

Electronic Supplementary Information

Divergent Methods for Polyester and Polycarbonate Depolymerization with a Cobalt Catalyst

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1. General Considerations

All manipulations of air and water sensitive compounds were carried out under a nitrogen atmosphere in a Vacuum Atmospheres OMNI-LAB glovebox. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian 400, Mercury 400, or 500. Chemical shifts (δ) for ^1H NMR spectra were referenced to the residual protons on deuterated chloroform (7.26 ppm) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to the residual chloroform (77.16 ppm). Parr reactions were performed in a Parr MRS 5000 Multireactor containing 75 mL total volume vessels with glass liners and PTFE-coated stir bars. Size-exclusion chromatography (SEC) analyses were conducted using an Agilent 1260 Infinity II SEC System equipped with a Wyatt DAWN HELEOS-II and a Wyatt Optilab T-rEX as well as an Agilent 1260 Infinity autosampler and UV-detector. The SEC system was equipped with two Agilent PolyPore columns (5 micron, 4.6 mmID) run in series which was calibrated using monodisperse polystyrene standards, eluted with THF at 30°C at 0.3 mL/min. The number average molar mass and dispersity values were determined from multi-angle light scattering (MALS) using dn/dc values calculated by 100% mass recovery method from the refractive index (dRI) and light scattering (LS) signals.

2. Materials

Solvents used in air-free reactions (tetrahydrofuran, diethyl ether, and dichloromethane) were purchased from Fisher, sparged under ultrahigh purity (UP) grade argon, and passed through two columns of drying agent in a JCMeyer solvent purification system and dispensed directly into the glovebox. All other solvents were used without further purification. The deuterated NMR solvents, CDCl_3 , was purchased from Cambridge Isotope Laboratories and were used as received. CDCl_3 suitable for air-sensitive compounds was dried by stirring over calcium chloride for five days, followed by three freeze-pump-thaw cycles and vacuum transferred into a flame-dried Straus flask and stored in a glovebox under N_2 atmosphere. Compounds 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine (L-DIPP),¹ 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine (L-MES),² 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine cobalt(II) dichloride (DIPP),³ and 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine cobalt(II) chloride (MES)² were synthesized following literature procedure. All other reagents and chemicals were obtained from commercial vendors (Sigma-Aldrich, Fisher, Acros Organics, KOPTEC, and VWR) and were used without further purification.

2.1 Names and vendors for materials used in this study

δ -Valerolactone (Sigma Aldrich)	Poly(propylene carbonate) (Sigma Aldrich)
2,6-Diacetylpyridine (Sigma Aldrich)	Poly(dioxanone) (Sigma Aldrich)
2,6-Diethylaniline (Sigma Aldrich)	Poly(trimethylene carbonate) (Sigma Aldrich)
2,6-Diisopropylaniline (Sigma Aldrich)	Poly(caprolactam) (Sigma Aldrich)
2,4,6-Trimethylaniline (Sigma Aldrich)	Poly(bisphenol A carbonate) (unused compact disc) (Amazon)
Aluminum isopropoxide (Sigma Aldrich)	
CoCl_2 (Acros Organics)	Poly(ethylene terephthalate (pre-consumer beverage lids) (EcoProducts)
Mesitylene (Sigma Aldrich)	

3. Synthesis

3.1. Synthesis of 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine (L-DEP). The synthesis methods are derived from literature procedures for L-DIPP and L-MES with slight modifications.^{1,2} To a 100 mL round-bottom flask, 2,6-diacetylpyridine (1.50 g, 9.2 mmol), a Teflon-coated stir bar, and 25 mL ethanol were added. Once dissolved, 2,6-diethylaniline (3.46 mL, 22.3 mmol) was then added to the flask followed by ~15 drops of glacial acetic acid. The solution was then refluxed for 16 hours at 85°C. Upon cooling to room temperature, the product crystallized from ethanol. The solid was then filtered and washed three times with ~25 mL cold ethanol each time. The product was dried by rotary evaporation and product was confirmed by ¹H and ¹³C NMR. ¹H NMR (500 MHz, CDCl₃) δ 8.48 (d, *J* = 7.8 Hz, 2H), 7.93 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 4H), 7.07 – 7.02 (m, 2H), 2.44 (dq, *J* = 15.3, 7.6 Hz, 4H), 2.35 (dt, *J* = 14.9, 7.5 Hz, 4H), 2.26 (s, 6H), 1.18 – 1.13 (m, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.13, 155.22, 137.04, 131.36, 126.09, 123.50, 122.39, 46.76, 24.75, 16.98, 13.89. T_d = 237°C. IR Peaks (in cm⁻¹): 2971 w, 2926 w, 2874 w, 1638 s, 1588 w, 1567 w, 1452 s, 1437 m, 1407 w, 1364 s, 1321 w, 1301 w, 1241 m, 1198 m, 1122 m, 1100 m, 1077 m, 1060 w, 993 w, 965 w, 876 m, 826 s, 816 m, 807 w, 768 vs, 766 vs, 744 m, 684 w, 630 w, 527 w.

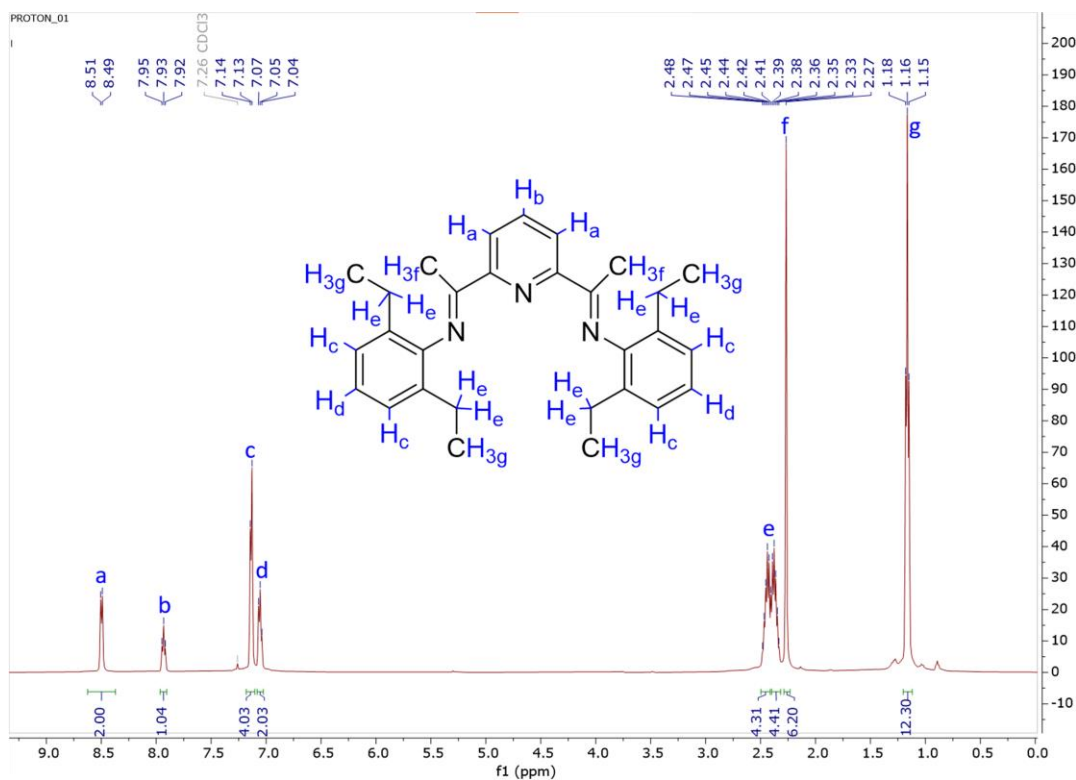


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectrum of DEP-H.

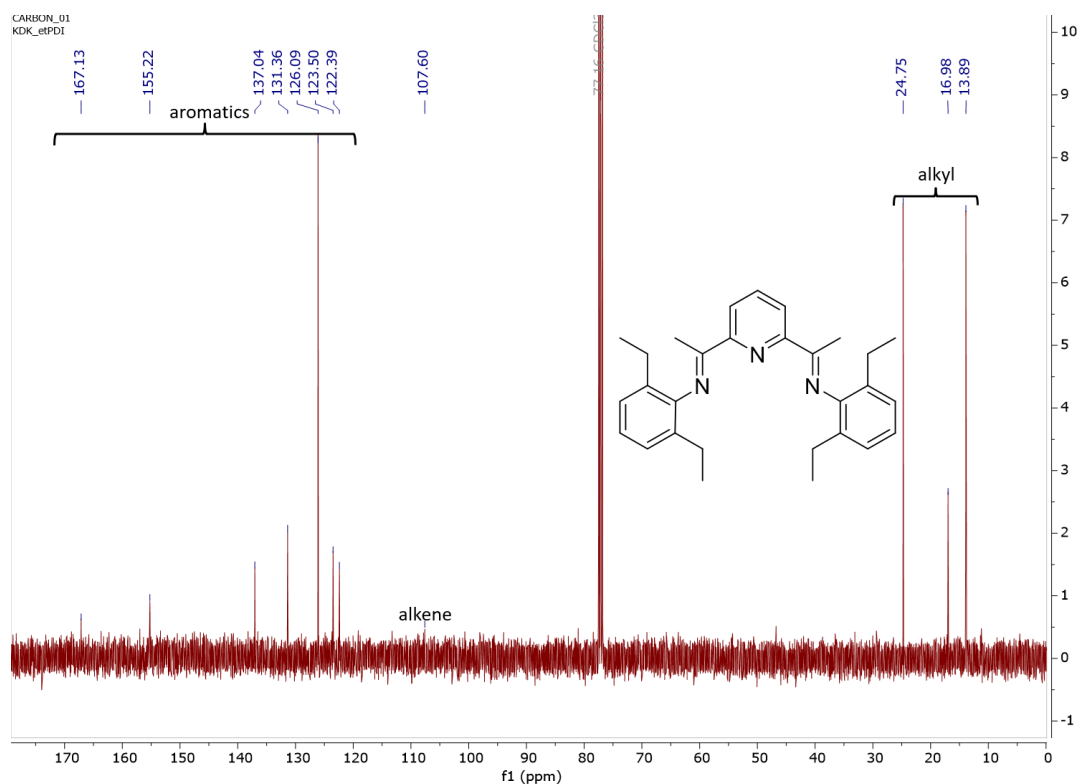


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) spectrum of DEP-H.

3.2. Synthesis of 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine cobalt(II) chloride (DEP). The synthesis methods are derived from literature procedures for MES and DIPP with slight modifications.^{2,3} Under a N_2 atmosphere, to an 8 mL vial, L-DEP (103 mg, 0.25 mmol) and ~1.25 mL THF were added and shaken until dissolved (transparent light yellow solution). To another 8 mL vial, CoCl_2 (33.5 mg, 0.25 mmol), ~1.25 mL THF, and a small Teflon-coated stir bar were added and began stirring until dissolved (murky blue solution). The dissolved ligand solution was then added dropwise to the vial containing CoCl_2 and stirred for 7 hours at room temperature. 5 mL diethyl ether was added to the vial, shaken, then the green solution was poured into a medium frit and transferred solids into a 20 mL vial. Solids were dried under vacuum at room temperature, giving a light brown powder. Concentrated in THF and maintained at -30°C for two weeks to give small yellow, brown crystals; 94% yield. ^1H NMR (500 MHz, CD_2Cl_2) δ 111.44 (s, 2H), 40.72 (s, 1H), 8.27 (s, 4H), 5.34 (s, 17H), 2.83 – 2.03 (m, 7H), 1.62 (d, $J = 2.8$ Hz, 28H), 1.27 (s, 21H), 1.02 – 0.69 (m, 22H), -10.09 (s, 2H), -19.07 (s, 13H), -36.33 (s, 2H). IR Peak (in cm^{-1}): 2963 m, 2952 w, 2872 w, 1621 w, 1584 m, 1461 m, 1459 m, 1448 s, 1433 w, 1374 s, 1319 w, 1262 vs, 1210 s, 1200 w, 1107 w, 1098 w, 1064 w, 1027 w, 906 w, 868 w, 813 s, 803 vs, 779 vs, 772 m, 742 m, 555 w. Anal. Calcd for $\text{C}_{29}\text{H}_{35}\text{Cl}_2\text{CoN}_3$: C, 62.71; H, 6.35; N, 7.57. Found: C, 62.68; H, 6.36; N, 6.95.

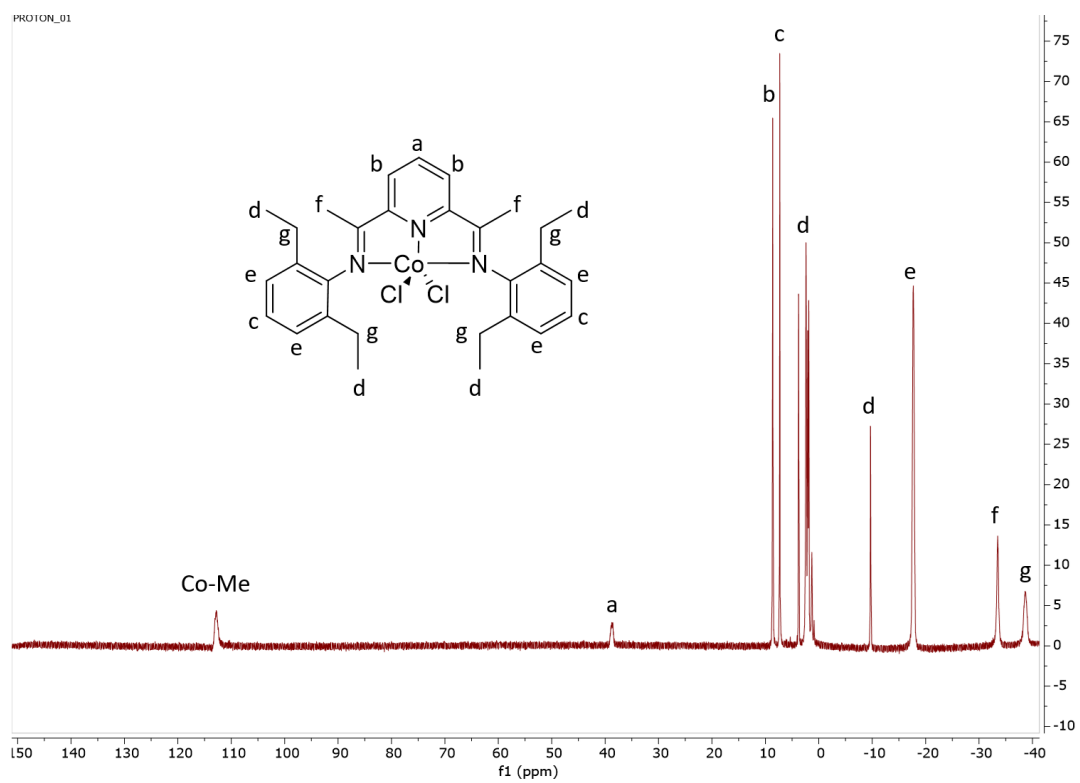
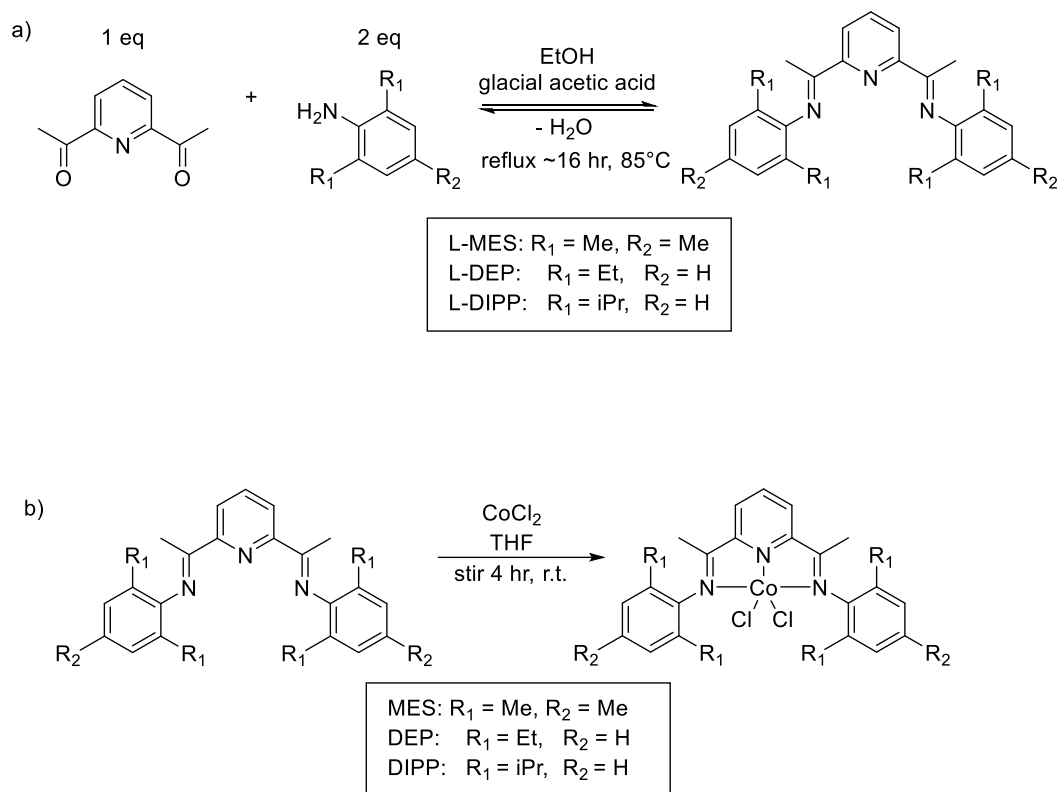


