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Supporting Information

Closed-loop Chemical Recycling of Poly(ε-caprolactone) by Tuning Reaction Parameters

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Experimental Procedures

Materials

All of the poly(ε-caprolactone) (PCL) products were purchased from commercial sources and used as received. Benzyl alcohol (BnOH, > 99.9%) was received from Alfa Aesar, distilled by cryo-distillation over calcium hydride (CaH_2). The BnOH was dissolved into a 1 M solution of toluene as the initiator. Catalyst $Mg(HMDS)_2$ is laboratory-made. The ε-caprolactone (ε-CL) used for polymerization was purified after degradation or purchase from Aladdin Reagent Co. Ltd. (Shanghai, China). All dry solvents were redistilled after collected from solvent purification system and then stored over molecular sieves (4 Å) in a glovebox for no longer than 1 month. Chromatographic tetrahydrofuran was purchased from Honeywell LTD for the analysis of GPC measurements. All other chemicals were commercially available and used after appropriate purification.

Instrumentation

NMR: Nuclear magnetic resonance measurements were performed at room temperature on Bruker Advance instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), $CDCl_3$ and C_6D_6 was used as an internal reference.

GPC: Molecular weights (M_n) and dispersities ($Đ$) of the polymers were determined by gel permeation chromatography (GPC, Agilent 1260 LC, USA) using THF as the eluent (flow rate: 1 mL/min, at 40 °C) and the sample concentration was 1 mg/mL.

MALDI-TOF: Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating in a positive ion, linear mode. The sample solutions (10 mg/mL in THF), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) solution (10 mg/mL in THF) and sodium trifluoroacetate aqueous solution (5 mg/mL) were mixed in a volume ratio of 5:25:1, 1μL of which was then deposited on the target plate and dried before measurement.

DSC: Differential scanning calorimetry (DSC) measurements were performed on DSC 3500 Sirius. Temperature was calibrated with $C_{10}H_{16}$, indium, tin, bismuth and zinc standard. Measurements were performed under N_2 atmosphere with a flow rate of 20 mL/min. Each sample with a mass of 10 mg was used for the measurement. The typical procedures for the measurements of samples were as follows: in the first heating scan, samples were heated from -80 °C to 100 °C at a heating rate of 10 °C/min. In the second heating scan, samples were cooled to -80 °C at 10 °C/min and kept at -80 °C for 5 min to eliminate any thermal history, and subsequently reheated to 100 °C at 10 °C/min.

General procedure for the preparation of $Mg(HMDS)_2$

Under argon atmosphere protection, di-n-butylmagnesium (50.0 mL, 1 mol/L in hexane, 50 mmol, 1 equiv.) and hexamethyldisilazane (21.0 mL, 100 mmol, 2 equiv.) in 50 mL hexane. The reaction mixture was stirred and refluxed at 110 °C for 3 h. Removed from heat and cooled to ambient temperature, then the solvent was removed in vacuum to give a white solid of $Mg[N(SiMe_3)_2]_2$ (10.1 g, 58%). ^1H NMR (400 MHz, C_6D_6, 298 K) δ 0.16 (s), 0.38 (s), 0.45 (s).

General procedure for the polymerization of ε-caprolactone

In a typical polymerization reaction, a dry 5 mL Schlenk tube was first introduced into an argon-filled glovebox. $Mg[N(SiMe_3)_2]_2$ (6.9 mg, 20 μmol, 1 equiv.) and the initiator of BnOH solution (40 μL, 40 μmol, 2 equiv.) were added and stirred for five minutes. Polymerizations were carried out in toluene (or bulk). Then, ε-caprolactone ($[\varepsilon\text{-CL}]_0$ = 2 mol/L (or 8.7 mol/L), 912 mg, 8 mmol, 200 equiv.) was added. Polymerization was performed at 25 ℃ ~ 140 ℃. Monomer conversion was monitored by ^1H NMR spectrum and calculated by comparing the integration of the methylene signals of unreacted monomer to the methylene region of the polymer before precipitation. The polymerization products are obtained by rotary evaporation. ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (t, *J* = 6.7 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.69–1.59 (m, 4H), 1.44–1.32 (m, 2H).

General procedure for the depolymerization of poly(ε-caprolactone)

Depolymerization of poly(ε-caprolactone) was carried out in a round bottom flask. Poly(ε-caprolactone) products was added in atmospheric environment. Then, $Mg[N(SiMe_3)_2]_2$ (0.1 ~ 0.5 mol% with respect to the monomer repeat unit of poly(ε-caprolactone)) was loaded in a glovebox. Depolymerization was performed at 180 ℃ ~ 210 ℃ in 0.07 mbar. The depolymerized products were obtained by vacuum distillation. ^1H NMR (400 MHz, $CDCl_3$) δ 4.18 (t, 2H), *J* = 2.59 (t, 2H), 1.81 (m, *J* = 10.8, 5.3, 3.2, 2.8 Hz, 2H), 1.72 (m, *J* = 6.7, 4.7, 2.9 Hz, 4H).

General procedure for the polymerization-depolymerization cycle of ε-CL

First, the polymerization of CL is carried out. In a typical polymerization reaction, a dry 50 mL round bottom flask was first introduced into an argon-filled glovebox. $Mg[N(SiMe_3)_2]_2$ (173 mg, 0.5 mmol, 1 equiv.) and the initiator of BnOH solution (1 mL, 1 mmol, 2 equiv.) were added and stirred for five minutes. Then, ε-caprolactone (11.4 g, 100 mmol, 200 equiv.) was added. Polymerization was performed at 140 ℃. Monomer conversion was monitored by ^1H NMR spectrum and calculated by comparing the integration of the methylene signals of unreacted monomer to the methylene region of the polymer before precipitation. After polymerization, depolymerization is carried out in the same reaction system. Depolymerization was performed at 210 ℃ in 0.07 mbar. The depolymerized

products were obtained by vacuum distillation.

General procedure for the reuse experiment of $Mg(HMDS)_2$ in depolymerization of PCL

First, the reaction flask and collection flask were weighed (round bottom flask). For the first cycle, poly(ε-caprolactone) granules (88 mmol, 10 g, M_n = 24 kg/mol, $Đ$ = 1.84) and stir bars was added in atmospheric environment. In a glove box, the catalyst $Mg[N(SiMe_3)_2]_2$ (0.088 mmol, 30.4 mg) was added. The reaction was started by heating in a sand bath to 210 °C in an argon atmosphere. It reacts at this temperature for 10 hours. The mass of the product in the collection vial was then weighed and the product was determined by ^{1}H NMR (400 MHz, $CDCl_3$). In the second cycle, poly(ε-caprolactone) granules (88 mmol, 10 g, M_n = 24 kg/mol, $Đ$ = 1.84) was added under argon protection. It reacts at this temperature for 10 hours. The mass of the product in the collection vial was then weighed and the product was determined by ^{1}H NMR. In the third cycle, poly(ε-caprolactone) granules (88 mmol, 10 g, M_n = 24 kg/mol, $Đ$ = 1.84) was added under argon protection. It reacts at this temperature for 10.5 hours. The mass of the product in the collection vial was then weighed and the product was determined by ^{1}H NMR spectrum.

General procedure for the polymer-monomer-polymer close-loop cycle for PCL

The depolymerization of poly(ε-caprolactone) was carried out in a round bottom flask under high vacuum and 210 °C. Poly(ε-caprolactone) products (200 mmol, 22.8 g) was added in atmospheric environment. Then, $Mg[N(SiMe_3)_2]_2$ (0.2 mmol, 69 mg) was loaded in a glovebox. The depolymerized product was determined by ^{1}H NMR spectrum (400 MHz, $CDCl_3$). Subsequently, the product ε-caprolactone monomer (171.9 mmol, 19.6 g) was purified by distillation under reduced pressure (1 mbar) at 75 °C. In a typical polymerization reaction, a dry 250 mL Schlenk tubes was first introduced into an Argon-filled glovebox. $Mg[N(SiMe_3)_2]_2$ (0.43 mmol, 148 mg) and the initiator of BnOH solution (0.86 mmol, 0.86 mL) was added and stirred for five minutes. Polymerizations were carried out in toluene. Then, ε-caprolactone ($[ε\text{-}CL]_0$ = 2 mol/L, 171.9 mmol, 19.6 g) monomer after purification was added. Polymerization was performed at 25 ℃. Monomer conversion was monitored by ^{1}H NMR spectrum. The polymerized products were obtained by rotary evaporation. Final shaping at 80 °C.

General procedure for exploring the ceiling temperature of ε-caprolactone polymerization

First, the polymerization of ε-CL is carried out. In a typical polymerization reaction, a dry 10 mL round bottom flask was first introduced into an argon-filled glovebox. $Mg[N(SiMe_3)_2]_2$ (17.3 mg, 0.05 mmol, 1 equiv.) and the initiator of BnOH solution (0.1 mL, 0.1 mmol, 2 equiv.) were added. Then, toluene (5 mL, solution polymerization) and ε-caprolactone (1.14 g, 10 mmol, 200 equiv.) was added. Polymerization was performed at 60 °C, 80 °C, 100

°C, 120 °C and 140 °C. Monomer conversion was monitored by ^{1}H NMR spectrum and calculated by comparing the integration of the methylene signals of unreacted monomer to the methylene region of the polymer. The methylene peak of ε-CL was confirmed by adding a small amount of ε-caprolactone in the reaction system to determine the peak position. Because the methylene peak of ε-CL overlapped with the satellite peak of the methylene peak of PCL, the peak area of ε-caprolactone was subtracted from one overlapping satellite peak by another unoverlapping satellite peak. Finally, the entropy and enthalpy changes of ε-caprolactone polymerization were obtained by the Van't Hoff plot of $\ln[\varepsilon\text{-CL}]_{eq}$ versus 1/T. Thus, the ceiling temperature of ε-caprolactone polymerization was obtained by equation 2.

$$\ln[\varepsilon\text{-CL}]_{eq} = \Delta H_p^\circ/RT - \Delta S_p^\circ/R \quad \text{.....(1)}$$

$$\Delta G = \Delta H_p^\circ - \Delta S_p^\circ/T \quad \text{.....(2)}$$

Scheme S1.

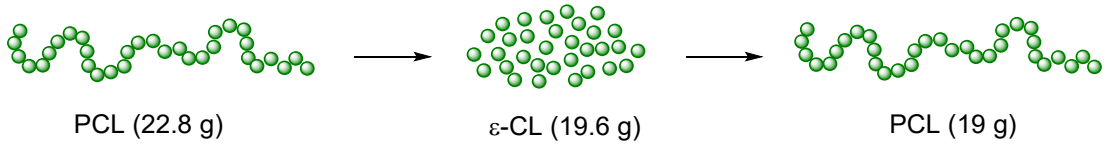


Table S1. Optimization of depolymerization conditions of poly(ε-caprolactone)

Entry[a]	$[\varepsilon\text{-CL}]_0/[\text{Cat.}]_0$	Pressure [mbar]	n[b] [mmol]	Time [h]	Temp. [℃]	Conv.[c] [%]	Yield[d] [%]
1	50:1	1013	10	10	180	>99	<5
2	50:1	0.07	10	10	180	>99	39
3[e]	50:1	0.07	10	10	180	>99	20
4	50:1	0.07	44	10	180	>99	70
5	1000:1	0.07	100	10	210	>99	84

[a] Conditions: depolymerizations were carried out in bulk, catalyst (0.1-2 mol% with respect to the monomer repeat unit of poly(ε-caprolactone)), pressure: 0.07 mbar. Raw materials for thermoplastic granule (M_n = 24 kg/mol, $Đ$ = 1.84). [b] Moles of ε-CL monomer. [c] Conversion was measured by ^{1}H NMR. [d] The ε-caprolactone monomer yield was measured by weighing. [e] Polyethylene glycol monomethyl ether was used as solvent.

Table S2. Depolymerization of poly(ε-caprolactone) by other conditions

Entry[a]	$[\varepsilon\text{-CL}]_0/[\text{Cat.}]_0$	n[b] [mmol]	Time [h]	Temp. [℃]	Conv.[c] [%]	Yield[d] [%]
1[e]	50:1	10	8	180	>99	60
2	50:1	10	11	100	0	0
3	50:1	10	8	180	>99	70
4[f]	250:1	44	9	210	>99	< 5
5	250:1	88	12	180	>99	82
6	500:1	200	6	210	>99	89

[a] Conditions: depolymerizations were carried out in bulk, catalyst (0.1-5 mol% with respect to the monomer repeat unit of poly(ε-caprolactone)), pressure: 0.07 mbar. Raw materials for thermoplastic granule (M_n = 24 kg/mol, $Đ$ = 1.84). [b] Moles of ε-CL monomer. [c] Conversion was measured by ^{1}H NMR. [d] The ε-caprolactone monomer yield was measured by weighing. [e] Raw materials for cleaned poly(ε-caprolactone) factory waste. [f] Pressure: 2 mbar.

Table S3. Polymerization of ε-caprolactone

Entry[a]	[M]:[Cat.]:[I]	Temp. [°C]	Time [h]	Conv.[b] [%]	$M_{n,calcd}$[c] [kg/mol]	$M_{n,GPC}$[d] [kg/mol]	$Đ$[d]
1	400:1:4	25	7	>99	11.4	16.4	1.3
2	1000:1:2	100	8	93	53	35.7	1.4
3[e]	400:1:1	100	3	>99	45.6	37.1	1.8

[a] Polymerizations were carried out in toluene, $[\varepsilon\text{-CL}]_0$ = 2 mol/L, catalyst: $Mg(HMDS)_2$, Initiator: benzyl alcohol. [b] Conversion was determined by ^1H NMR. [c] Calculated molecular weight based on $[M]_0/[I]_0$ ratio and conversion. [d] Apparent number-average molar mass ($M_{n,GPC}$) and dispersity ($Đ$) values were determined by GPC in THF at 40 °C using polystyrene standards for calibration, and corrected using the factor 0.56 for PCL. [e] Initiator: terephthalyl alcohol.

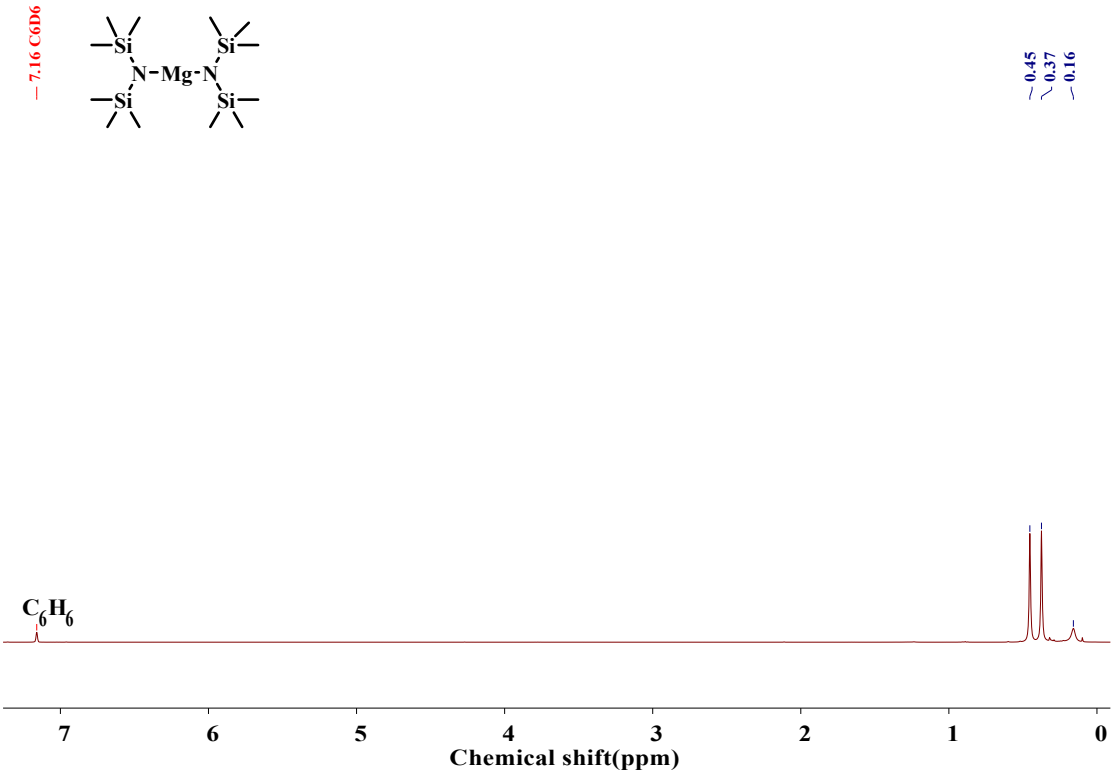


Figure S1. ^1H NMR spectrum of $Mg(HMDS)_2$ (400 MHz, C_6D_6, 25 °C).

