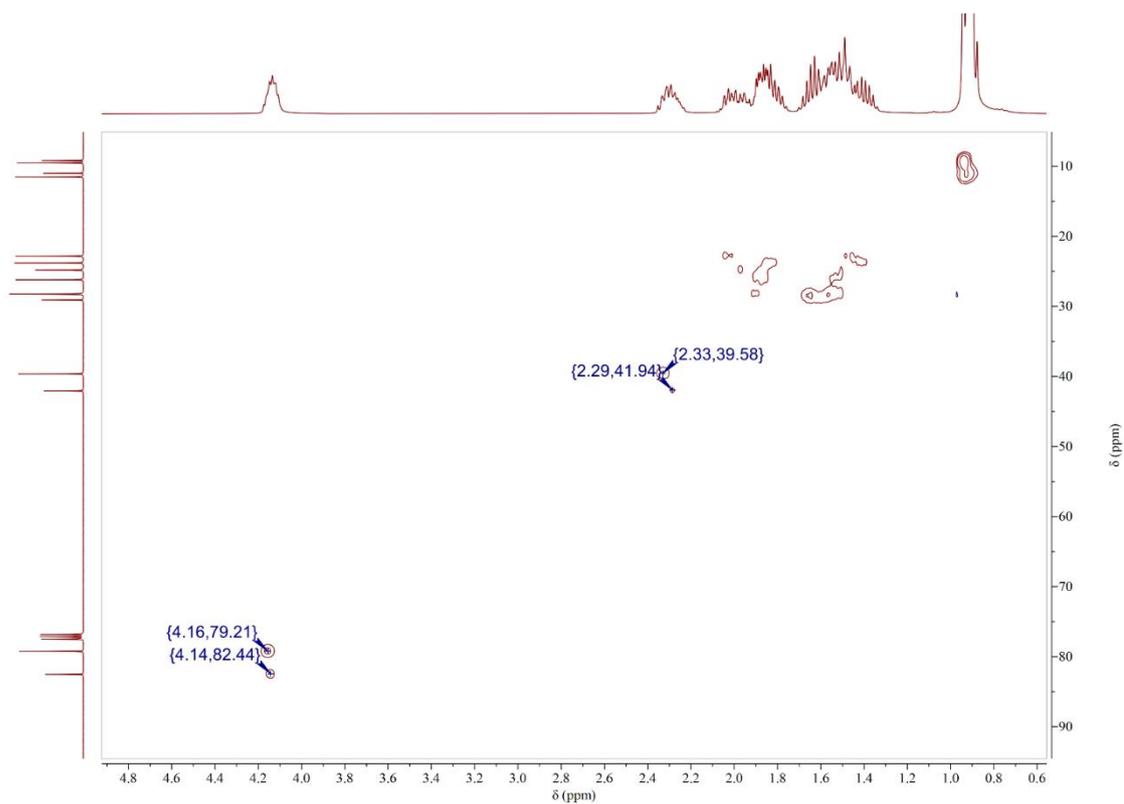


Figure S4. ^1H - ^{13}C HSQC spectrum of **HL** monomer (CDCl_3 , 25°C). Each of the characteristic methine proton signals correspond to two adjacent carbon signals in ^{13}C NMR spectrum, which again confirmed the existence of two pairs of diastereoisomers.

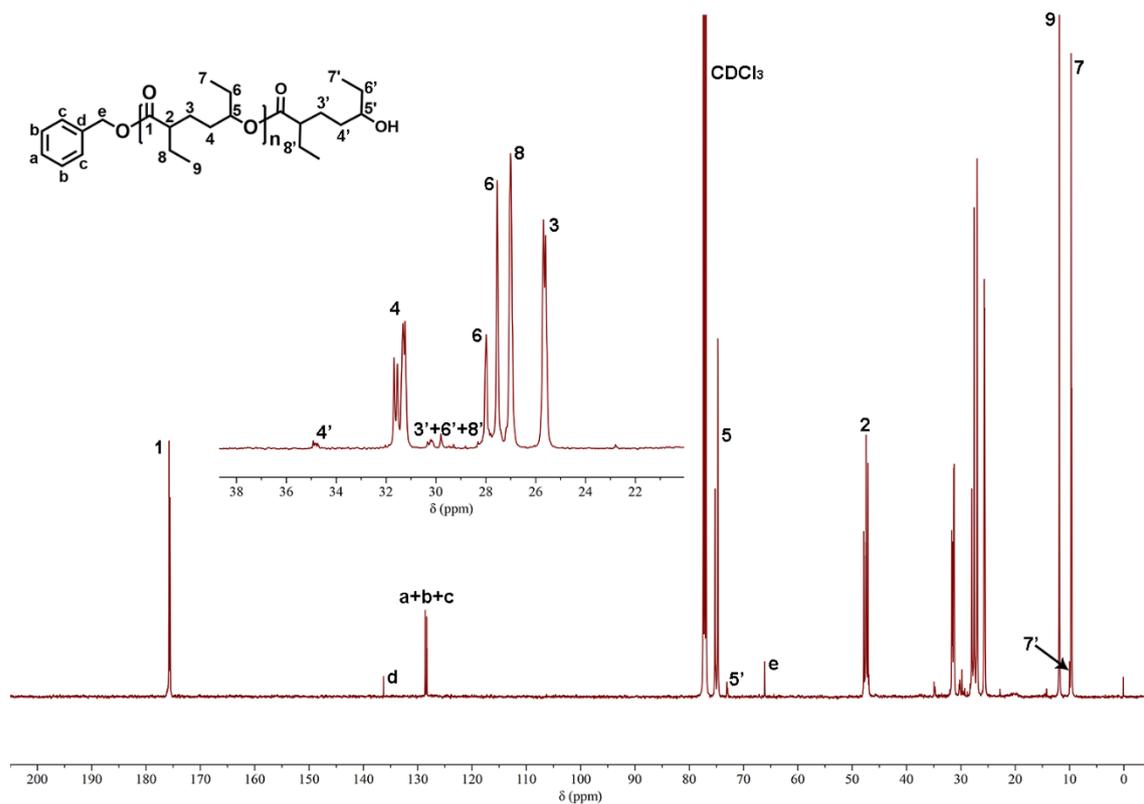


Figure S5. ¹³C NMR spectrum of polyHL produced at a ratio of [HL]/[^tBu-P₄]/[BnOH] = 25/0.1/1 (CDCl₃, 125 MHz, 25°C). $M_n = 4.1 \text{ kg mol}^{-1}$, $D = 1.11$.

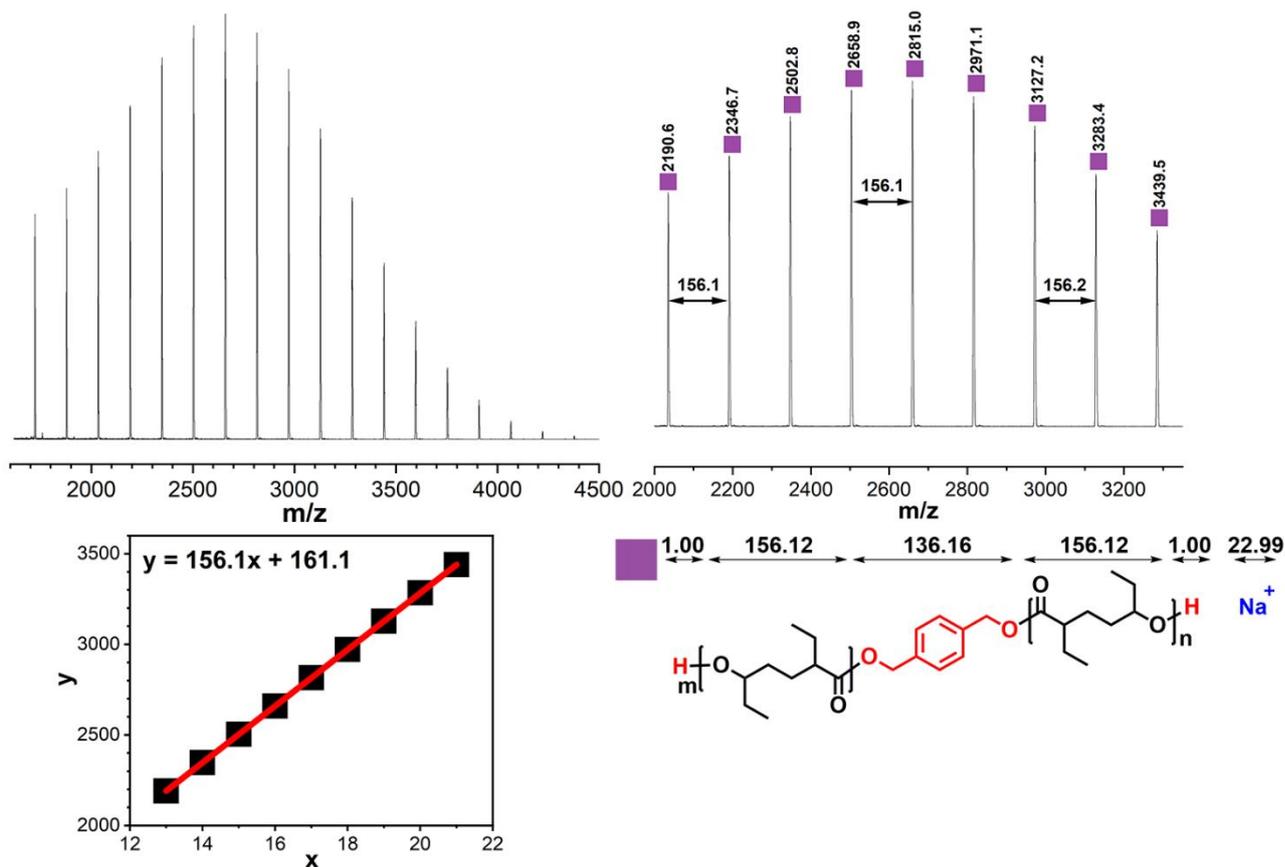


Figure S6. MALDI-TOF mass spectra of polyHL produced by $[\text{HL}]/[\text{'Bu-P}_4]/[1,4\text{-BDM}] = 15/0.5/1$, $[\text{HL}]_0 = 5.3 \text{ M}$ in THF, $T = -25^\circ\text{C}$. Monomer conversion = 83%. M_n (GPC) = 3.75 kg mol^{-1} , $\mathcal{D} = 1.13$.

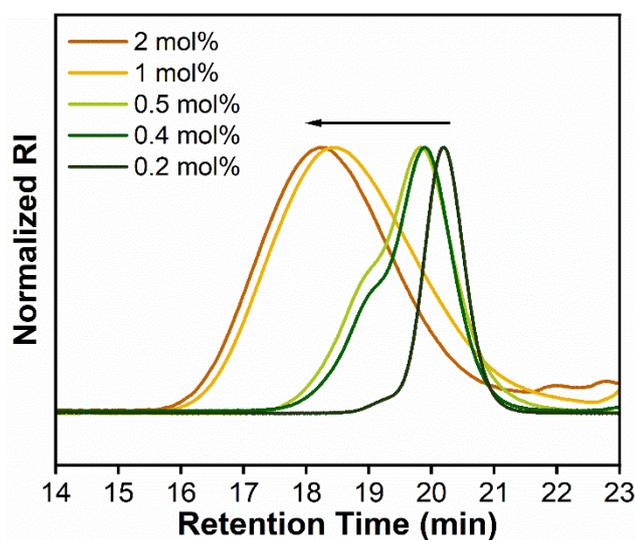


Figure S7. GPC traces of polyHL produced by different loading of 'Bu-P₄. $[\text{HL}]/[\text{BnOH}] = 50/1$. As the loading of the phosphazene base increases, bimodal distribution came out.

