

Supporting Information

Linear not Cyclic – Unravelling an Anionic Initiation Pathway for Lewis Pair Polymerization of Lactones

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Table of Contents

Methods	3
Materials and reagents	3
Instrumentation and characterization	3
Synthesis of PPDL by ZnEt ₂ -DBU	4
Polymerization kinetics.....	5
Preparation of the ZnEt ₂ treated PDL FT-IR samples	5
Supporting data.....	6
Table S1. Control polymerization reactions.	6
Figure S1. ¹ H and ¹³ C NMR analysis of high molecular weight PPDL.....	6
Figure S2. MALDI-TOF MS analysis of low molecular weight PCL.....	7
Figure S3. NMR tube preparation method to record <i>in-situ</i> NMR spectra.....	7
Figure S4. <i>In-situ</i> ¹ H NMR of δVL treated with ZnEt ₂ -DBU Lewis Pair	7
Figure S5. <i>In-situ</i> ¹ H NMR of γBL treated with ZnEt ₂ -DBU Lewis Pair.....	8
Figure S6. <i>In-situ</i> ¹ H NMR of εCL treated with ZnEt ₂ -DBU Lewis Pair.....	8
Figure S7. FT-IR analysis of ZnEt ₂ treated PDL.....	9
Figure S8. <i>In-situ</i> ¹ H NMR of ZnEt ₂ -DBU adduct.	10
Figure S9. Hypothesised reaction mechanism for ZnEt ₂ -DBU initiated polymerization of PDL.	10
Figure S10. ¹ H NMR of PPDL synthesized by ZnEt ₂ -DBU in toluene at 120 °C.....	11
Figure S11. HSQC NMR spectroscopy of PPDL synthesized at 120 °C.	12
Figure S12. HMBC NMR spectroscopy of PPDL synthesized at 120 °C.	13
Figure S13. COSY NMR spectroscopy of PPDL synthesized at 120 °C.	14
Figure S14. ¹ H NMR of PCL synthesized by ZnEt ₂ in the absence of DBU.	15
Table S2. Specifications for polymers used for viscometry.	15
Figure S15. Viscosity of PPDL with number average molecular weight.....	16
Figure S16. <i>In-situ</i> ¹³ C NMR of δVL treated with ZnEt ₂ -DBU Lewis Pair	17
Figure S17. <i>In-situ</i> ¹³ C NMR of γBL treated with ZnEt ₂ -DBU Lewis Pair.....	17
Figure S18. ¹³ C NMR of P(δVL) synthesized with ZnEt ₂ -DBU Lewis Pair.....	18
Figure S19. SEC analysis of P(δVL) synthesized with ZnEt ₂ -DBU Lewis Pair.....	18
Figure S20. ¹ H NMR of P(δVL) synthesized with ZnEt ₂ -DBU Lewis Pair.....	18
Figure S21. SEC analysis of PPDL synthesized using various ratios of ZnEt ₂ to DBU	19
Figure S22. End group analysis of PPDL synthesized with γBL-ZnEt ₂ -DBU initiation system.....	20
Figure S23. SEC analysis of P(εCL) synthesized using ZnEt ₂ -DBU Lewis Pair.	20

Methods

Materials and reagents

The manipulation of all air or moisture sensitive reagents was performed inside a N₂-filled glovebox. All glassware and stirring bars were oven dried prior to use, unless otherwise mentioned. Purification of δ -valerolactone (δ VL), γ -butyrolactone (γ BL), and ϵ -caprolactone (ϵ CL) (99%, Sigma-Aldrich) was performed by drying over CaH₂ (93%, Thermo Scientific) for 18 hours, followed by vacuum distillation. The distillate was stored inside a glovebox over activated molecular sieves (4 Å). Pentadecalactone (PDL) (98%, Sigma-Aldrich) was dried over P₂O₅ for at least 7 days prior to use. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (>99%, Sigma-Aldrich), diethyl zinc 15 wt.% in toluene (Sigma-Aldrich), and anhydrous toluene (99%, Sigma-Aldrich) were stored under nitrogen atmosphere and used without further purification. HCl 2 M in anhydrous Et₂O (99%, Sigma-Aldrich) was stored at 11 °C, trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (>99%, Sigma-Aldrich) was stored in a desiccator over activated alumina, and NaOTf (98%, Sigma-Aldrich) and tetrahydrofuran (THF) (inhibitor free, >99%, Sigma Aldrich) were stored under ambient conditions and used without further purification.

Instrumentation and characterization

Nuclear magnetic resonance (NMR)

¹H, ¹³C, ¹H-¹H correlation, and ¹H-¹³C correlation NMR spectra were recorded in CDCl₃ on a 400 MHz Bruker Avance III HD instrument at room temperature. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent signal (CHCl₃: ¹H, δ = 7.26 ppm, ¹³C, δ = 77.2 ppm). ¹H NMR spectra recorded in toluene were referenced to the methyl group of toluene (CH₃ toluene: 2.36 ppm).

Size exclusion chromatography (SEC)

SEC elugrams were obtained on a Malvern GPCMAX instrument containing a PLgel 5 μ m guard column (7.5 x 50 mm) and two PLgel 5 μ m MIXED-D (300 x 7.5 mm) columns. HPLC grade CHCl₃ containing 2% (v/v) toluene was used as eluent at 35 °C. Polystyrene standards with a narrow dispersity

(162-364,000 g mol⁻¹) were used as calibration. Samples were prepared at ~3 mg mL⁻¹ for a 100 µL injection volume.

Matrix assisted laser desorption/ionization time of flight mass spectroscopy (MALDI TOF MS)

MALDI TOF MS spectra were recorded on an ultrafleXtreme MALDI TOF/TOF with a smartbeam-II laser operating at a wavelength of 355 nm (Bruker Daltonik), controlled by FlexControl software (Bruker Daltonik). Sample preparation was performed as follows: low molecular weight polymer was dissolved in chloroform (5 mg mL⁻¹), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile matrix was dissolved in THF (100 mg mL⁻¹), and NaOTf was dissolved in THF (10 mg mL⁻¹). These 3 solutions were then mixed as: 40 µL polymer, 10 µL NaOTf, and 60 µL matrix. The resulting solution was spotted on stainless steel MALDI target plate and left to dry.

Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectra were recorded in the 600–4000 cm⁻¹ region for 16 scans on a Perkin-Elmer spotlight 400 FT-IR system equipped with a MKII heated Diamond 45° ATR Top Plate crystal.

Viscometry

Viscometry was performed on a Lauda iVisc Viscosimeter (Version 1.01) equipped with an Ubbelohde type viscometer at a capillary constant of 0.009582 mm² s⁻². Polymer samples were dissolved at a concentration of 0.1 g mL⁻¹ in CHCl₃ and loaded using a glass pipette. The Hagenbach kinetic energy correction was employed for the analysis of a statistical significance samples (p<0.005) consisting of 5 repetitions.

Synthesis of PPDL by ZnEt₂-DBU

A typical polymerization procedure was as follows: an oven-dried glass vial was charged with PDL (1 g, 4.16 mmol, 50 equiv.), dissolved in anhydrous toluene (2.08 mL, 1.80 g), and treated with ZnEt₂ 15 wt.% in toluene (68.5 mg, 0.083 mmol, 1 equiv.) and DBU (25.3 mg, 0.166 mmol, 2 equiv.). The vial was equipped with a septum and quickly transferred out of the glovebox onto a preheated sand bath at 90 °C for polymerization and determination of kinetics. After a determined time, HCl (2 M) in

anhydrous Et₂O (208 μL, 0.416 mmol, 5 equiv.) was added to the reaction vial to stop the reaction, the polymers were isolated by precipitation from cold MeOH and dried for 24 hours *in vacuo* to yield a white fluffy solid. Typical yield = 0.96 g (96%). ¹H NMR (400 MHz, CDCl₃) δ 4.05 (t, *J* = 6.7 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.61 (m, 4H), 1.37 – 1.23 (m, 20H). ¹³C NMR (101 MHz, CDCl₃) δ 174.1, 77.3, 64.5, 34.5, 29.8, 29.7, 29.7, 29.7, 29.6, 29.4, 29.4, 29.3, 28.8, 26.1, 25.2.

Polymerization kinetics

To monitor the polymerization rate of PDL, samples were withdrawn from the crude mixture during polymerization for ¹H NMR spectroscopy and SEC analysis. Initially, samples were obtained through the septum using clean needles and syringes. As the solution turned too viscous, the reaction vials were decapped under a flow of nitrogen, where oven dried glass pipettes were used to draw samples. The drawn samples were quenched by dissolution in cold undried CHCl₃ or CDCl₃. ¹H NMR analysis was performed immediately after sample preparation in the deuterated solvent and conversion was determined by comparative integration of the methylene peaks of the monomer (PDL δ = 4.14 ppm, εCL δ = 4.26, δVL δ = 3.63) and polymer (PPDL δ = 4.06 ppm, P(εCL) δ = 4.06, P(δVL) δ = 3.88).

For δVL, γBL, and εCL, kinetics were monitored by in-situ ¹H NMR analysis at room temperature.

Preparation of the ZnEt₂ treated PDL FT-IR samples

An oven dried glass vial was charged with PDL (94 mg, 0.391 mmol, 1 equiv.), DBU (53 mg, 0.391 mmol, 1 equiv.), and ZnEt₂ 15 wt% in toluene (288 mg, 0.391 mmol, 1 equiv.). The vial was capped and the solution transferred outside the glovebox onto a preheated sand bath at 120 °C, where the solution was left for 2 hours. During this time, the solution solidified to form a yellow/orange clear solid. FT-IR analysis was performed directly on this solid.

In the case where the FT-IR product were quenched, HCl (2 M) in Et₂O (200 μL) was added and the solution was stirred mechanically with a glass pipette until a white dispersion was obtained. The solvent was then removed *in vacuo* to yield a white powder. FT-IR analysis were performed directly on the white powder.