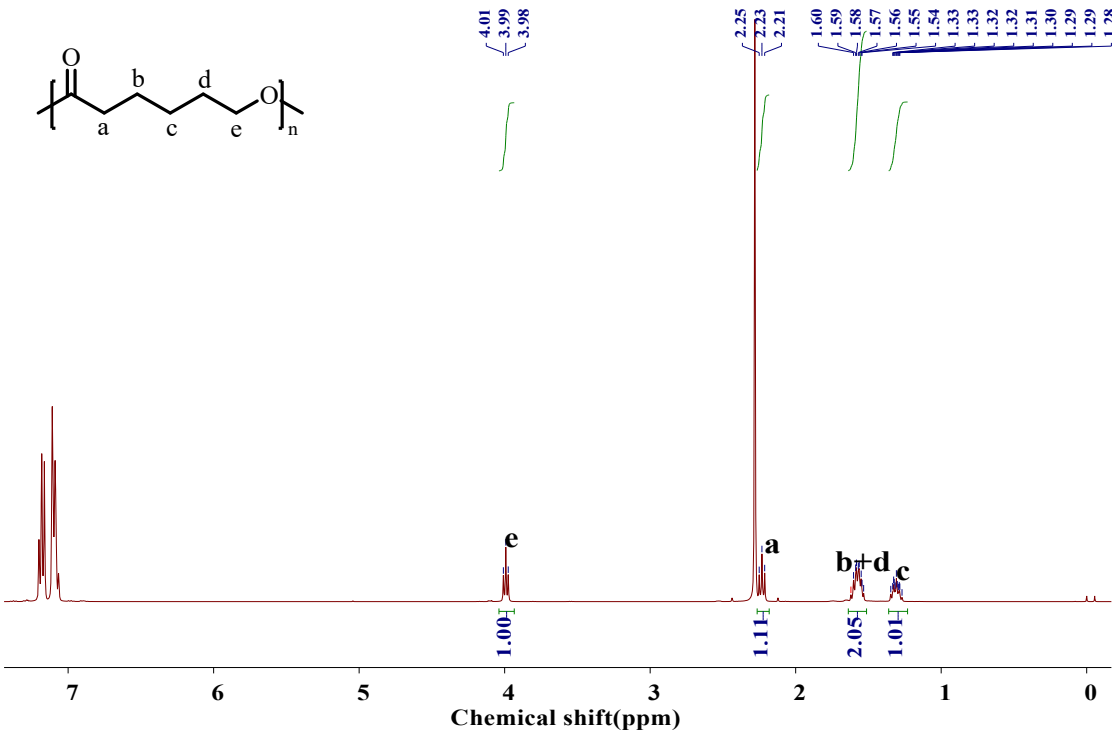


Figure S2. ^{1}H NMR spectrum of PCL (400 MHz, $CDCl_3$, 25 °C). (Table 1, entry 1)

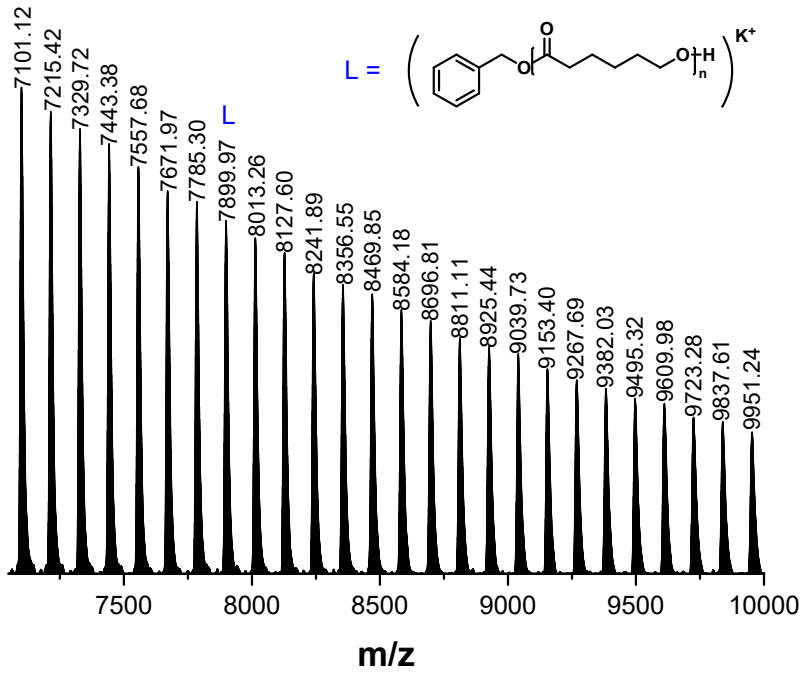
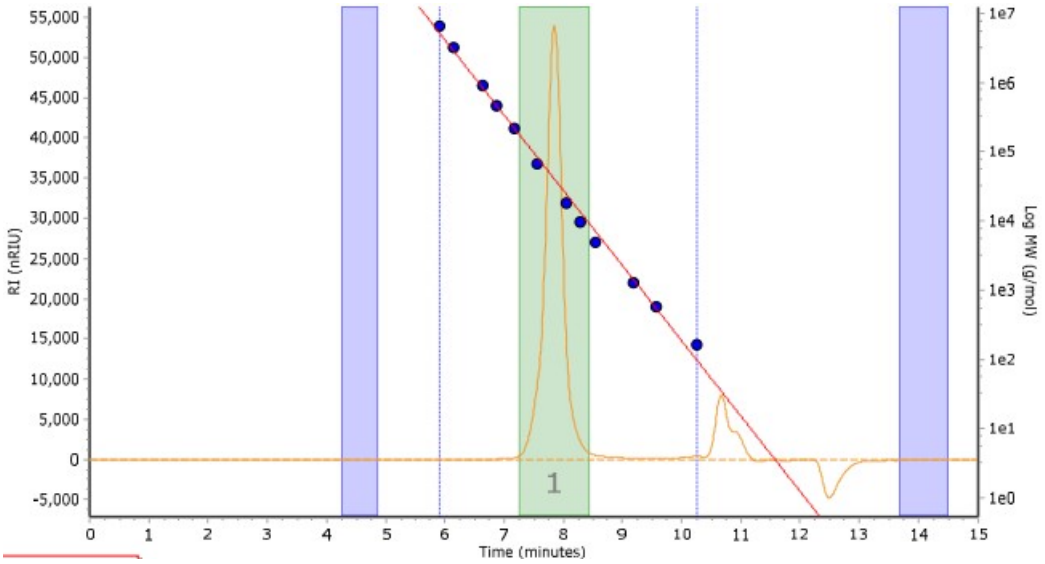


Figure S3. MALDI-TOF analysis for PCL induced by benzyl alcohol. (Table 1, entry 1)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	40044	37065	44492	53849	66385	52242	1.2

Figure S4. GPC analysis for PCL (flow rate: 1 mL/min, at 40 °C). (Table 1, entry 1)

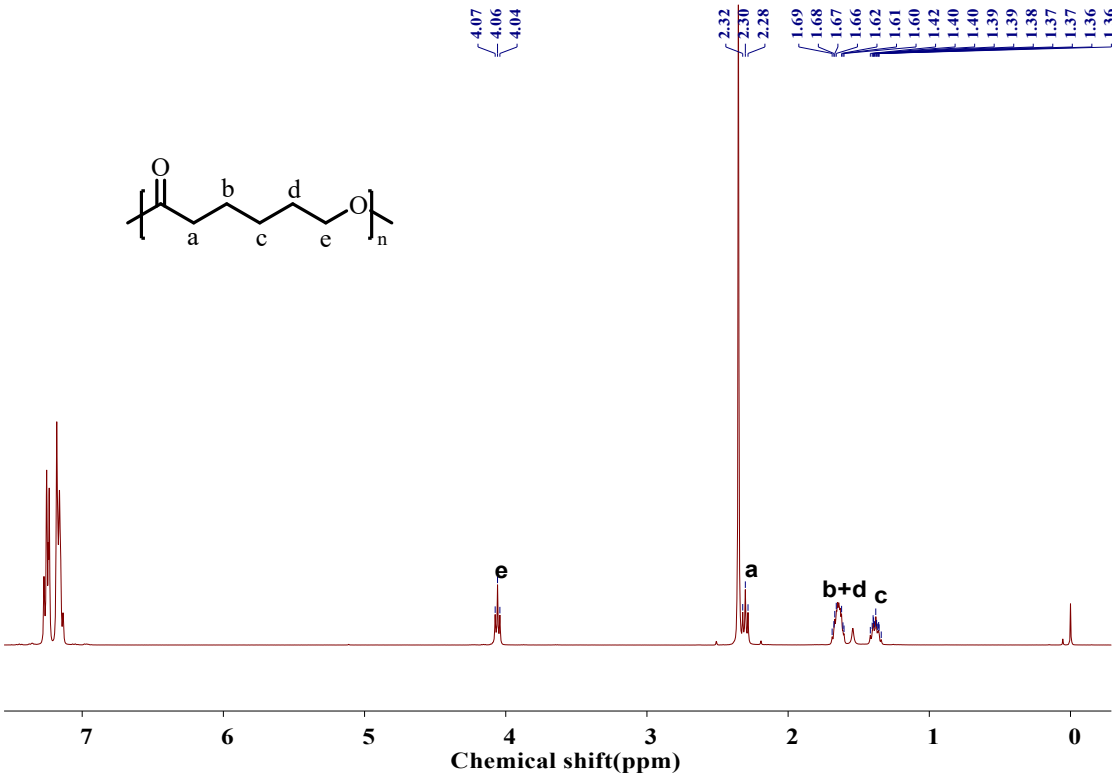
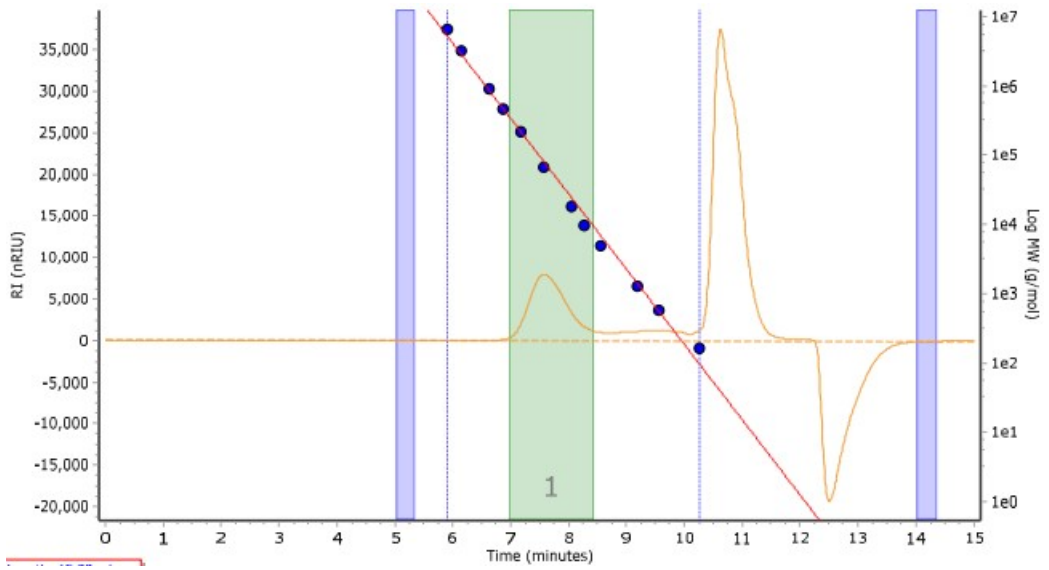


Figure S5. ^{1}H NMR spectrum of PCL (400 MHz, $CDCl_3$, 25 °C). (Table 1, entry 2)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	78076	44573	77985	118107	157475	112330	1.75

Figure S6. GPC analysis for PCL (flow rate: 1 mL/min, at 40 °C). (Table 1, entry 2)

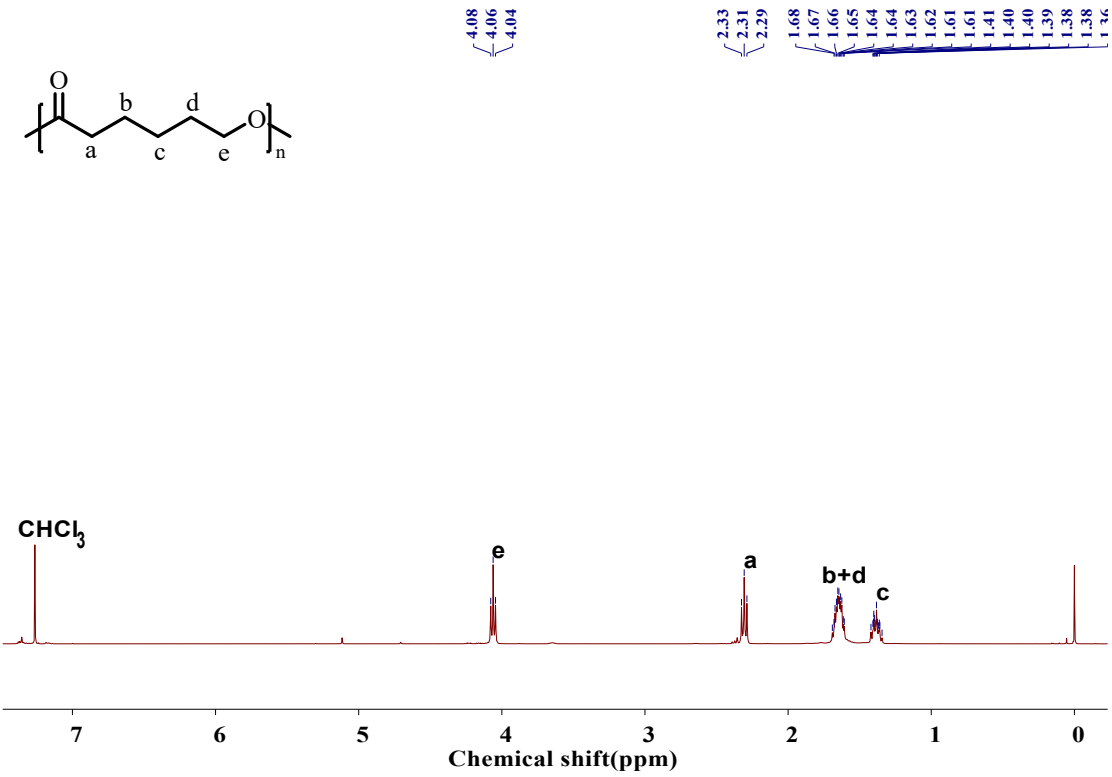
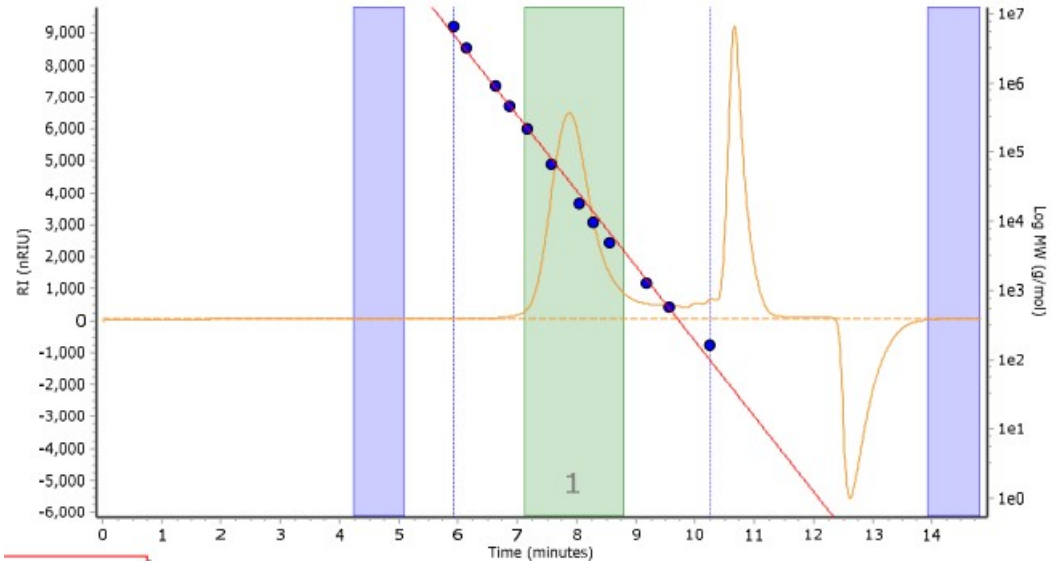


Figure S7. ^{1}H NMR spectrum of PCL (400 MHz, $CDCl_3$, 25 °C). (Table 1, entry 3)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	36838	21713	42845	71308	102373	66976	1.973

Figure S8. GPC analysis for PCL (flow rate: 1 mL/min, at 40 °C). (Table 1, entry 3)