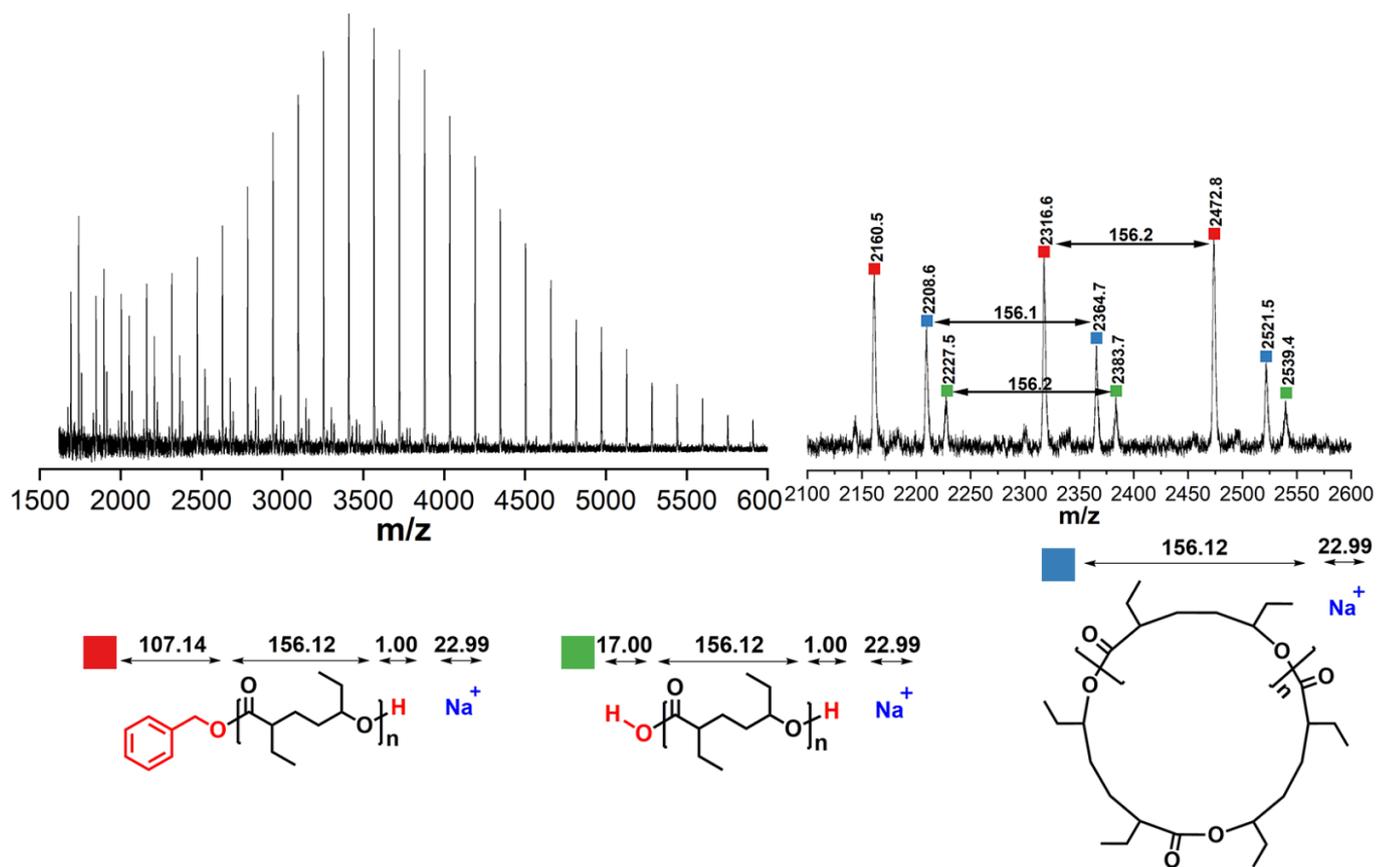


Figure S8. MALDI-TOF mass spectra of polyHL produced by $[\text{HL}]/[\text{tBu-P}_4]/[\text{BnOH}] = 50/0.5/1$, $[\text{HL}]_0 = 5.3$ M in THF, $T = -25^\circ\text{C}$. To generate low MW polymer, the reaction was quenched at low monomer conversion.

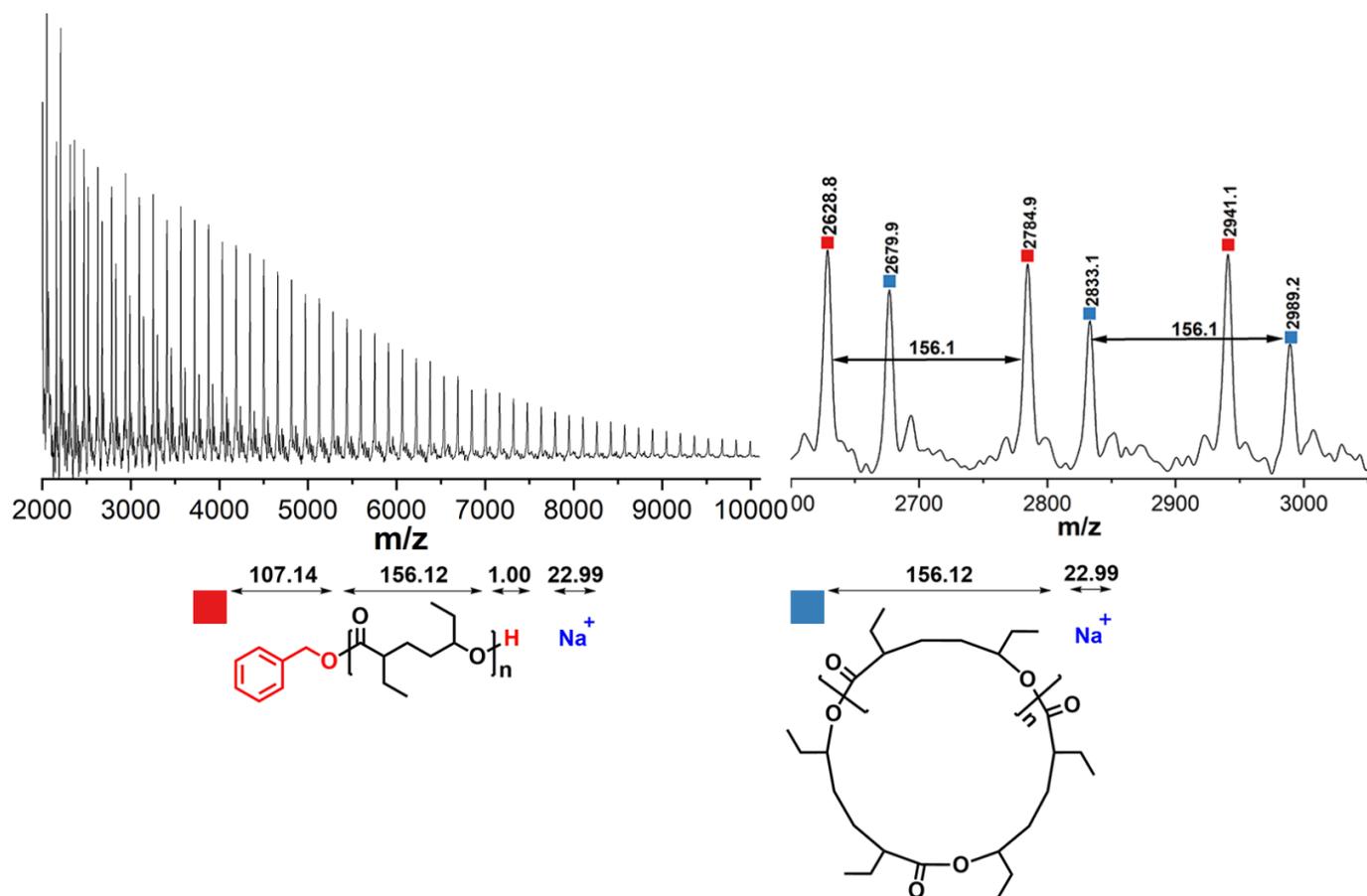


Figure S9. MALDI-TOF mass spectra of polyHL produced by $[\text{HL}]/[\text{tBu-P}_4]/[\text{BnOH}] = 50/1/1$, $[\text{HL}]_0 = 5.3 \text{ M}$ in THF, $T = -25^\circ\text{C}$. To generate low MW polymer, the reaction was quenched at low monomer conversion.

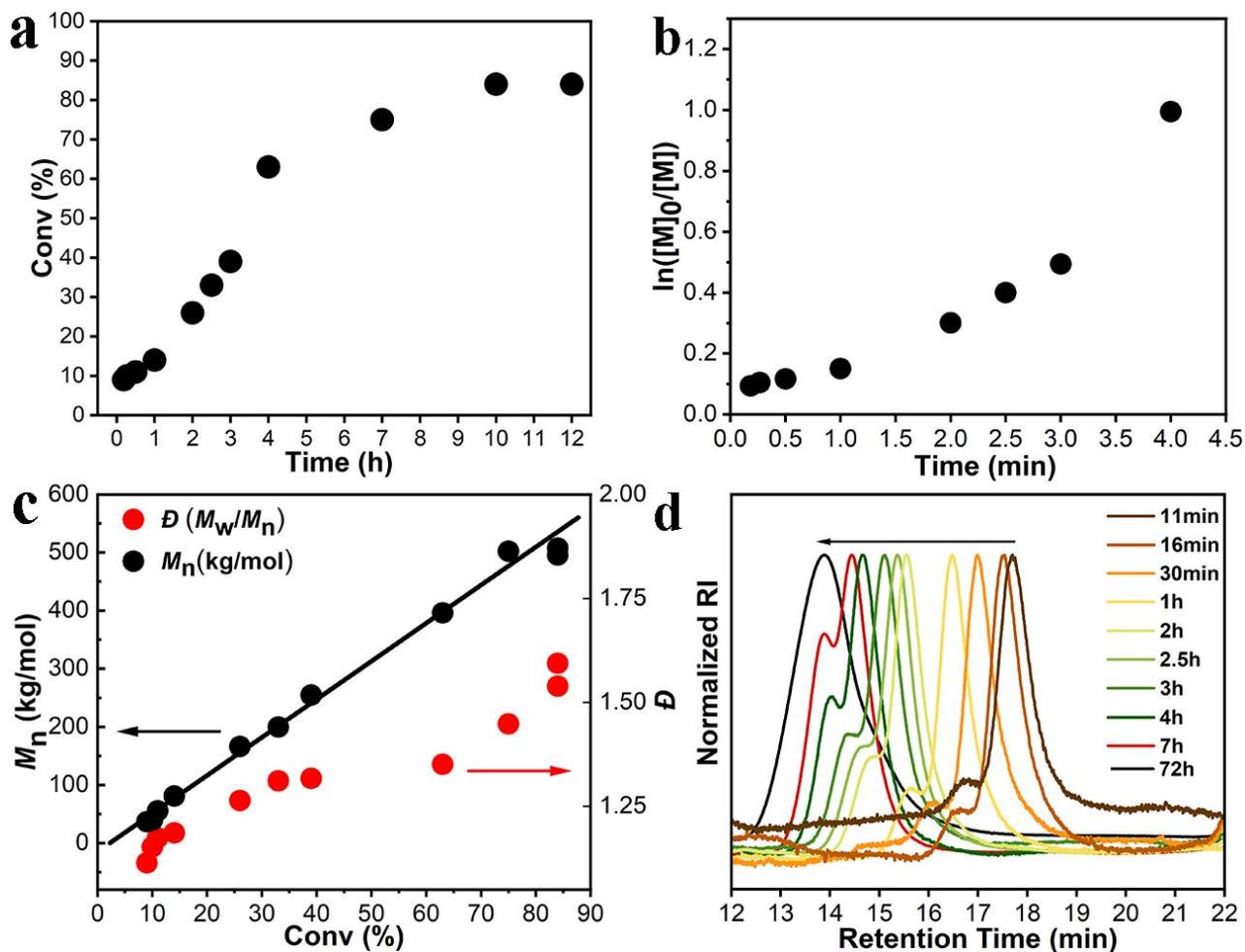


Figure S10. ROP of HL catalyzed by *t*Bu-P₄ alone. (a) Plot of HL conversion versus time. (b) Semilogarithmic kinetic plots of $\ln([M]/[M]_0)$ versus time. (c) Plot of molecular weight (M_n) and \bar{D} versus HL conversion. (d) GPC traces of polyHL obtained at different polymerization time. $[\text{HL}]/[\text{tBu-P}_4] = 50/1$, $[\text{HL}]_0 = 4.0 \text{ M}$ in THF, $T = -25^\circ\text{C}$.