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectrum of DEP.



Scheme S1. General synthetic route for a) ligands and b) catalysts used in this study.

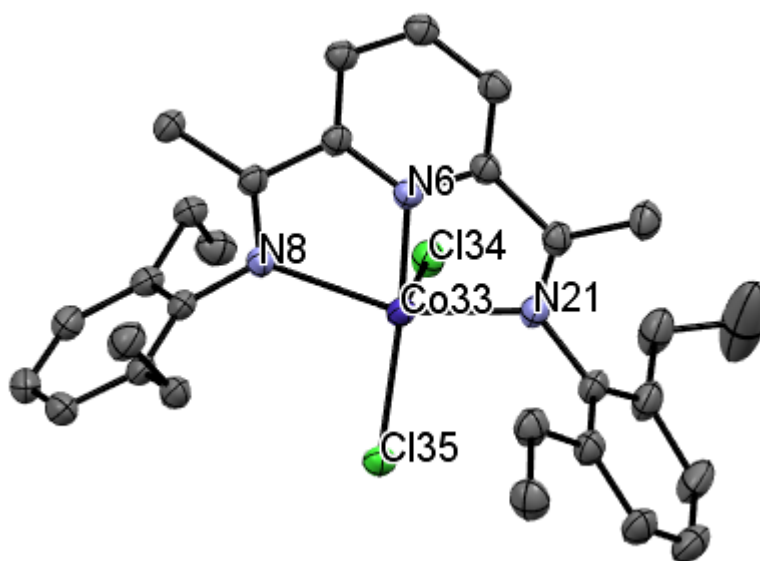


Figure S4. Thermal ellipsoid plot of (^{Et}PDI)CoCl₂·THF, drawn at the 50% probability level. Hydrogen atom and solvates are omitted for clarity. Selected bond distances (Å) and angles (°): Co33-Cl34 = 2.2854(9); Co33-Cl35 = 2.2635(7); Co33-N6 = 2.048(2); Co33-N8 = 2.233(2); Co33-N21 = 2.201(2); Cl34-Co33-Cl35 = 117.07(3); N8-Co33-N21 = 146.22(9); N6-Co33-N8 = 74.51(9); N6-Co33-N21 = 74.78(9). Reproduced from the CIF file having CCDC No. 2292414.

Table S1. Crystallographic information for CCDC No. 2292414.

(^{Et}PDI)CoCl₂·THF	
Formula	C ₃₁ H ₃₅ Cl ₂ CoN ₃ O
Crystal Habit, Color	Plated, yellow
Crystal Size (mm)	0.15 x 0.7 x 0.5
MW (g/mol)	595.45
Crystal system	Monoclinic
Space group	P 2 ₁ /c
a (Å)	12.9918(3)
b (Å)	14.8082(3)
c (Å)	15.5276(3)
α (°)	90
β (°)	95.746(2)
γ (°)	90
V (Å ³)	2972.27(11)
Z	4
T(K)	128(30)
λ (Å)	1.54184
GOF	1.026
Density (calcd) (g/cm ³)	1.331
Absorption coefficient (mm ⁻¹)	6.394
F ₀₀₀	1244
Total no Reflections	28832
Unique Reflections	5929
Final R indices*	R ₁ = 0.0552 wR ₂ = 0.1561
Largest Diff. peak and hole (e ⁻ Å ⁻³)	0.58, -0.70

* For [$I > 2\sigma(I)$]

3.3 Synthesis of poly(valerolactone) (PVL). PVL was synthesized unintentionally during the drying process with CaH_2 at 180°C . This polymer was isolated by precipitation in MeOH and characterized by SEC ($M_n = 13.9$ kDa, $\text{Đ} = 1.343$). ^1H NMR (500 MHz, CDCl_3) δ 4.05 (m, 2H), 2.31 (m, 2H), 1.64 (m, 4H). ^{13}C NMR (500 MHz, CDCl_3) δ 173.34, 63.98, 33.75, 28.13, 21.48.

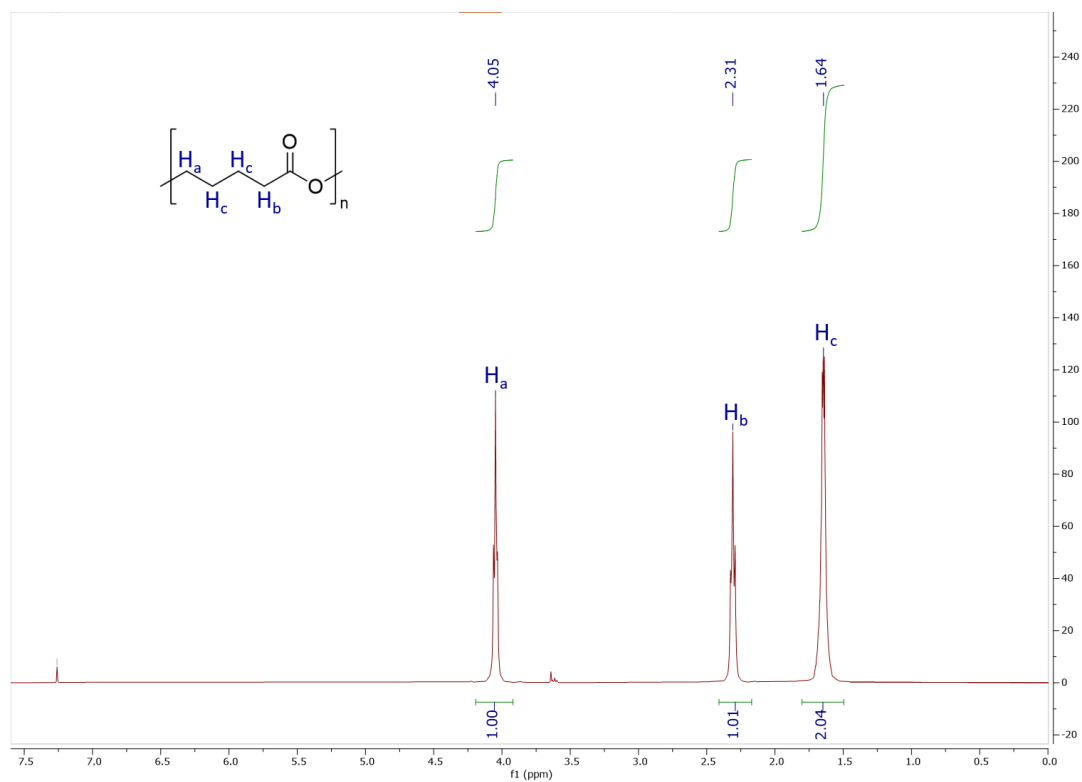


Figure S5. ^1H NMR characterization of poly(δ -valerolactone).

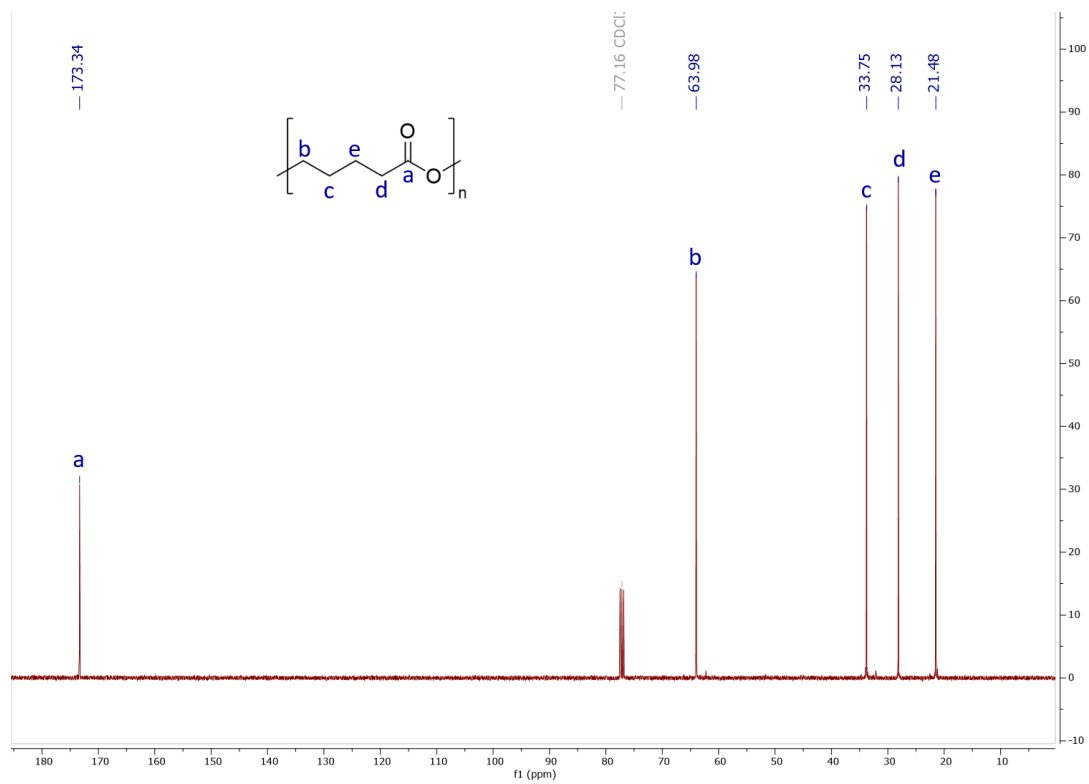


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of poly(δ -valerolactone).

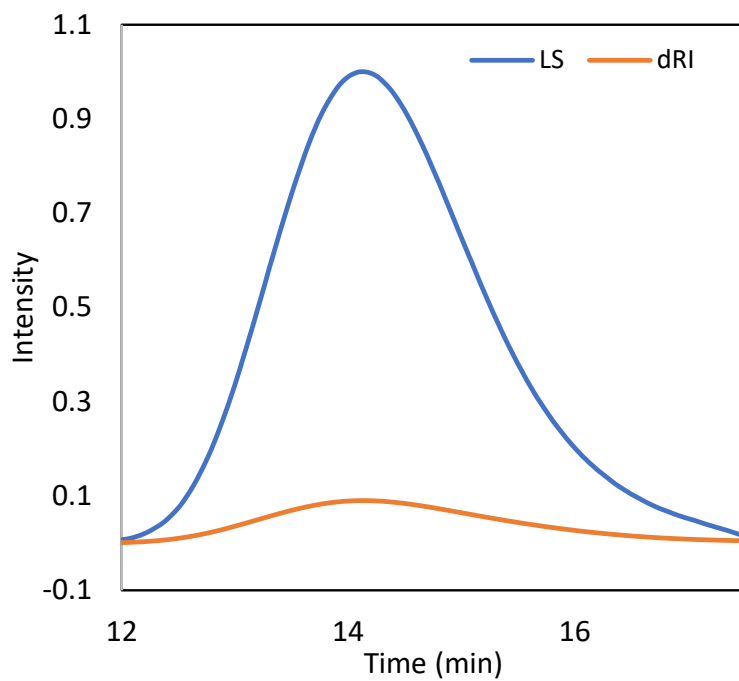


Figure S7. SEC characterization of synthesized poly(δ -valerolactone).

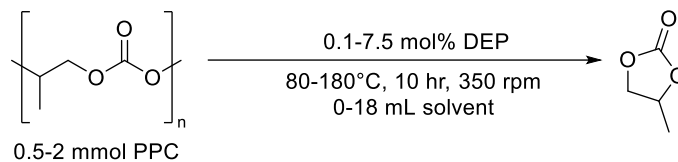
4. Depolymerization Design and Results

4.1 General Depolymerization Procedure

All depolymerization reactions were performed in the same general manner, modified from literature procedure.⁴ In Parr MRS 5000 reactor glass 30 mL liners, 0.25-7.5 mol% of catalyst with respect to the repeat unit molar mass of the polymer, 0-5 mol % KO^tBu with respect to the repeat unit molar mass of the polymer, 1-4 mmol of polymer, and a Teflon-coated magnetic stir bar were added. To this, 3.0-18.0 mL solvent was syringed in, followed by 0-8.0 mL ¹PrOH and rapidly sealed in the Parr vessel. Reactions involving KO^tBu were performed under a N₂ atmosphere glovebox during weighing and addition of any solvents, while air-stable reactions were performed on the lab benchtop. The Parr vessel was placed in the Parr reactor, then set to react at a given temperature for a given amount of time, stirred at 350 rpm. All reactions, regardless of air-sensitivity during weighing and preparation, were worked up in air, on the lab benchtop. The Parr vessel was allowed to cool to room temperature, then a measured aliquot was removed, rotary evaporated to remove reaction solvents (if any). Remaining product(s) were then characterized using CDCl₃ in ¹H and ¹³C{¹H} NMR, with some products' yield obtained by adding an exact 9-10 uL mesitylene as an internal standard in each NMR sample for those involving CDP of poly(propylene carbonate) (PPC). The 3H of the methyl peak of mesitylene and that of propylene carbonate and PPC all are in 1:1 ratios, allowing for the moles of product to be calculated proportionally using the measured aliquot compared to the measured total solution of the reaction. For all other depolymerization reactions, yield was determined by NMR integration. In some noted cases, remaining polymer was examined using SEC.