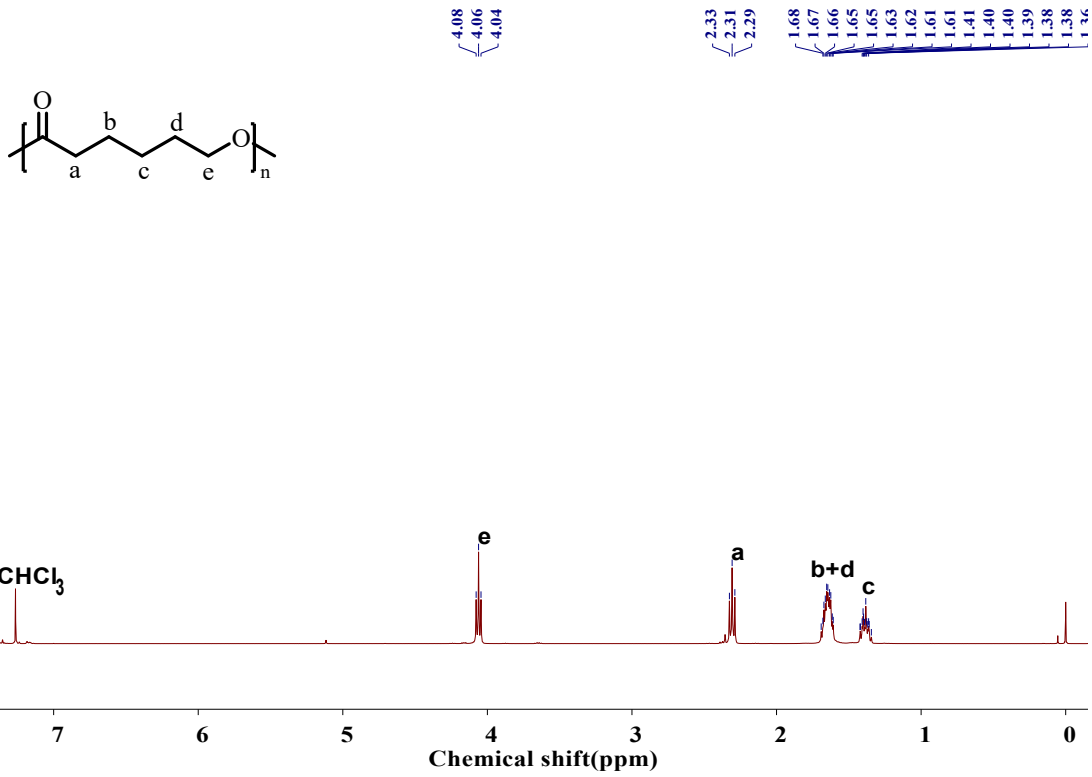
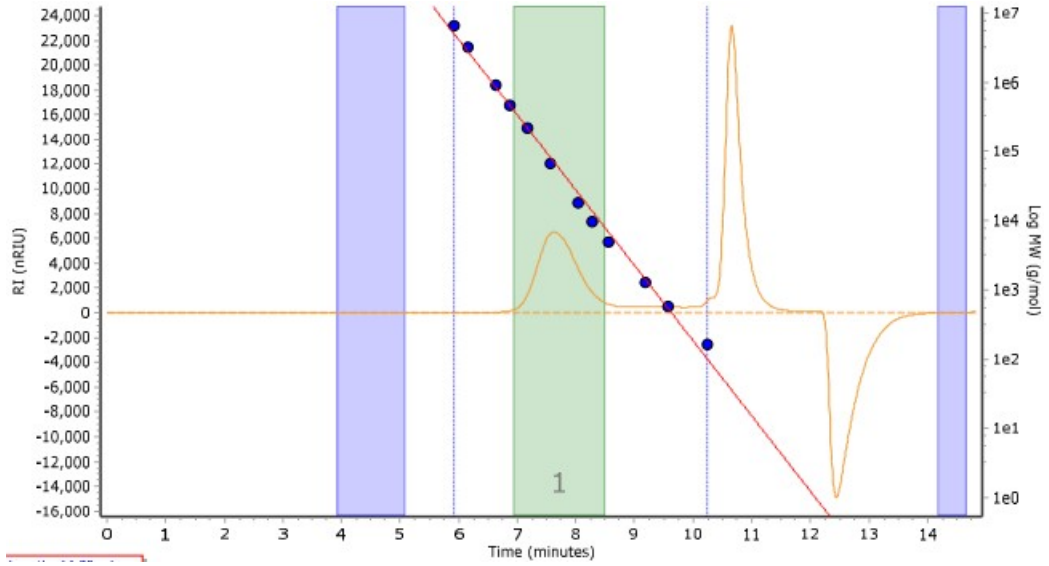


Figure S9. ^{1}H NMR spectrum of PCL (400 MHz, $CDCl_3$, 25 °C). (Table 1, entry 4)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	68889	40010	73221	117427	164727	110749	1.83

Figure S10. GPC analysis for PCL (flow rate: 1 mL/min, at 40 °C). (Table 1, entry 4)

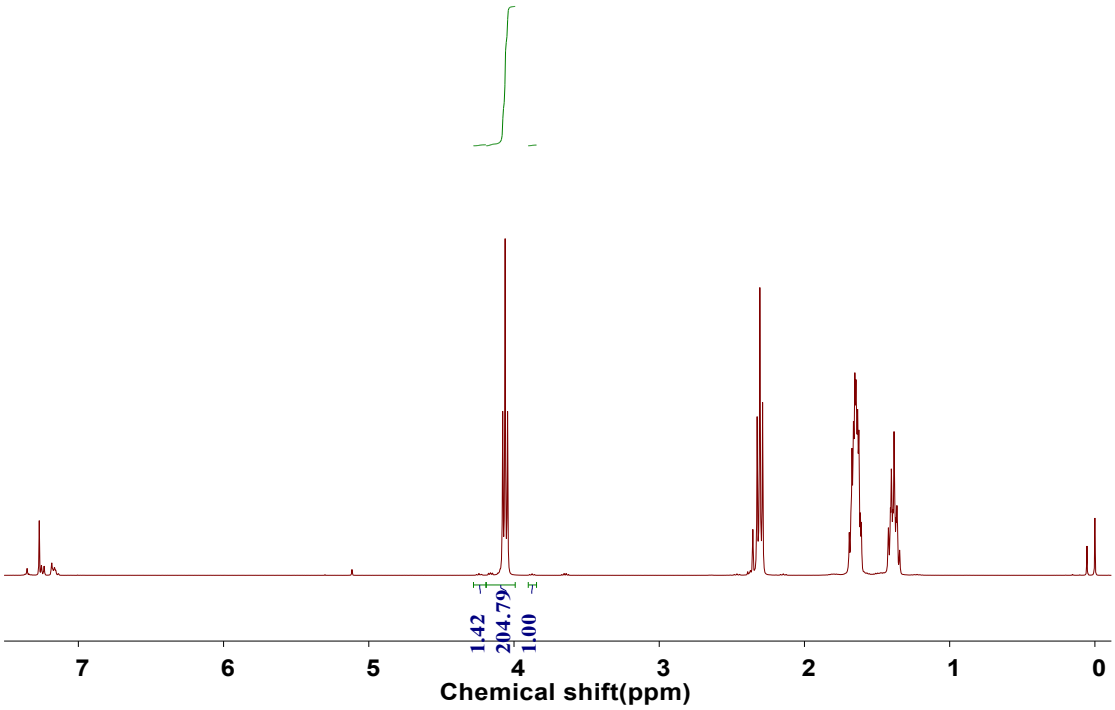


Figure S11. ^{1}H NMR spectrum of equilibrium monomer concentration of ε-caprolactone bulk polymerization at 110 ℃ (400 MHz, $CDCl_3$, 25 °C).

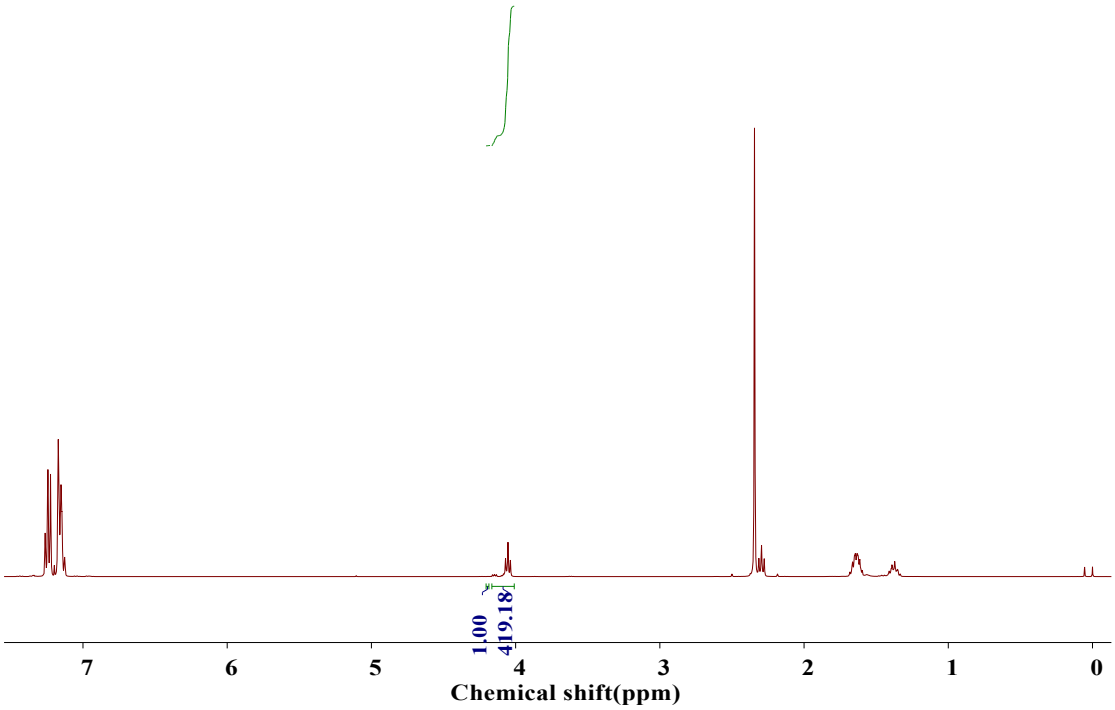


Figure S12. ^{1}H NMR spectrum of equilibrium monomer concentration of ε-caprolactone solution polymerization at 120 ℃ (400 MHz, $CDCl_3$, 25 °C, Figure 1).

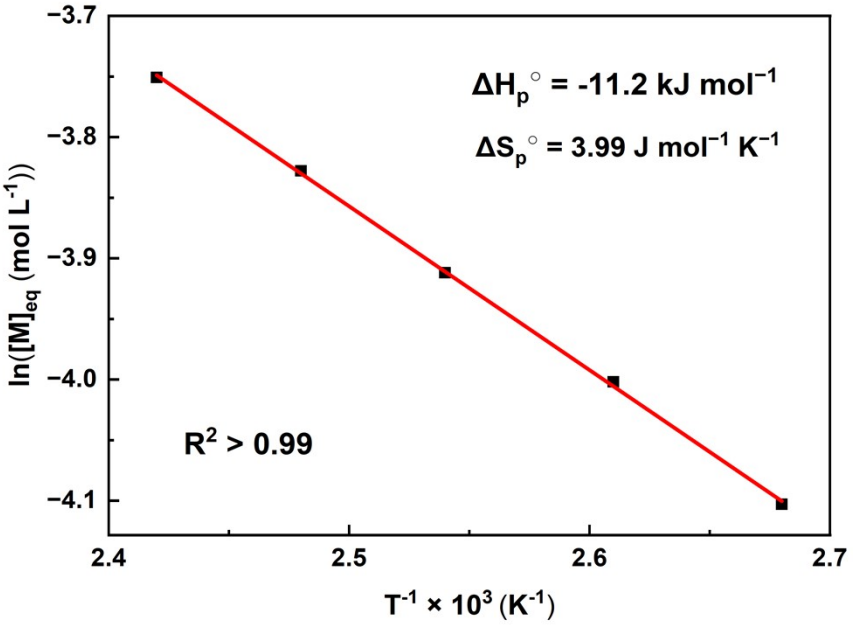


Figure S13. Van't Hoff plot of the $Mg(HMDS)_2$-catalyzed ROP of ε-CL in bulk.

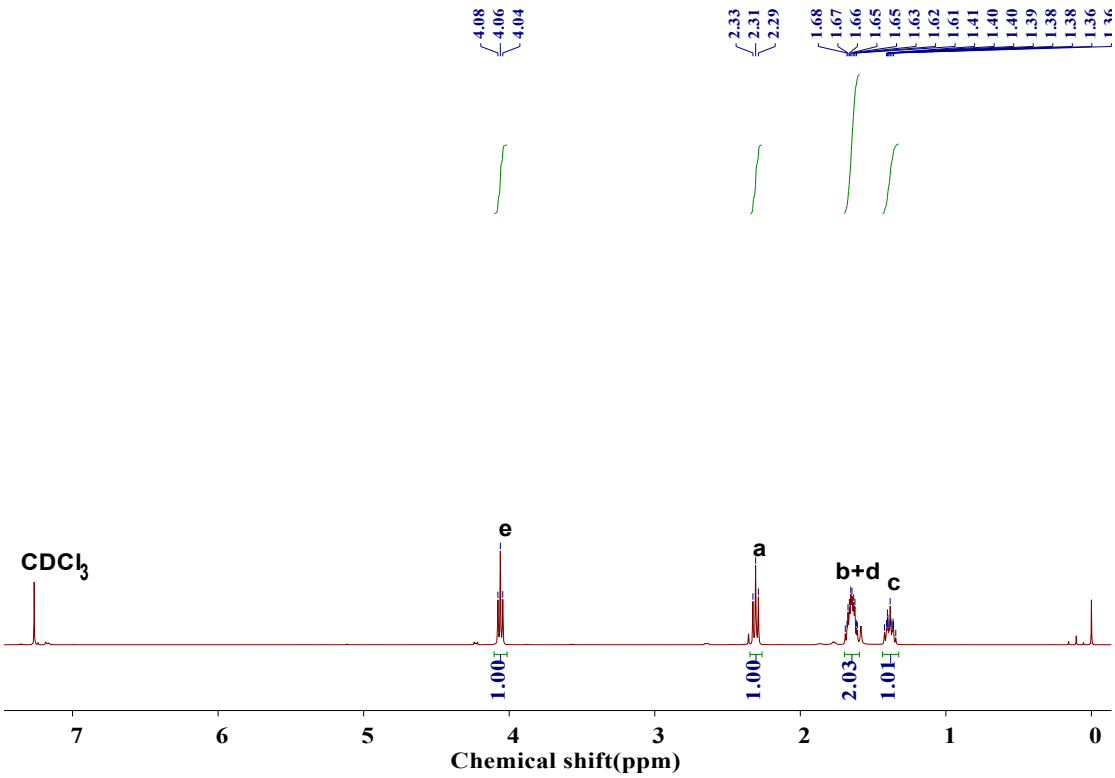
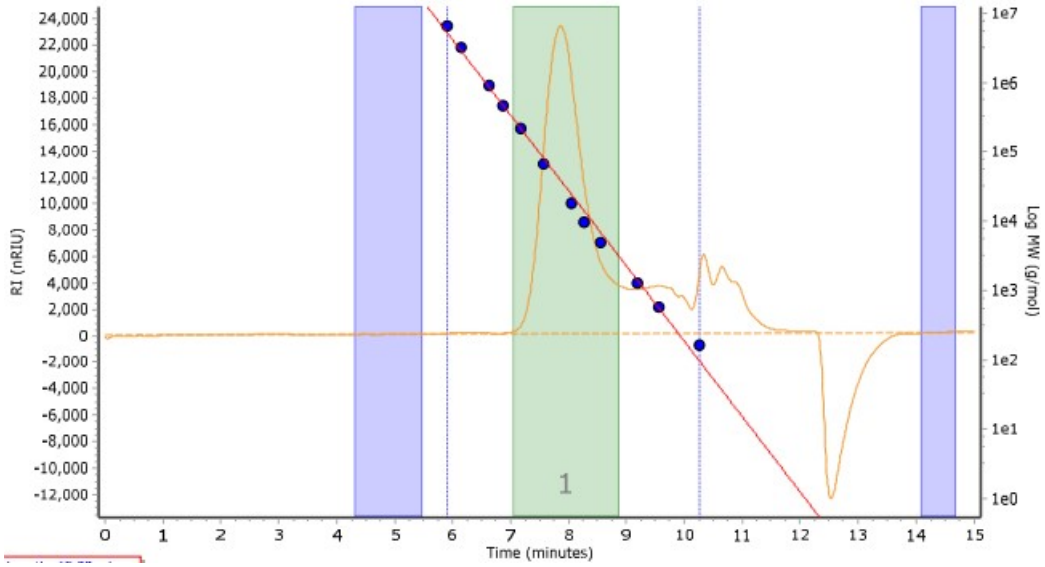


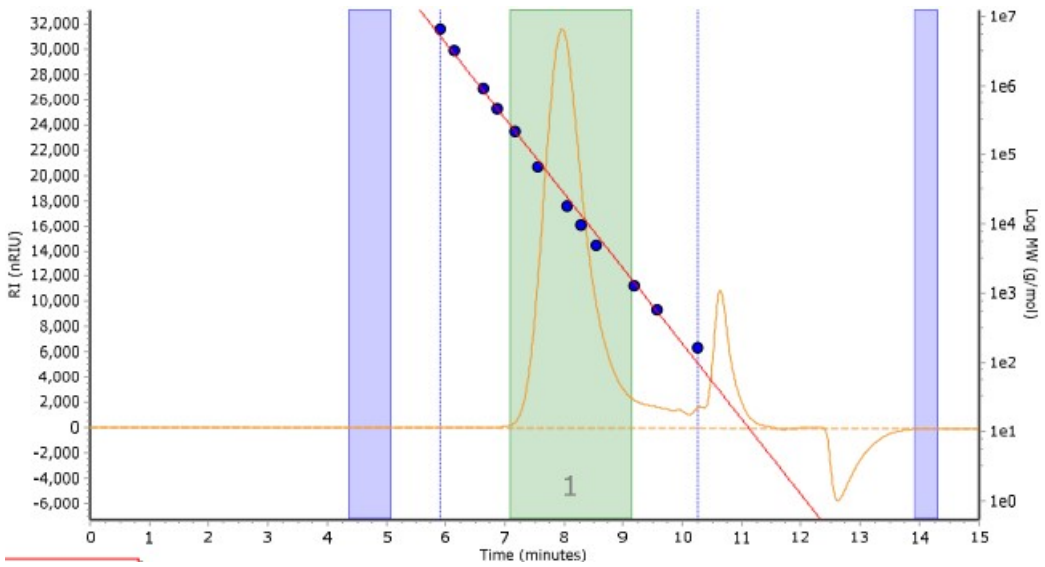
Figure S14. ^{1}H NMR spectrum of PCL (400 MHz, $CDCl_3$, 25 °C). (Table 2, entry 1)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	38407	19326	40796	67714	97581	63682	2.111

Figure S15. GPC analysis for PCL (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 1)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	29900	14068	32894	57407	85885	53639	2.338

Figure S16. GPC analysis for the depolymerization PCL (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 1)