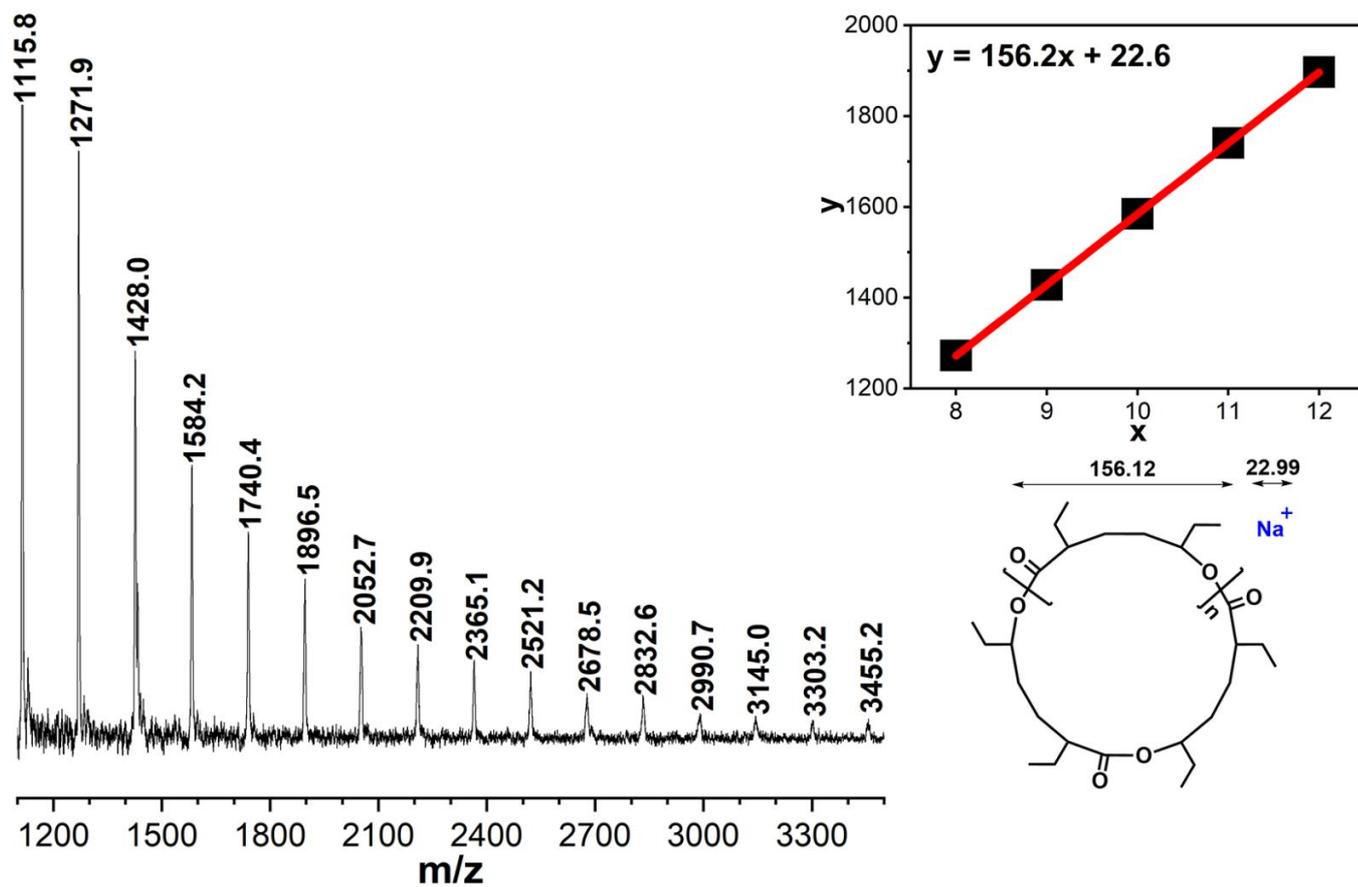


Figure S11. MALDI-TOF mass spectra of polyHL produced by $[\text{HL}]/[\text{t-Bu-P}_4]/[\text{BnOH}] = 50/1/0$, $[\text{HL}]_0 = 4.0 \text{ M}$ in THF, $T = -25^\circ\text{C}$. To generate low MW polymer, the reaction was quenched at low monomer conversion.

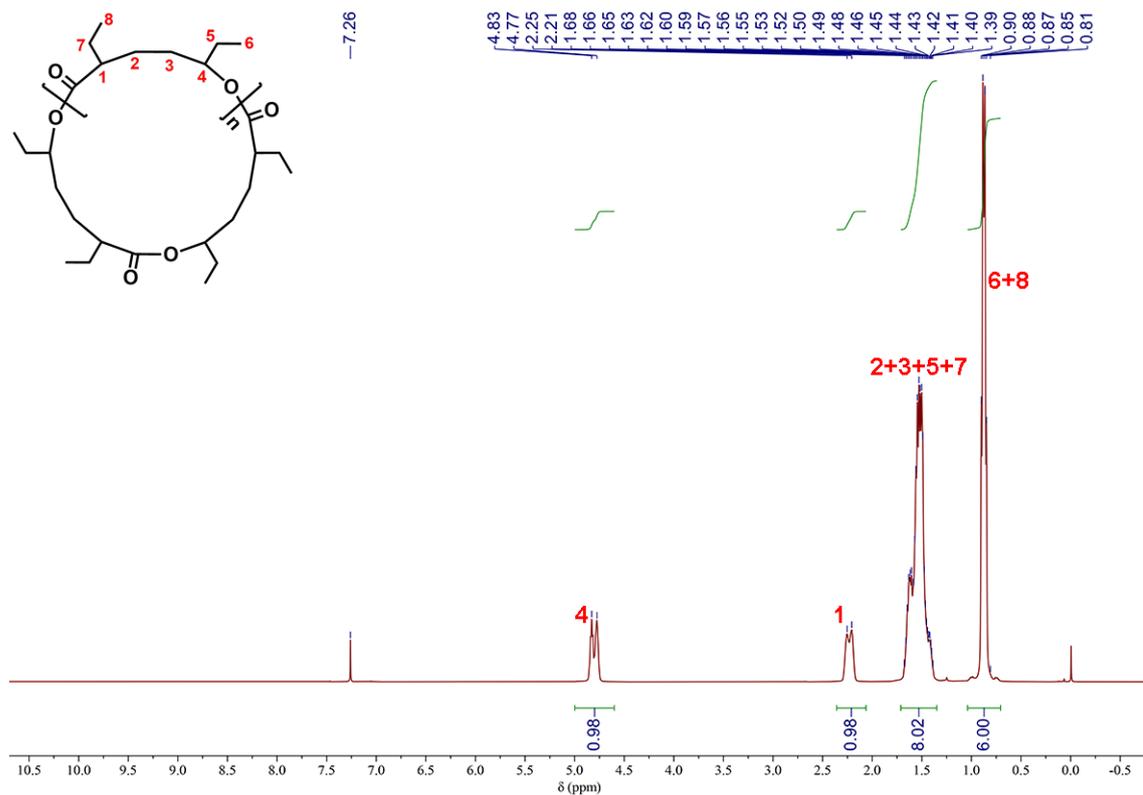


Figure S12. ¹H NMR spectrum of cyclic polyHL produced at a ratio of [HL]/[tBu-P₄] = 50/1, (CDCl₃, 500 MHz, 25°C).

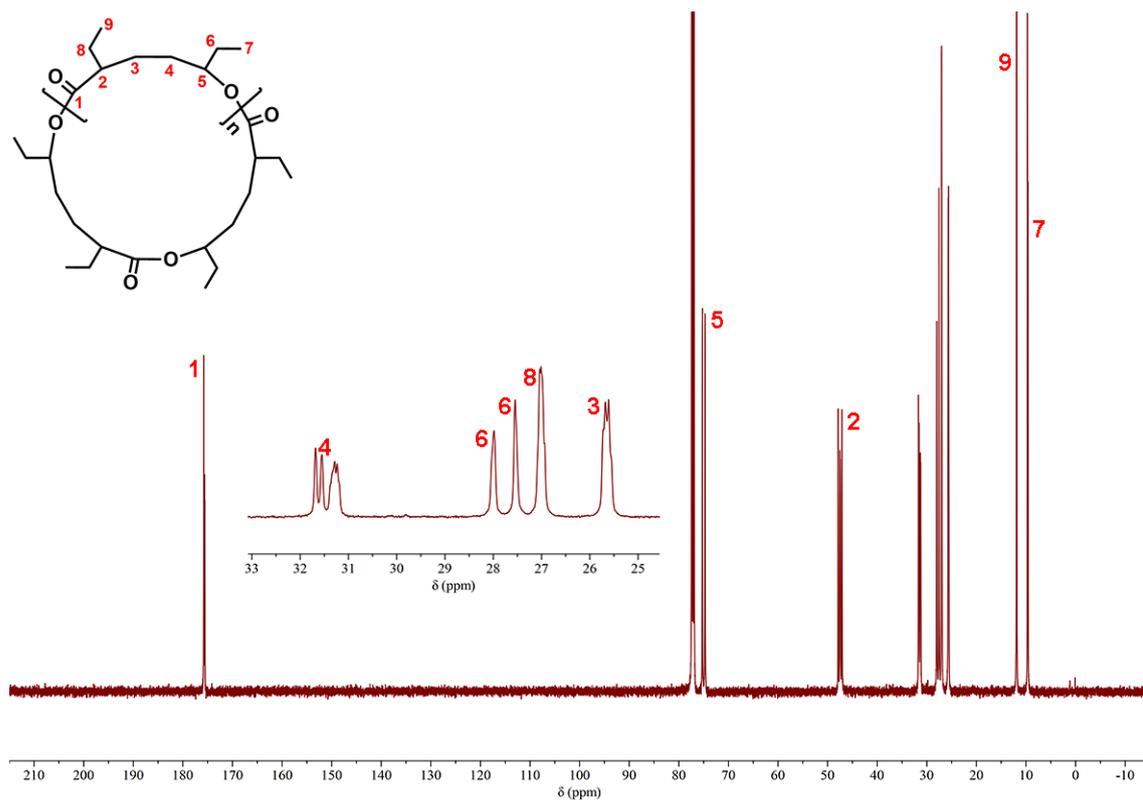


Figure S13. ^{13}C NMR spectrum of cyclic polyHL produced at a ratio of $[\text{HL}]/[\text{tBu-P}_4] = 50/1$, (CDCl_3 , 125MHz, 25°C).