4.2 Depolymerization of PPC under various conditions for optimization

Table S2. Depolymerization of PPC results after varying single parameter under standard conditions.^a



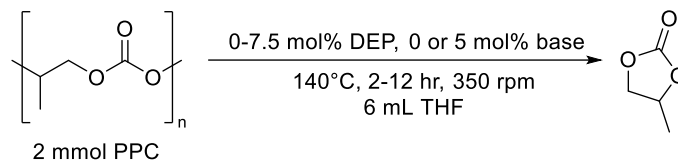
Entry	PPC (in mmol)	Catalyst Loading (mol %)	Solvent (mL)	Temperature (°C)	Yield ^b
1	2	5	6	80	2
2	2	5	6	100	38
3	2	5	6	120	41
4 ^c	2	5	6	140	68(4)
5	2	5	6	160	>99
6 ^c	2	5	3	140	87(4)
7 ^c	2	5	6	140	68(4)
8 ^c	2	5	12	140	87(8)
9 ^c	2	5	18	140	31(12)
10	4	5	6	140	86
11	2	5	6	140	66
12	1	5	6	140	99
13	0.5	5	6	140	30
14 ^c	2	0.5	6	140	17(7)
15 ^c	2	1	6	140	34(10)
16 ^c	2	2.5	6	140	35(19)
17 ^c	2	5	6	140	68(4)
18 ^c	2	7.5	6	140	30(18)

^aConditions: 0.1-7.5 mol% DEP with respect to repeat unit molar mass of polymer, 0.5-2mmol PPC, 3-18.0 mL THF, 80-160°C, run at 350 rpm for 10 hours in Parr reactor. ^bDetermined ¹H NMR spectroscopy using mesitylene as an internal standard. ^cExperiments run in at least duplicate.

Table S3. Conditions for prior work reporting depolymerization of PPC.

Prior Work	Catalyst	Catalyst Loading (mol %)	Solvent	Solvent (mL)	Time (h)	Temperature (°C)	Conversion (%)
Kuran ⁵	ZnEt ₂	41	Hexanes:1,4-dioxane	5:60	16.7	30	50
Kerton ⁶	BCF	5	DCM	3	3	130	>99
Darensbourg ⁷	<i>n</i> Bu ₄ NN ₃	4	d-toluene	1	1	100	>99

Table S4. Depolymerization of PPC under varying amounts base, catalyst loadings, and time, characterized by SEC.^a



Entry	DEP (mol%)	KO ^t Bu (mol%)	NaO ^t Bu (mol%)	Time (hours)	%Yield ^{b,c}	M _n (kDa) ^{c,d}	M _w (kDa) ^{c,d}	Đ ^{c,d}
1	5	5	0	2	74(0)	13(8)	22(11)	1.82(21)
2	5	5	0	4	85(3)	5(1)	10(4)	1.97(24)
3	5	5	0	6	91(2)	9(3)	46(36)	4(2)
4	5	5	0	8	92(2)	43(38)	68(60)	1.61(4)
5	5	5	0	10	85(2)	13(11)	24(22)	1.78(14)
6	5	5	0	12	92(2)	3(2)	4(3)	2.23(77)
7	5	0	5	2	40(14)	21.3(5)	33(5)	1.54(27)
8	5	0	5	4	58(15)	18(8)	33(17)	1.75(18)
9	5	0	5	6	50(12)	26(14)	43(27)	1.55(18)
10	5	0	5	8	44(12)	32(7)	57(10)	1.77(5)
11	5	0	5	10	86(1)	117(106)	147(122)	1.84(63)
12	5	0	5	12	65(16)	83(69)	101(83)	1.24(2)

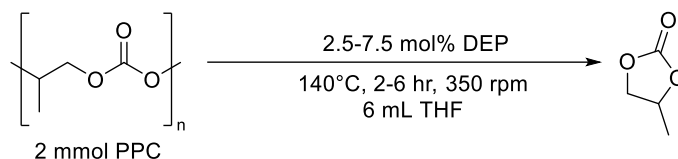
^aConditions: 0-7.5 mol% DEP, 0 or 5 mol% KO^tBu, 0 or 5 mol% NaO^tBu loadings with respect to repeat unit molar mass of the polymer, 2 mmol PPC, 6.0 mL THF, run 2-12 hours at 350 rpm and 140°C in Parr reactor unless otherwise noted. Reactions with KO^tBu performed in N₂ atmosphere, otherwise performed in air. ^bDetermined ¹H NMR spectroscopy using mesitylene as an internal standard. ^cExperiments run in duplicate, numbers represent averages with standard deviations in parentheses. ^dDetermined by size exclusion chromatography (SEC) in THF using a Wyatt DAWN HELEOS II MALS detector.

Table S5. Control reactions for depolymerization of PPC.^a

Entry	DEP (mol%)	KO ^t Bu (mol%)	NaO ^t Bu (mol%)	Starting Material	Yield PC (%) ^b
1 ^c	5	0	0	2 mmol PC	>99
2 ^c	0	5	0	2 mmol PC	>99
3	0	5	0	2 mmol PPC	41
4	0	0	5	2 mmol PPC	66

^aConditions: 5 mol% DEP or base used with respect to repeat unit molar mass of starting material, as noted, 2 mmol PPC or PC as noted, in 6.0 mL THF, run 10 hours at 350 rpm and 140°C in Parr reactor. Reactions with KO^tBu performed in N₂ glovebox atmosphere, otherwise performed in air. ^bDetermined with ¹H NMR spectroscopy using mesitylene as an internal standard. ^cReactions performed as controls to ensure DEP and KO^tBu do not polymerize PC to PPC under similar reaction conditions.

Table S6. Depolymerization of PPC under varying amount catalyst loadings and time, characterized by SEC.^a



Entry	DEP (mol%)	Time (hours)	%Yield ^b	M _n (kDa) ^c	M _w (kDa) ^c	Đ ^c
1	2.5	2	14	52.7	85.6	1.624
2	2.5	6	61	3.6	11.1	3.103
3	7.5	2	59	4.7	8.8	1.898
4	7.5	6	73	2.5	7.3	2.963

^aConditions: 2.5-7.5 mol% DEP loadings with respect to repeat unit molar mass of the polymer, 2 mmol PPC, 6.0 mL THF, run 2-6 hours at 350 rpm and 140°C in Parr reactor. Reactions performed in air. ^bDetermined ¹H NMR spectroscopy using mesitylene as an internal standard. ^cDetermined by size exclusion chromatography (SEC) in THF using a Wyatt DAWN HELEOS II MALS detector.

Table S7. Duplicate 2h interval reactions of the depolymerization of PPC with DEP.^a

Entry	Time (hr)	%Yield ^b	% Yield Avg. ^c	M _n (kDa) ^d	M _n Avg. ^{c,d}	M _w (kDa) ^d	M _w Avg. ^{c,d}	Đ ^d	Đ Avg. ^{c,d}
1	0	n/a	n/a	75.7	67(8)	151.5	147(4)	2.002	2.21(21)
2		n/a		58.9		142.8		2.425	
3	2	33	29(5)	53.7	48(6)	94.2	89(5)	1.755	1.89(14)
4		24		41.5		84.3		2.034	
5	4	38	34(4)	50.5	56(5)	86.9	95(8)	1.720	1.715(5)
6		30		60.5		103.5		1.710	
7	6	46	47(1)	36.8	40(4)	59.3	61(1)	1.614	1.52(10)
8		48		43.8		62.1		1.416	
9	8	51	52(1)	29.3	29.1(2)	40.6	42(1)	1.387	1.43(5)
10		53		28.9		42.7		1.477	
11	10	67	70(5)	24.6	24.8(2)	33.6	33.6(0)	1.364	1.356(8)
12		75		25.0		33.6		1.348	
13 ^e	12	94	96(2)	n/a	n/a	n/a	n/a	n/a	n/a
14 ^e		98		n/a		n/a		n/a	

^aConditions: 5 mol% DEP or base used with respect to repeat unit molar mass of PPC, 2 mmol PPC, in 6.0 mL THF, run 2-12 hours at 350 rpm and 140°C in Parr reactor. Reactions performed in air. ^bDetermined with ¹H NMR spectroscopy using mesitylene as an internal standard. ^cExperiments run in duplicate, numbers represent averages with standard deviations in parentheses. ^dDetermined by size exclusion chromatography (SEC) in THF using a Wyatt DAWN HELEOS II MALS detector. ^eDue to high depolymerization, polymer sample for SEC could not be obtained.

Figure S8. Labeling for various polymers (a) and their products following cyclodepolymerization (b) and solvolytic depolymerization (c).

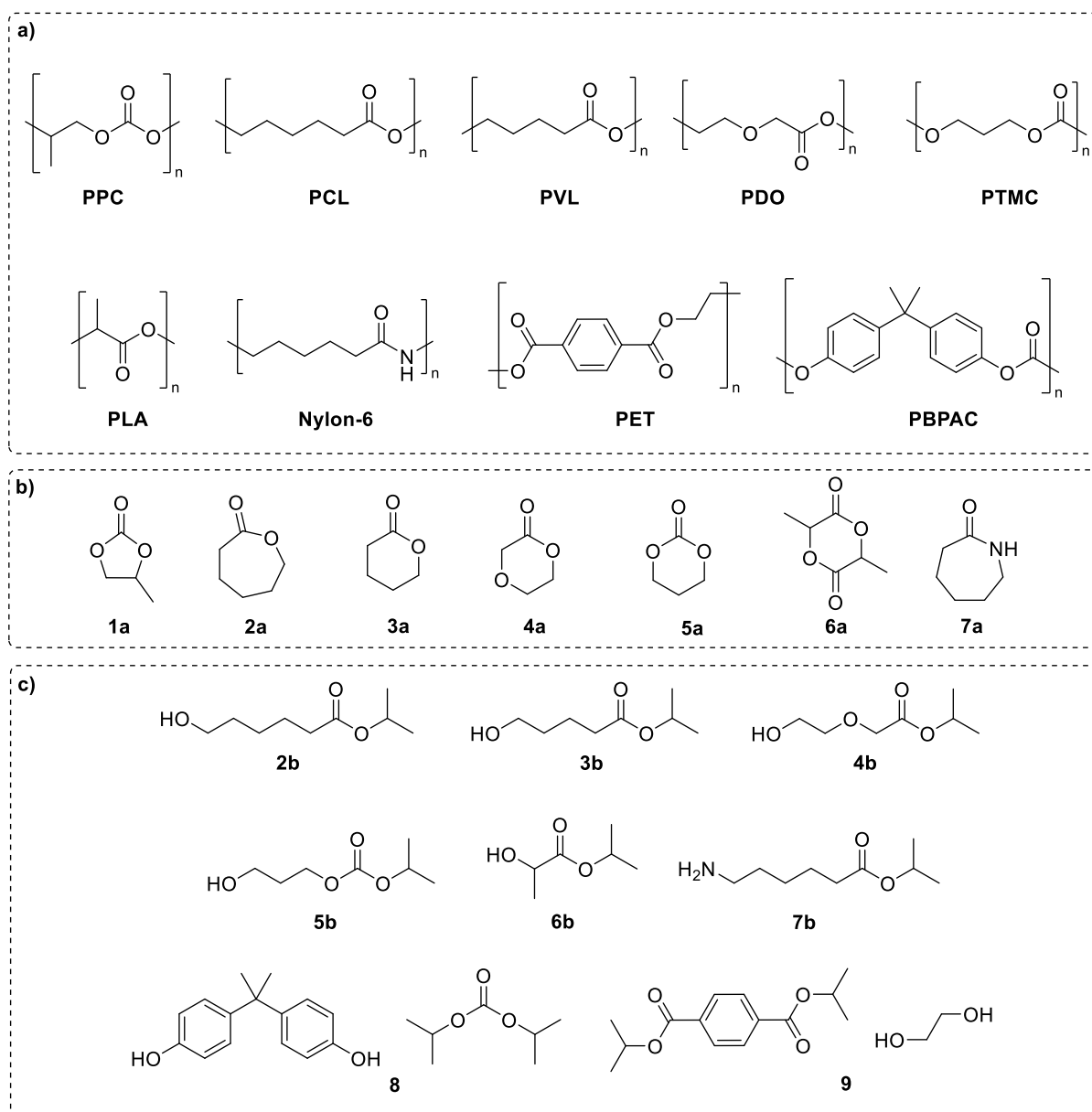
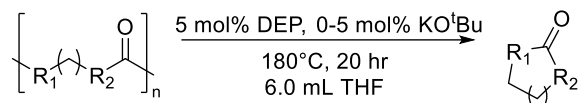
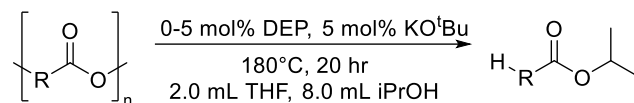


Table S8. Cyclodepolymerization of various polymers using DEP under varying conditions.^a

Entry	Polymer	KO ^t Bu (mol%)	Product	% Yield ^b
1^c	PPC	0	1a	>99
2^c	PPC	5	1a	>99
3	PCL	0	2a	11
4	PCL	5	2a	8
5	PVL	0	3a	84
6^c	PVL	0	3a	73
7^c	PVL	5	3a	58
8	PDO	0	4a	>99
9	PDO	5	4a	>99
10^d	PTMC	0	5a	>0
11^d	PTMC	5	5a	>0
12	PLA	0	6a	42
13	PLA	5	6a	38
14	Nylon-6	0	7a	0
15	Nylon-6	5	7a	0

^aConditions: 5 mol% DEP and 0-5mol% KO^tBu loadings with respect to repeat unit molar mass of the polymer, 2 mmol polymer, 6.0 mL THF, run 20 hours at 350 rpm and 180°C in Parr reactor, unless otherwise noted. Reactions with KO^tBu performed in N₂ atmosphere, otherwise performed in air. ^bDetermined ¹H NMR spectroscopy using peak integrations. ^cPerformed at 140°C. ^dPresence of cyclic monomer is observed in small quantities in the NMR, but not enough to determine an accurate yield.

Table S9. Solvolysis of various polymers using KO^tBu under varying conditions.^a

Entry	Polymer	DEP (mol%)	Product	% Yield ^b
1 ^c	PPC	5	1a	>99
2 ^c	PPC	0	1a	>99
3	PCL	5	2b	>99
4	PCL	0	2b	>99
5	PVL	5	3b	78
6	PVL	0	3b	85
7	PDO	5	4b	61
8	PDO	0	4b	82
9	PTMC	5	5b	>99
10	PTMC	0	5b	0
11	PLA	5	6b	70
12	PLA	0	6b	>99
13	Nylon-6	5	7b	0
14	Nylon-6	0	7b	0
15	PBPAC	5	8	>99
16	PBPAC	0	8	48
17	PET	5	9	>99
18	PET	0	9	>99

^aConditions: 5 mol% KO^tBu, 0-5 mol% DEP used with respect to repeat unit molar mass of polymer, 2 mmol polymer, in 2.0 mL THF and 8.0 mL iPrOH, run 20 hours at 350 rpm and 180°C in Parr reactor. Reactions with KO^tBu performed in N₂ atmosphere, otherwise performed in air. ^bDetermined ¹H NMR spectroscopy using peak integrations. ^cNote, no solvolytic depolymerization product observed in yield, only cyclodepolymerization product.