Supporting data

Table S1. Polymerization reactions of ZnEt₂ or DBU with CL or PDL at different temperatures. Monomer concentration = 2 M with [monomer]/[ZnEt₂ or DBU] = 50/1.

Entry	Solution	Reaction time (h)	Reaction temperature (°C)	Conversion (%) ^a
1	ZnEt ₂ + CL	6	120	99
2	ZnEt ₂ + CL	9	90	98
3	ZnEt ₂ + PDL	4	120	0
4	DBU + CL	6	120	0
5	DBU + PDL	6	120	0
6	ZnEt ₂ + 2 DBU + PDL	6	22	0

^a determined by ¹H NMR of the crude sample.

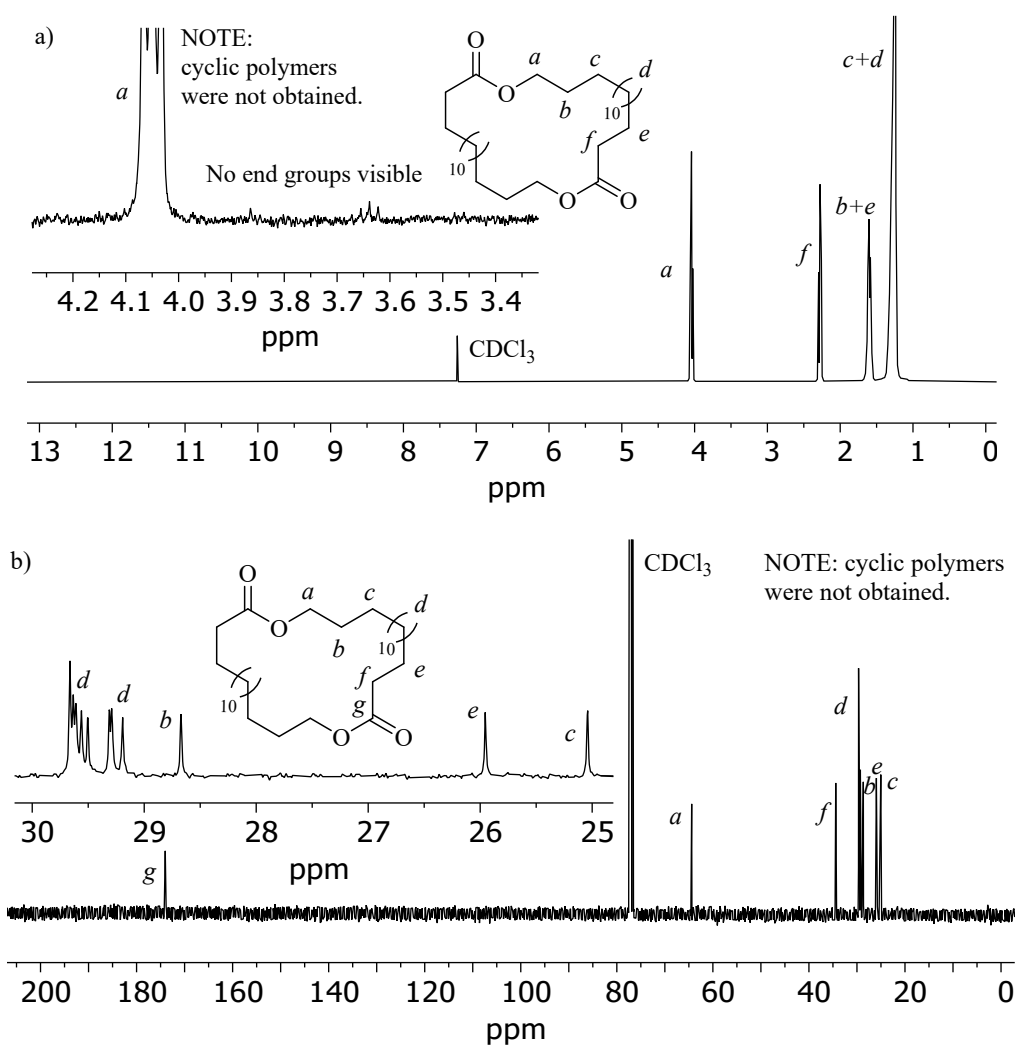


Figure S1. Analysis of PPDL synthesized by ZnEt_2 -DBU Lewis pair at 90°C in toluene. a) ^1H NMR (400 MHz, 298 K, CDCl_3). b) ^{13}C NMR (101 MHz, 298 K, CDCl_3). End-groups of high molecular weight polymers are not visible, which may be interpreted as cyclic polymer.

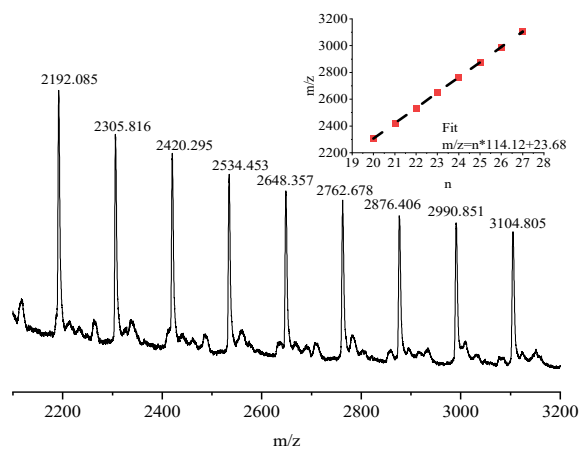


Figure S2. MALDI-TOF MS analysis of low molecular weight PCL synthesized at 90°C in toluene using $[\text{CL}]_0 = 1.5\text{ M}$ and $[\text{CL}]/[\text{ZnEt}_2] = 25/1$. Reaction was terminated using HCl in anhydrous Et_2O .

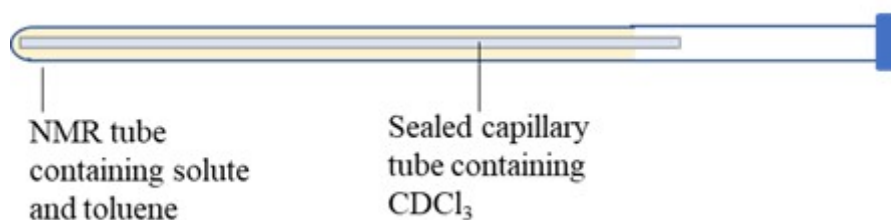


Figure S3. NMR tube preparation method to record ^1H NMR spectra in toluene.

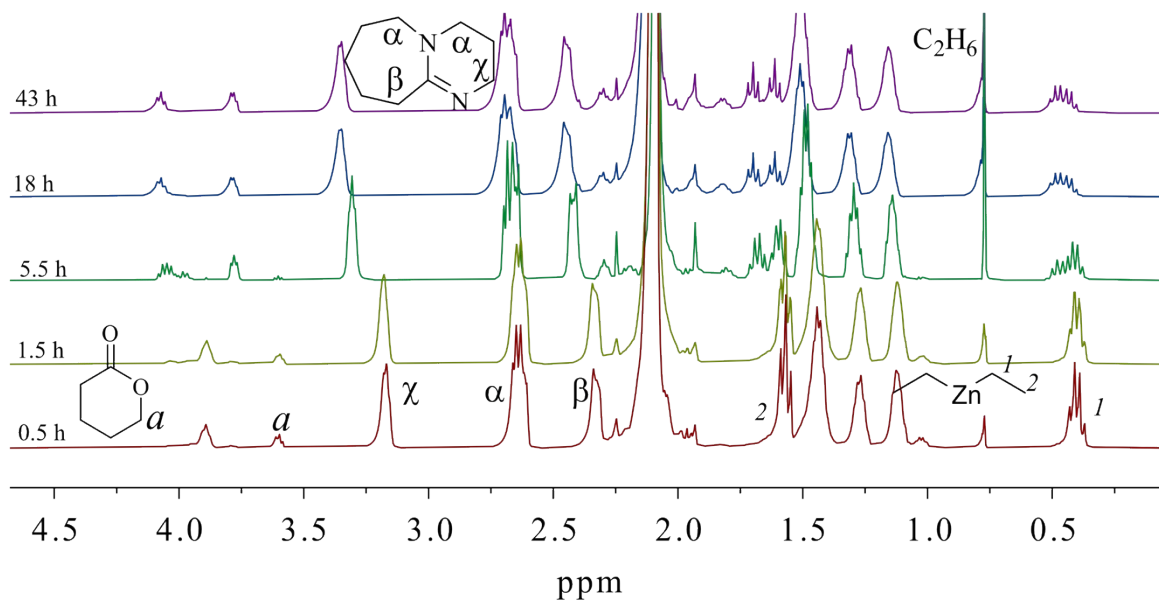


Figure S4. In-situ ^1H NMR (298 K, 400 MHz, toluene) of a solution of $[\delta\text{VL}]/[\text{ZnEt}_2]/[\text{DBU}] = 1/1/2$ in toluene at room temperature with spectra recorded over time.