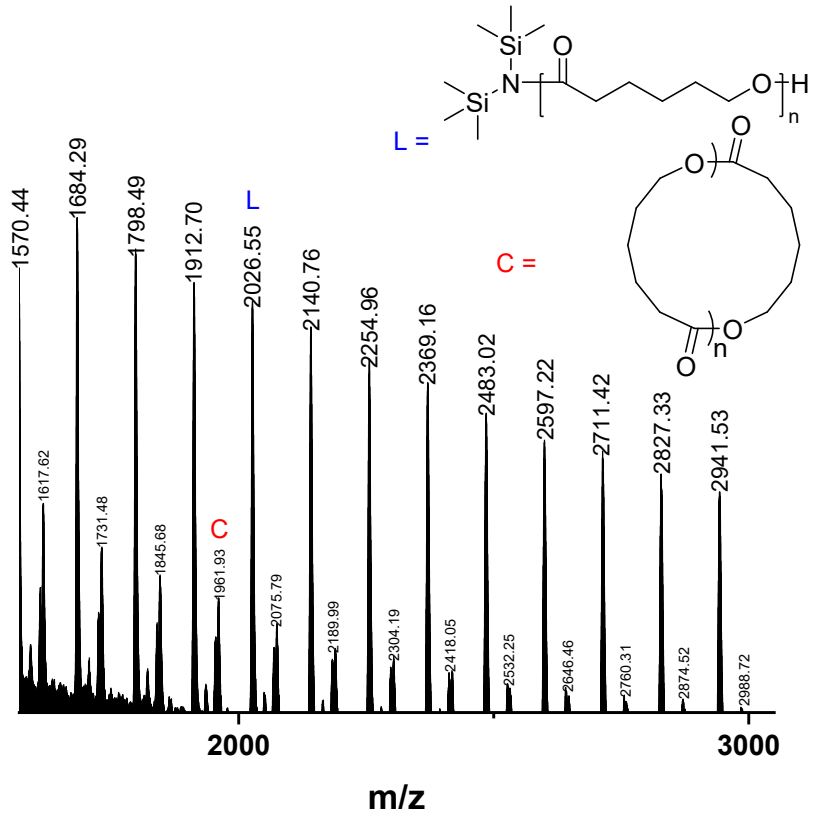


Figure S17. MALDI-TOF analysis for the depolymerization PCL. (Table 2, entry 1)

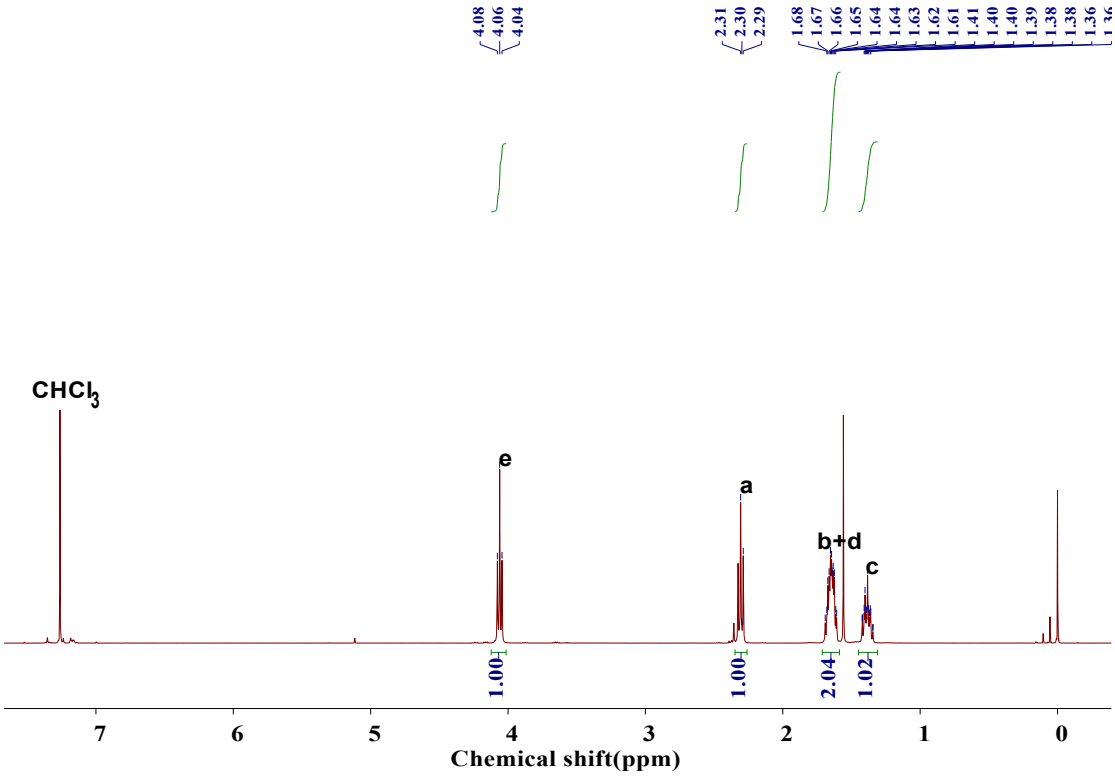
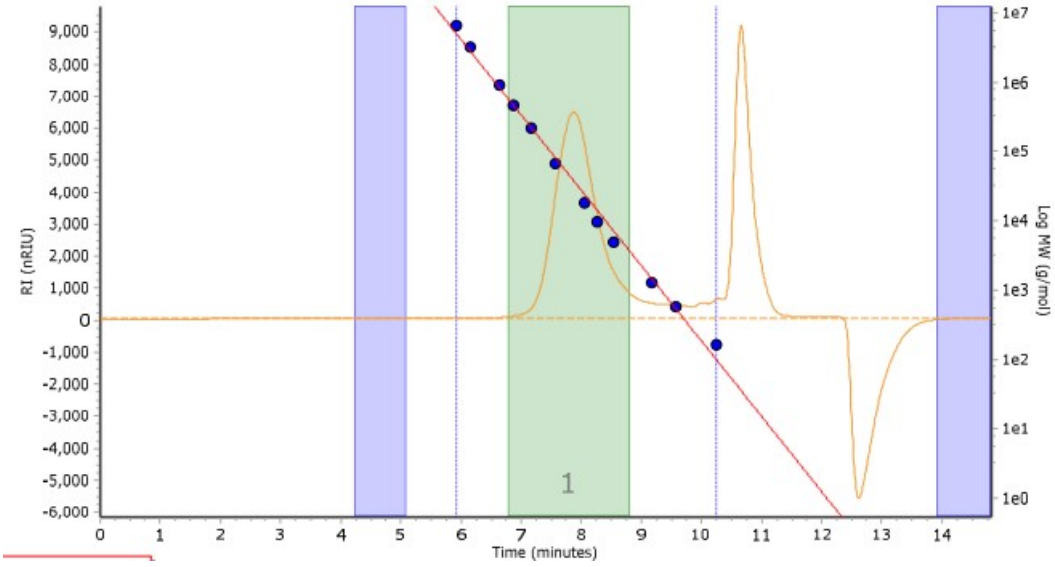


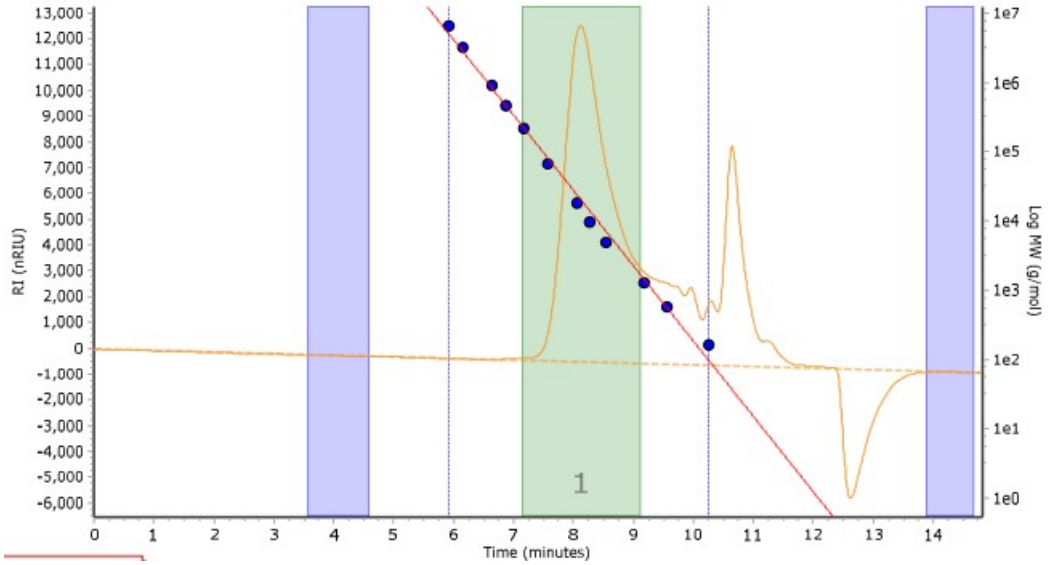
Figure S18. ^{1}H NMR spectrum of PCL (400 MHz, $CDCl_3$, 25 °C). (Table 2, entry 2)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	36838	21848	44825	85970	162053	78036	2.052

Figure S19. GPC analysis for PCL (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 2)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	20114	8212	18875	35180	59904	32432	2.298

Figure S20. GPC analysis for the depolymerization PCL (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 2)

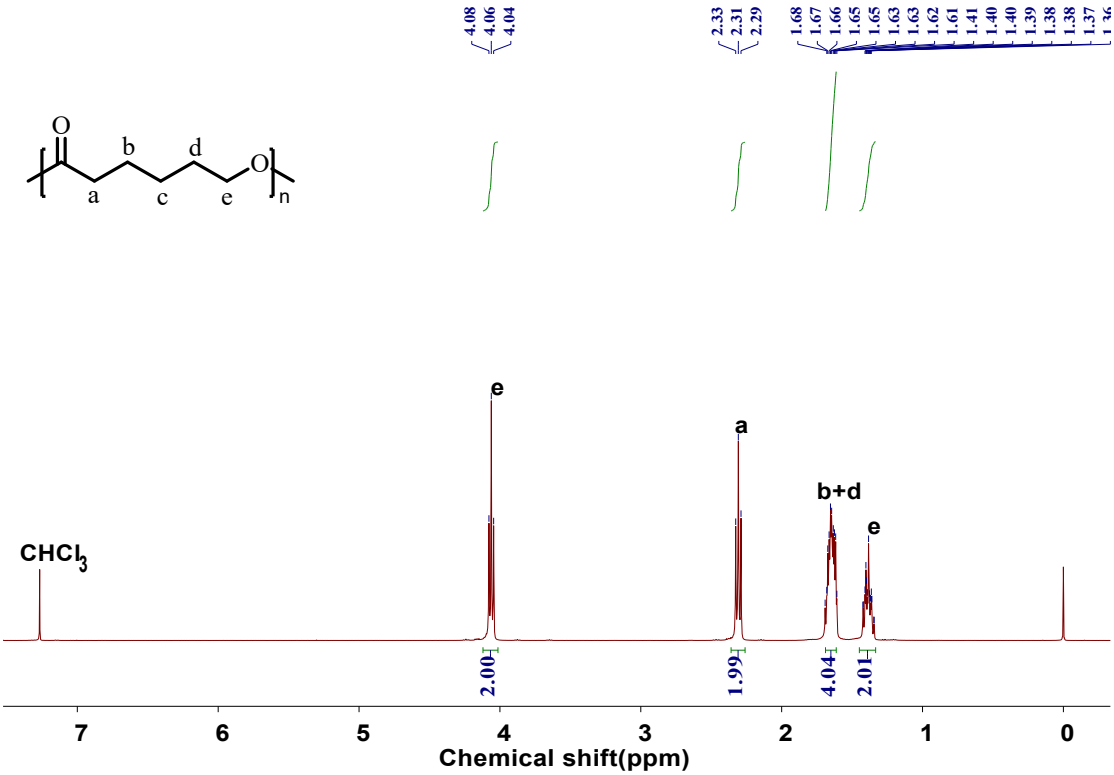
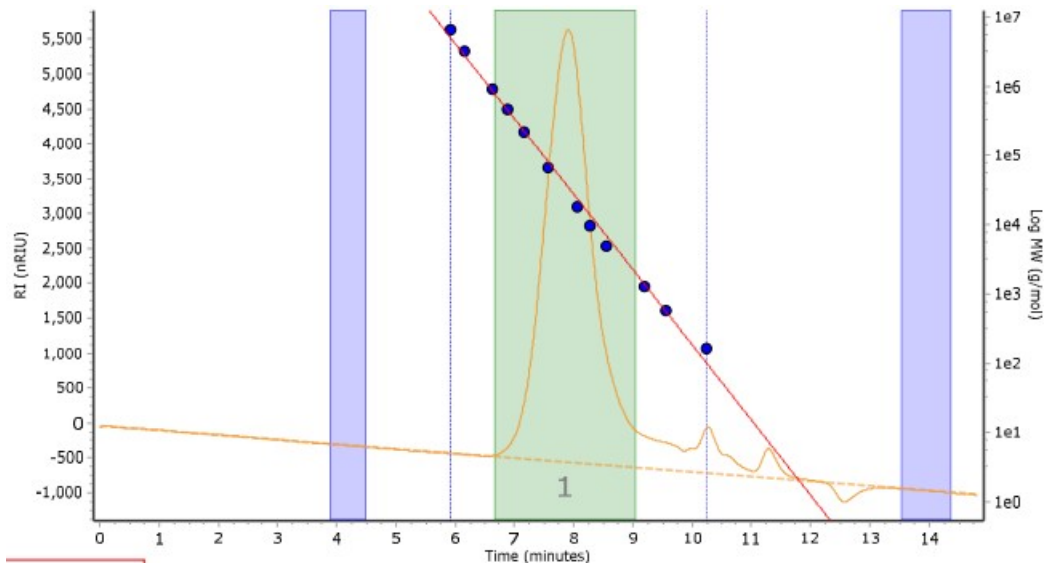


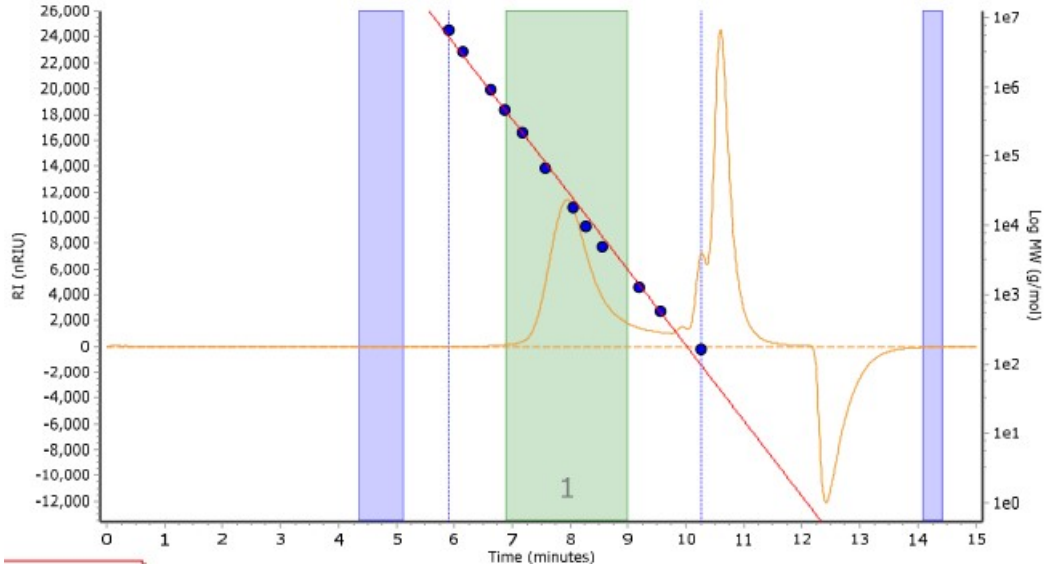
Figure S21. ^{1}H NMR spectrum of PCL (400 MHz, $CDCl_3$, 25 °C). (Table 2, entry 3)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	34602	18023	50822	118917	232035	106085	2.82

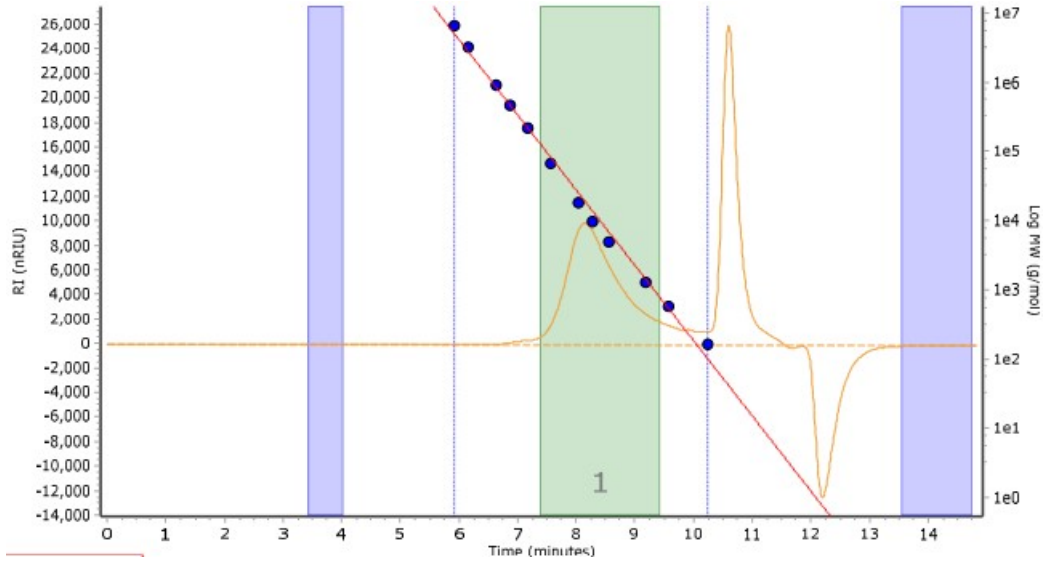
Figure S22. GPC analysis for PCL (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 3)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	30530	14538	35288	73049	139905	65893	2.427