5. Characterization of Depolymerizations

5.1 NMR Characterizations

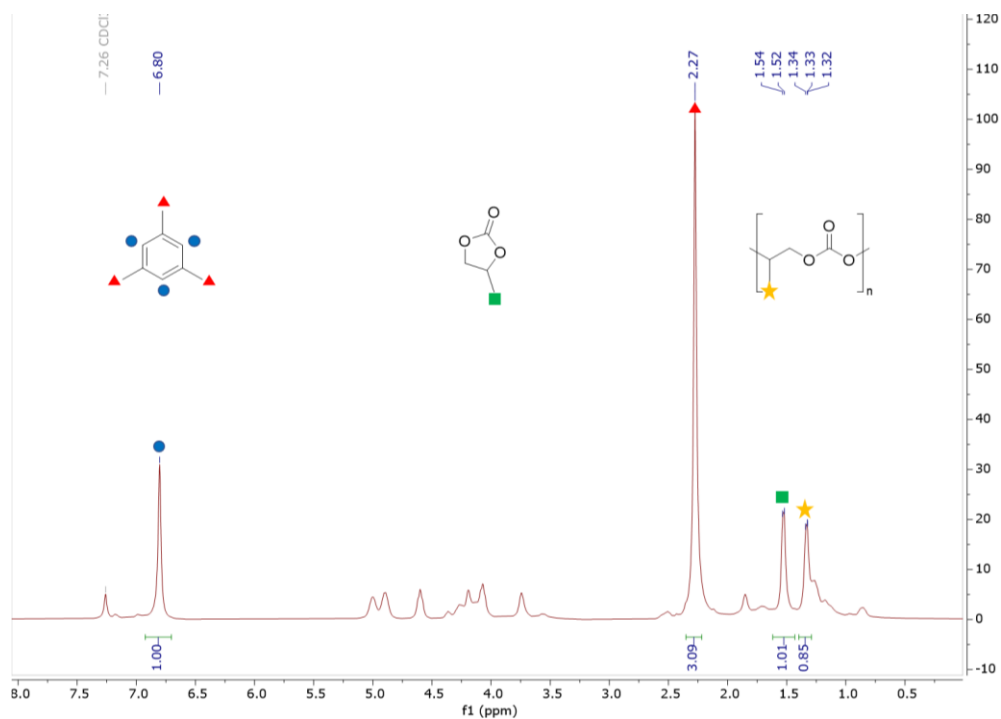


Figure S9. ^1H NMR with 58% yield by internal standard and 54% by NMR ratio. Yield with internal standard was calculated by proportioning 3H peak with the known amount of mesitylene with the methyl peak from the propylene carbonate in the measured aliquot.

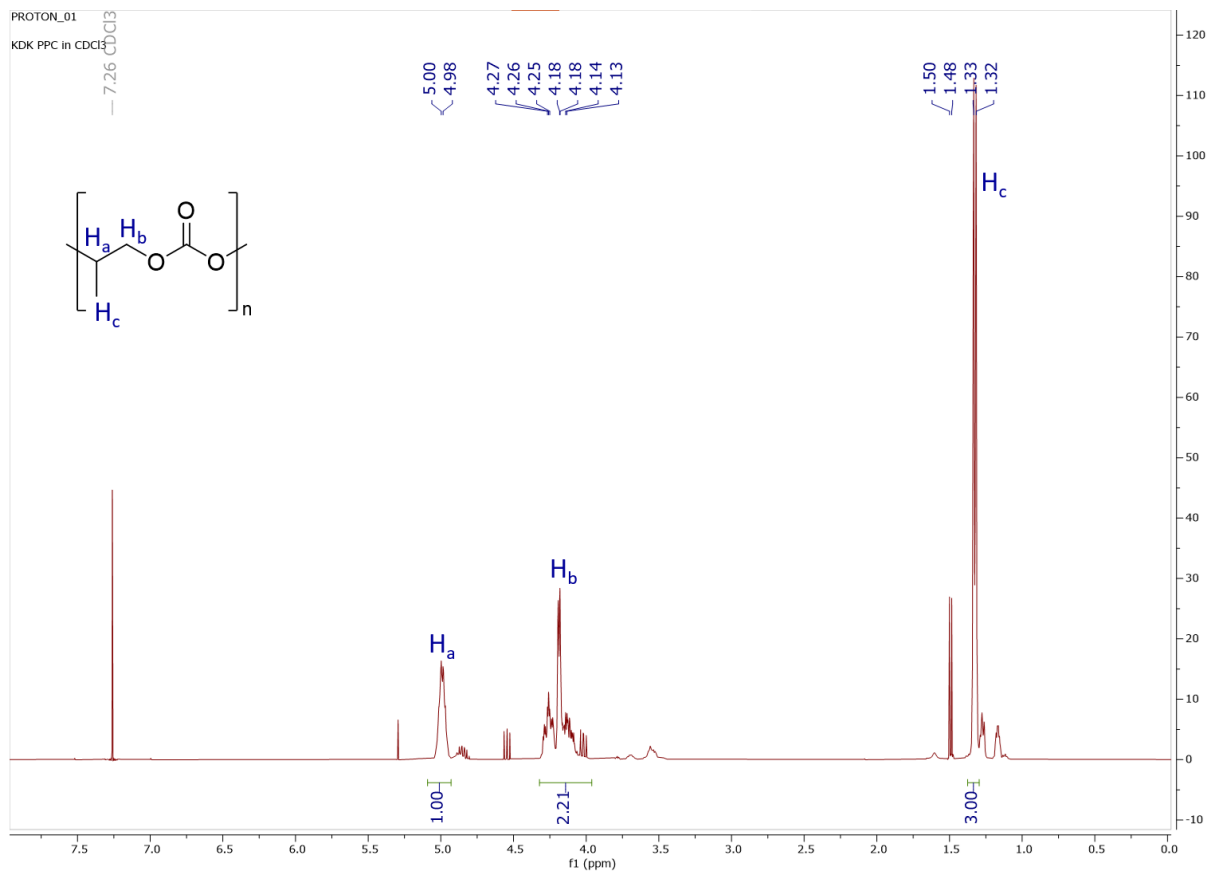


Figure S10. ¹H NMR characterization of poly(propylene carbonate) (PPC).

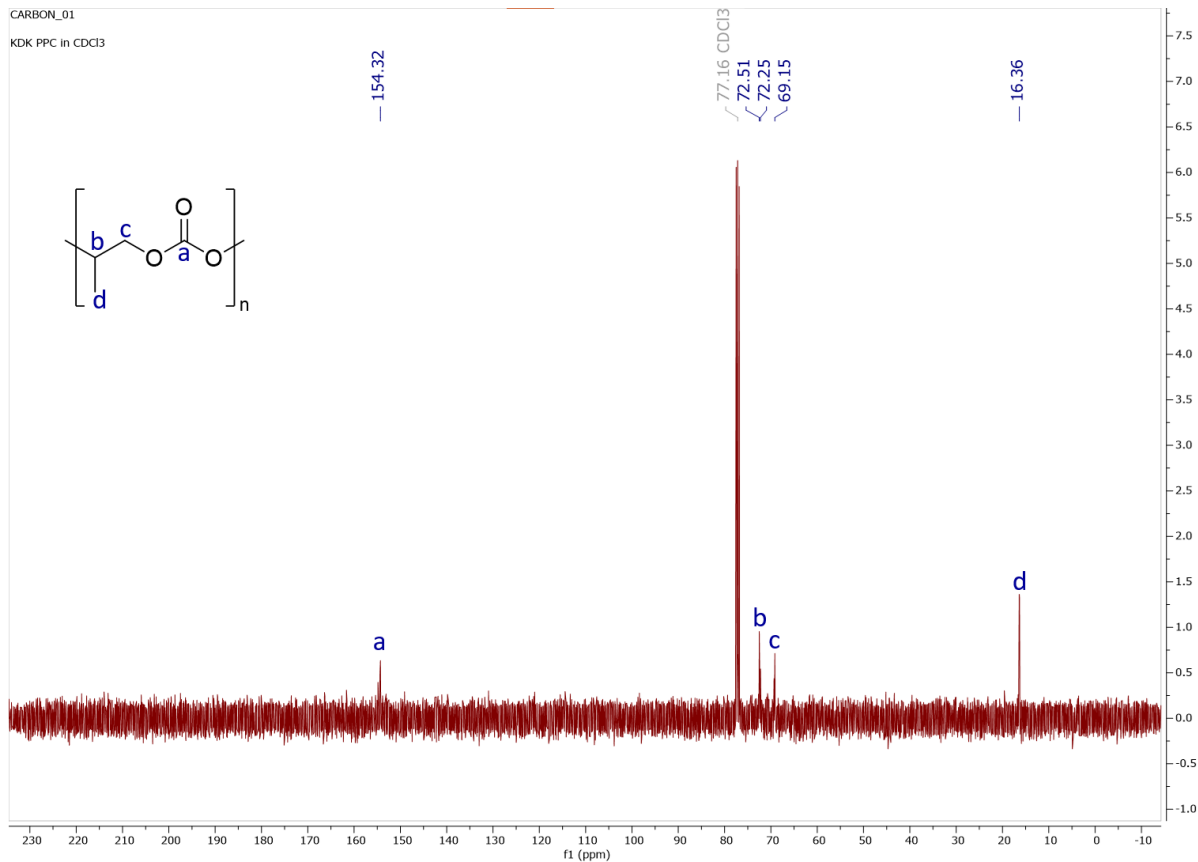


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of poly(propylene carbonate) (PPC).

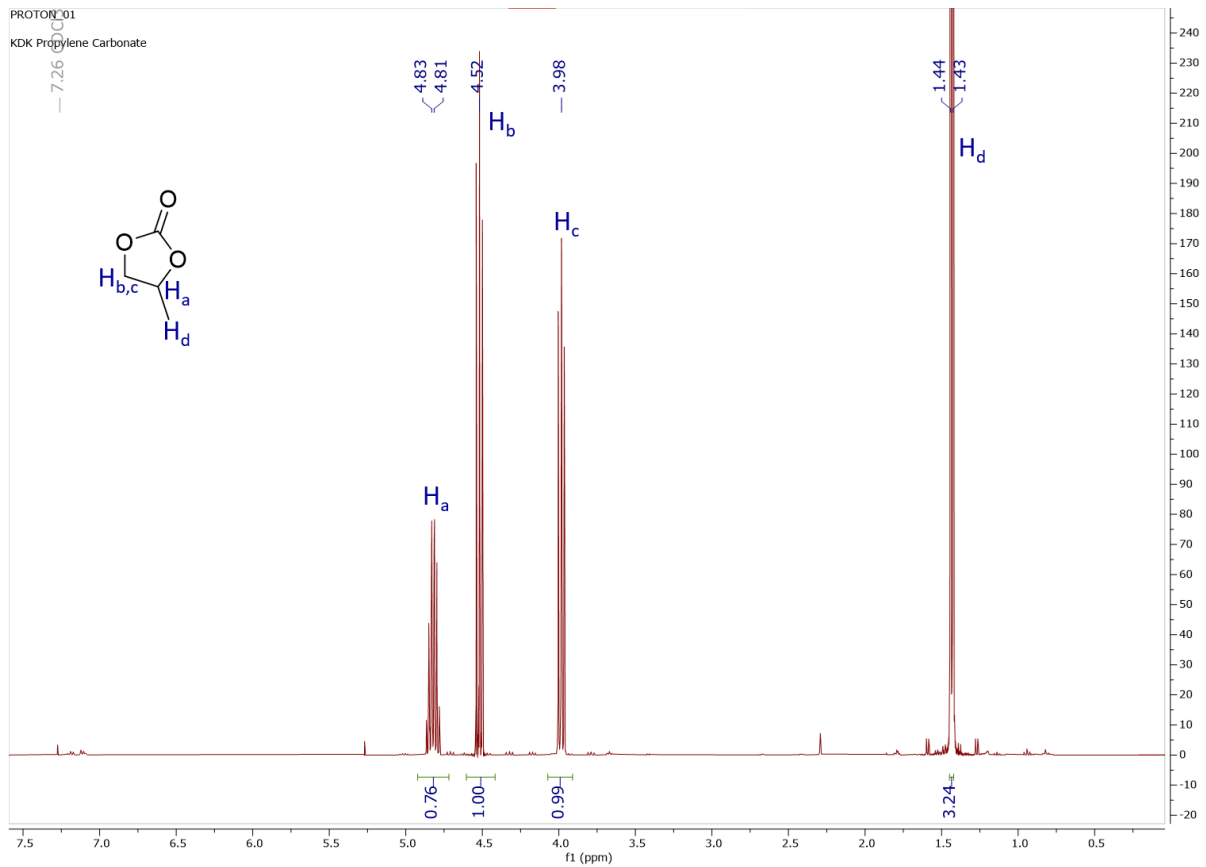


Figure S12. ¹H NMR characterization of propylene carbonate (**1a**).

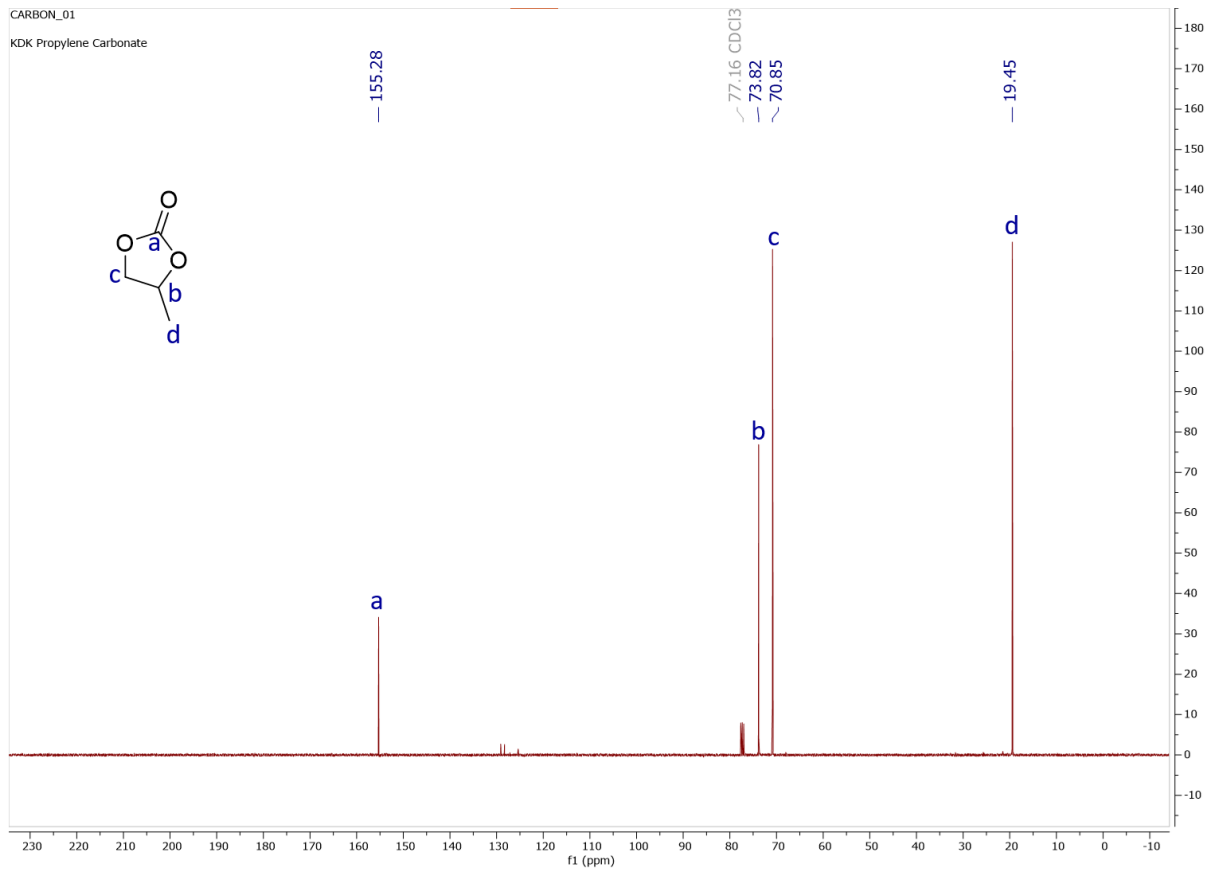


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of propylene carbonate (**1a**).