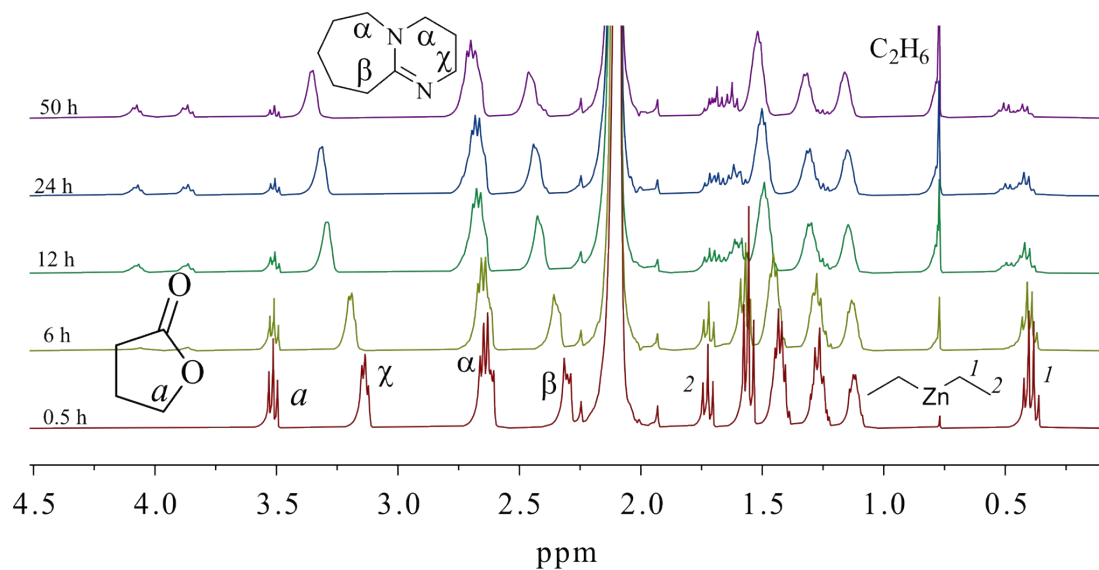


Figure S5. In-situ ^1H NMR (298 K, 400 MHz, toluene) of a solution of $[\gamma\text{BL}]/[\text{ZnEt}_2]/[\text{DBU}] = 1/1/2$ in toluene at room temperature with spectra recorded over time.

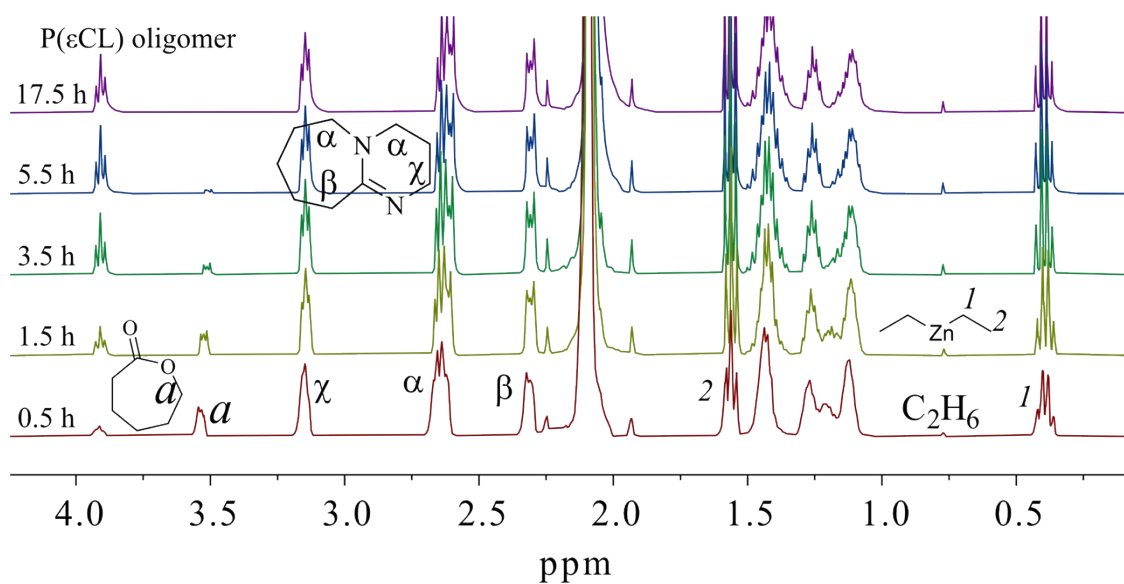


Figure S6. In-situ ^1H NMR (298 K, 400 MHz, toluene) of a solution of $[\text{CL}]/[\text{ZnEt}_2]/[\text{DBU}] = 1/1/2$ in toluene at room temperature with spectra recorded over time.

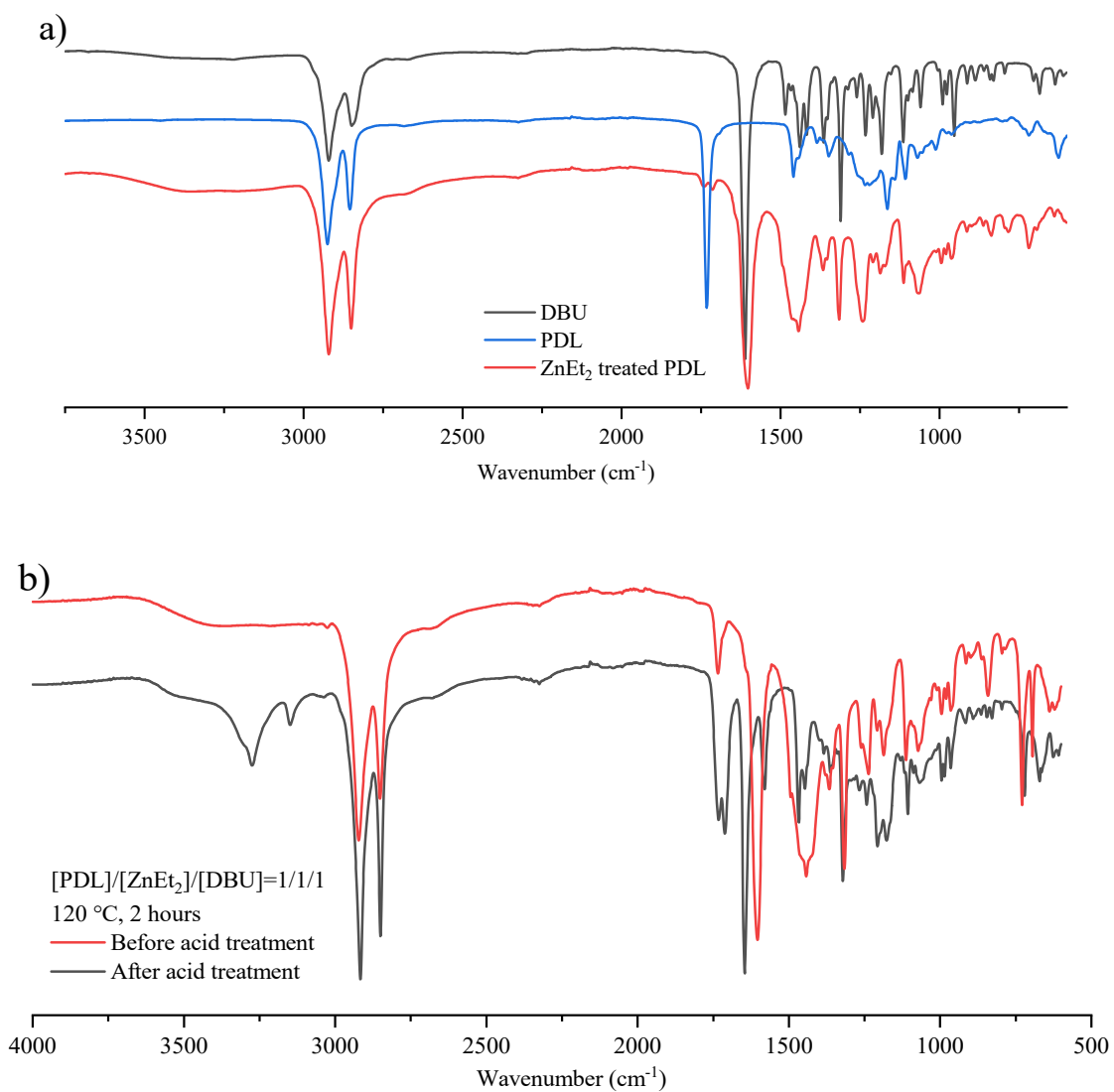


Figure S7. FT-IR spectra of DBU, PDL, and reaction product of [PDL]/[ZnEt₂]/[DBU] = 1/1/1 heated to 120 °C in bulk for 2 h. a) compared to DBU and PDL and b) compared to acid treated reaction product.

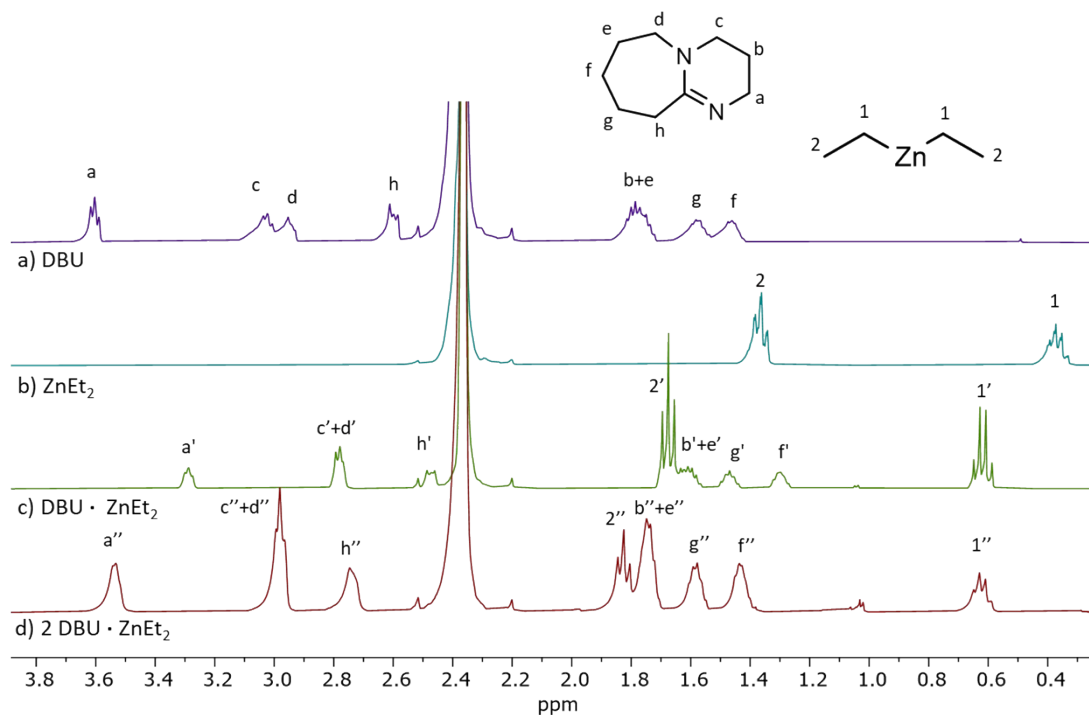


Figure S8. ^1H NMR (400 MHz, 298 K, CDCl_3) recorded in toluene containing a sealed capillary tube containing CDCl_3 present in the NMR tube as schematically drawn in Figure S3. Recorded spectra: a) DBU, b) ZnEt_2 , c) $\text{DBU} \cdot \text{ZnEt}_2$ adduct, and d) $2 \text{ DBU} \cdot \text{ZnEt}_2$ adduct. Ingredients were mixed and no additional heating was required. The large peak at 2.36 ppm is from the toluene.