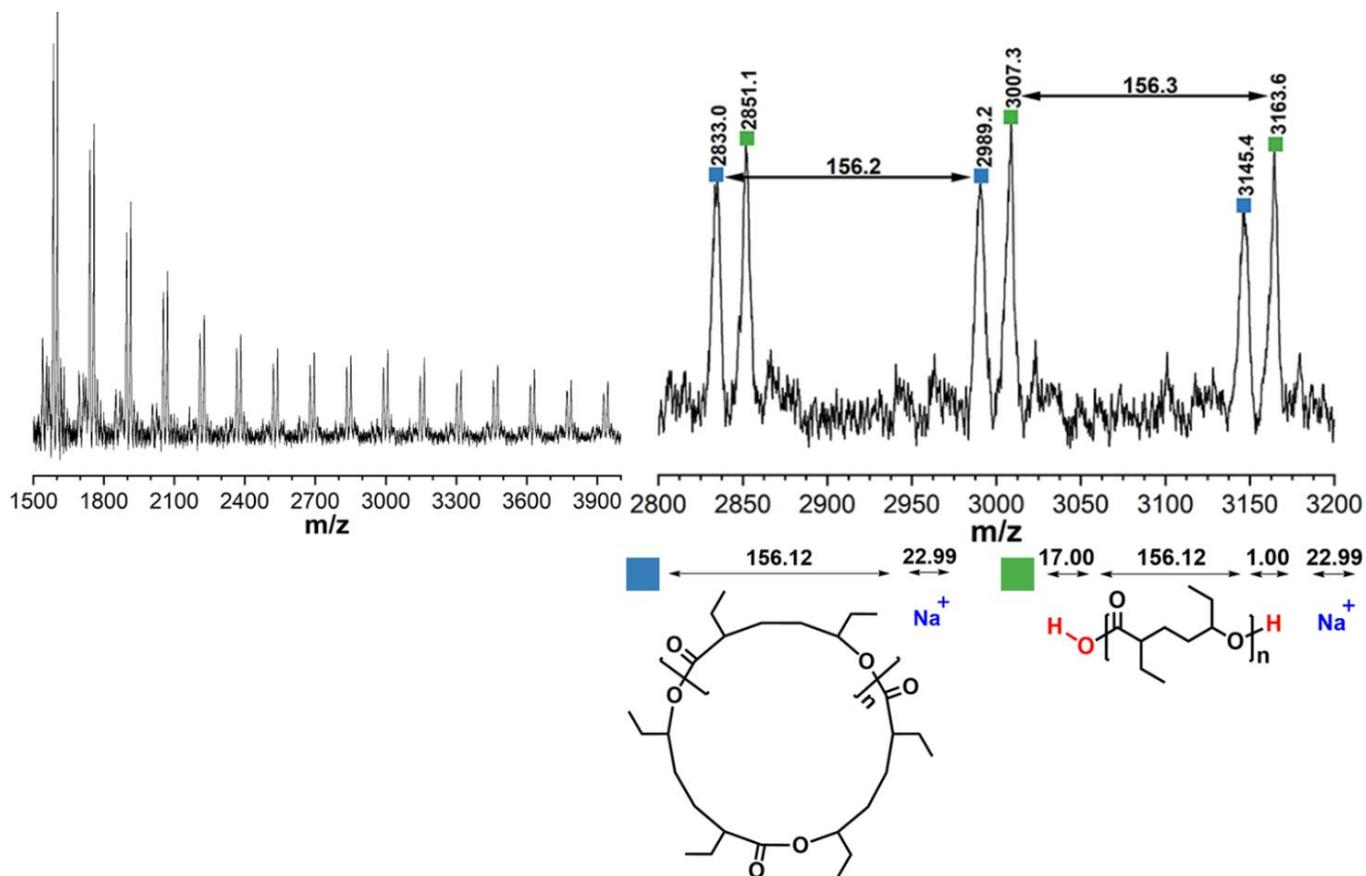


Figure S14. MALDI-TOF mass spectra of polyHL produced by [HL]/[*t*Bu-P₄]/[BnOH] = 50/1/0, [HL]₀ = 4.0 M in THF, *T* = -25°C. To generate low MW polymer, the reaction was quenched at low monomer conversion. The water initiated linear mass peak was detected because the HL monomer employed in this reaction was not rigorously dried. The water content of HL monomer was estimated to be ~100 ppm by Karl Fischer moisture titrator.

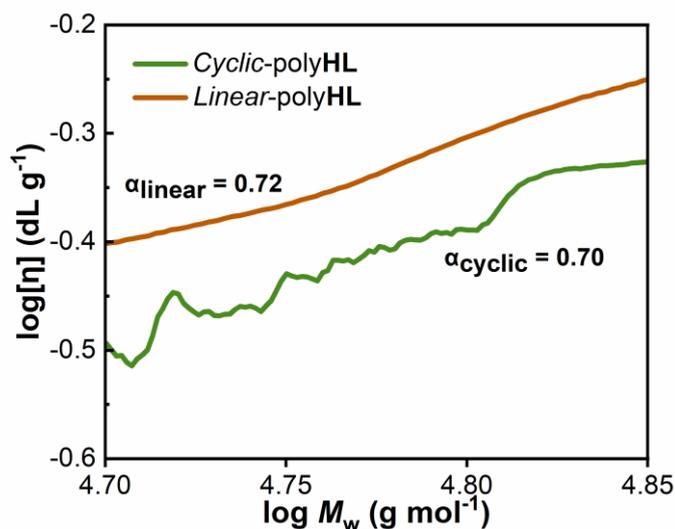


Figure S15. Mark-Houwink plots of the linear (brown line) and cyclic polyHLs (green line). The Mark-Houwink exponent α was also calculated and exhibited. The putative cyclic polyHL was synthesized at a ratio of [HL]/[*t*Bu-P₄]/[BnOH] = 20/1/0 in THF ([HL]₀ = 4.0 M) at -25°C for 1 h, and the resultant polyHL had a $M_n = 52036 \text{ g mol}^{-1}$, $\mathcal{D} = 1.184$; whereas the linear polyHL acted as a counterpart was prepared at a ratio of [HL]/[*t*Bu-P₄]/[BnOH] = 300/0.3/1 in THF ([HL]₀ = 4.0 M) at -25°C for 48 h. The linear polyHL had a $M_n = 56856 \text{ g mol}^{-1}$, $\mathcal{D} = 1.071$.

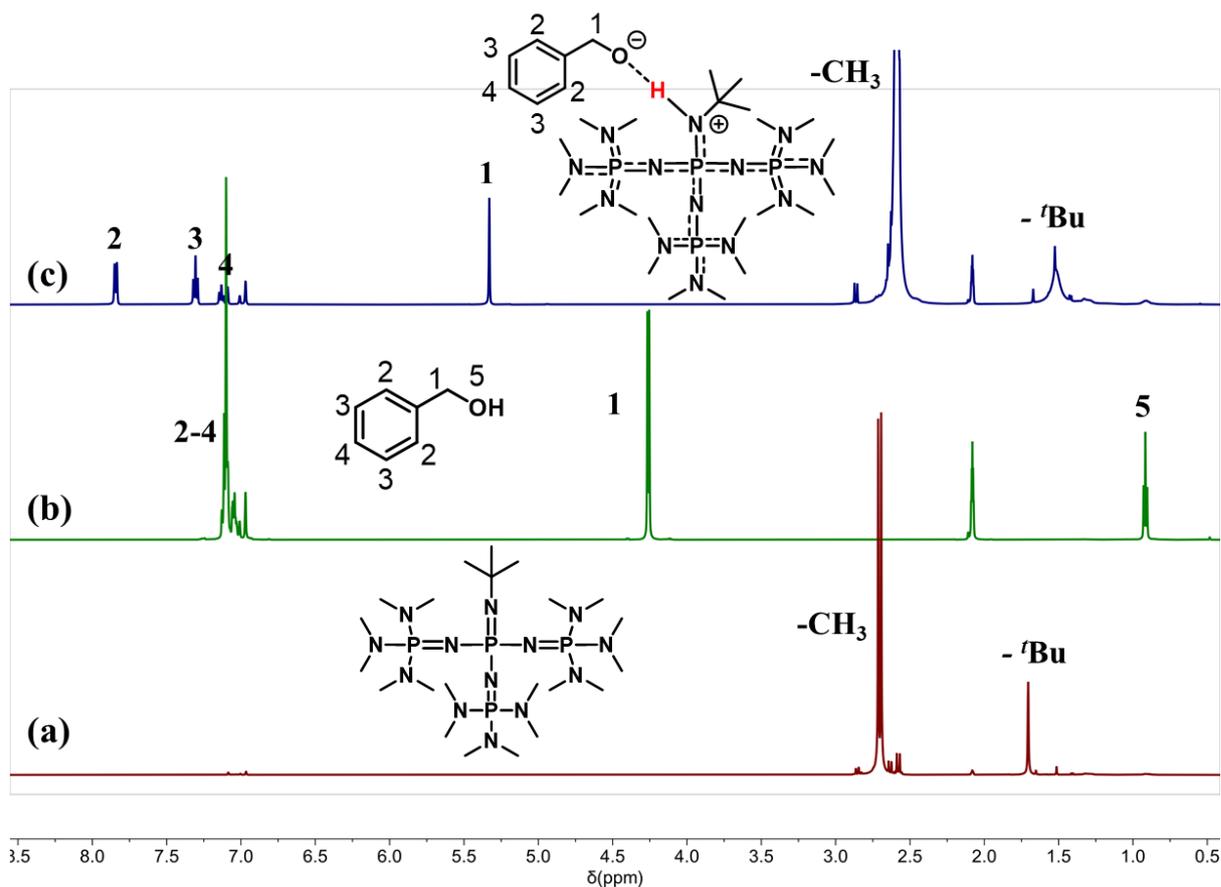


Figure S16. ^1H NMR spectrum ($\text{toluene-}d_8$, 500 MHz, 25°C): (a) $t\text{Bu-P}_4$; (b) BnOH; (c) $[t\text{Bu-P}_4]/[\text{BnOH}] = 1/1$. The NMR spectra were collected after sufficiently oscillation in order to assure the reaction stoichiometric was complete. The proton signal in $[t\text{Bu-P}_4\text{H}^+\cdots\text{OBn}]$ was not detected, this should be attributed to the rapid proton exchange at 25°C.

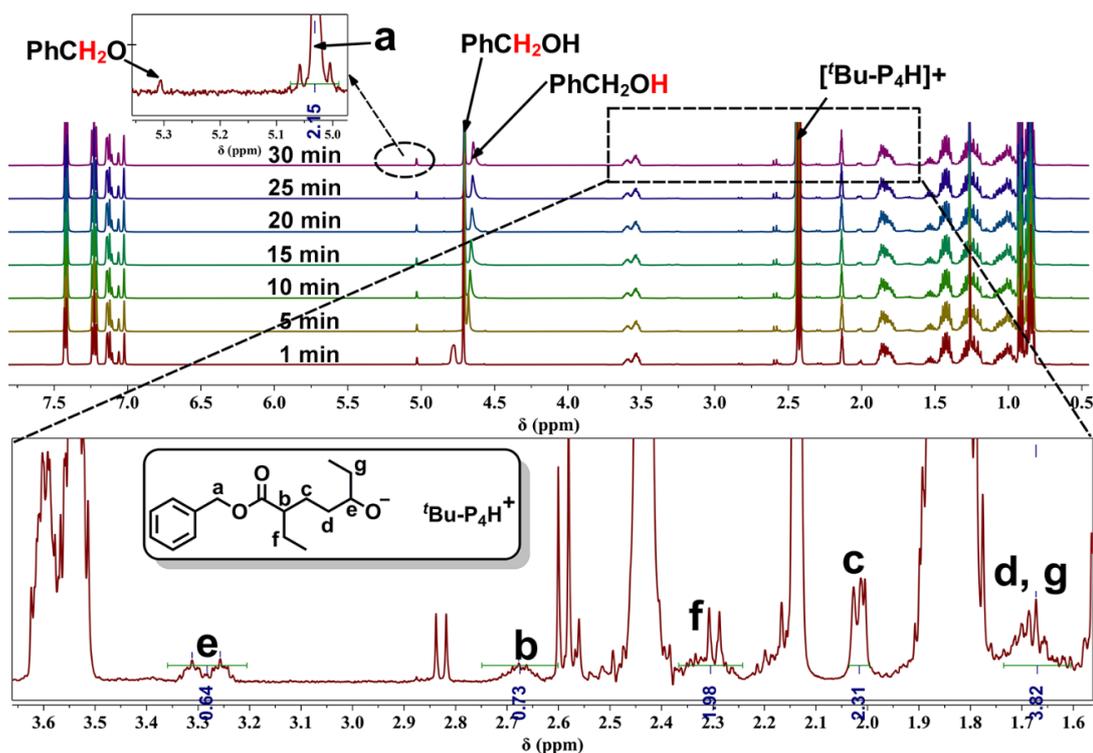


Figure S17. *In-situ* ^1H NMR spectroscopies of chain-initiation stage at a ratio of $[\text{HL}]/[\text{BnOH}] = 1/1$ catalyzed by 10 mol% of $^t\text{Bu-P}_4$ (toluene- d_8 , 500 MHz, 25°C). The *in-situ* ^1H NMR spectra were gathered immediately at one-minute intervals for the very first 30 min (top, partially showed). The assignment of putative ring-opened intermediate detected in the ^1H NMR spectroscopy (bottom).