Figure S23. GPC analysis for the depolymerization PCL at 6 h (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 3)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	18893	5717	18467	37287	56038	34602	3.23

Figure S24. GPC analysis for the depolymerization PCL at 12 h (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 4)

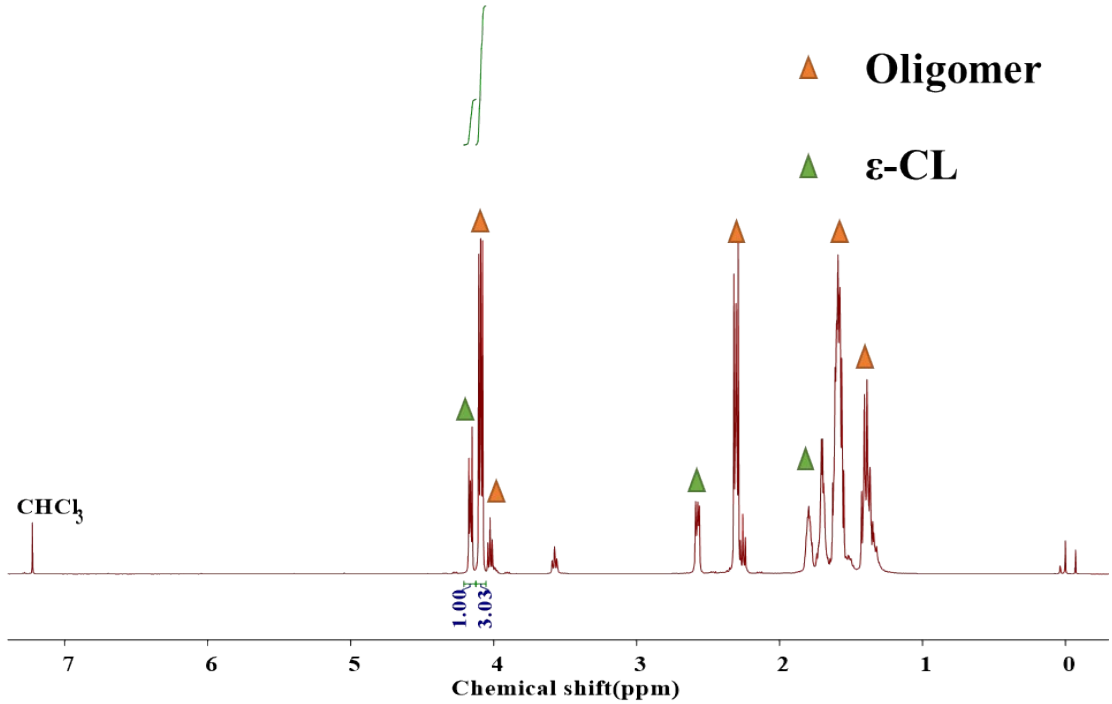


Figure S25. ^{1}H NMR spectrum of the residual product after depolymerization at 180 ℃ in 0.07 mbar (400 MHz, $CDCl_3$, 25 °C).

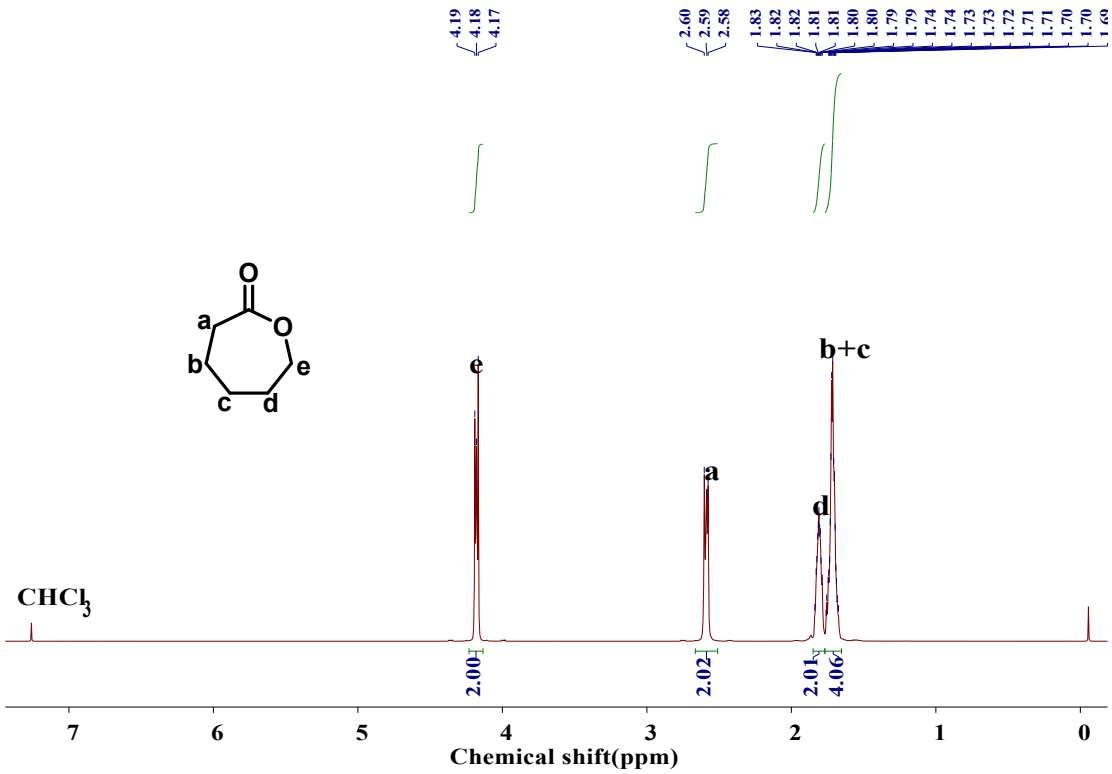


Figure S26. ^{1}H NMR spectrum of ε-CL monomer after degradation (400 MHz, $CDCl_3$, 25 °C).

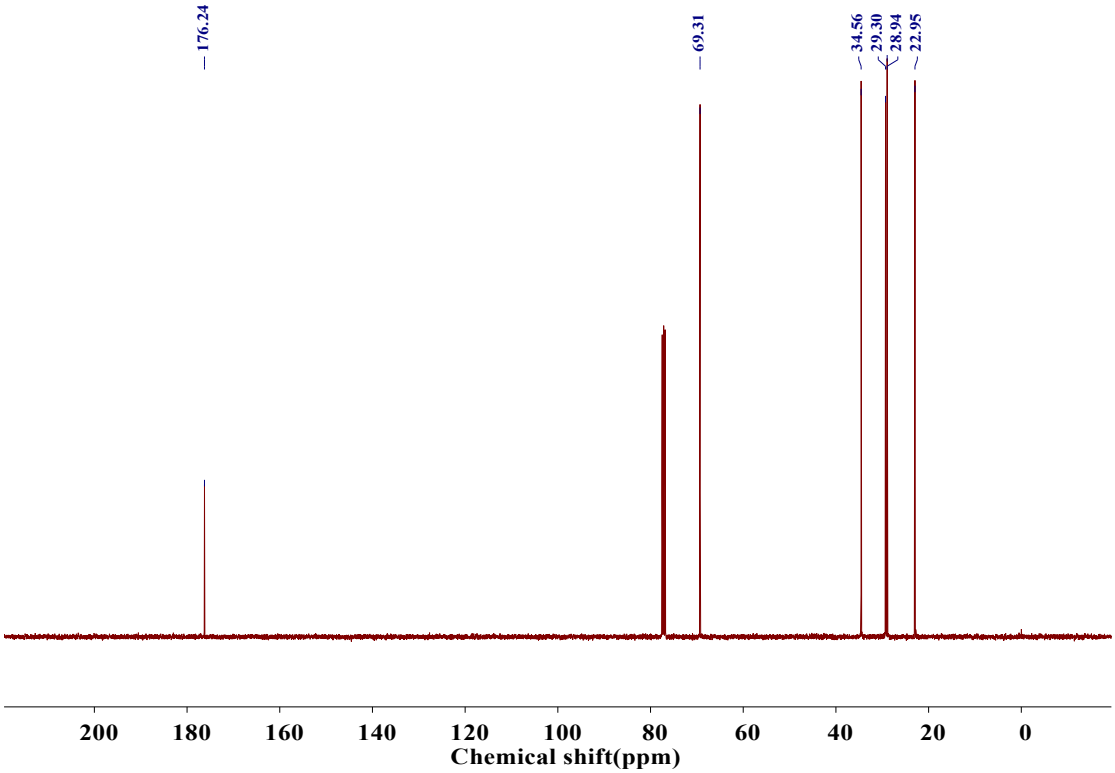


Figure S27. ^{13}C NMR spectrum of ε-CL monomer after degradation (100 MHz, $CDCl_3$, 25 °C).

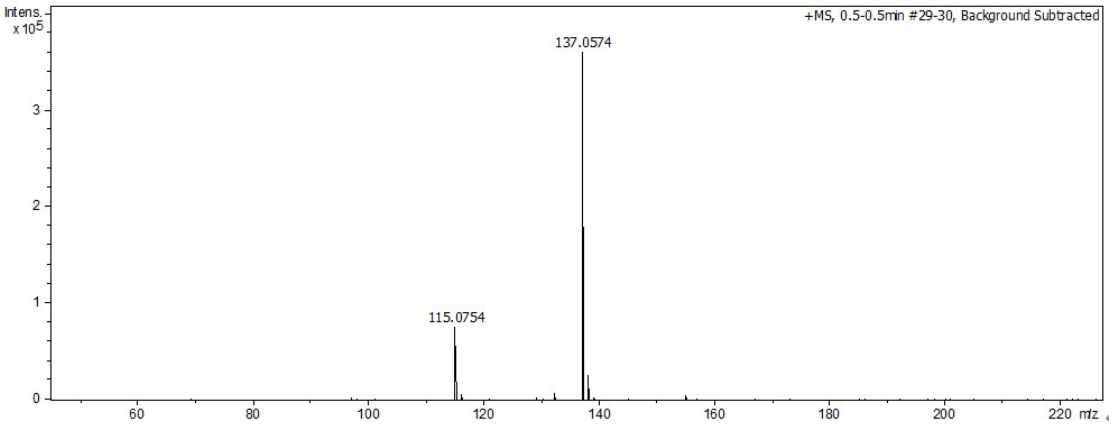
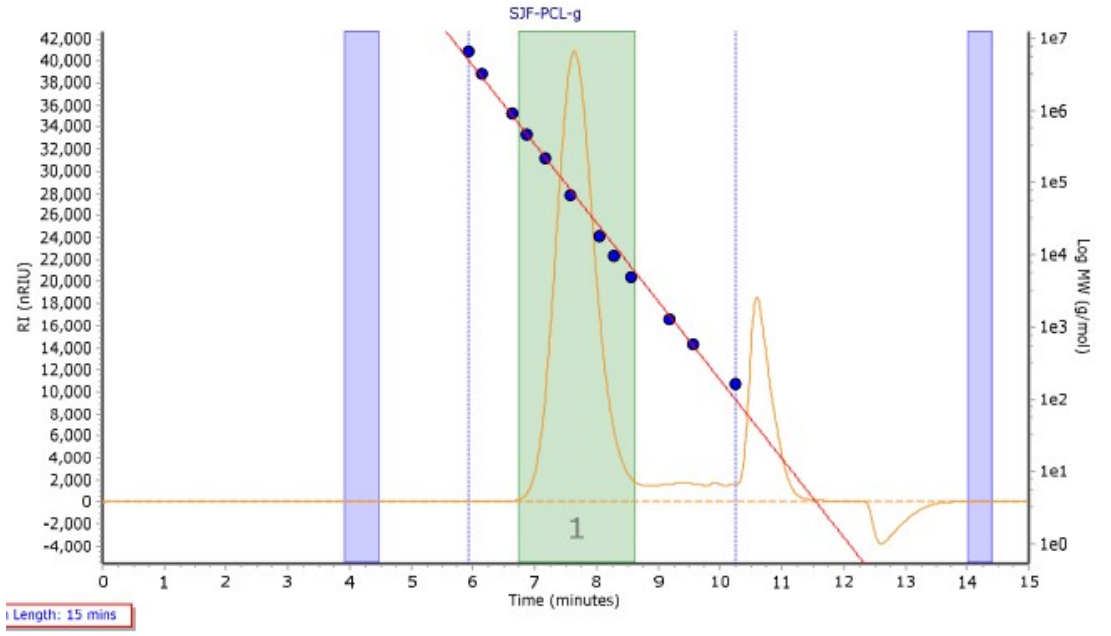


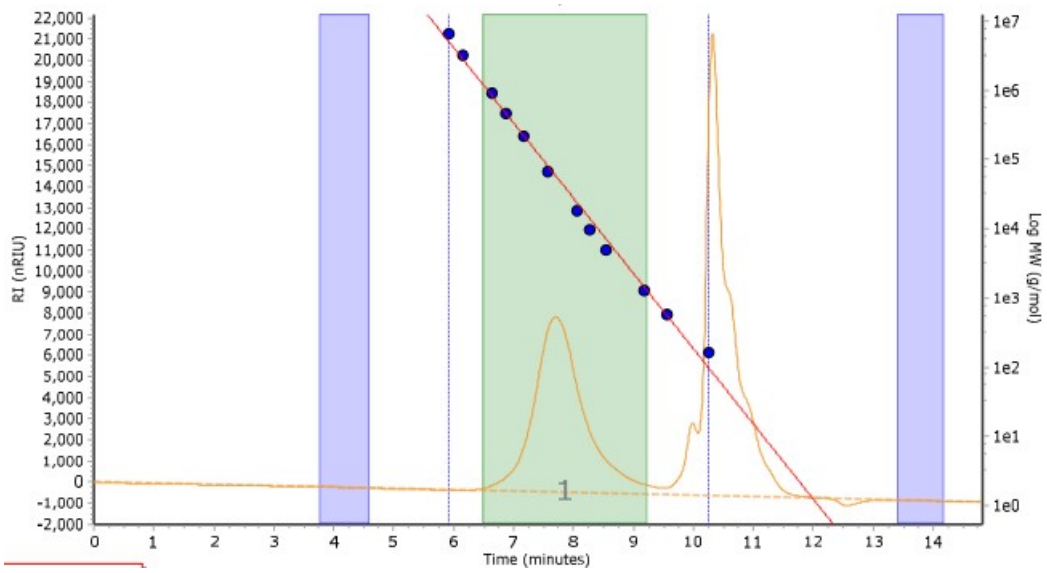
Figure S28. Mass spectrometry (MS) of ε-CL monomer by evaporation (Acetonitrile (HPLC), 180 ℃).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	67466	43179	79439	130213	195743	121843	1.84

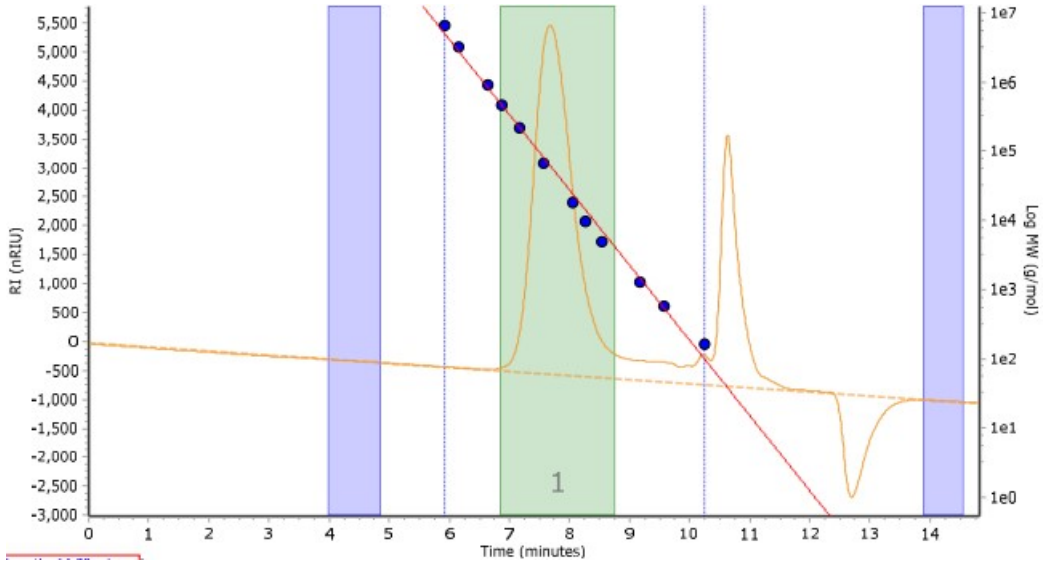
Figure S29. GPC analysis for PCL granule (flow rate: 1 mL/min, at 40 °C). (Table 3, entries 1-4)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	57094	19811	77475	215466	458917	187655	3.911