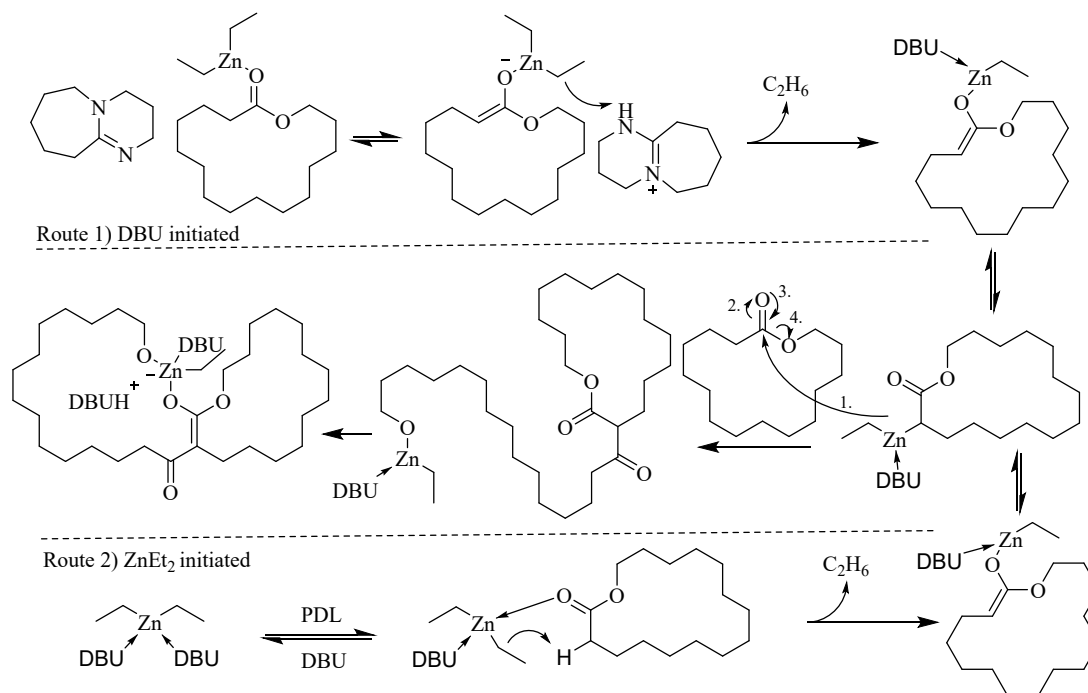


Figure S9. Hypothesised reaction mechanisms for ZnEt_2 -DBU polymerization of PDL.

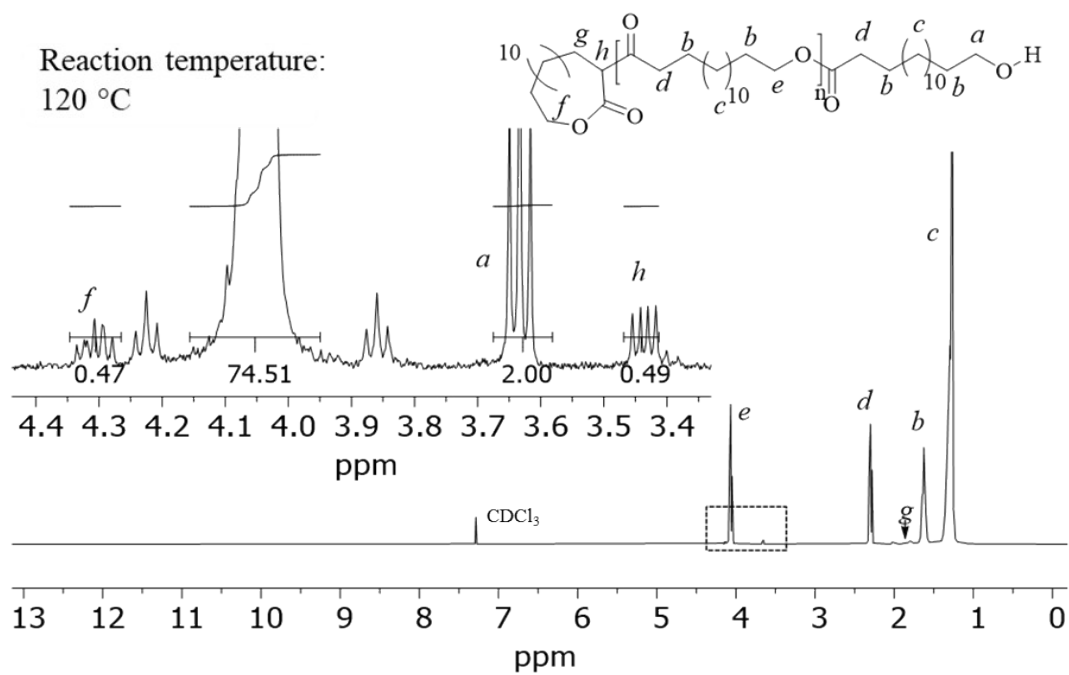


Figure S10. Typical ¹H NMR of PPDL polymer synthesized by [PDL]/[ZnEt₂]/[DBU] = 25/1/2 in toluene at 120 °C and [PDL]₀ = 2 M. Isolated from precipitation in methanol and recorded in CDCl₃ (400 MHz, 298 K, CDCl₃).

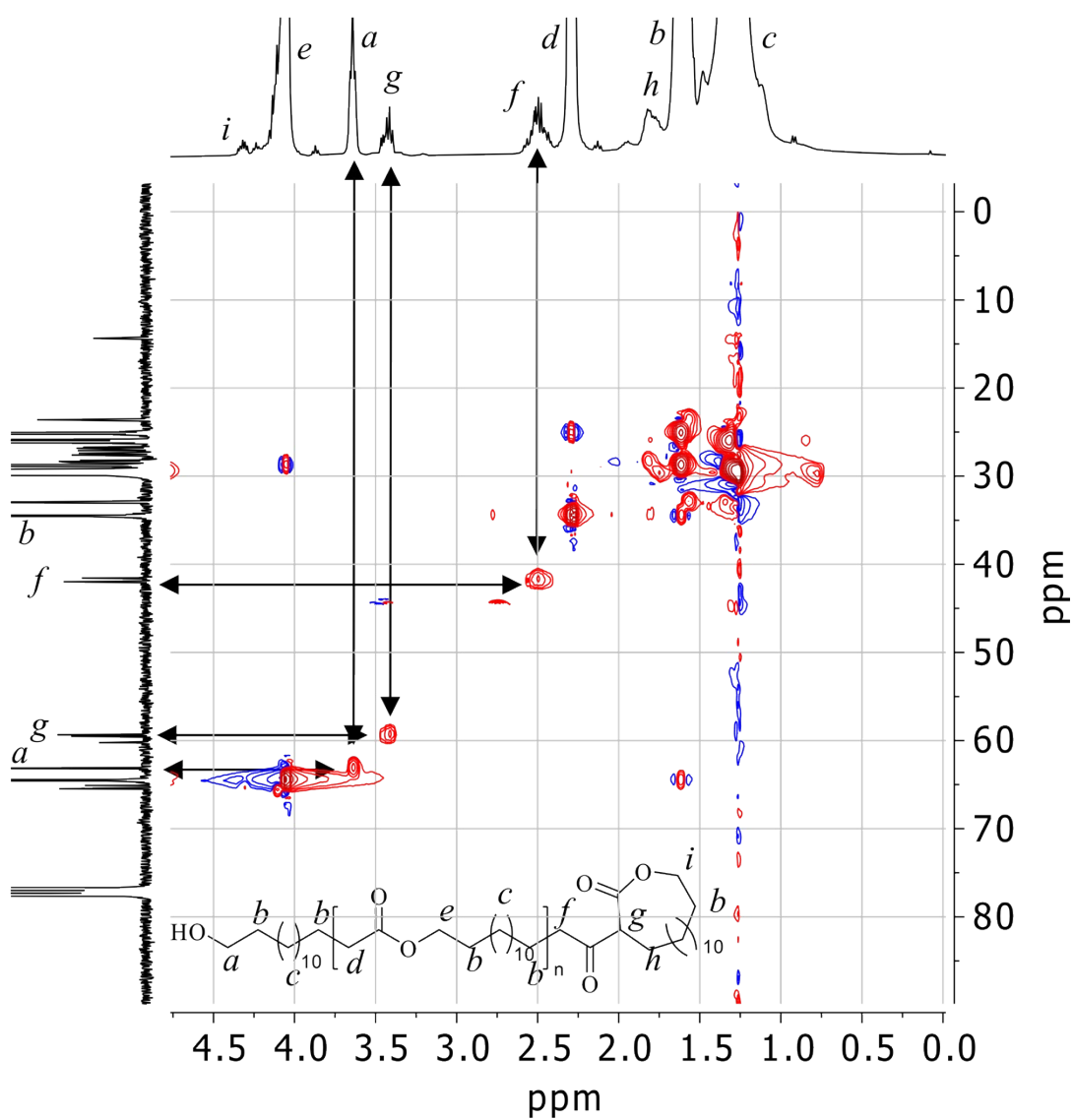


Figure S11. ^1H - ^{13}C heteronuclear single quantum coherence (HSQC) NMR spectroscopy graph (400 MHz, 298 K, CDCl_3) of low molecular PPDL synthesized by $[\text{PDL}]/[\text{ZnEt}_2]/[\text{DBU}] = 15/1/2$ at 120 $^\circ\text{C}$ in toluene.