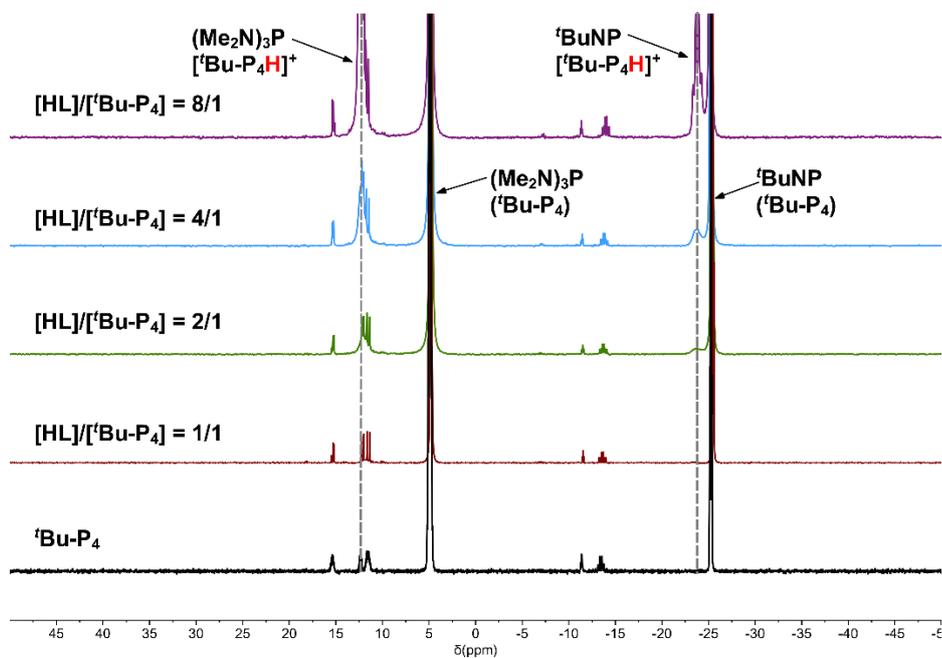


Figure S18. ^{31}P NMR spectrum of the mixture of **HL** and $^t\text{Bu-P}_4$ in varied feed ratios (toluene- d_8 , 25°C, no polymerization took place).

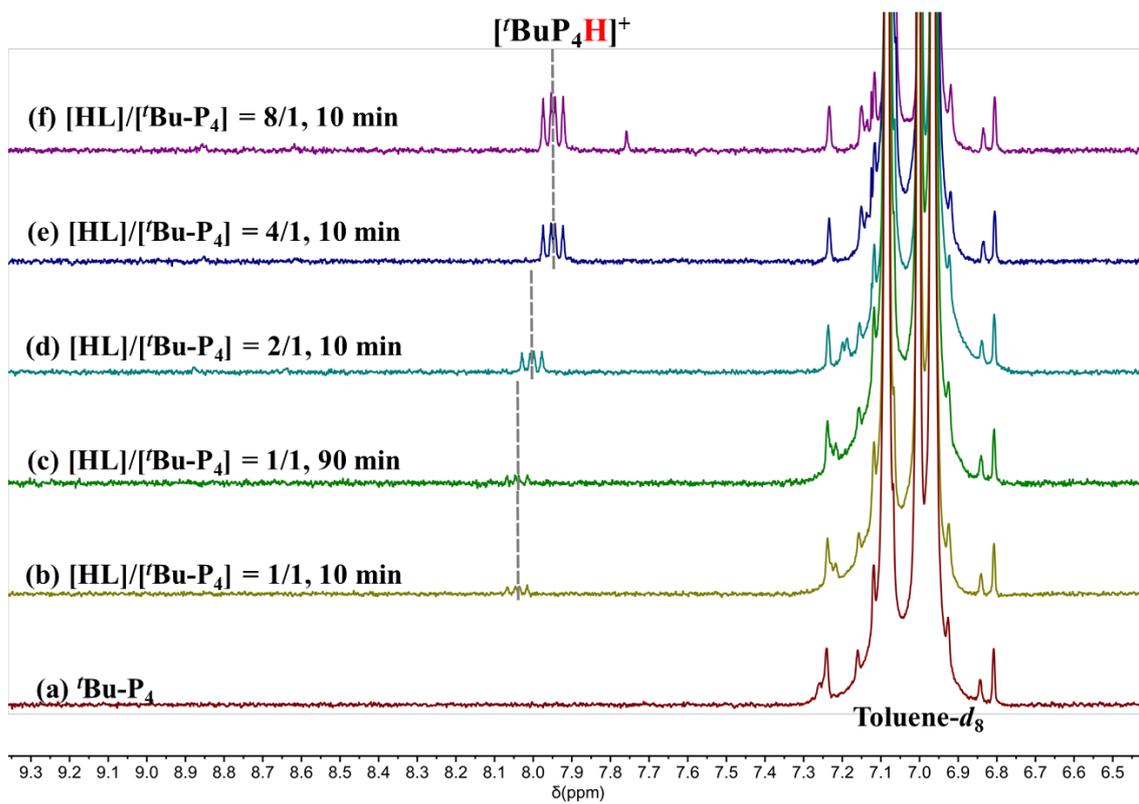


Figure S19. ^1H NMR spectrum ($\text{toluene-}d_8$, 25°C) of the reaction between tBu-P_4 and **HL** at varied feed ratios (partial enlarged view).

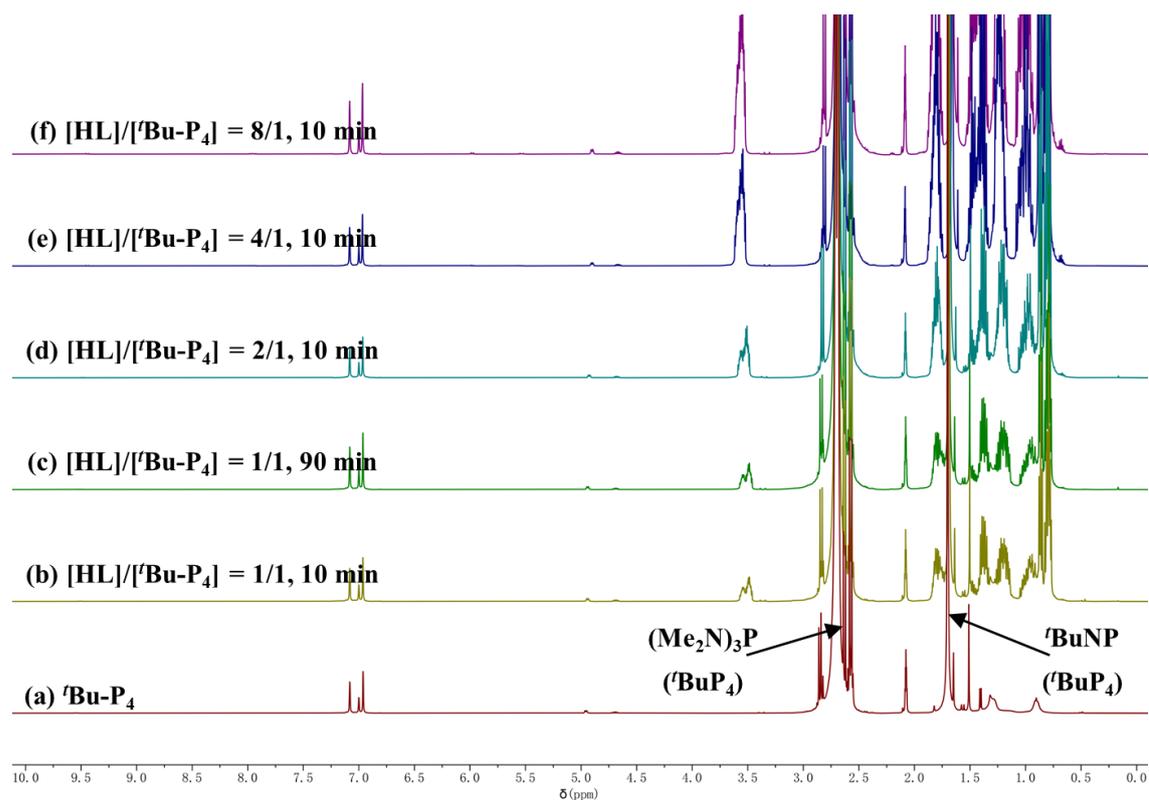


Figure S20. ¹H NMR spectrum (toluene-*d*₈, 25°C) of the reaction between ^tBu-P₄ and HL at varied feed ratios (overview). At this diluted reaction condition, no polymerization was detected.

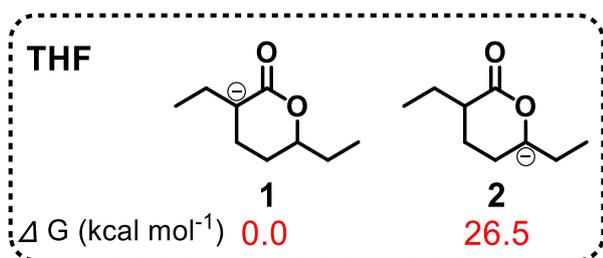


Figure S21. Deprotonation energies of HL calculated by DFT calculations.

6-311+g** solvent: tetrahydrofuran

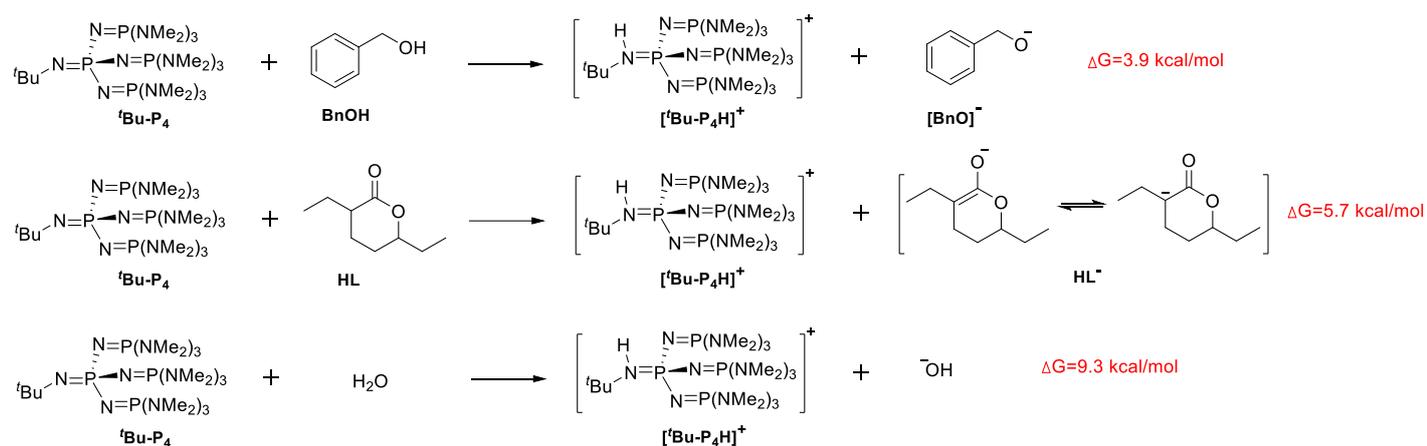


Figure S22. Calculated free energy of deprotonation reactions of BnOH, HL and water by $t\text{Bu-P}_4$.

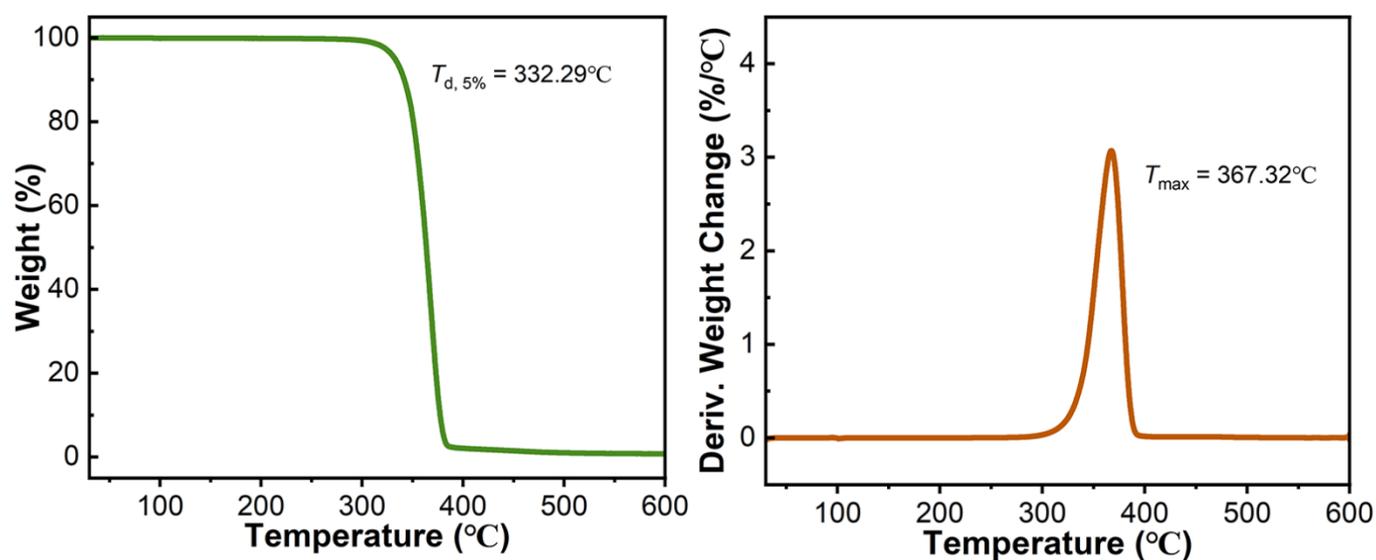


Figure S23. TGA and DTG of cyclic polyHL produced by $t\text{Bu-P}_4$ alone at a ratio of $[\text{HL}]/[t\text{Bu-P}_4] = 10/1$ at -25°C for 30 min. $M_n = 21.7 \text{ kg mol}^{-1}$, $D = 1.13$.