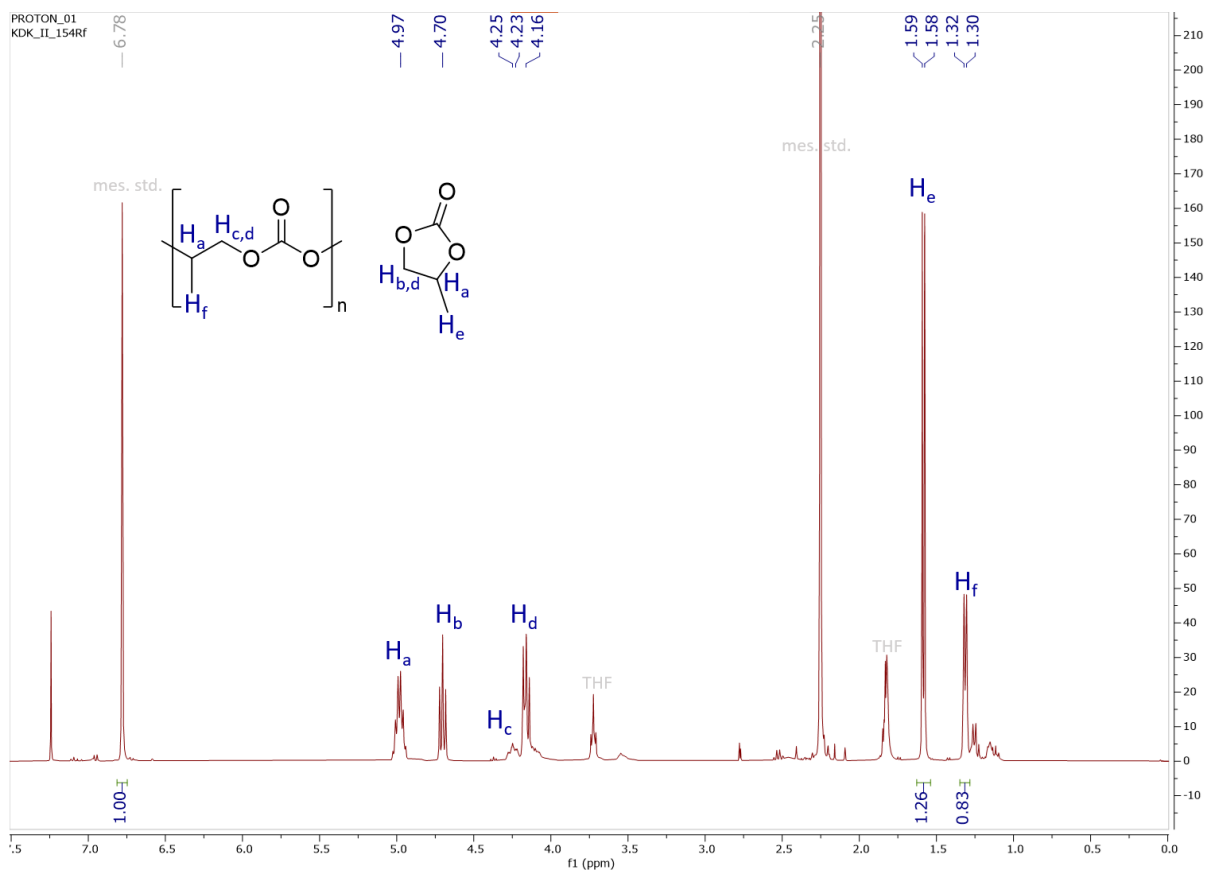


Figure S14. ^1H NMR of depolymerization product of PPC to propylene carbonate (**1a**) with DEP, representing a mixed product of 59% yield **1a** by internal standard and 60% by NMR integration.

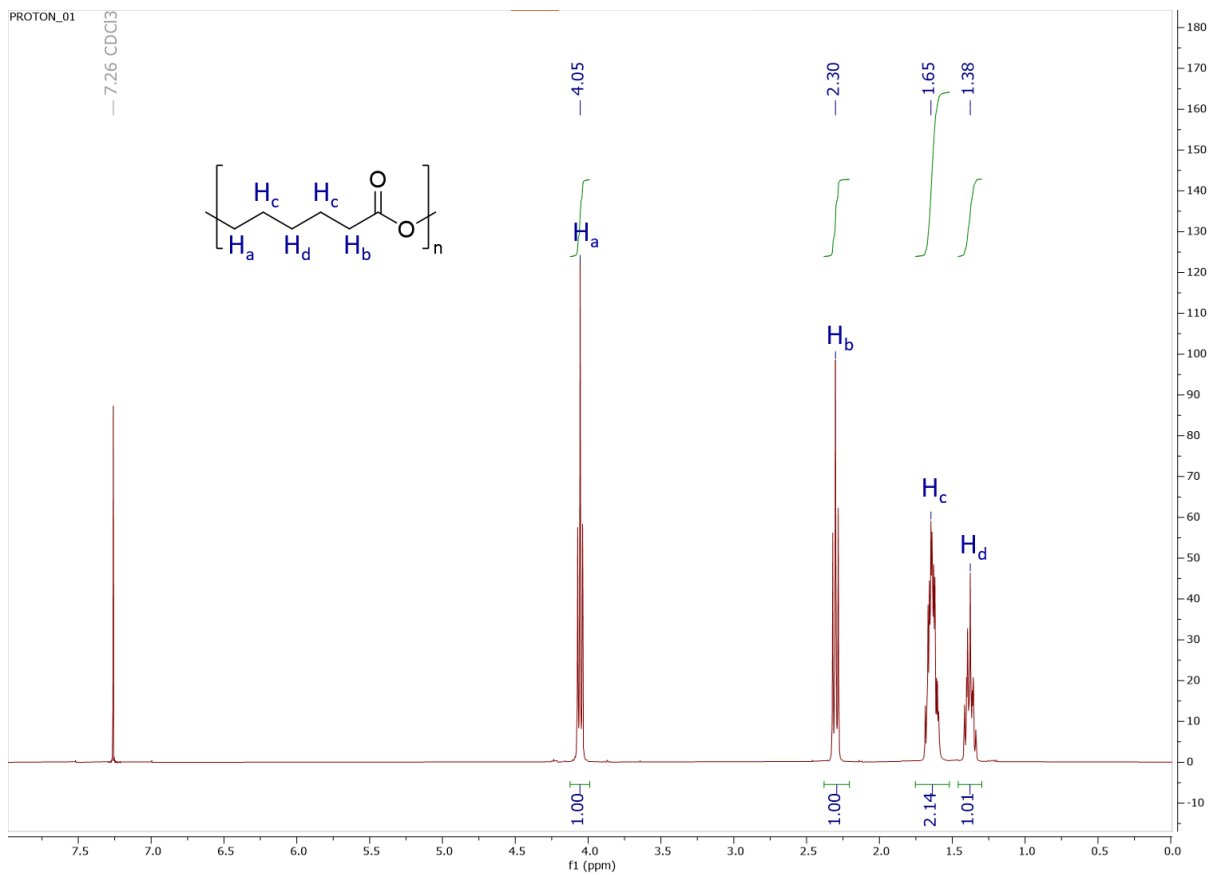


Figure S15. 1H NMR characterization of poly(ϵ -caprolactone) (PCL).

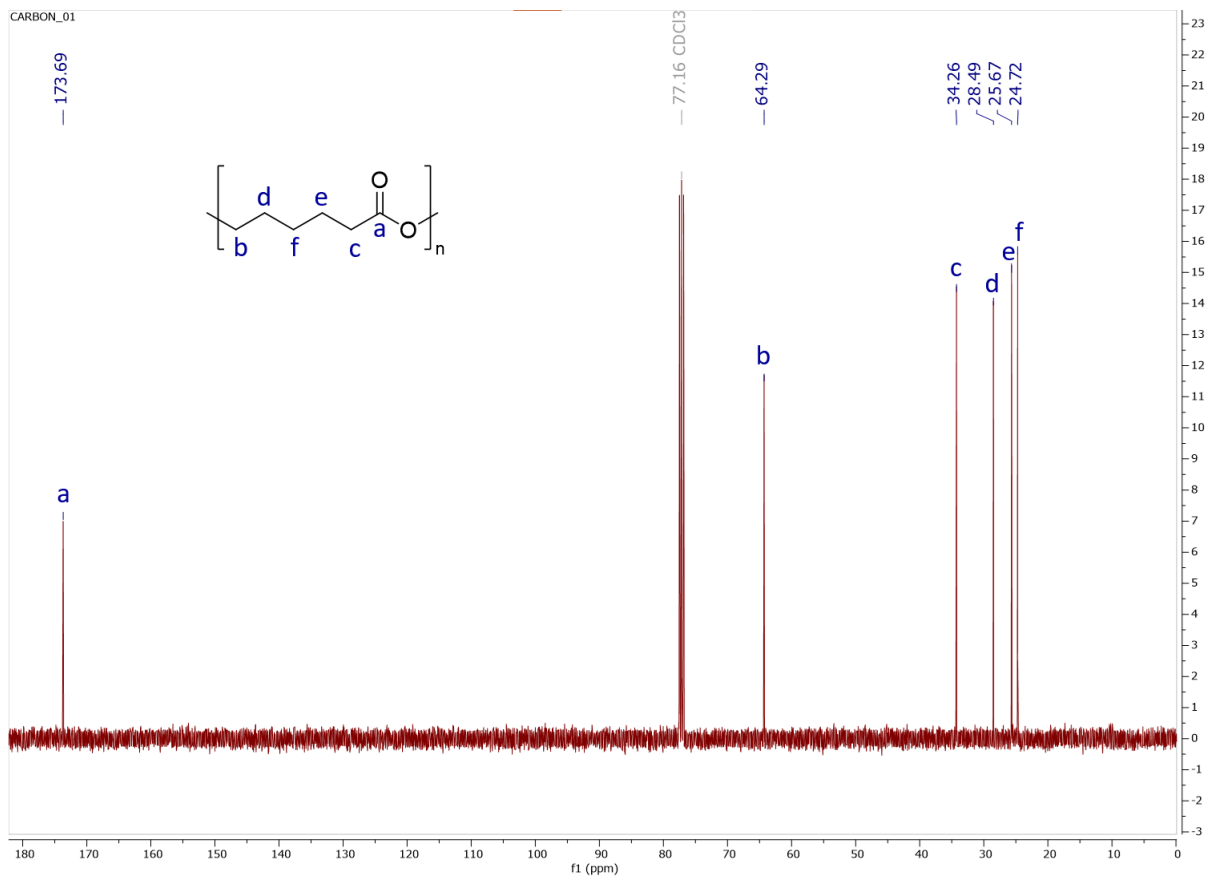
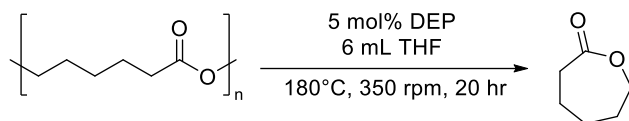


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of poly(ϵ -caprolactone) (PCL).



Scheme S3. General reaction conditions for the cyclodepolymerization of poly(ϵ -caprolactone) (**PCL**) to ϵ -caprolactone (**2a**) with DEP.

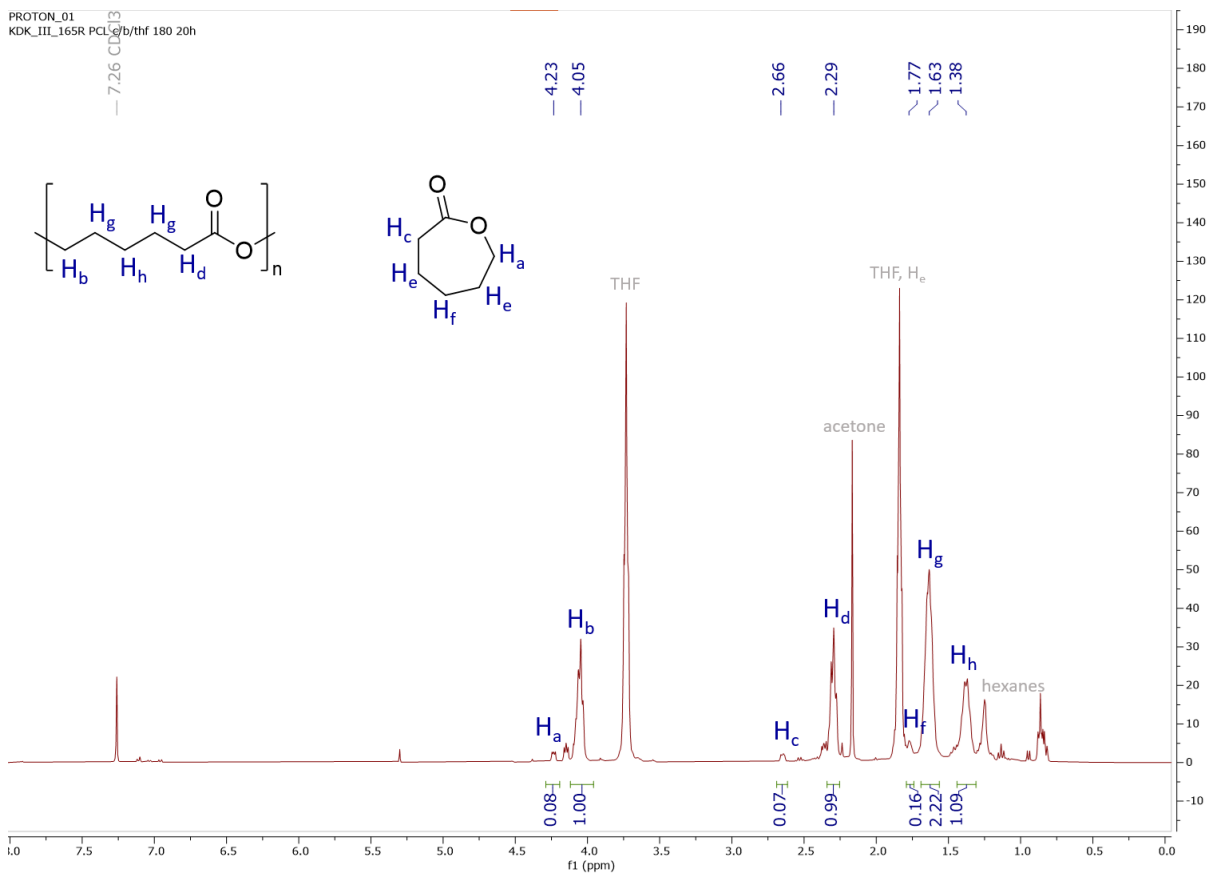
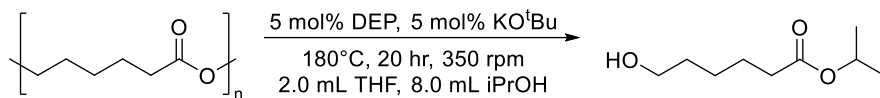


Figure S17. ^1H NMR of depolymerization product of PCL to ϵ -caprolactone (**2a**) with DEP with solvent impurities, representing 8% conversion to **2a** by NMR integration.