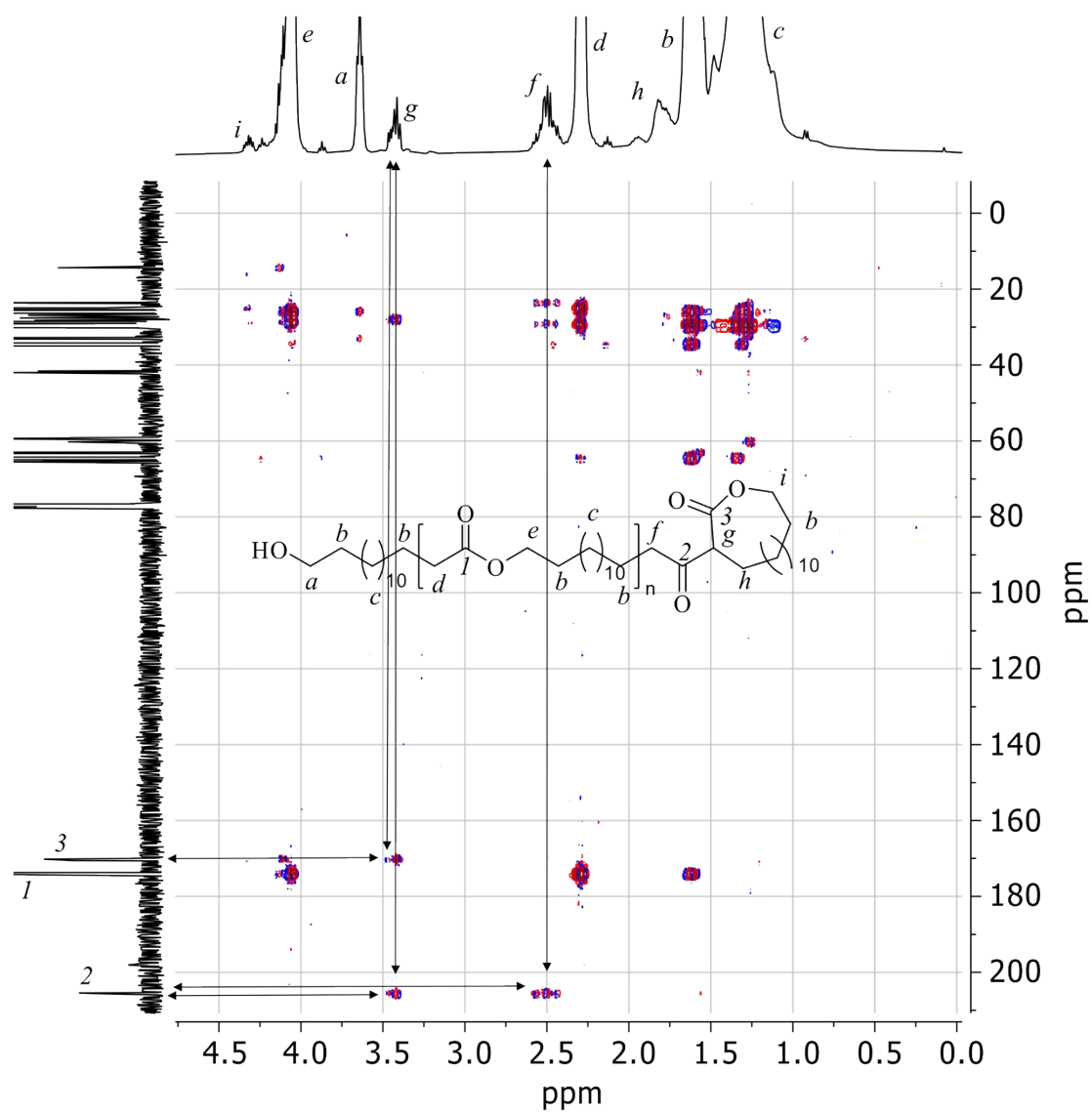


Figure S12. ^1H - ^{13}C heteronuclear multiple-bond correlation (HMBC) NMR spectroscopy (400 MHz, 298 K, CDCl_3) of PPDL synthesized by $[\text{PDL}]/[\text{ZnEt}_2]/[\text{DBU}] = 15/1/2$ at 120 $^\circ\text{C}$ in toluene.

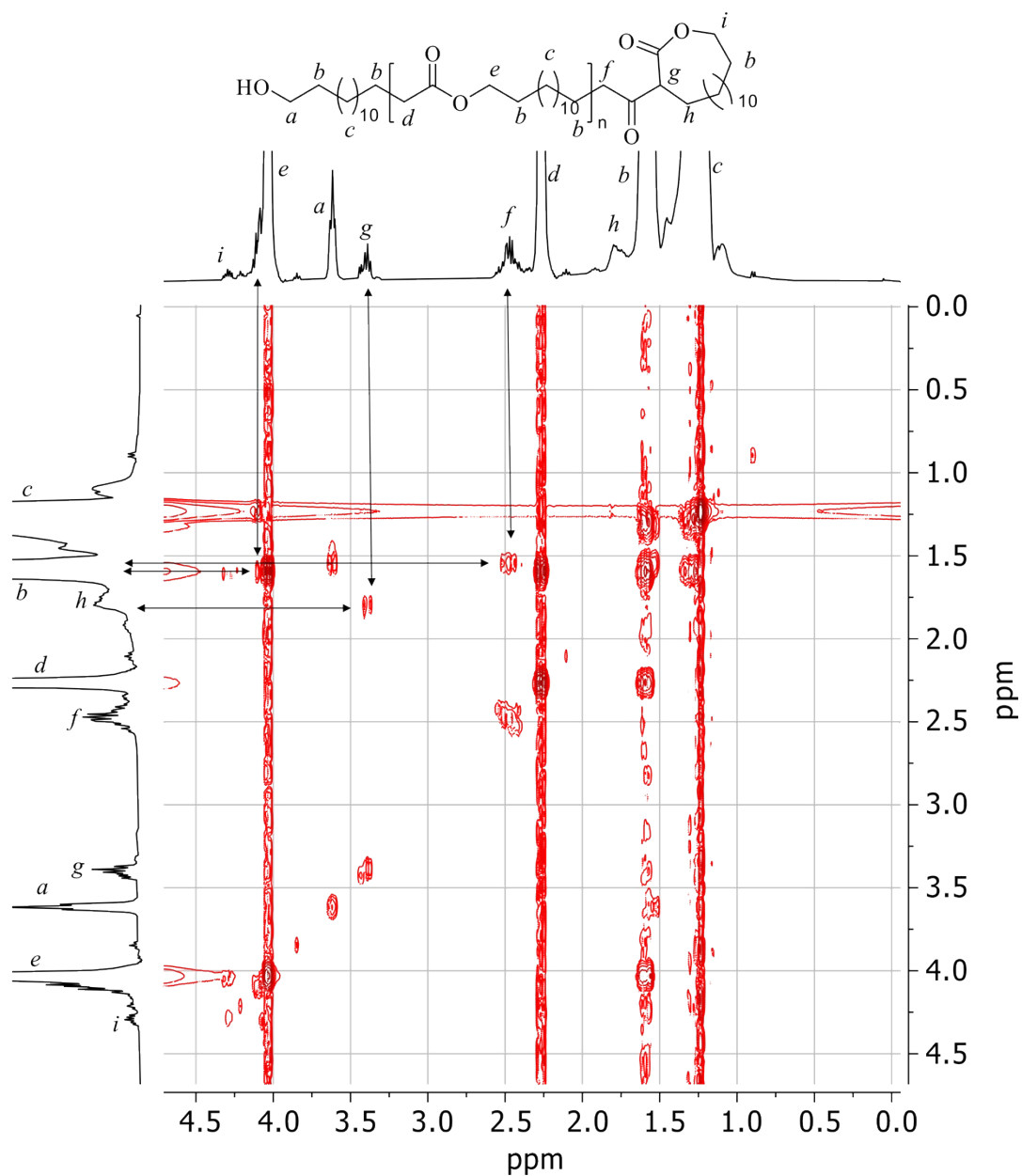


Figure S13. ^1H - ^1H homonuclear correlation (COSY) NMR spectroscopy (400 MHz, 298 K, CDCl_3) of PPDL synthesized by $[\text{PDL}]/[\text{ZnEt}_2]/[\text{DBU}] = 15/1/2$ at 120 °C in toluene.