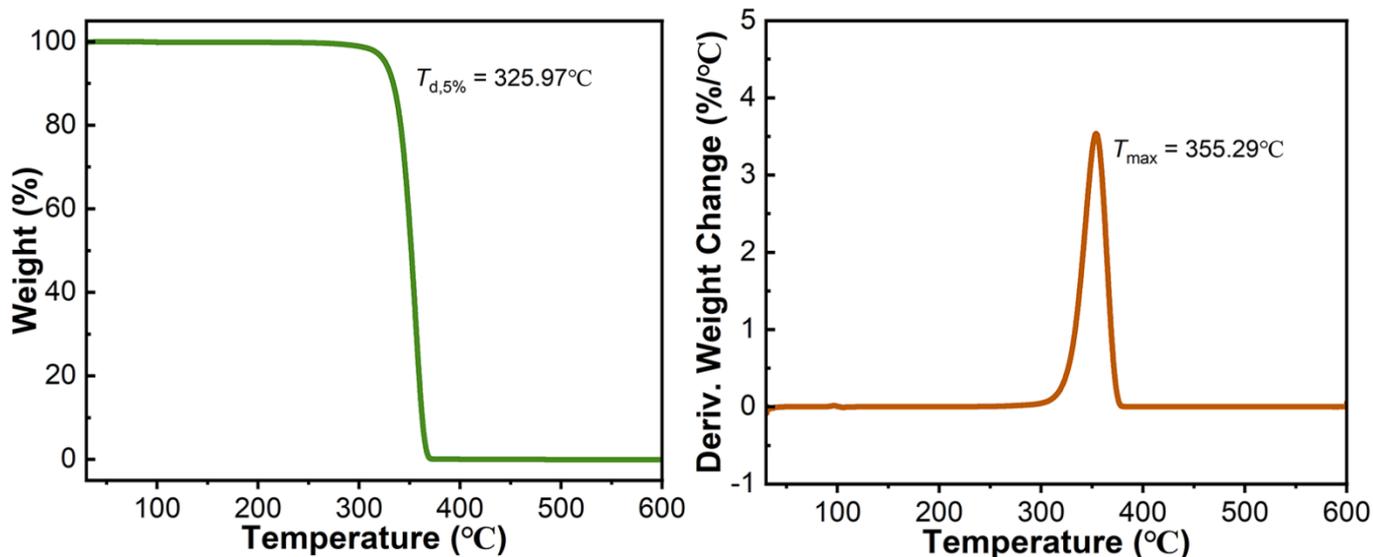


Figure S24. TGA and DTG of linear polyHL produced by $t\text{-Bu-P}_4$ at a ratio of $[\text{HL}]/[t\text{-Bu-P}_4]/[\text{BnOH}] = 100/0.2/1$ at -25°C for 12 h. $M_n = 19.6 \text{ kg mol}^{-1}$, $D = 1.08$ (Table 1, run 15).

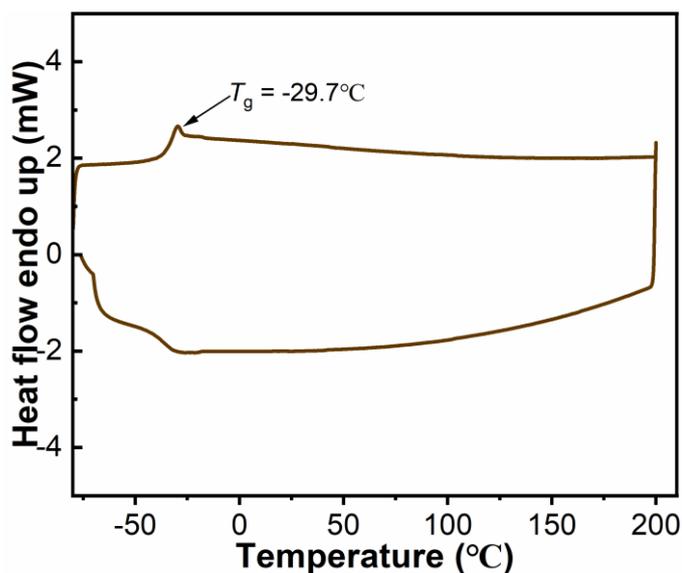


Figure S25. DSC curves of cyclic polyHL produced by $t\text{-Bu-P}_4$ alone at a ratio of $[\text{HL}]/[t\text{-Bu-P}_4] = 10/1$ at -25°C for 30 min.

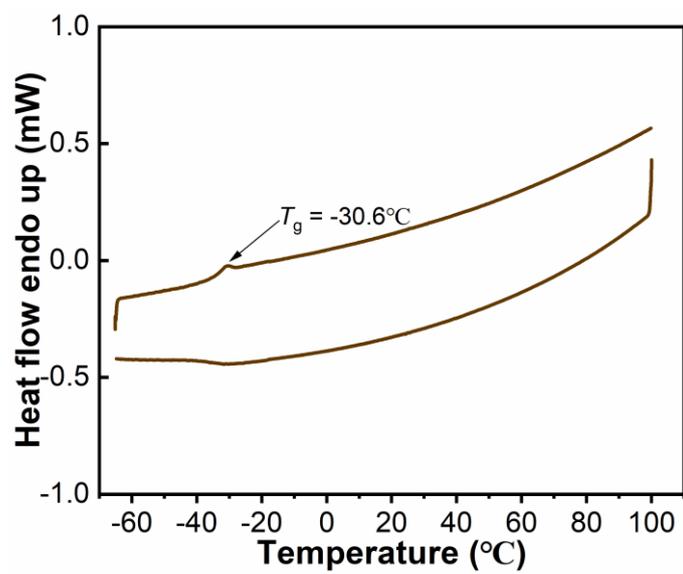


Figure S26. DSC curves of linear polyHL produced by ^tBu-P₄ at a ratio of [HL]/[^tBu-P₄]/[BnOH] = 100/0.2/1 at -25°C for 12 h. $M_n = 19.6 \text{ kg mol}^{-1}$, $D = 1.08$ (Table 1, run 15).

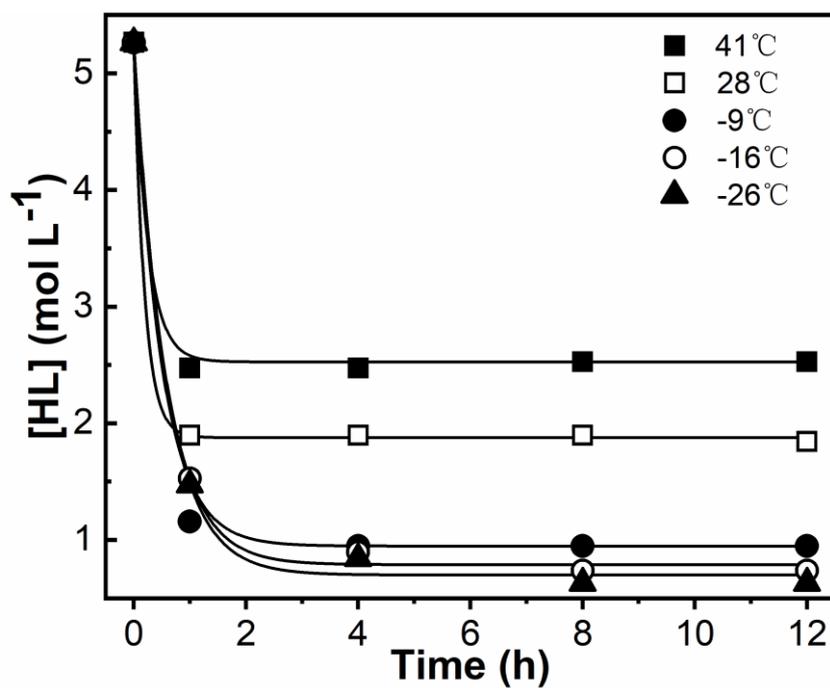


Figure S27. Plot of **HL** monomer concentration as a function of time during ROP at different temperatures. Conditions: **HL** = 0.104 g, $[\text{HL}]/[\text{'Bu-P}_4]/[\text{BnOH}] = 50/0.1/1$, $[\text{HL}]_0 = 5.3 \text{ M}$ in THF.

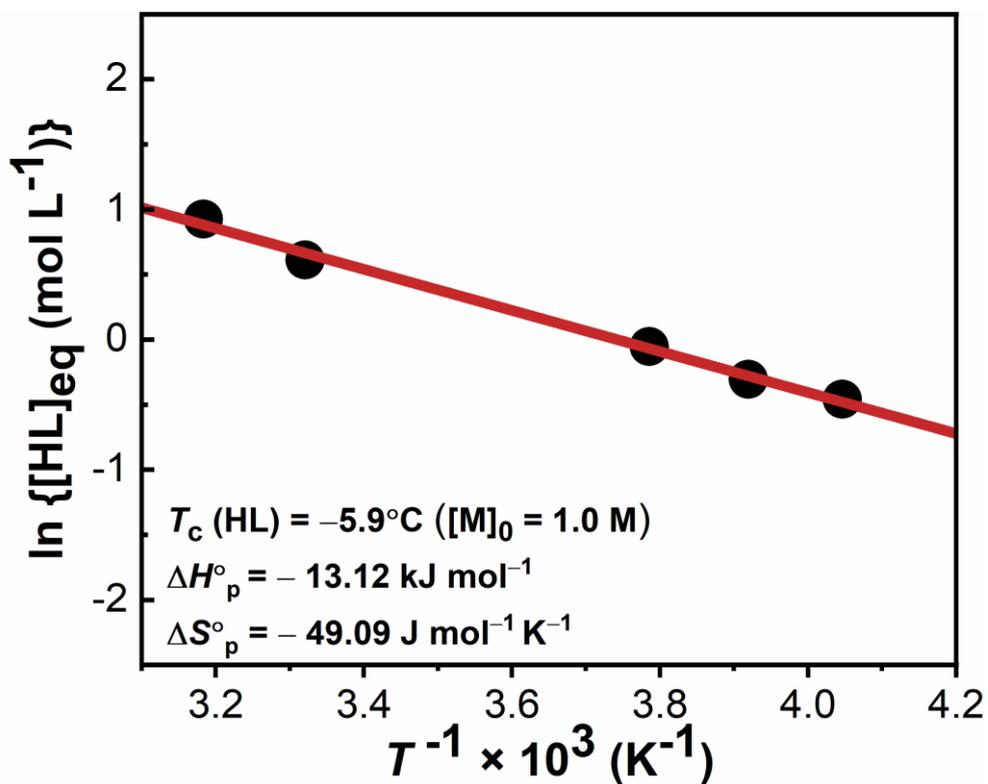


Figure S28. Van't Hoff plot of $\ln[\text{HL}]_{\text{eq}}$ versus the reciprocal of the absolute temperature (T^{-1}).