Scheme S4. Reaction conditions for the solvolysis of poly(ϵ -caprolactone) (**PCL**) to 2-isopropyl 6-hydroxyhexanoate (**2b**) with DEP.

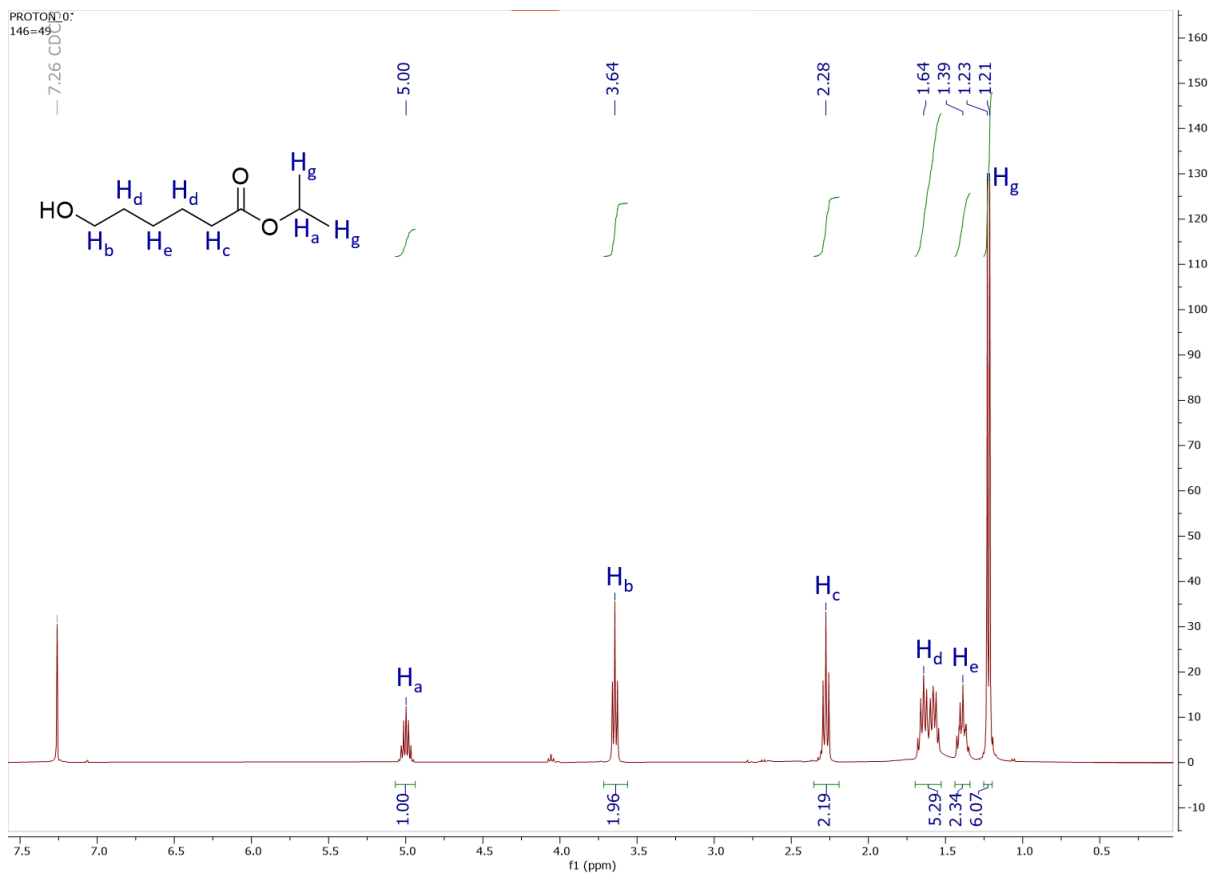


Figure S18. ^1H NMR characterization of solvolysis of poly(ϵ -caprolactone) (**PCL**) to 2-isopropyl 6-hydroxyhexanoate (**2b**).

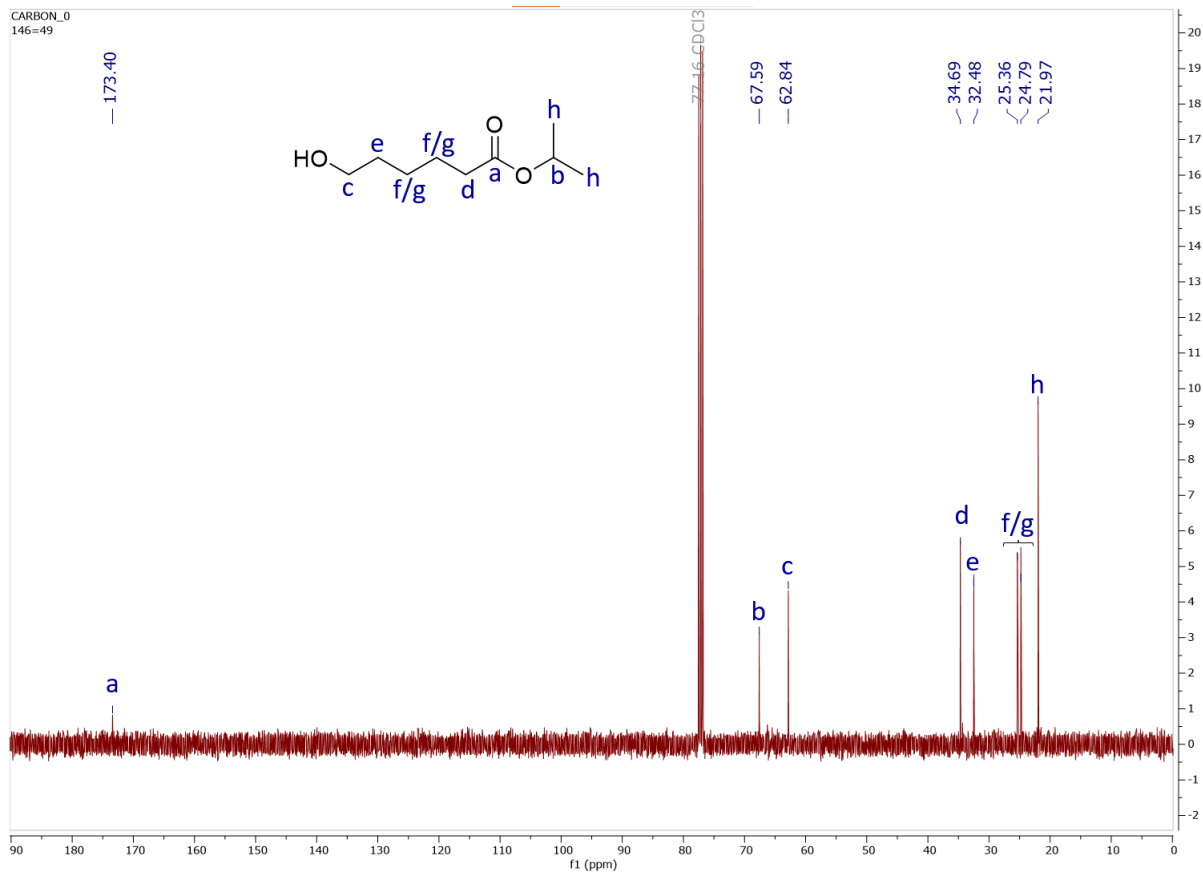


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of solvolysis of poly(ϵ -caprolactone) (PCL) to 2-isopropyl 6-hydroxyhexanoate (**2b**).

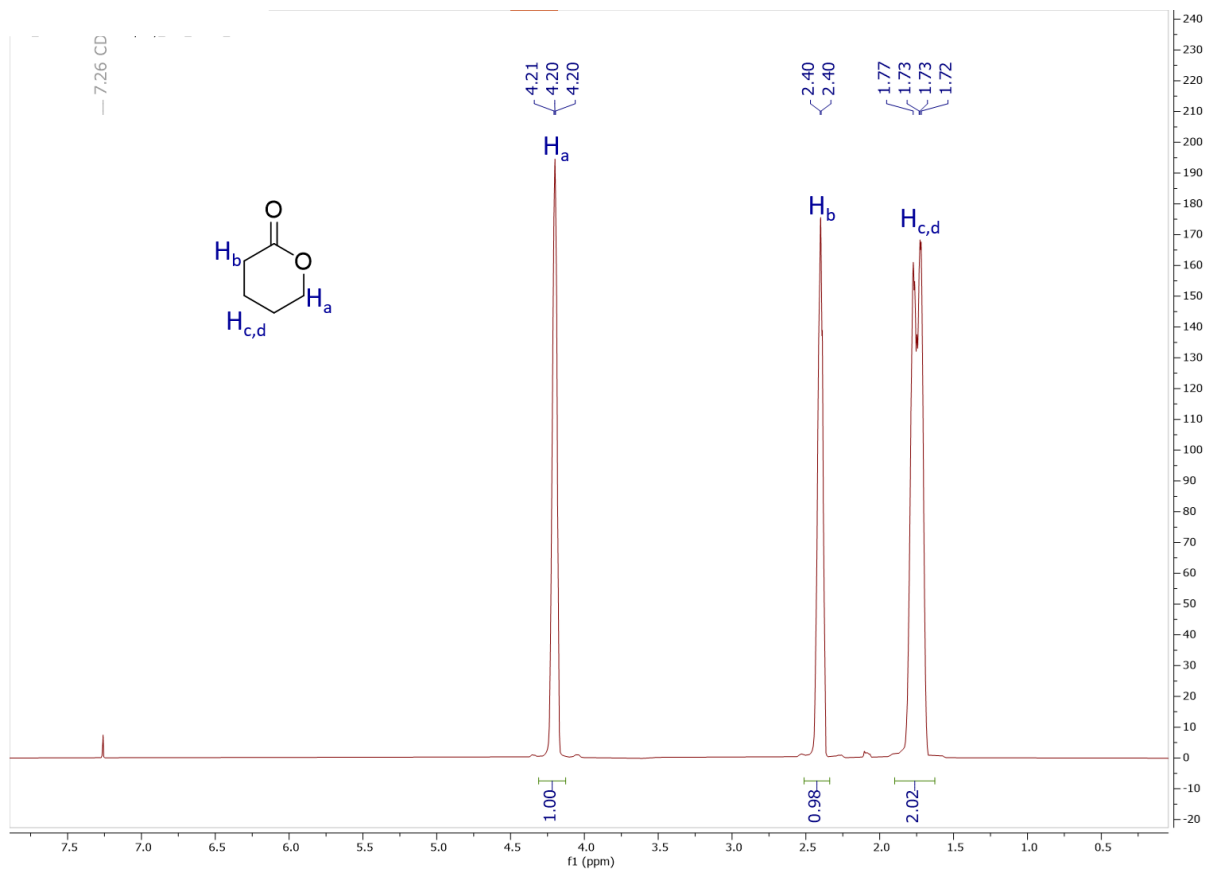
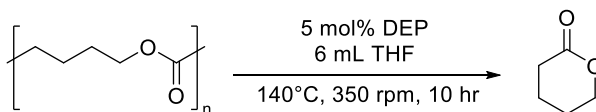


Figure S20. ^1H NMR characterization of δ -valerolactone (**3a**).



Scheme S5. General reaction conditions for the cyclodepolymerization of poly(valerolactone) (**PVL**) to δ -valerolactone (**3a**) with DEP.

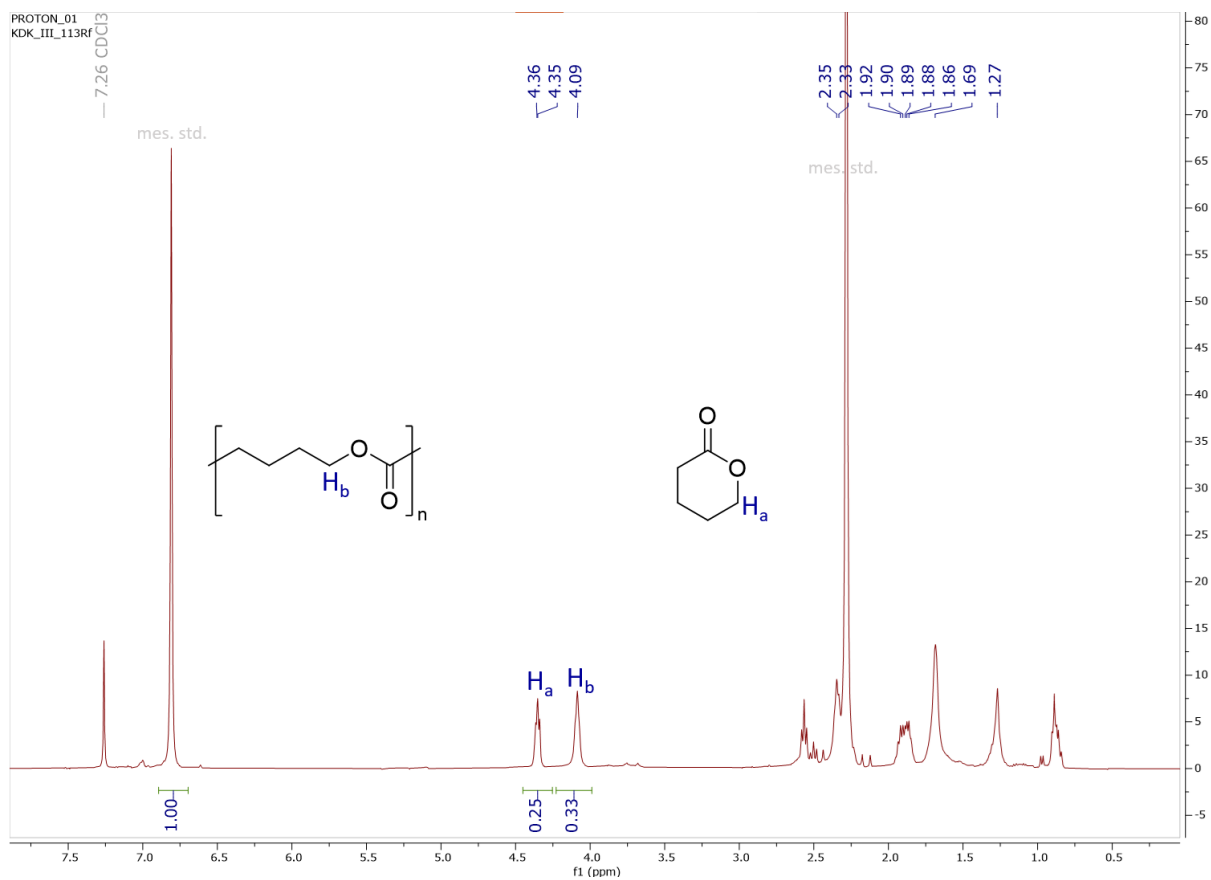
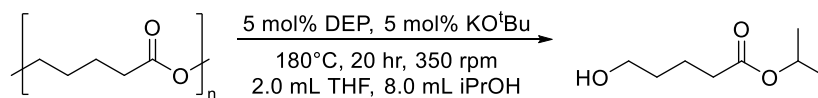


Figure S21. ¹H NMR of depolymerization product of PVL to δ -valerolactone (**3a**) with DEP with solvent impurities, representing 43% conversion to **3a** by NMR integration.