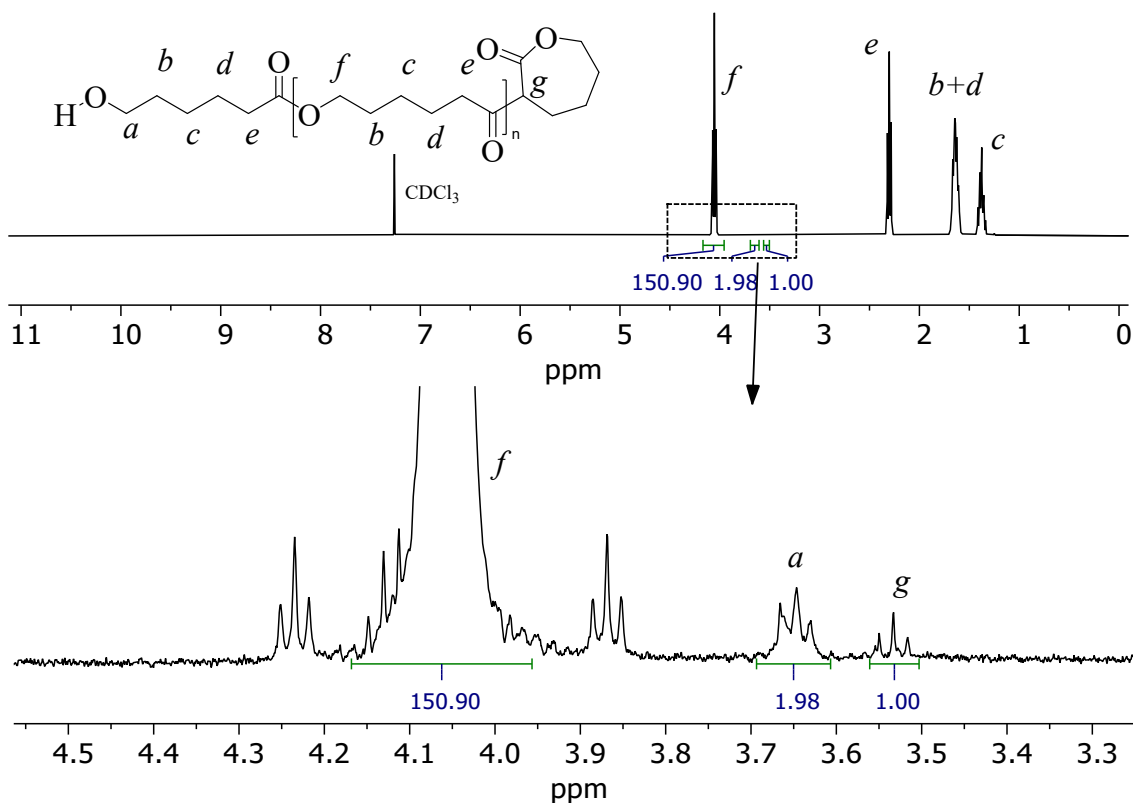


Figure S14. ^1H NMR (400 MHz, 298 K, CDCl_3) of PCL polymer synthesized by $[\text{CL}]/[\text{ZnEt}_2] = 50/1$ at 120 °C in the absence of DBU.

Table S2. Polymer samples used for viscosity analysis.

Catalyst	T (°C)	$M_{n,\text{theory}}$ (kg mol^{-1})	DP^a	M_n (kg mol^{-1}) ^a	M_n (kg mol^{-1}) ^b	\mathcal{D}^b
ZnEt ₂ -DBU	120	8.7	32	7.7	24.5	1.86
ZnEt ₂ -DBU	120	11.4	43	9.4	37.1	1.89
ZnEt ₂ -DBU	120	22.4	73	17.5	72.5	1.60
ZnEt ₂ -DBU	120	33.5	114	27.4	102.5	1.75
^t BuOLi ^c	120	12.0	50	12.0	42.5	1.79
^t BuOLi ^c	120	18.0	78	18.7	70.5	1.78
^t BuOLi ^c	120	29.1	120	28.8	97.6	1.70
^t BuOLi ^c	120	33.6	140	33.7	117.1	1.67

^aDetermined by ^1H NMR (400 MHz, 298 K, CDCl_3).

^bDetermined by SEC analysis versus polystyrene standards (0.5 mL min⁻¹, 3 mg mL⁻¹, CHCl_3).

^cUsed to generate PPDL of known linear topology. $[\text{PDL}] = 2 \text{ M}$ in toluene treated with desired quantity ^tBuOLi and heated for 2 hours at 120 °C.

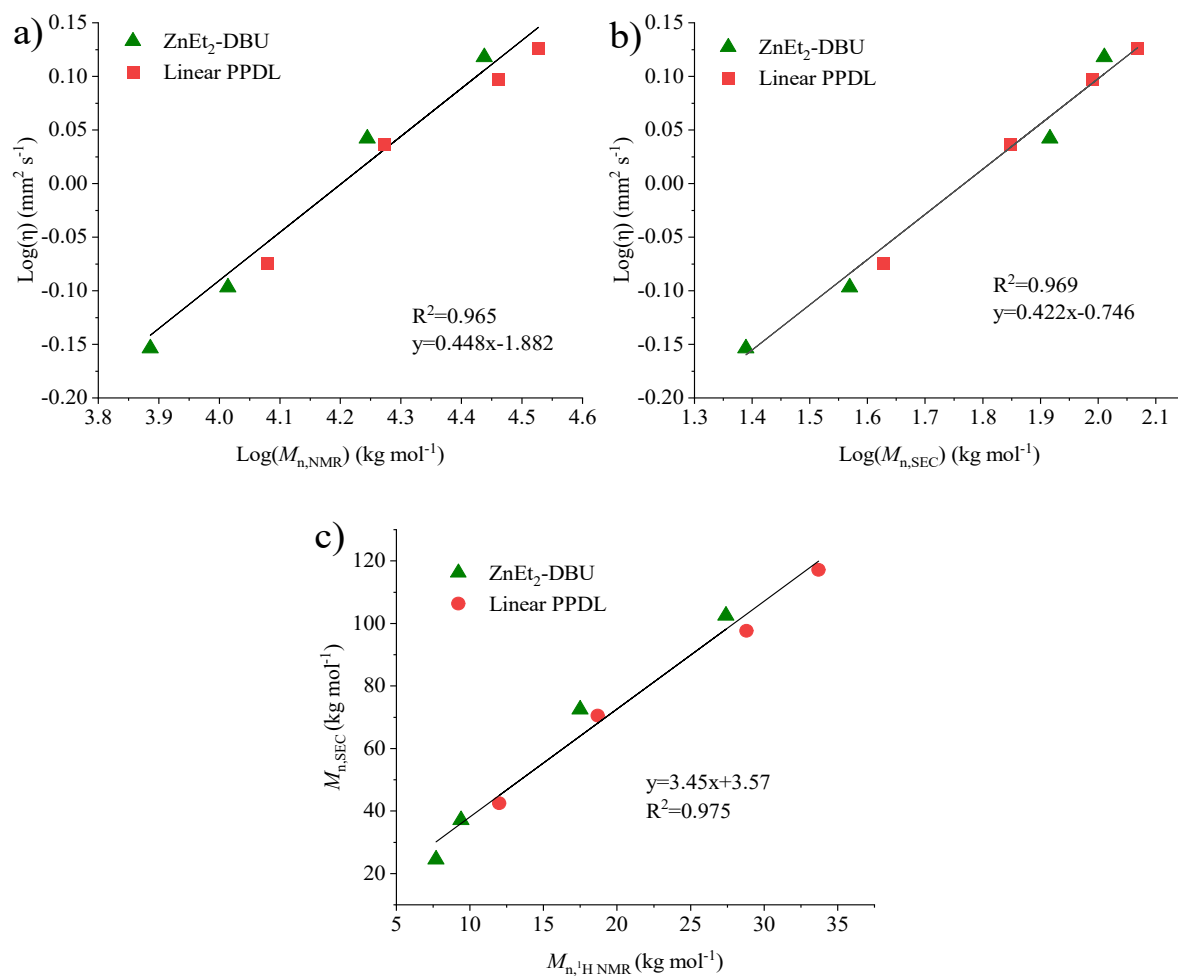


Figure S15. Viscometry (Ubbelohde, $0.009582 \text{ mm}^2 \text{ s}^{-2}$, $0.1 \text{ g mL}^{-1} \text{ CHCl}_3$) analysis of PPDL synthesized by $\text{ZnEt}_2\text{-DBU}$ at 120°C compared to a linear PPDL sample synthesized by $^t\text{BuOLi}$ anionic initiator at 120°C . M_n was derived a) by ^1H NMR integration of the alcohol end group and ester repeating unit and b) from SEC versus polystyrene standards.