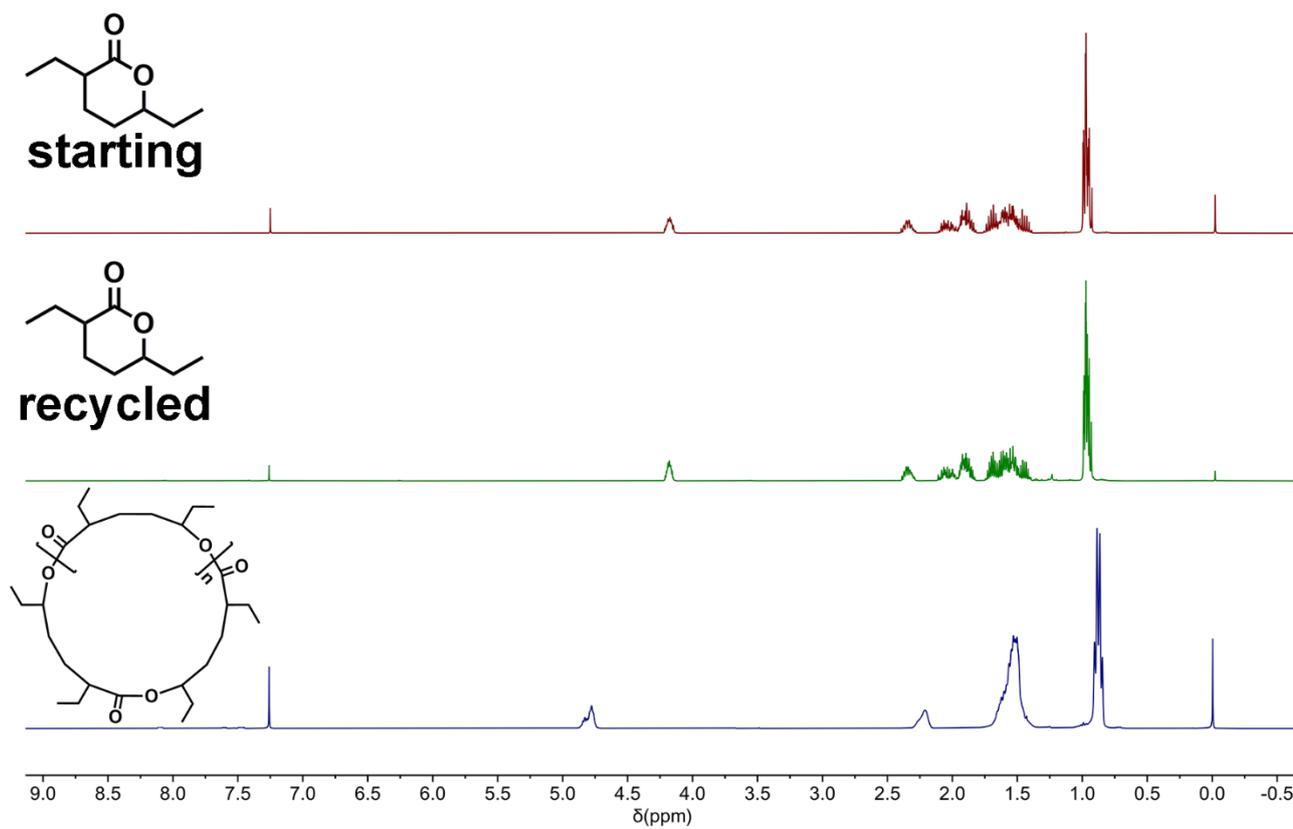


Figure S29. The ¹H NMR spectra of chemical recycling of high MW *cyclic-polyHL* by 3 mol% of La[N(SiMe₃)₂]₃ (Table S9, run 9). Bottom (blue), high MW *cyclic-polyHL* synthesized by ^tBuP₄ alone; middle (green), the colorless oil generated after purification; top (red), clean **HL** monomer employed for comparison.

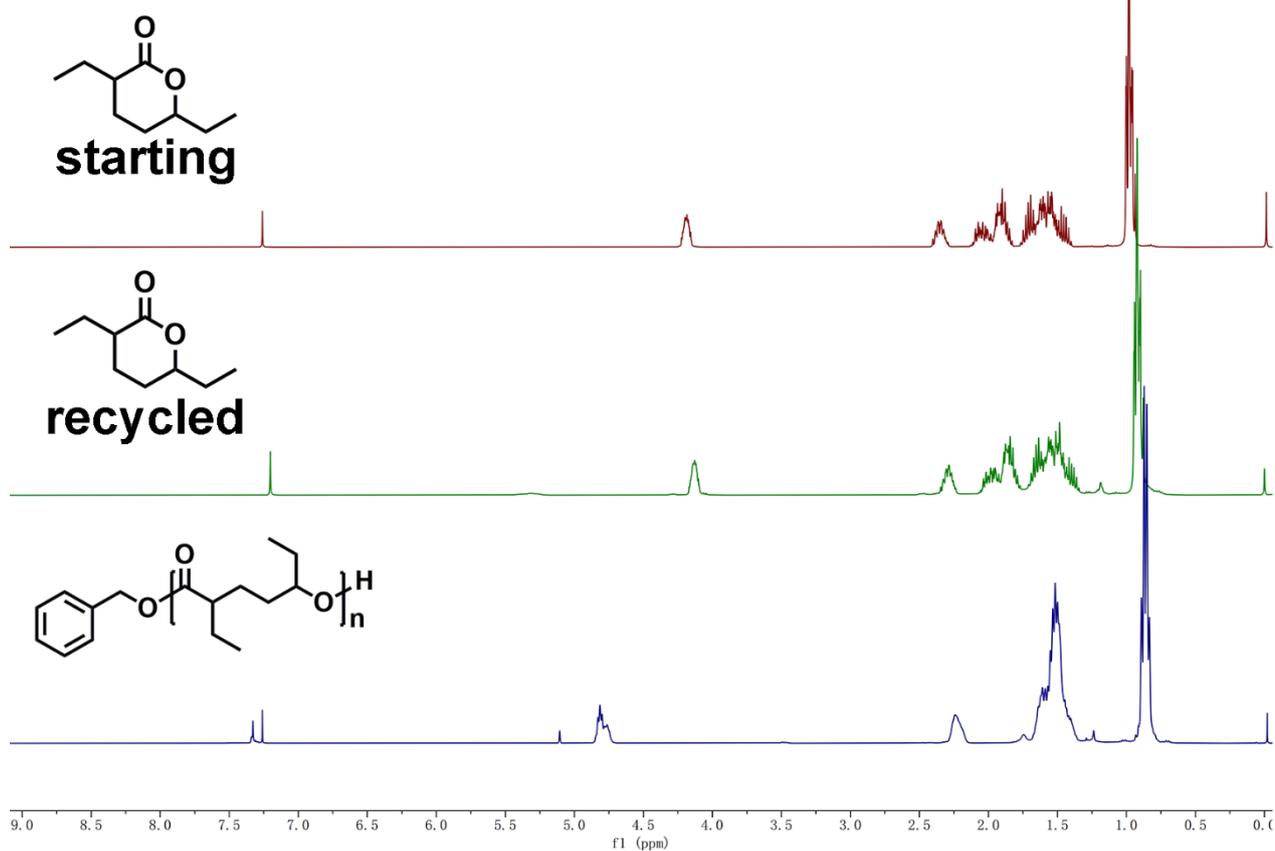
a

Figure S30. The ¹H NMR spectra of chemical recycling of linear poly**HL** by 5 mol% of ZnCl₂ at 160°C in *o*-DCB. Bottom (blue), linear poly**HL** synthesized by tBuP₄/BnOH at a ratio of 50/0.1/1 at -25°C in THF, $M_n = 9.2 \text{ kg mol}^{-1}$, $\mathcal{D} = 1.08$; middle (green), the colorless oil generated after purification; top (red), clean **HL** monomer employed for comparison.

Cartesian coordinates for 'Bu-P₄.

P	0.01534200	0.00120800	0.60077100
N	0.21707300	0.54837000	2.07492500
C	-0.26595700	0.02134200	3.34782700
C	0.69486300	0.52638200	4.44902800
C	-1.67468000	0.58181300	3.66274700
C	-0.32298400	-1.52401800	3.42848200
H	1.70178900	0.11647300	4.30496100
H	0.76737200	1.61975900	4.40685800
H	0.34724100	0.23847900	5.45104600
H	-2.37736100	0.29095900	2.87669500
H	-2.05648800	0.21549200	4.62722600
H	-1.64272500	1.67748900	3.70244200
H	-0.64188900	-1.85585000	4.42676000
H	-1.02776700	-1.92898600	2.69366600
H	0.66180100	-1.95833300	3.22425700
N	0.88421500	-1.37367300	0.21096800
P	2.22949800	-1.93247600	-0.31592000
N	2.67741300	-1.74865900	-1.95395200
N	3.61337200	-1.30433900	0.46242500
N	2.14869200	-3.63317200	-0.20377800
N	0.50393200	1.17764400	-0.48432000
N	-1.53448200	-0.43145600	0.21222700
P	-2.87191600	-0.88240100	-0.38963300
P	0.67579300	2.73900700	-0.41463900
N	1.25799300	3.35276500	-1.89871100
N	-3.30289300	0.04215300	-1.75888900
N	-2.92194700	-2.55508800	-0.71136100

N	1.77229900	3.27957200	0.74143300
N	-0.74125400	3.64810800	-0.24201700
N	-4.28805600	-0.71603300	0.54153900
C	-1.00260100	4.95147800	-0.83850100
H	-0.22866400	5.20188400	-1.56460200
H	-1.97906400	4.94350000	-1.34632000
H	-1.03774700	5.74426300	-0.07203700
C	-1.68866900	3.28709200	0.81138500
H	-1.41336900	2.33459400	1.26711800
H	-1.69894700	4.05470700	1.60221700
H	-2.70311100	3.20829600	0.39635900
C	-4.79624300	0.63124200	0.81329200
H	-5.87823900	0.57587900	0.99462400
H	-4.32216200	1.07807100	1.70008200
H	-4.61701100	1.28494000	-0.04148400
C	-4.50495000	-1.61714200	1.67785900
H	-4.04577100	-1.23312200	2.60024800
H	-5.58484500	-1.72173800	1.85047500
H	-4.08594600	-2.60239100	1.46959600
C	-4.55764600	-0.16439700	-2.47586300
H	-4.87102700	0.78393500	-2.93518600
H	-4.46326700	-0.90957100	-3.28358700
H	-5.34386000	-0.48813400	-1.79152800
C	-2.23067000	0.53149200	-2.62100400
H	-1.32805800	0.71372700	-2.03531600
H	-1.99762500	-0.17917600	-3.43363900
H	-2.54809700	1.47570200	-3.08567100
C	-1.68174000	-3.25505000	-1.03263500
H	-1.54666700	-3.36076800	-2.12298800

H	-0.82559500	-2.71934000	-0.61958100
H	-1.71178000	-4.26567200	-0.60039600
C	-4.10799600	-3.22360500	-1.23653700
H	-4.09211500	-3.29687200	-2.33677900
H	-4.15505100	-4.24705700	-0.83706700
H	-5.01538600	-2.69803900	-0.93453600
C	1.38980400	-4.24693200	0.88447500
H	0.59488100	-3.57518400	1.20600800
H	0.94390500	-5.18718500	0.53109100
H	2.03091400	-4.48152400	1.75083700
C	3.22080800	-4.49226300	-0.69801200
H	3.95919200	-4.73375900	0.08442600
H	2.79023500	-5.44033200	-1.05045400
H	3.73862200	-4.02034200	-1.53456200
C	1.78253200	-2.35818200	-2.94508300
H	0.89148600	-1.73843300	-3.13045100
H	2.32768600	-2.47175800	-3.89095200
H	1.45518800	-3.34324300	-2.60886900
C	3.12851200	-0.42379100	-2.39923100
H	2.28500300	0.26753400	-2.52807000
H	3.81688800	0.01093700	-1.67362700
H	3.65209800	-0.53649000	-3.35770300
C	4.96109900	-1.74943500	0.10578100
H	5.67450100	-0.94113200	0.31741000
H	5.27568600	-2.63214000	0.68660400
H	5.02049300	-1.99202100	-0.95639900
C	3.49337100	-0.98682600	1.88928700
H	4.25229000	-0.23735800	2.14902300
H	2.50811900	-0.56921600	2.10570100