Scheme S6. Reaction conditions for the solvolysis of poly(δ -valerolactone) (**PVL**) to 2-isopropyl 6-hydroxypentanoate (**3b**) with DEP.

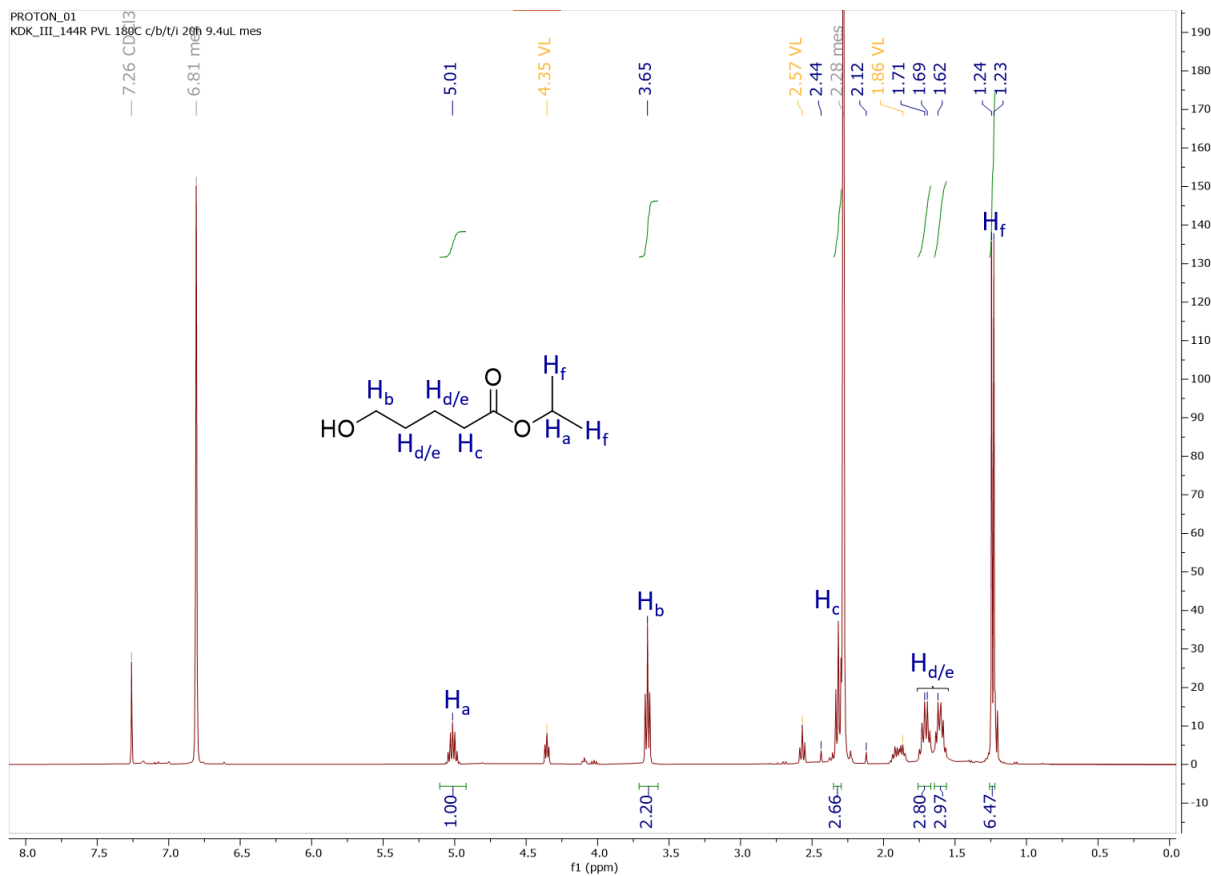


Figure S22. ¹H NMR characterization of solvolysis of poly(δ -valerolactone) (**PVL**) to 2-isopropyl 6-hydroxypentanoate (**3b**).

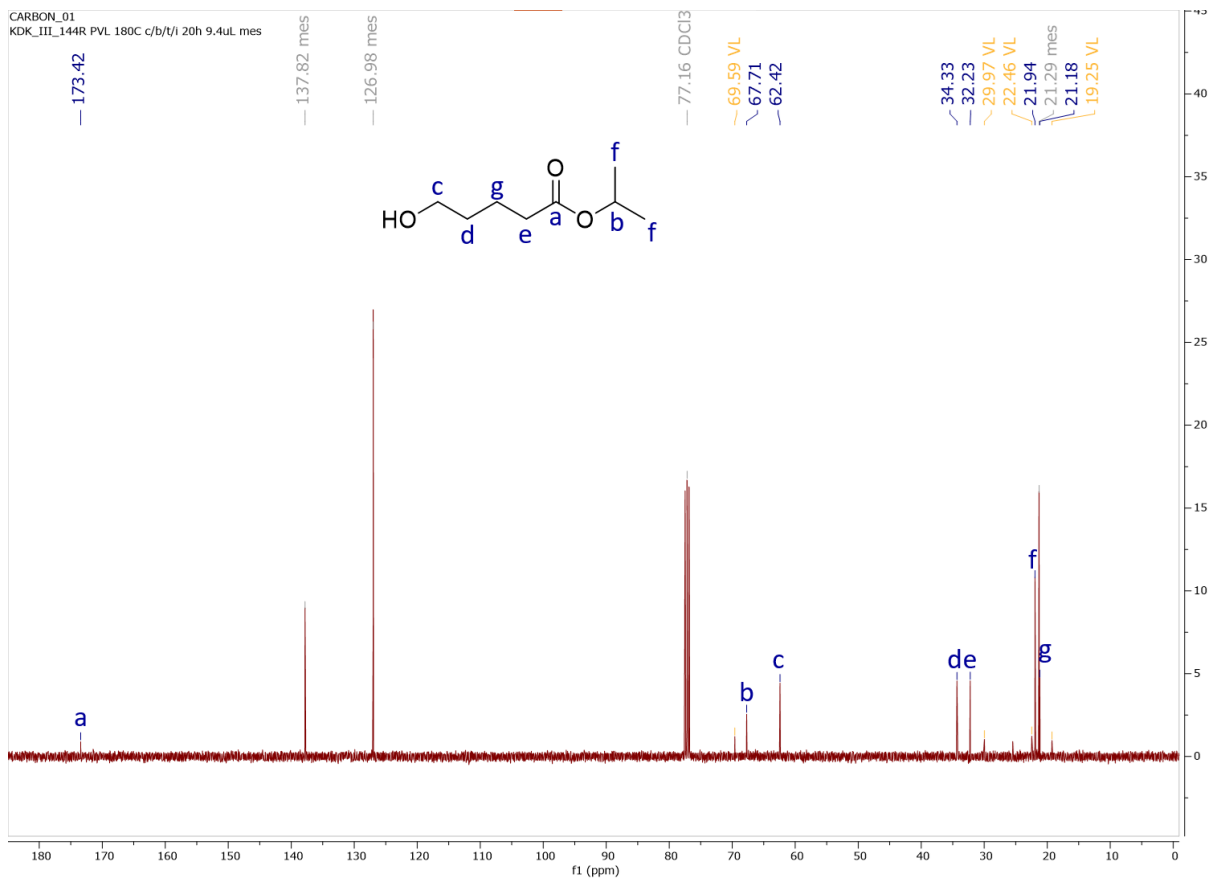
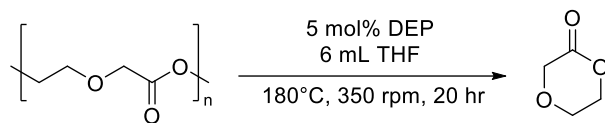


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of solvolysis of poly(δ -valerolactone) (PVL) to 2-isopropyl 6-hydroxypentanoate (**3b**).



Scheme S7. General reaction conditions for the cyclodepolymerization of poly(dioxanone) (PDO) with DEP.

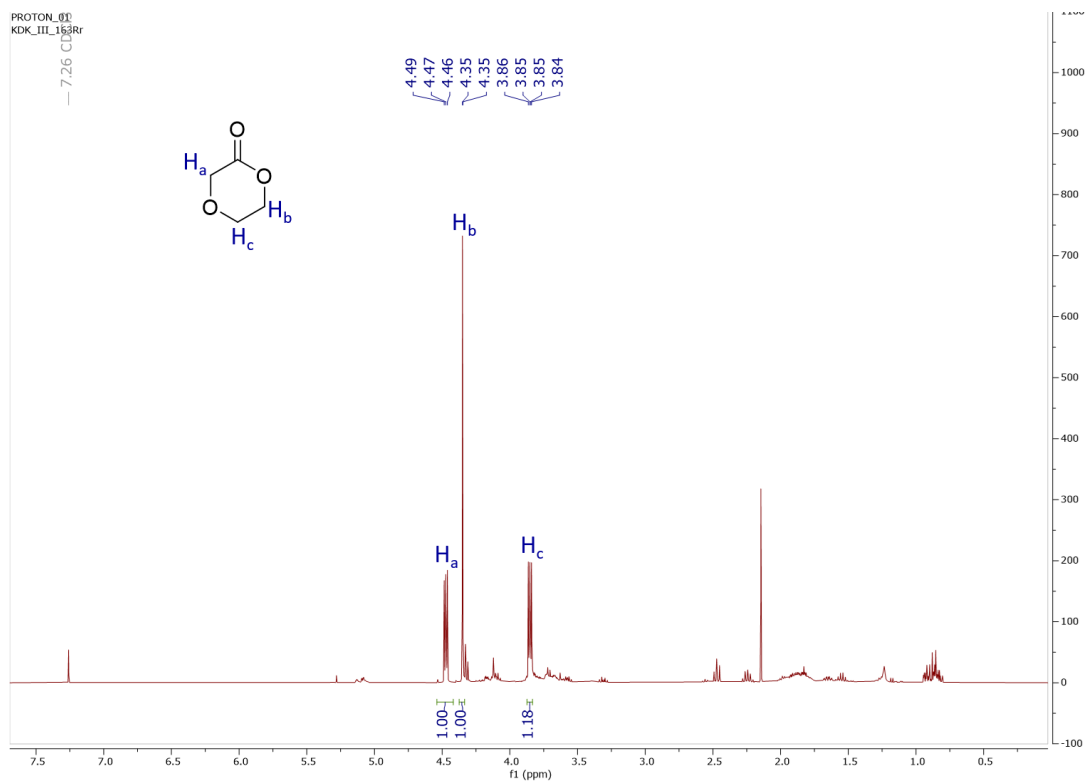


Figure S24. ^1H NMR of depolymerization product of PDO to quantitative yield of 1,4-dioxanone (4a) with DEP with solvent impurities.

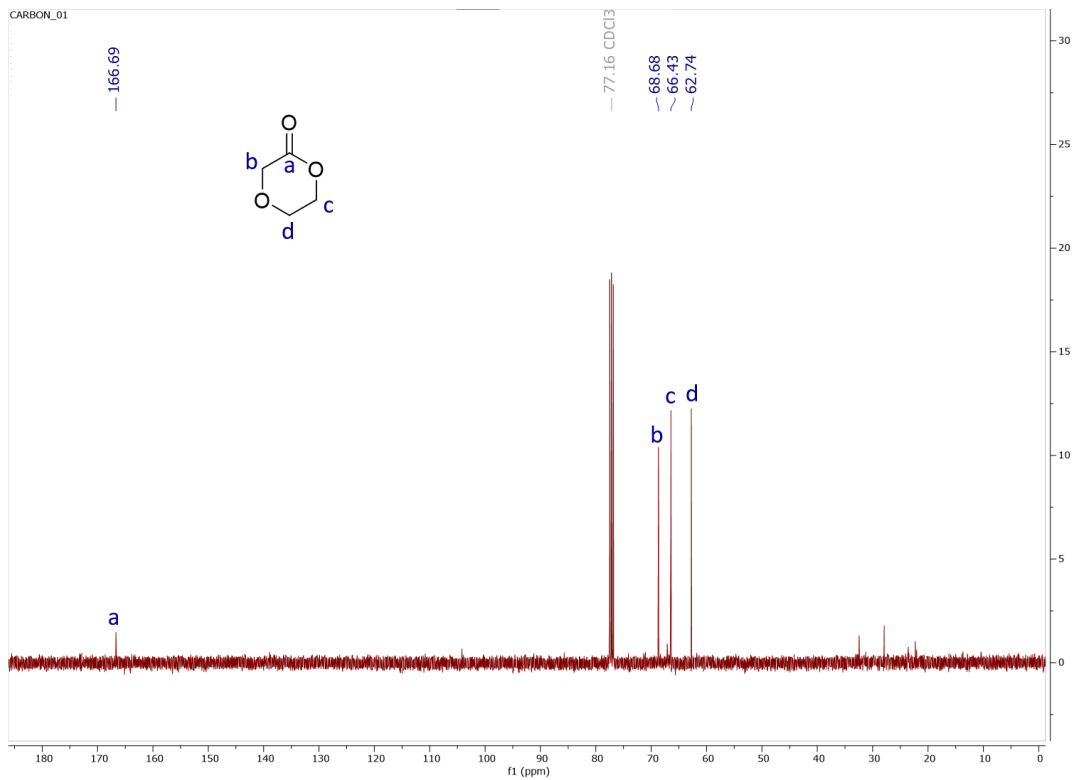
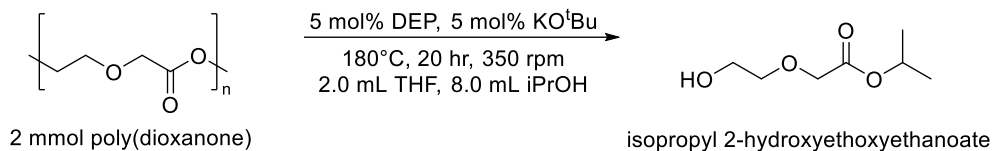


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR of depolymerization product of PDO to quantitative yield of 1,4-dioxanone (**4a**) with DEP with solvent impurities.