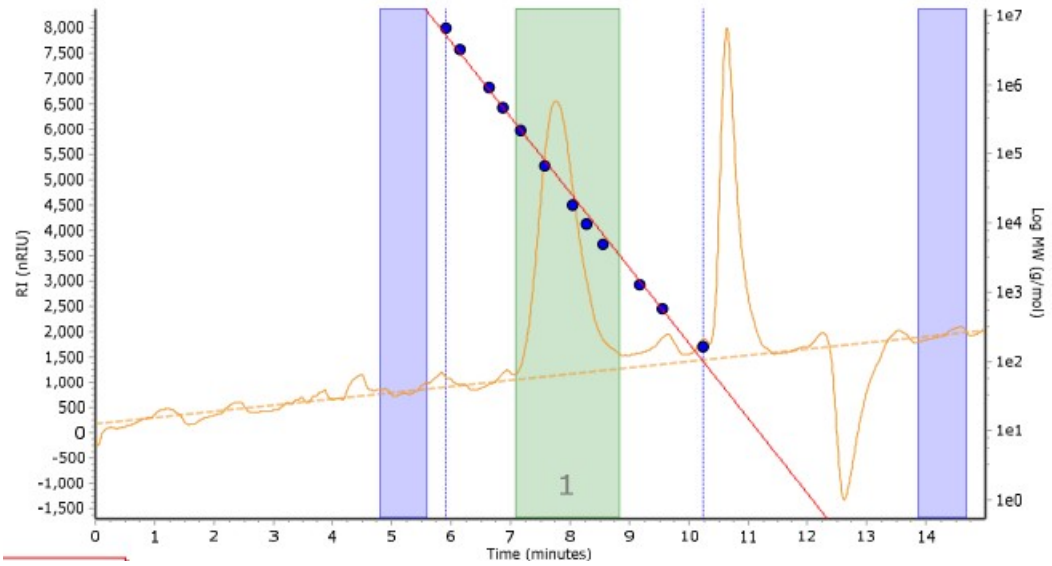
Figure S30. GPC analysis for the depolymerization of PCL in the presence of $Zn(HMDS)_2$ (flow rate: 1 mL/min, at 40 °C). (Table 3, entry 1)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	60782	32298	63382	102434	150682	96254	1.962

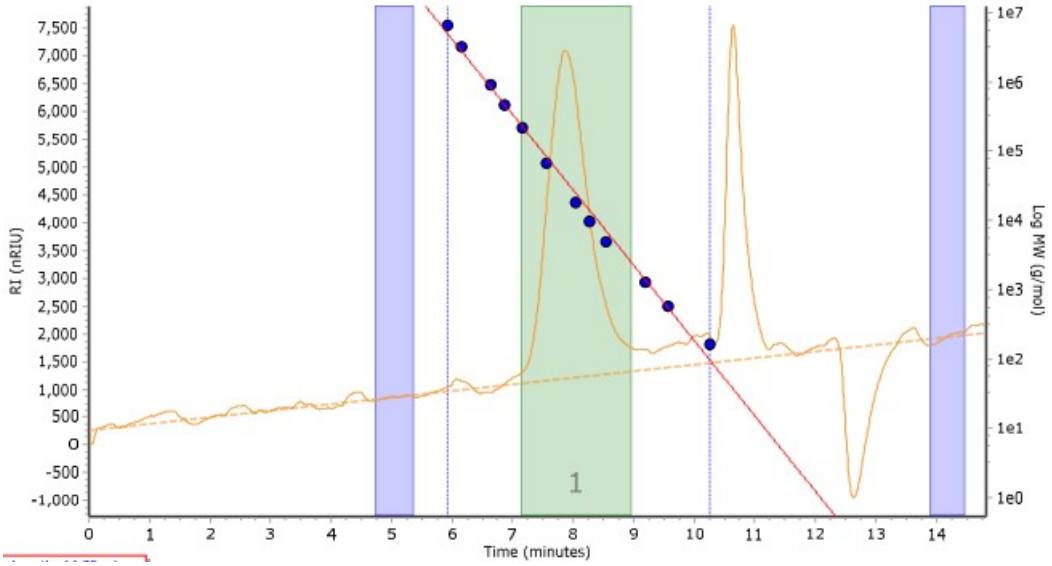
Figure S31. GPC analysis for the depolymerization of PCL at 1 h with 4% conversion (flow rate: 1 mL/min, at 40 °C).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	49335	27200	51715	79925	108856	75814	1.901

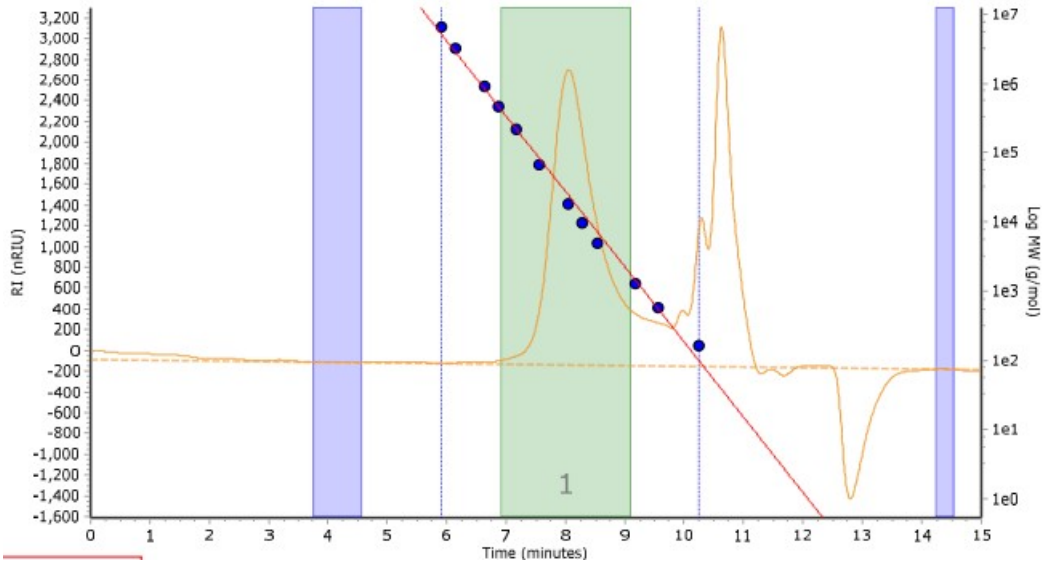
Figure S32. GPC analysis for the depolymerization of PCL at 3 h with 10% conversion (flow rate: 1 mL/min, at 40 °C).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	37614	19626	40436	66024	93807	62187	2.06

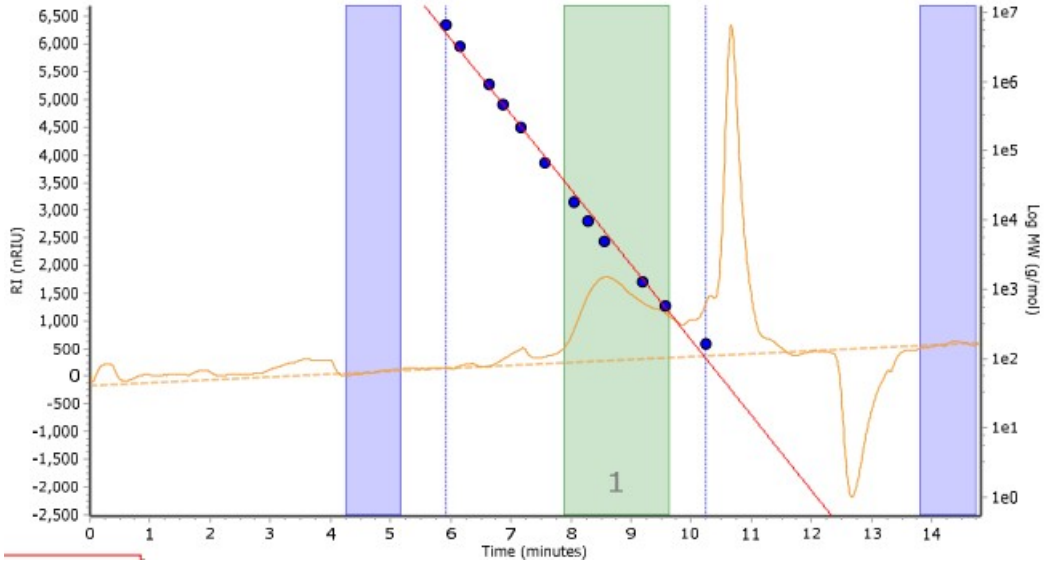
Figure S33. GPC analysis for the depolymerization of PCL at 6 h with 27% conversion (flow rate: 1 mL/min, at 40 °C).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	23768	10338	26370	63427	144050	55438	2.551

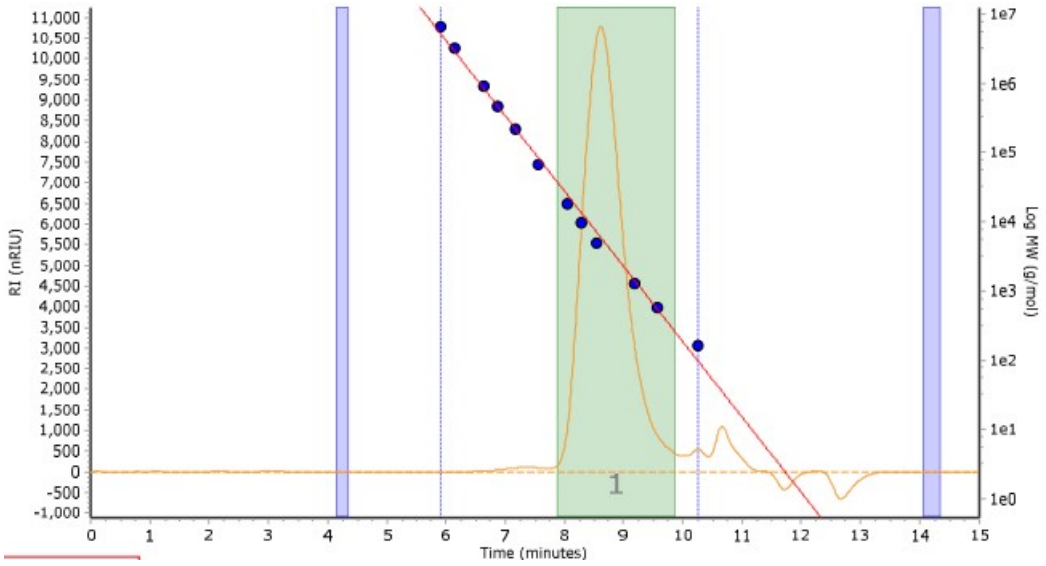
Figure S34. GPC analysis for the depolymerization of PCL at 10 h with 48% conversion (flow rate: 1 mL/min, at 40 °C).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	6384	2156	6694	13943	19900	13000	3.105

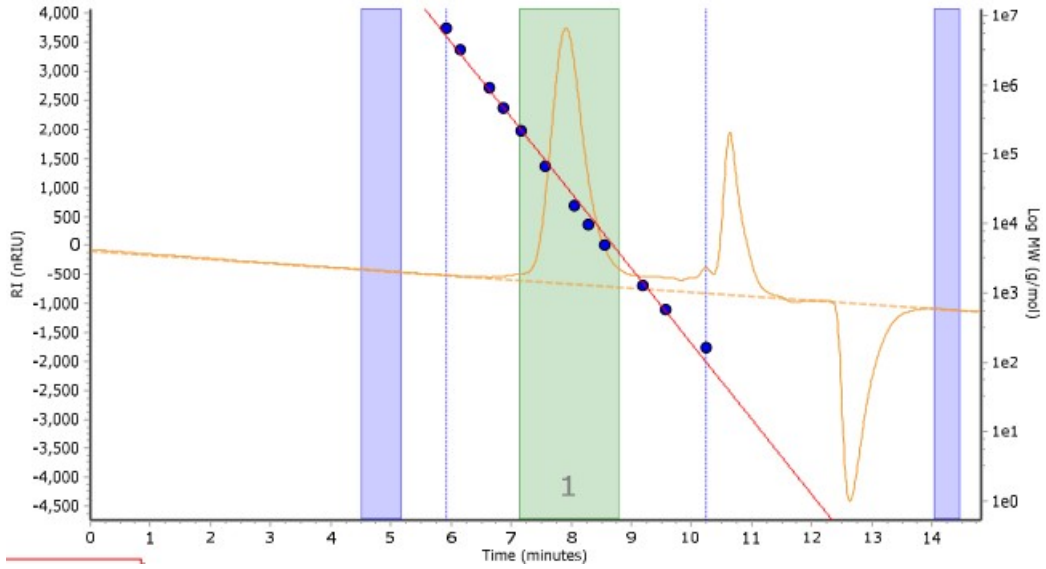
Figure S35. GPC analysis for the depolymerization of PCL at 13 h with 70% conversion (flow rate: 1 mL/min, at 40 °C).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	5873	2923	6397	10325	14269	9762	2.189

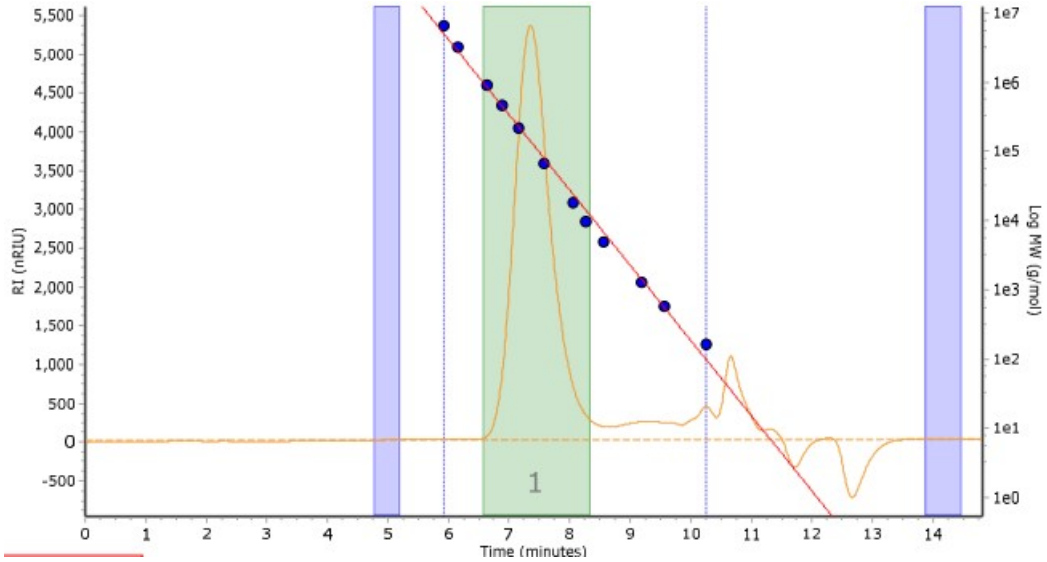
Figure S36. GPC analysis of molecular weight PCL (2000 g/mol) (flow rate: 1 mL/min, at 40 °C). (Table 3, entry 5)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	33888	21890	36696	56347	82955	53053	1.676

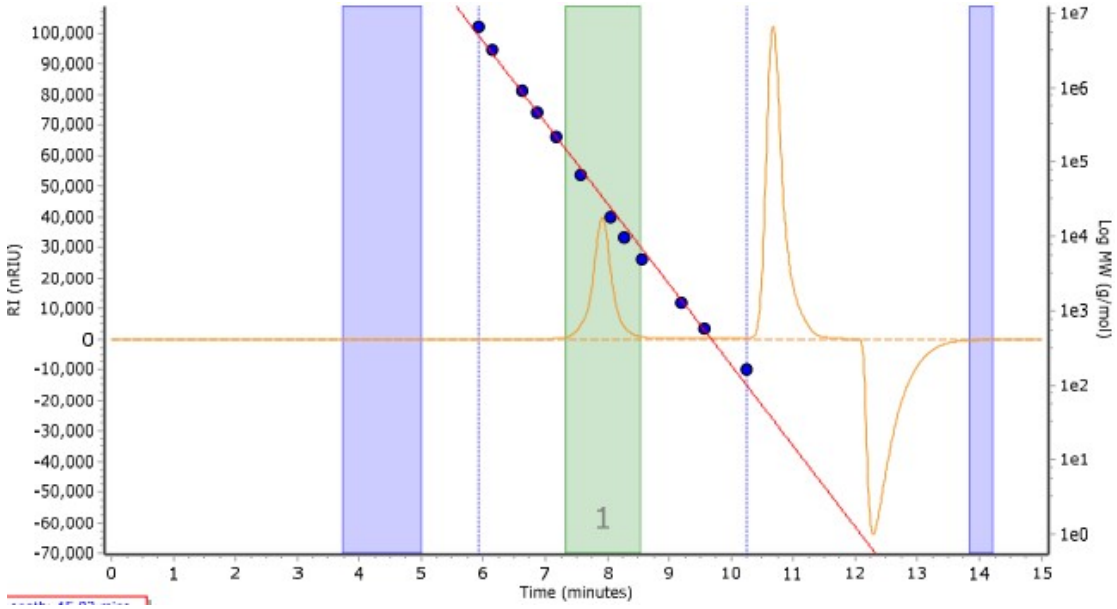
Figure S37. GPC analysis of molecular weight PCL (10000 g/mol) (flow rate: 1 mL/min, at 40 °C). (Table 3, entry 6)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	137148	84770	148370	225146	311843	213374	1.75

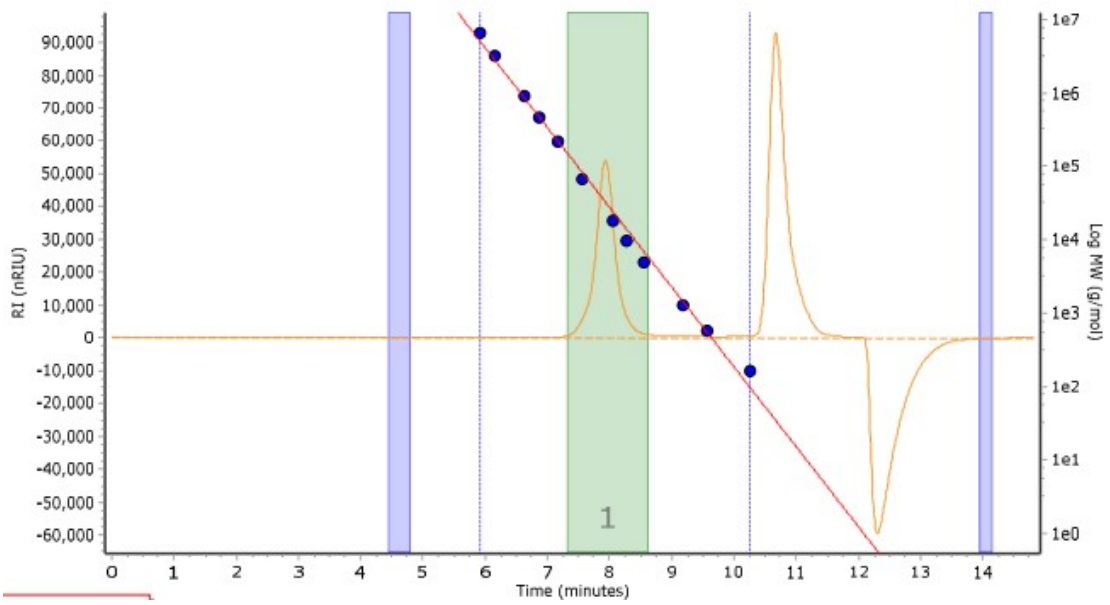
Figure S38. GPC analysis of molecular weight PCL (50000 g/mol) (flow rate: 1 mL/min, at 40 °C). (Table 3, entry 7)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	33188	29613	36702	45600	57491	44076	1.239