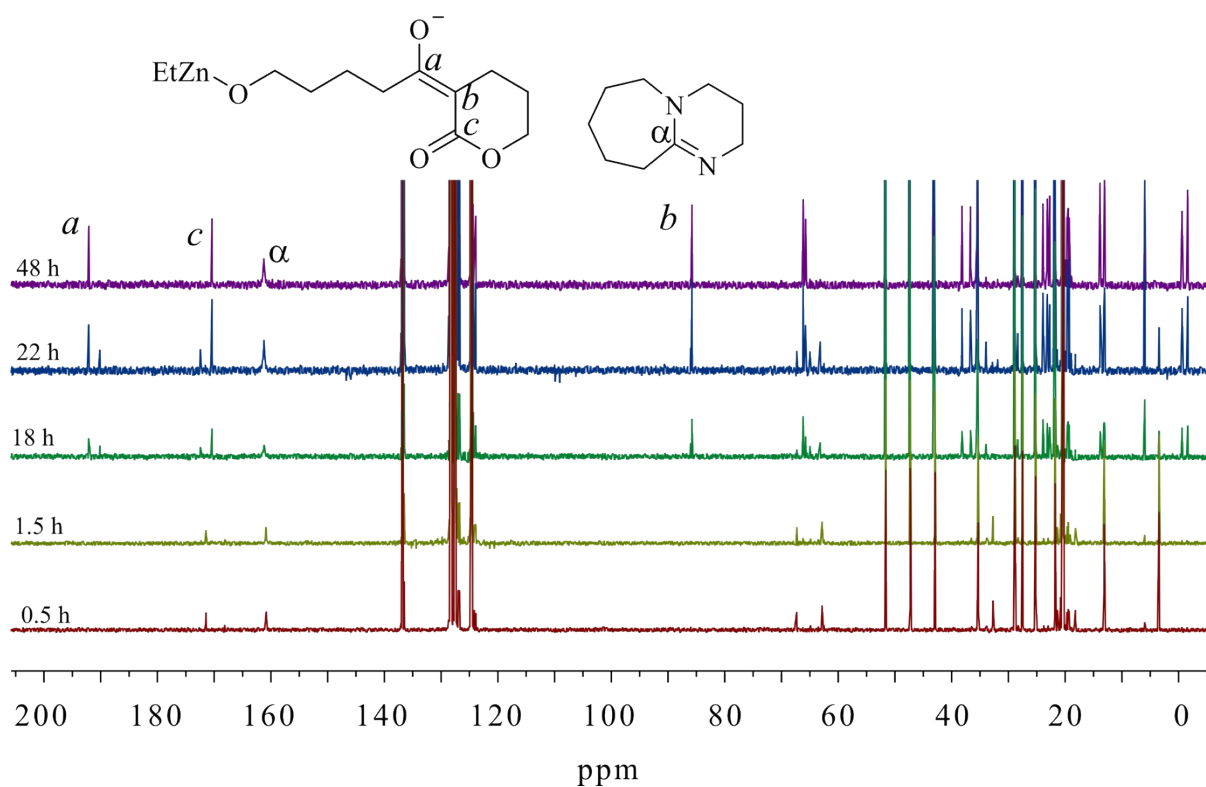


Figure S16. In-situ ^{13}C NMR (101 MHz, 298 K, toluene) analysis of the reaction of $[\delta\text{VL}]/[\text{ZnEt}_2]/[\text{DBU}] = 1/1/2$ in toluene at room temperature over time.

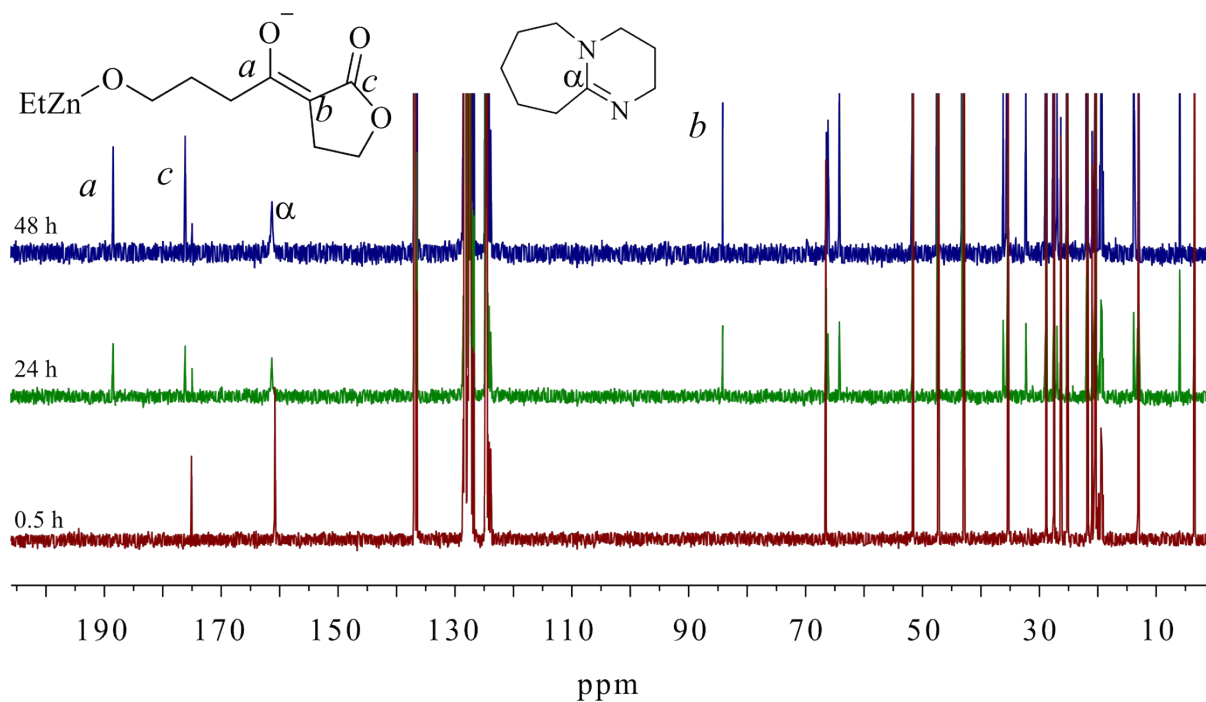


Figure S17. In-situ ^{13}C NMR (101 MHz, 298 K, toluene) analysis of the reaction of $[\gamma\text{BL}]/[\text{ZnEt}_2]/[\text{DBU}] = 1/1/2$ in toluene at room temperature over time.

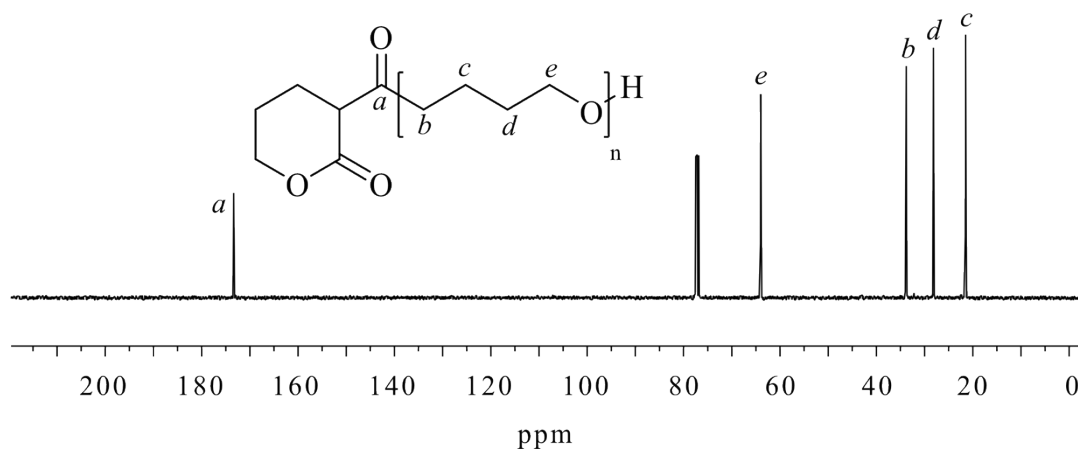


Figure S18. ^{13}C NMR (101 MHz, 298 K, CDCl_3) analysis of $P(\delta\text{VL})$ synthesized by $[\delta\text{VL}]/[\text{ZnEt}_2]/[\text{DBU}] = 50/1/2$ in toluene $[\delta\text{VL}]_0 = 2 \text{ M}$ at room temperature after 18 hours and obtained by precipitation in heptane.

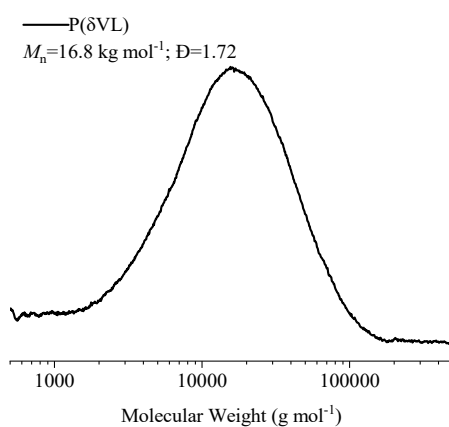


Figure S19. SEC elugram (CHCl_3) of $P(\delta\text{VL})$ synthesized by $[\delta\text{VL}]/[\text{ZnEt}_2]/[\text{DBU}] = 50/1/2$ in toluene $[\delta\text{VL}]_0 = 2 \text{ M}$ at room temperature after 18 hours and obtained by precipitation in heptane.

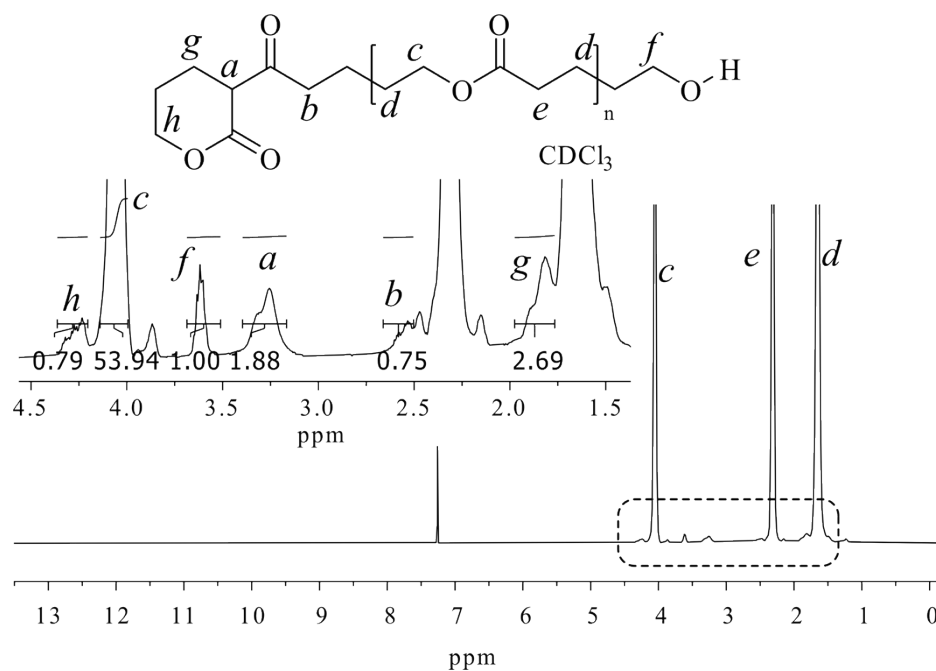


Figure S20. ^1H NMR (400 MHz, 298 K, CDCl_3) analysis of $P(\delta\text{VL})$ synthesized by $[\delta\text{VL}]/[\text{ZnEt}_2]/[\text{DBU}] = 50/1/2$ in toluene $[\delta\text{VL}]_0 = 2 \text{ M}$ at room temperature after 18 hours and obtained by precipitation in heptane.