H	3.66531800	-1.87280200	2.52432300
C	2.84674700	2.42916600	1.23935200
H	2.66777500	2.15889300	2.28684700
H	2.89732600	1.50732300	0.66087000
H	3.81169800	2.95623000	1.15845000
C	1.67089900	4.55804200	1.42787100
H	2.58196200	5.15913800	1.27584100
H	0.81979100	5.13363200	1.06348500
H	1.54361400	4.40221400	2.50981900
C	2.69281700	3.51730600	-2.11124600
H	3.18495300	2.58523800	-2.43395400
H	2.85236700	4.27181700	-2.89311600
H	3.17289600	3.86615600	-1.19539700
C	0.54412400	2.97570900	-3.11716600
H	0.74400400	3.72213500	-3.89804600
H	0.85033100	1.98730100	-3.49447700
H	-0.53170200	2.95132100	-2.93333600

Cartesian coordinates for $[\text{Bu-P}_4\text{H}]^+$

P	-0.00336600	-0.06395200	0.49834500
N	0.22546600	0.38934500	2.11915000
C	-0.45495700	-0.08509700	3.35673500
C	0.48189900	0.24620100	4.53399400
C	-1.79485200	0.65152000	3.55383300
C	-0.68535800	-1.60250000	3.30415700
H	1.43268300	-0.29000300	4.44461500
H	0.69734900	1.32192700	4.57700700
H	0.01692300	-0.03449600	5.48591800
H	-2.45475800	0.47526600	2.70122700

H	-2.29986800	0.31164300	4.46630700
H	-1.63241000	1.73302700	3.64584100
H	-1.14291600	-1.93435500	4.24278500
H	-1.35340200	-1.88072400	2.48396400
H	0.26016400	-2.13829400	3.17750000
N	0.78627700	-1.45336500	0.24010400
P	2.10401800	-2.10514500	-0.31412200
N	2.52861500	-1.89104700	-1.93351500
N	3.49836000	-1.55564900	0.48892700
N	1.88711000	-3.77760800	-0.22014100
N	0.62109000	1.16567700	-0.37826000
N	-1.56834300	-0.30441400	0.20946200
P	-2.94057100	-0.65324100	-0.44731300
P	0.91639100	2.71535500	-0.34764200
N	1.67428900	3.27052000	-1.74584000
N	-3.19401600	0.28418600	-1.83849200
N	-3.10775000	-2.31422000	-0.70544200
N	1.89450700	3.10050000	0.98040000
N	-0.44793500	3.69292800	-0.30281700
N	-4.32489500	-0.31141100	0.44670200
C	-0.49603400	5.07734700	-0.78432400
H	0.41786300	5.32992300	-1.32159300
H	-1.35080500	5.20190700	-1.46241800
H	-0.62426900	5.78223300	0.05008000
C	-1.59550700	3.33696700	0.53217900
H	-1.63024400	2.26254600	0.71059500
H	-1.57319100	3.86461500	1.49792000
H	-2.51811000	3.62067800	0.01139300
C	-4.78437700	1.07057300	0.61726100

H	-5.88036800	1.08195800	0.66834100
H	-4.39597700	1.51267300	1.54653400
H	-4.46750900	1.68679000	-0.22420700
C	-4.73970900	-1.17667700	1.55783100
H	-4.40578000	-0.77449400	2.52416800
H	-5.83506100	-1.24202500	1.57565700
H	-4.33043800	-2.17984100	1.43883000
C	-4.44528500	0.18077000	-2.59807600
H	-4.63594200	1.13748400	-3.10020200
H	-4.39759200	-0.60208200	-3.37021400
H	-5.28559900	-0.03038100	-1.93572600
C	-2.05220200	0.60513800	-2.69685300
H	-1.15110100	0.74568900	-2.10032600
H	-1.87033700	-0.17900900	-3.45015600
H	-2.26579300	1.53904400	-3.23228300
C	-1.93309900	-3.14017400	-0.98476600
H	-1.78473000	-3.27701200	-2.06799100
H	-1.03828600	-2.68899200	-0.55740000
H	-2.07813900	-4.13200800	-0.53725500
C	-4.34524700	-2.89430300	-1.23747800
H	-4.30503200	-3.00974000	-2.33087300
H	-4.49072200	-3.88974300	-0.79872900
H	-5.20876000	-2.27965300	-0.98068100
C	1.06851800	-4.36965700	0.84123700
H	0.32464500	-3.65265100	1.18420400
H	0.55474300	-5.25572000	0.44727800
H	1.68332500	-4.68667200	1.69778800
C	2.89885700	-4.70597300	-0.73582900
H	3.59648400	-5.03038300	0.05047000

H	2.39666700	-5.59891000	-1.12912800
H	3.46807200	-4.24883900	-1.54615100
C	1.65101700	-2.46987500	-2.96014300
H	0.81698100	-1.79551800	-3.20669100
H	2.23726100	-2.64081600	-3.87064100
H	1.24230200	-3.42310900	-2.62345900
C	3.09855800	-0.61017400	-2.37028800
H	2.31003900	0.12344400	-2.58481100
H	3.75191200	-0.19681700	-1.60210800
H	3.68581400	-0.77852400	-3.28107000
C	4.82587500	-2.06126300	0.10815300
H	5.57993900	-1.30953800	0.37144600
H	5.07834100	-2.99236800	0.63718700
H	4.88054300	-2.24355600	-0.96548300
C	3.39693700	-1.34527400	1.93984300
H	4.19793500	-0.66474300	2.25250200
H	2.43793200	-0.89294100	2.19348100
H	3.51707200	-2.28551400	2.50137400
C	3.03171800	2.25313600	1.36130100
H	3.04750500	2.12900700	2.45110300
H	2.94414000	1.26894600	0.90116100
H	3.98861000	2.70403800	1.05870700
C	2.00882600	4.47268200	1.48234300
H	2.83364000	5.02525300	1.00650600
H	1.08091700	5.02205400	1.32220800
H	2.20181500	4.44061400	2.56115500
C	3.13136100	3.35857000	-1.84842600
H	3.59137100	2.40673400	-2.15340900
H	3.38456000	4.11529700	-2.60011500

H	3.56783600	3.67204100	-0.90011400
C	1.01690700	3.03502900	-3.03561500
H	1.28390000	3.84199700	-3.72880200
H	1.32285200	2.07757500	-3.48180800
H	-0.06778400	3.02922600	-2.91385600
H	0.48319000	1.37070600	2.18935900

Cartesian coordinates for **BnOH**.

C	-1.87109900	1.01343800	-0.07164100
C	-0.50440000	1.29724400	-0.02316900
C	0.43850500	0.26393000	0.06572600
C	-0.00827000	-1.06270100	0.09252300
C	-1.37596500	-1.34800900	0.03674400
C	-2.31173600	-0.31324300	-0.04204600
H	-2.58962600	1.82645800	-0.14166800
H	-0.16845400	2.33244200	-0.05804700
H	0.72006900	-1.86532800	0.14554200
H	-1.70978200	-2.38277700	0.05343300
H	-3.37460300	-0.53743500	-0.08575700
C	1.90909700	0.60142600	0.17357300
H	2.15186000	0.85454700	1.21865800
H	2.12919900	1.48752700	-0.44072700
O	2.69466000	-0.51294300	-0.25152700
H	3.62726600	-0.32439600	-0.06948400

Cartesian coordinates for **BnO⁻**.

O	-2.67055200	-0.00032700	0.77352800
C	-2.06197800	0.00030200	-0.42550000
H	-2.30706800	-0.89291300	-1.08161900

H	-2.30702200	0.89421500	-1.08067600
C	-0.53021600	0.00018600	-0.27943900
C	0.18771500	-1.20054400	-0.15727200
C	0.18799800	1.20071400	-0.15708400
C	1.56853800	-1.20777000	0.06744500
H	-0.35774000	-2.14068600	-0.23478500
C	1.56883500	1.20757300	0.06765300
H	-0.35721300	2.14101100	-0.23447500
C	2.26980500	-0.00018600	0.18105700
H	2.10181700	-2.15512700	0.15326800
H	2.10233300	2.15479000	0.15365200
H	3.34512100	-0.00033100	0.35524300

Cartesian coordinates for **HL**.

C	0.56616800	-1.61374100	-0.29039900
C	-0.86351400	-1.37604200	0.19525800
C	-1.37713100	-0.00863300	-0.28239800
C	-0.34050700	1.11656200	-0.14737700
C	1.48505100	-0.52845600	0.25323500
H	-0.89007000	-1.41759400	1.29472600
H	-1.52890900	-2.16904400	-0.16352200
H	0.60220600	-1.61424400	-1.38946400
H	0.93810200	-2.58986900	0.04549500
H	1.51581600	-0.60045200	1.35118600
H	-1.54032900	-0.07600200	-1.37161900
O	-0.64433900	2.28816000	-0.21043200
C	-2.71346100	0.41400200	0.36194100
H	-2.94722600	1.42907100	0.02784600
H	-2.58041400	0.47042700	1.45185900

C	-3.88138000	-0.52318300	0.03171600
H	-4.81303200	-0.13977900	0.46371900
H	-3.73140200	-1.53508700	0.42631400
H	-4.03006400	-0.60528600	-1.05320000
O	0.97702100	0.80457200	-0.04443400
C	2.91020400	-0.58359100	-0.29372900
H	3.29027900	-1.59996700	-0.11891800
H	2.86827600	-0.44274900	-1.38226700
C	3.85973700	0.44300800	0.33384400
H	3.50665100	1.46370100	0.15863900
H	4.86514500	0.35054300	-0.09274000
H	3.94250100	0.29492400	1.41833100

Cartesian coordinates for **HL**

C	0.62508400	-1.63761700	-0.30343900
C	-0.78757000	-1.52751400	0.28234200
C	-1.29659000	-0.10786400	0.26086300
C	-0.50438500	0.99664300	-0.03375700
C	1.46020200	-0.45200000	0.18222000
H	-0.77629000	-1.94579700	1.31584400
H	-1.45609000	-2.20837000	-0.27934700
H	0.58532200	-1.59598800	-1.40198900
H	1.10297000	-2.58910200	-0.01986000
H	1.44479800	-0.45097300	1.29119500
O	-0.82324000	2.20486900	-0.12844000
C	-2.74122200	0.11188500	0.62093600
H	-2.87419600	1.15387000	0.94029300
H	-3.02196100	-0.52633000	1.48510000
C	-3.75231600	-0.17355500	-0.51491200

H	-4.79568100	-0.04103400	-0.17908700
H	-3.65263600	-1.20241100	-0.88994200
H	-3.57224300	0.50684600	-1.35642700
O	0.90491000	0.76421300	-0.28760100
C	2.91924500	-0.50368900	-0.28395000
H	3.35642400	-1.45955200	0.04522000
H	2.92826800	-0.50788100	-1.38390500
C	3.76747800	0.66450900	0.23239300
H	3.32942000	1.61701000	-0.08161300
H	4.79881200	0.60836400	-0.14389600
H	3.81017100	0.66390400	1.33056800

Cartesian coordinates for **H₂O**.

O	0.00000000	0.00000000	0.11729100
H	0.00000000	0.77129900	-0.46916500
H	0.00000000	-0.77129900	-0.46916500

Cartesian coordinates for **HO[•]**.

O	0.00000000	0.00000000	0.10831900
H	0.00000000	0.00000000	-0.86655200

Reference

1. Sharif, M., Jackstell, R., Dastgir, S., et al. (2017). Efficient and selective Palladium-catalyzed Telomerization of 1,3-Butadiene with Carbon Dioxide. *Chemcatchem* **9**, 542-546, <https://doi.org/10.1002/cctc.201600760>.
2. Save, M., Schappacher, M., and Soum, A. (2002). Controlled Ring-Opening Polymerization of Lactones and Lactides Initiated by Lanthanum Isopropoxide, 1. General Aspects and Kinetics. *Macromol. Chem. Phys.* **203**, 889-899, [https://doi.org/10.1002/1521-3935\(20020401\)203:5/6](https://doi.org/10.1002/1521-3935(20020401)203:5/6).
3. Schneiderman, D.K., and Hillmyer, M.A. (2016). Aliphatic Polyester Block Polymer Design. *Macromolecules* **49**, 2419-2428, 10.1021/acs.macromol.6b00211.