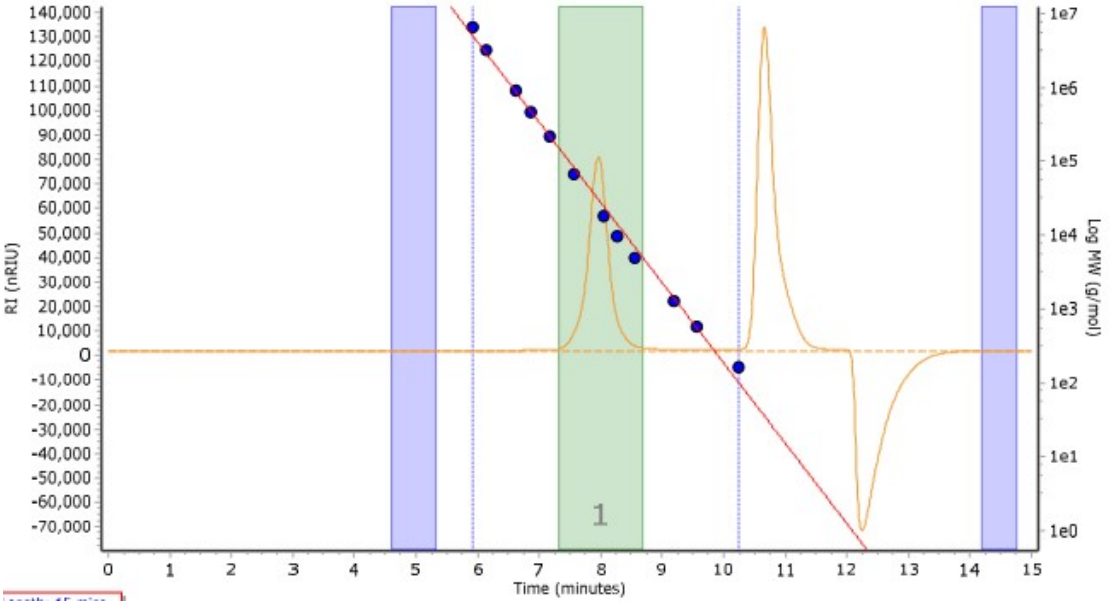
Figure S39. GPC analysis for the depolymerization of PCL at 15% conversion (flow rate: 1 mL/min, at 40 °C, Figure 4).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	31832	28118	35334	44274	56407	42736	1.257

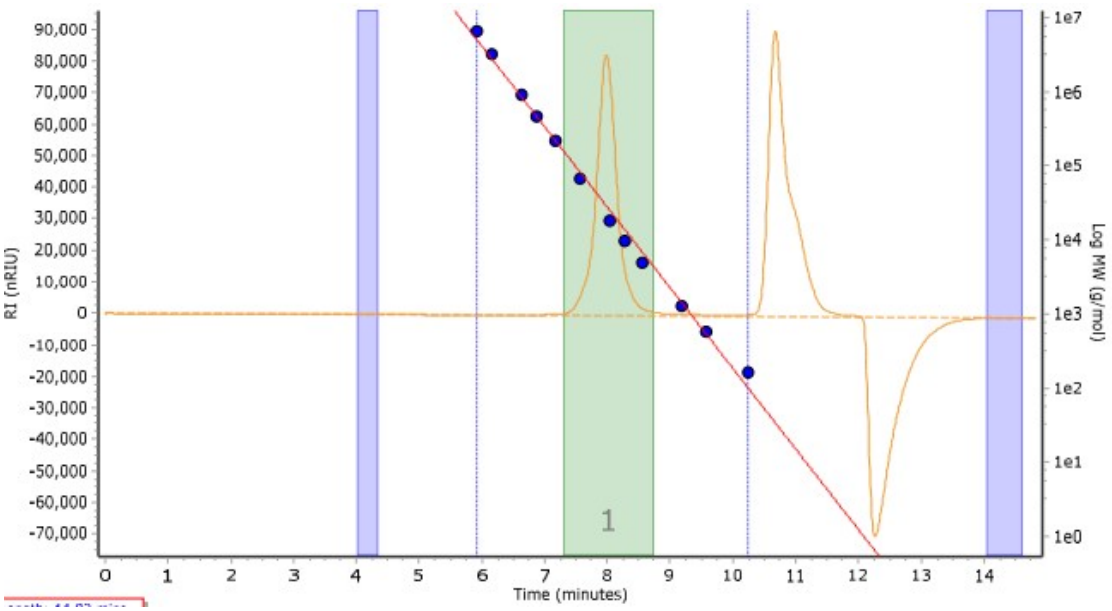
Figure S40. GPC analysis for the depolymerization of PCL at 20% conversion (flow rate: 1 mL/min, at 40 °C, Figure 4).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	29900	26190	33081	41699	53554	40208	1.263

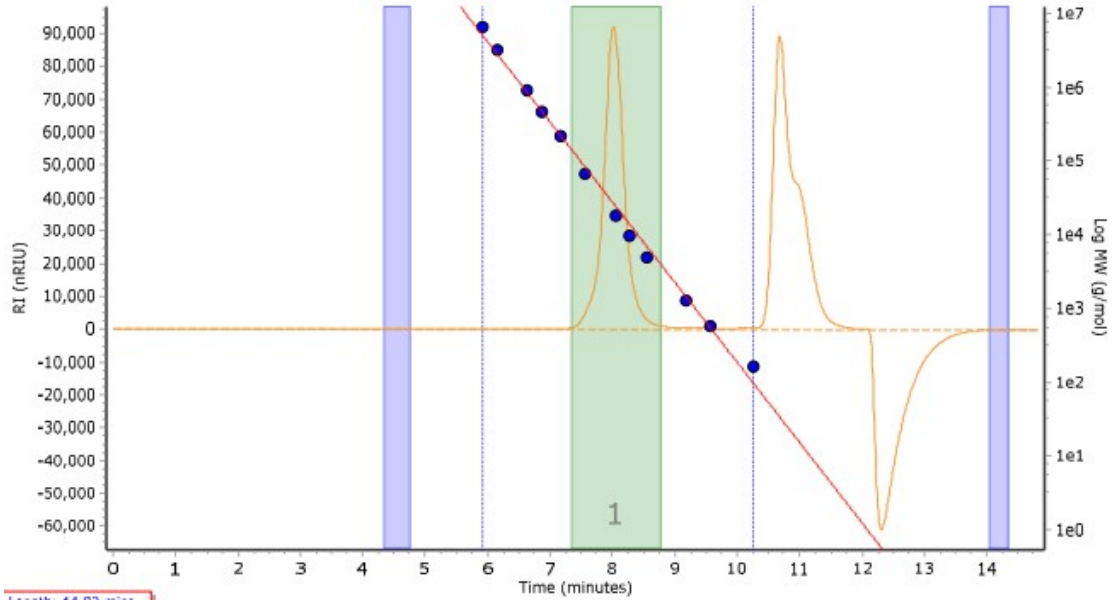
Figure S41. GPC analysis for the depolymerization of PCL at 25% conversion (flow rate: 1 mL/min, at 40 °C, Figure 4).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	28086	24470	31000	39312	51352	37841	1.267

Figure S42. GPC analysis for the depolymerization of PCL at 30% conversion (flow rate: 1 mL/min, at 40 °C, Figure 4).

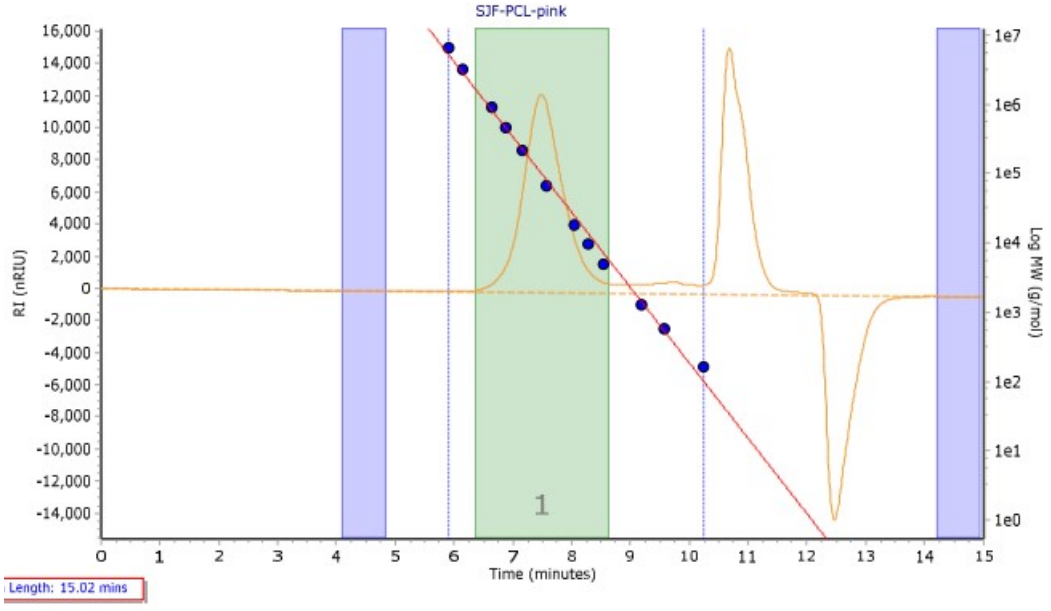


Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	25837	22581	28343	35709	46433	34402	1.255

Figure S43. GPC analysis for the depolymerization of PCL at 35% conversion (flow rate: 1 mL/min, at 40 °C, Figure 4).

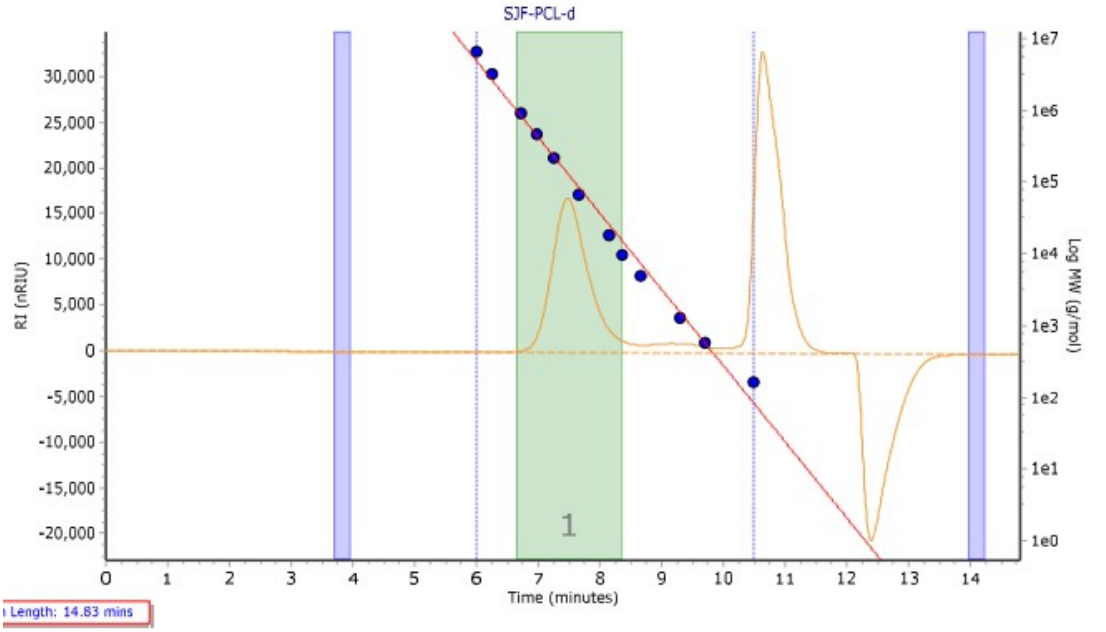
Figure S44. Three different PCL products. (a) nasal bridge plate. (b) 3D printing material (colors). (c) 3D printing material (white).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	98220	55715	126687	273899	551628	244009	2.274

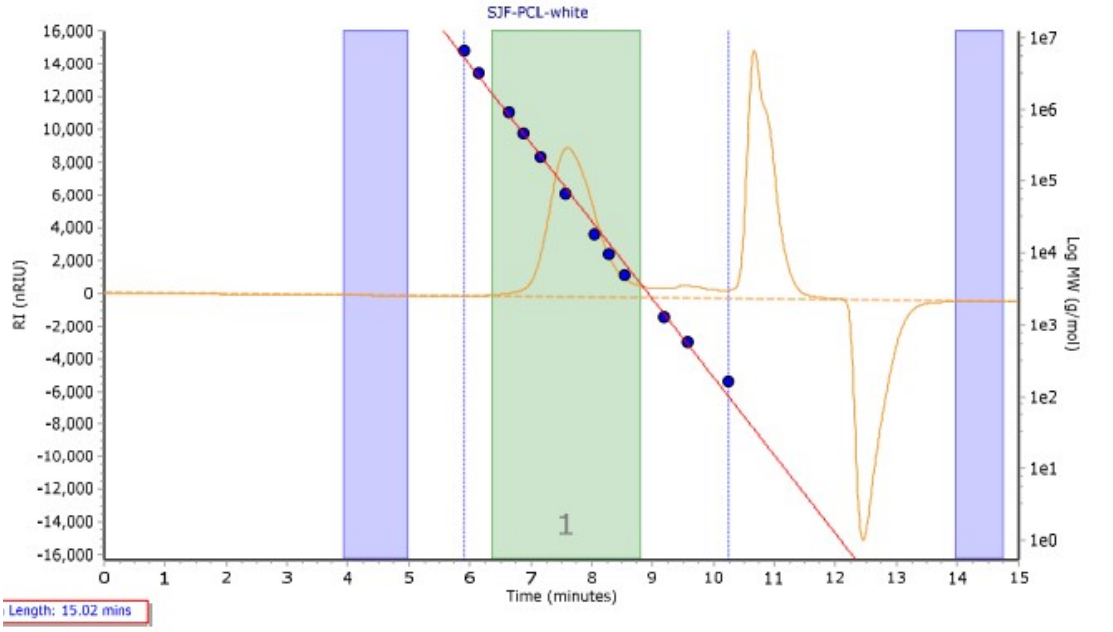
Figure S45. GPC analysis for nasal bridge plate (flow rate: 1 mL/min, at 40 °C). (Table 4, entry 1)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	127972	82101	136501	204984	289924	194025	1.663

Figure S46. GPC analysis for 3D printed material (colors) (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 2)



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	73339	32906	86486	238527	635102	201803	2.628

Figure S47. GPC analysis for 3D printed material (white) (flow rate: 1 mL/min, at 40 °C). (Table 2, entry 3)

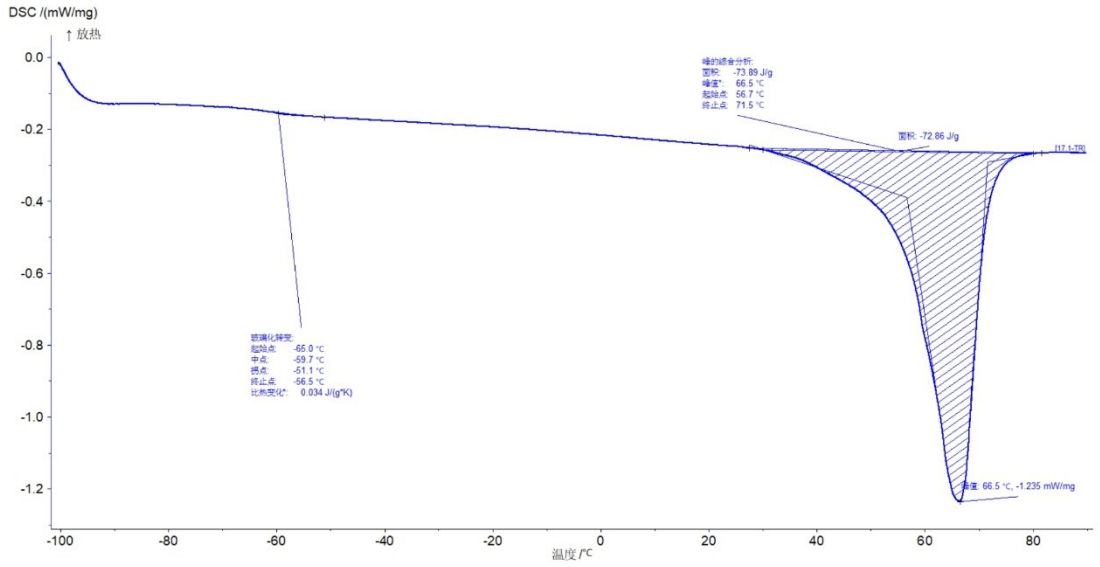


Figure S48. DSC analysis for nasal bridge plate in the first heating scan.