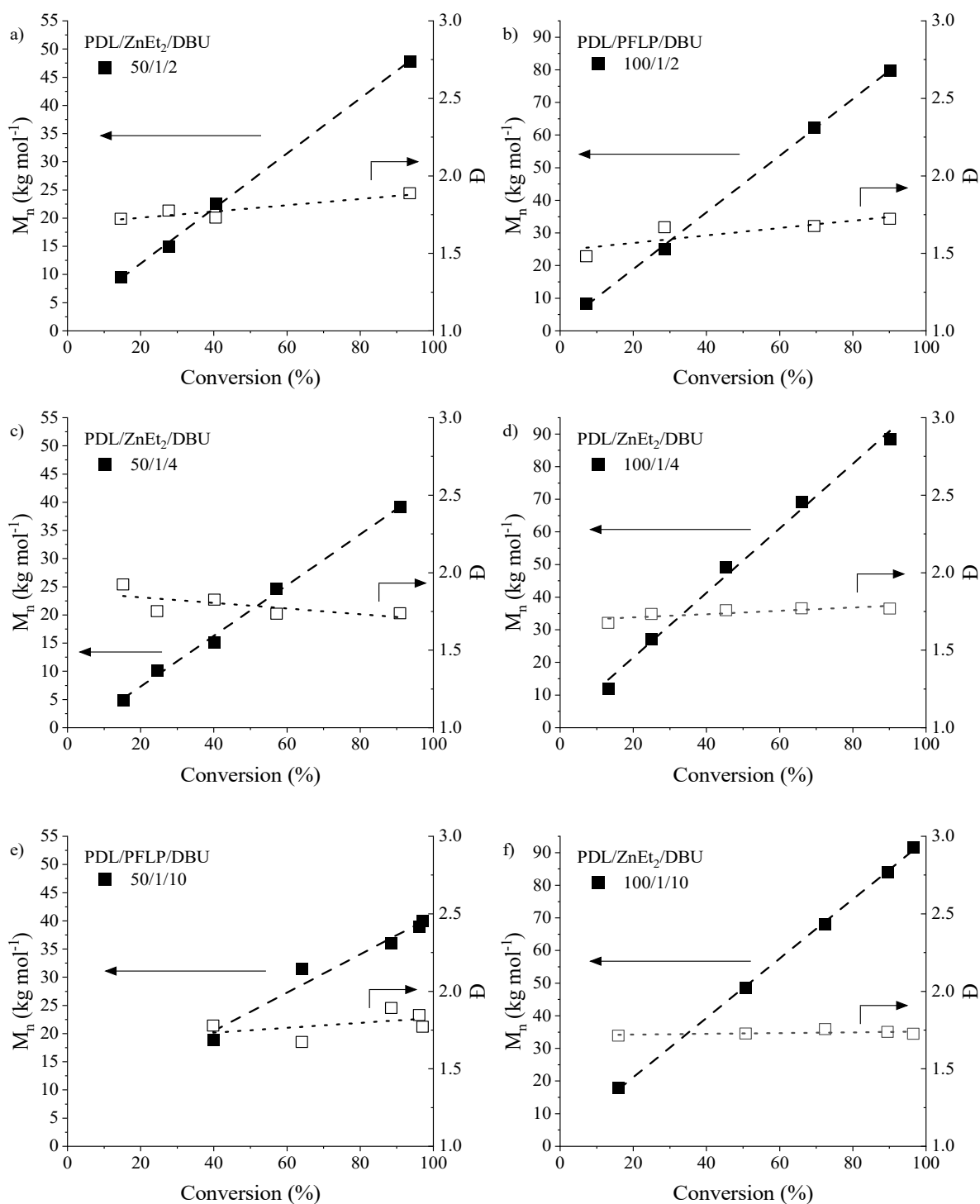


Figure S21. Number average molecular weight and dispersity to conversion of PPDL synthesized using ratios of ZnEt₂ to DBU ranging from 2 to 10. Conditions: [PDL] = 2 M in toluene at 90 °C. Reported values were obtained by SEC in CHCl₃ at a flow rate of 0.5 mL min⁻¹ versus narrow disperse polystyrene standards.

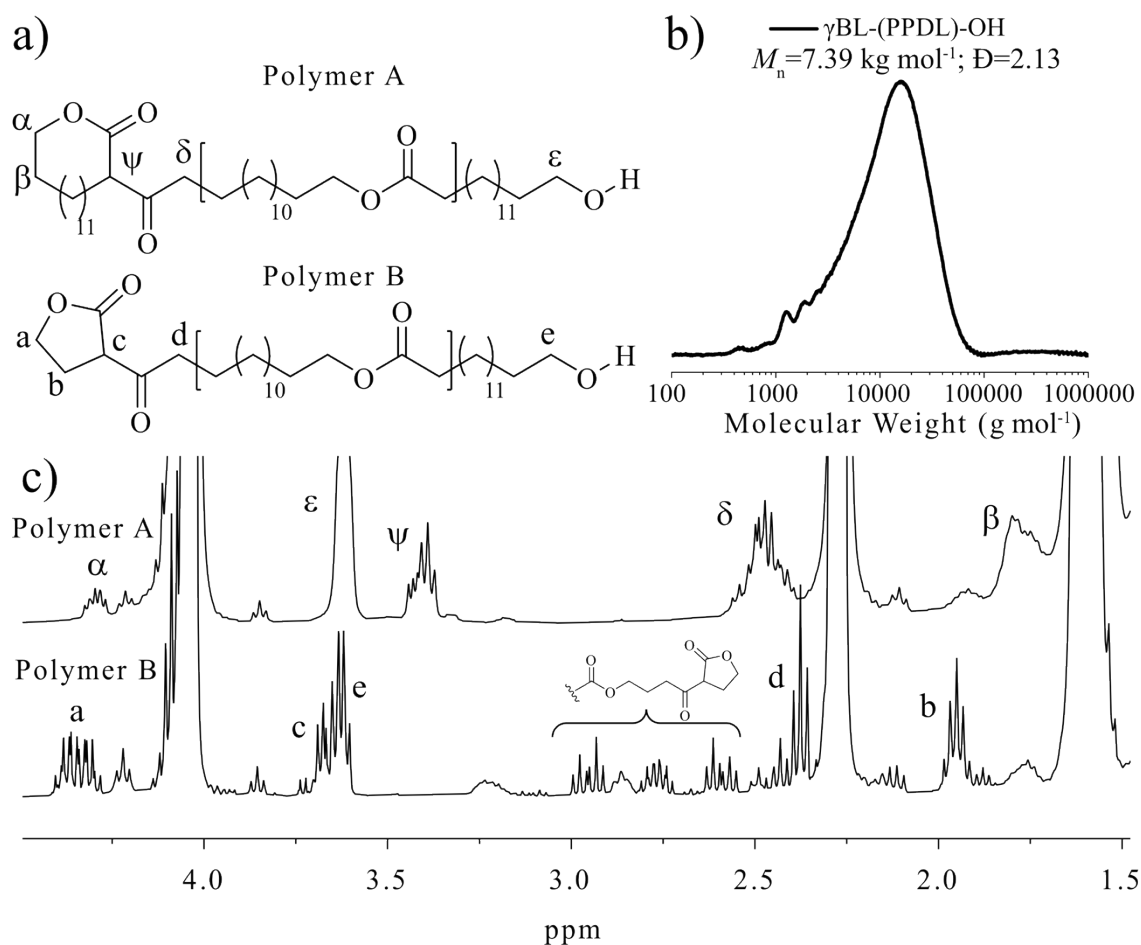


Figure S22. Low molecular weight PPDL synthesized by $[\text{PDL}]/[\text{ZnEt}_2]/[\text{DBU}]/[\gamma\text{BL}] = 10/1/2/3$ with $[\text{PDL}]_0 = 1.9 \text{ M}$ in toluene after heating to $90 \text{ }^\circ\text{C}$ for 1 hour. Polymer was obtained by dissolution in CHCl_3 and precipitation in MeOH ($2\times$). a) chemical structure of polymers synthesized in the absence (Polymer A) of γBL and presence (Polymer B) of γBL . b) SEC elugram (CHCl_3) of the synthesized PPDL. c) ^1H NMR (298K, 400 MHz, CDCl_3) of polymers A and B shown in 4a.

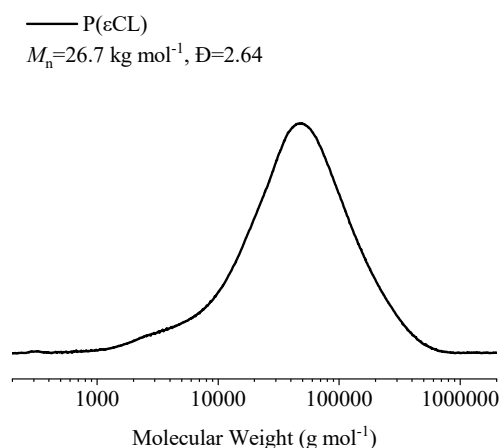


Figure 23. SEC elugram (CHCl_3) of $\text{P}(\epsilon\text{CL})$ synthesized by $[\epsilon\text{CL}]/[\text{ZnEt}_2]/[\text{DBU}] = 50/1/2$ in toluene $[\epsilon\text{CL}]_0 = 2 \text{ M}$ at room temperature after 18 hours and obtained by precipitation in heptane