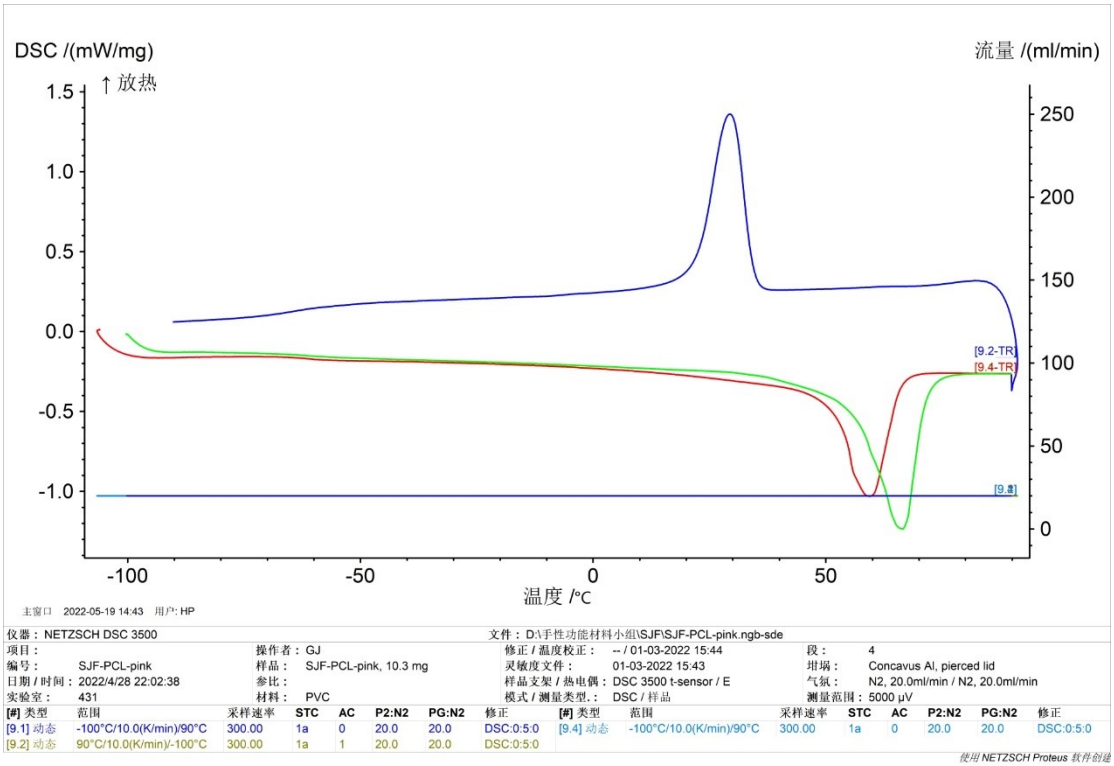


Figure S49. Overlay of the DSC curves of nasal bridge plate.

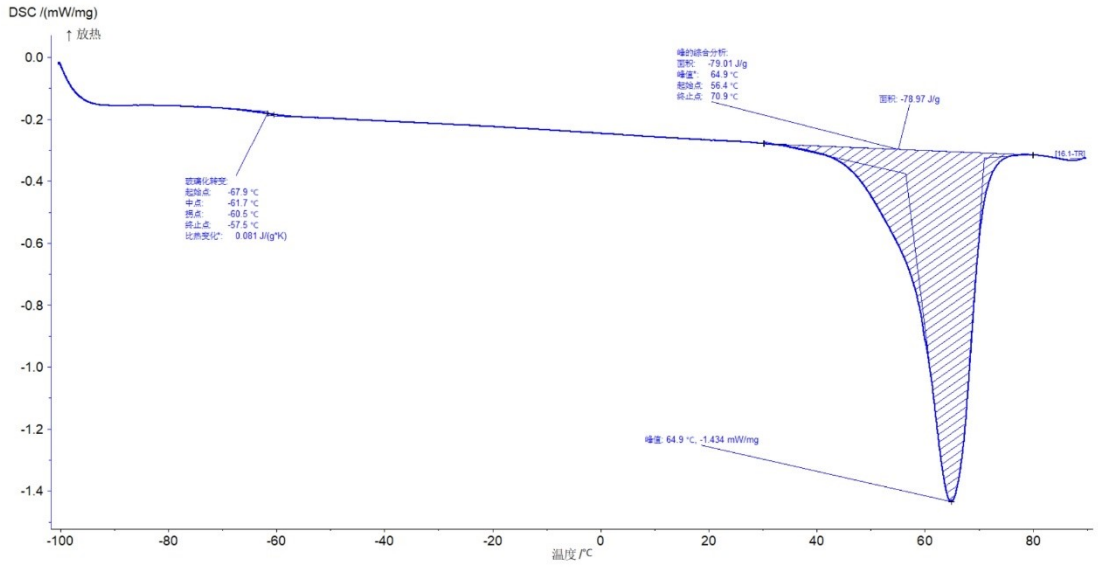


Figure S50. DSC analysis for 3D printed material (colors) in the first heating scan.

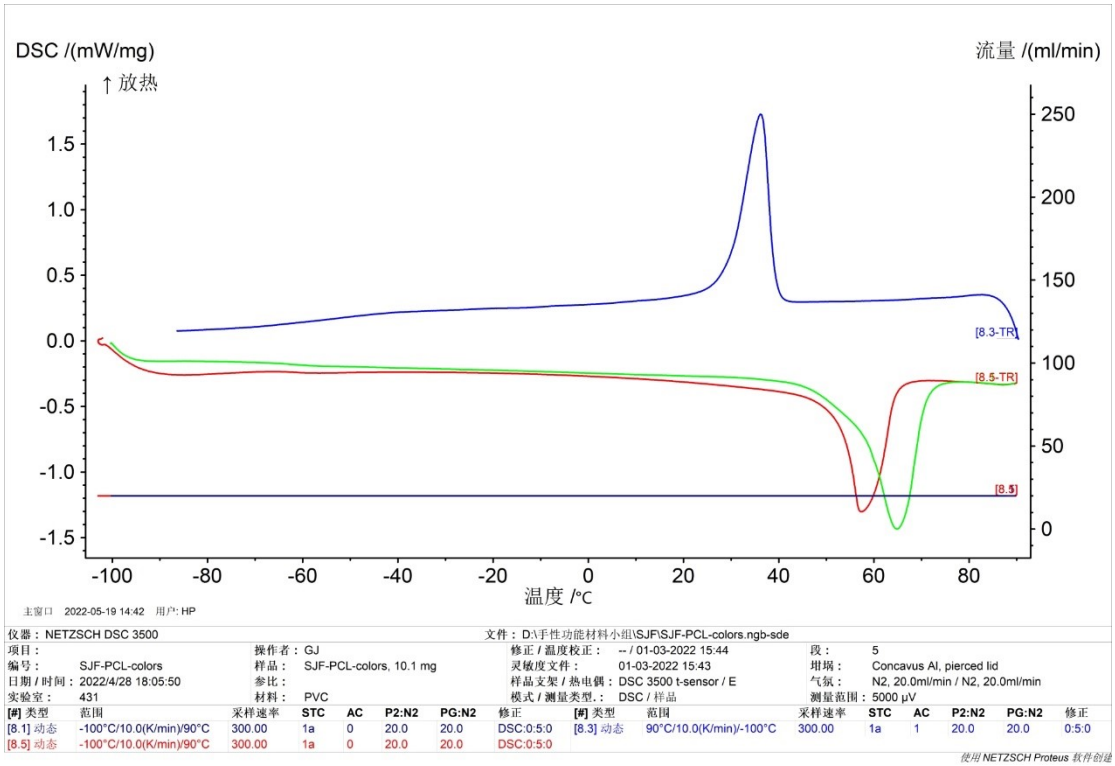


Figure S51. Overlay of the DSC curves of 3D printed material (colors).

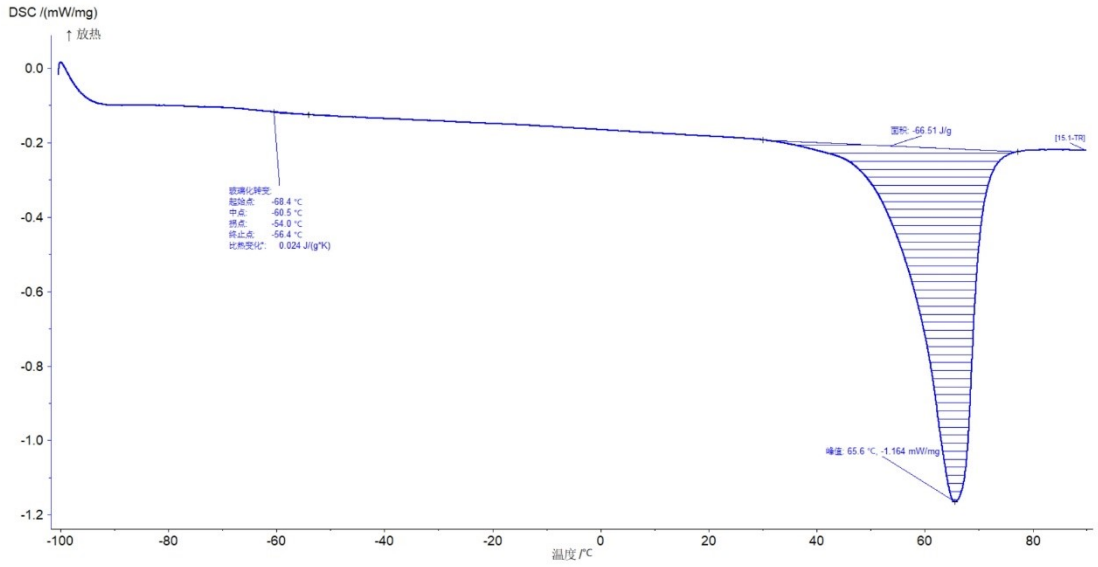


Figure S52. DSC analysis for 3D printed material (white) in the first heating scan.

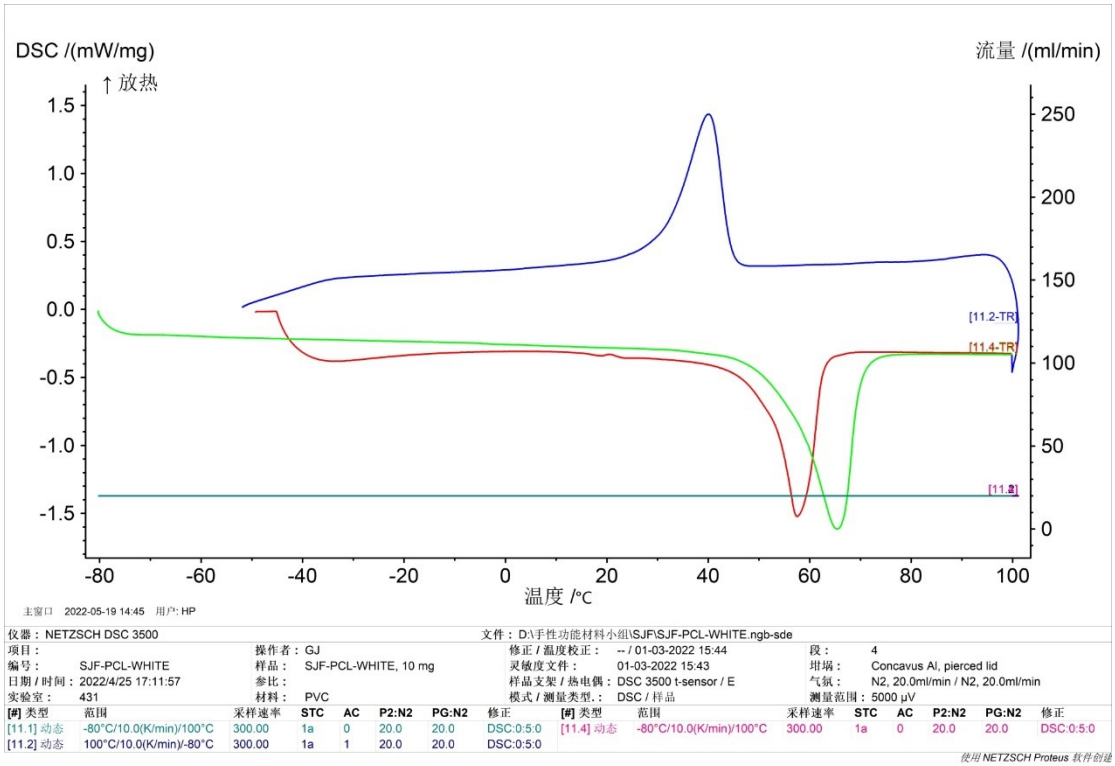


Figure S53. Overlay of the DSC curves of 3D printed material (white).

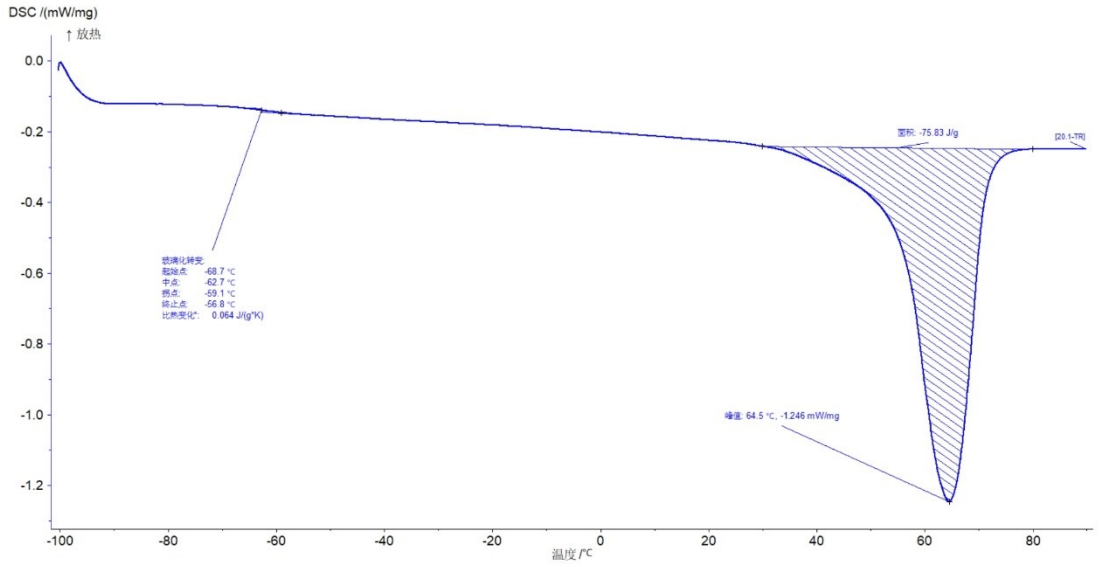


Figure S54. DSC analysis for the polymerized PCL in the first heating scan.

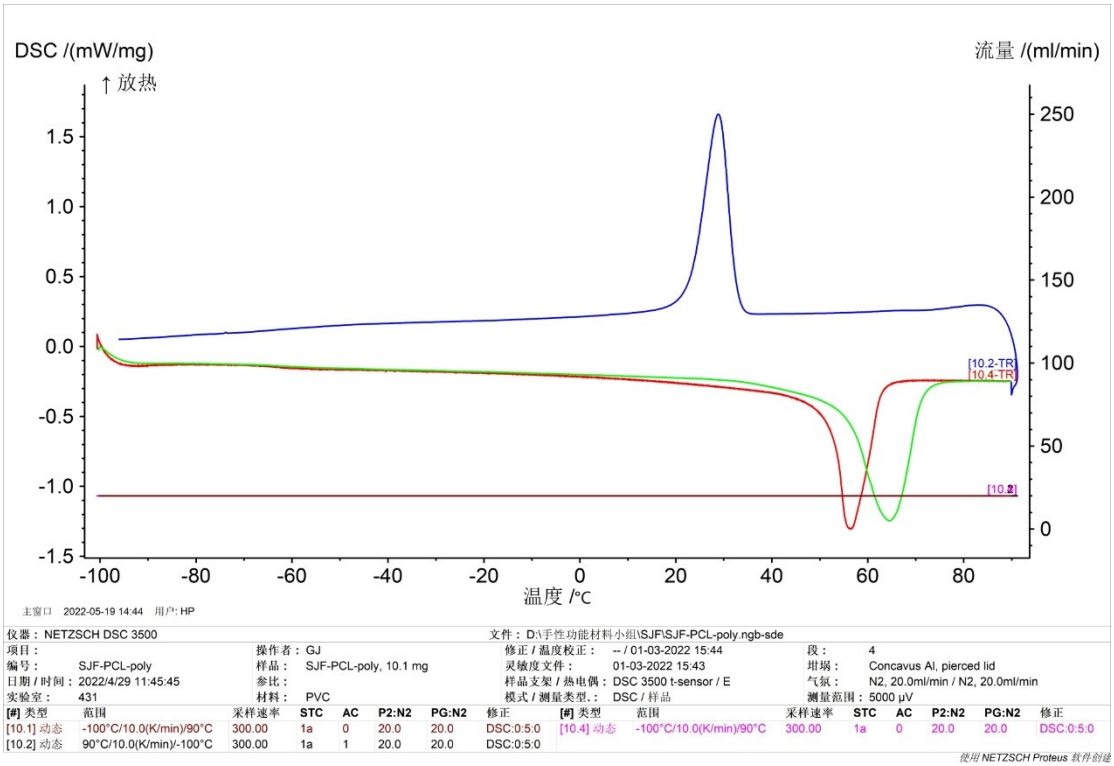


Figure S55. Overlay of the DSC curves of the polymerized PCL.