Scheme S8. Reaction conditions for the solvolysis of poly(dioxanone) (**PDO**) to isopropyl 2-hydroxyethoxyethanoate (**4b**) with DEP.

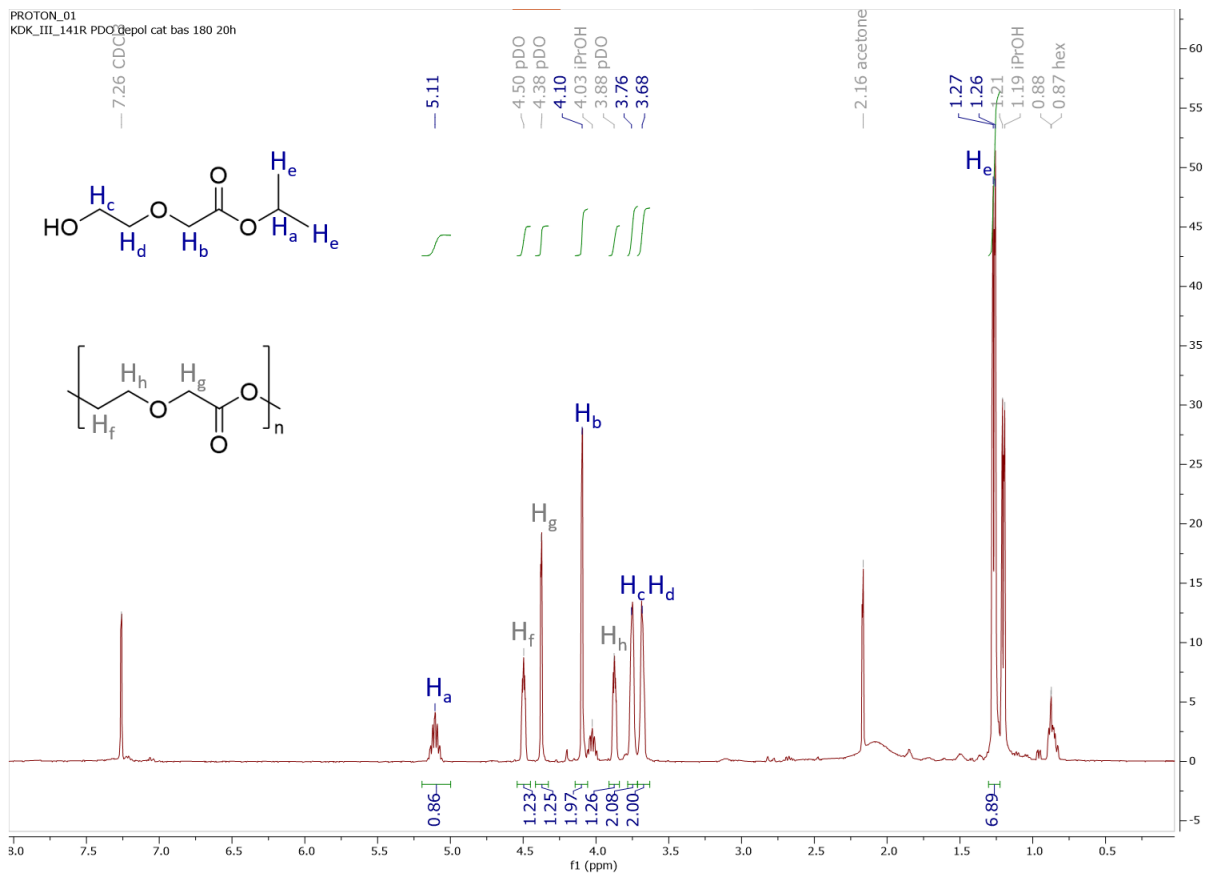


Figure S26. ¹H NMR characterization of solvolysis of PDO to isopropyl 2-hydroxyethoxyethanoate (**4b**), yielding 61% product by NMR integration.

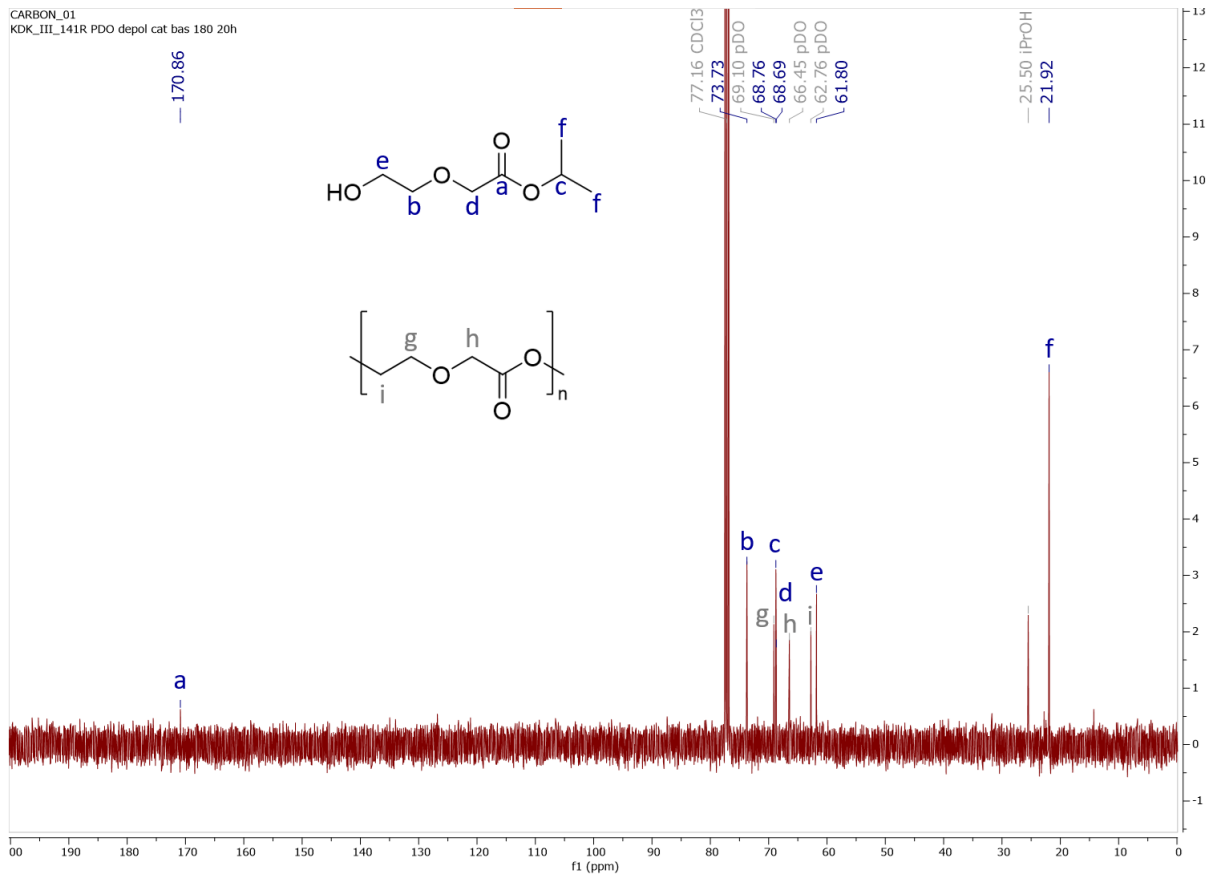


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of solvolysis of PDO to isopropyl 2-hydroxyethoxyethanoate (**4b**), yielding 61% product.

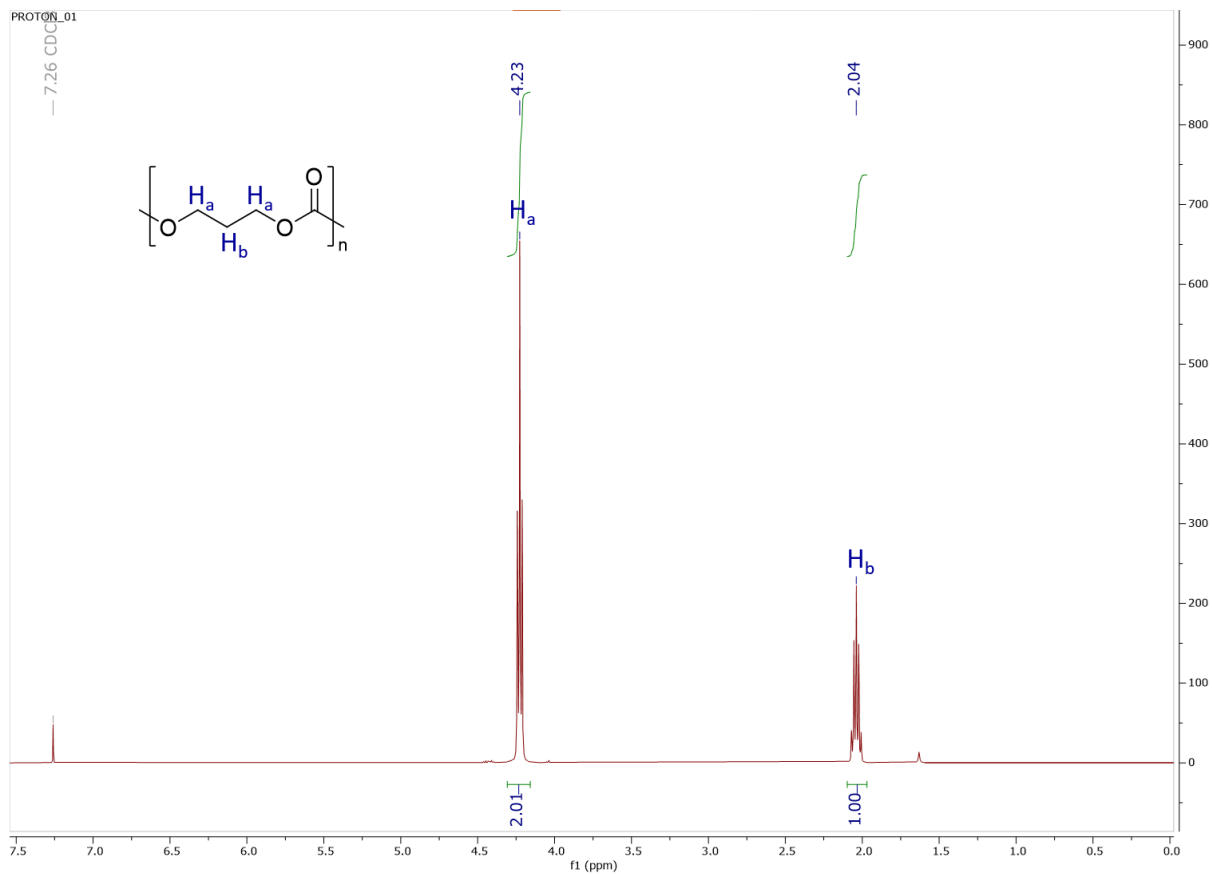


Figure S28. ¹H NMR characterization of poly(trimethylene carbonate) (PTMC).

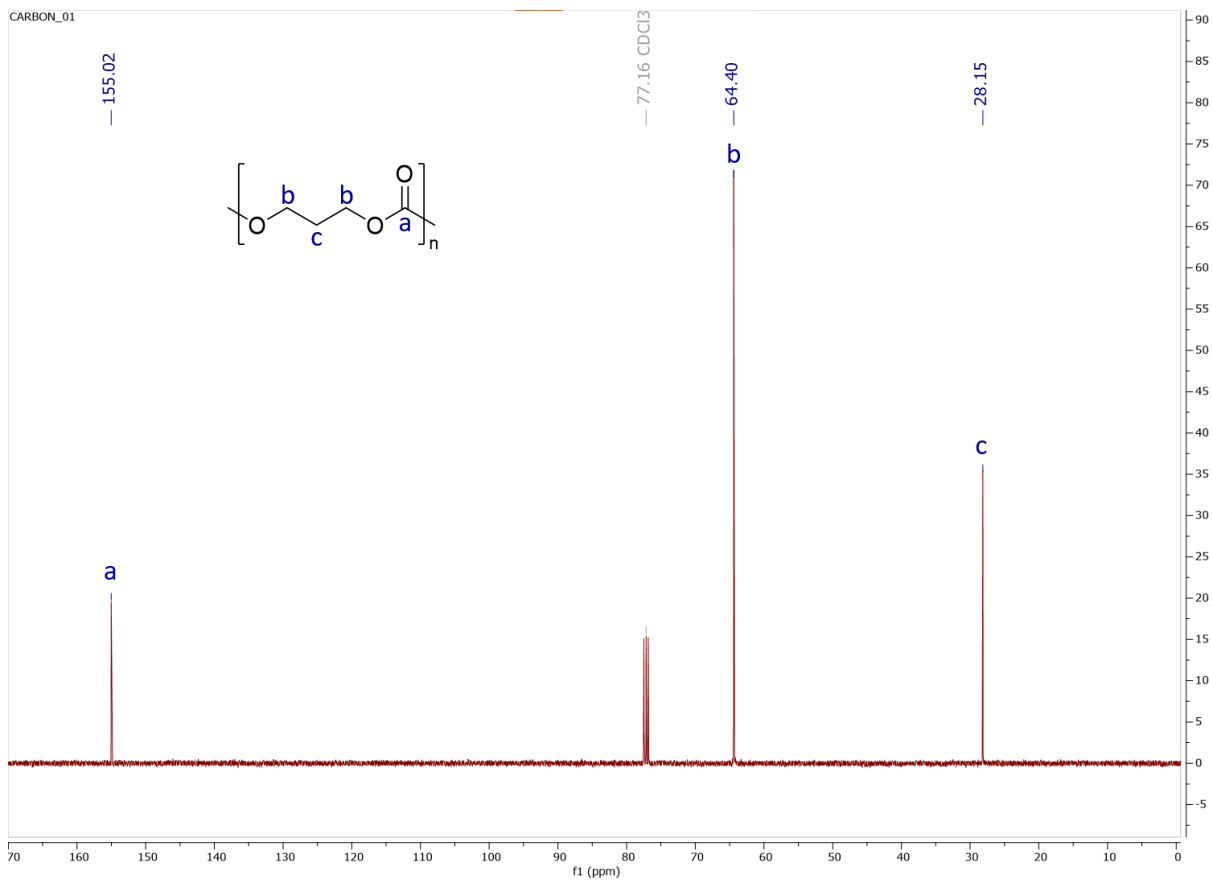
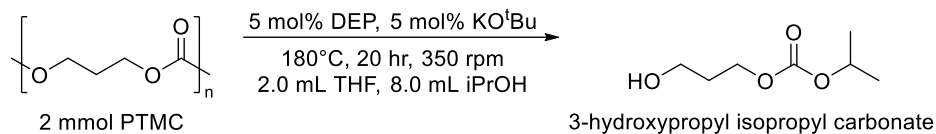


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of poly(trimethylene carbonate) (PTMC).



Scheme S9. Reaction conditions for the solvolysis of poly(trimethylene carbonate) (PTMC) to 3-hydroxypropyl isopropyl carbonate (**5b**) with DEP.

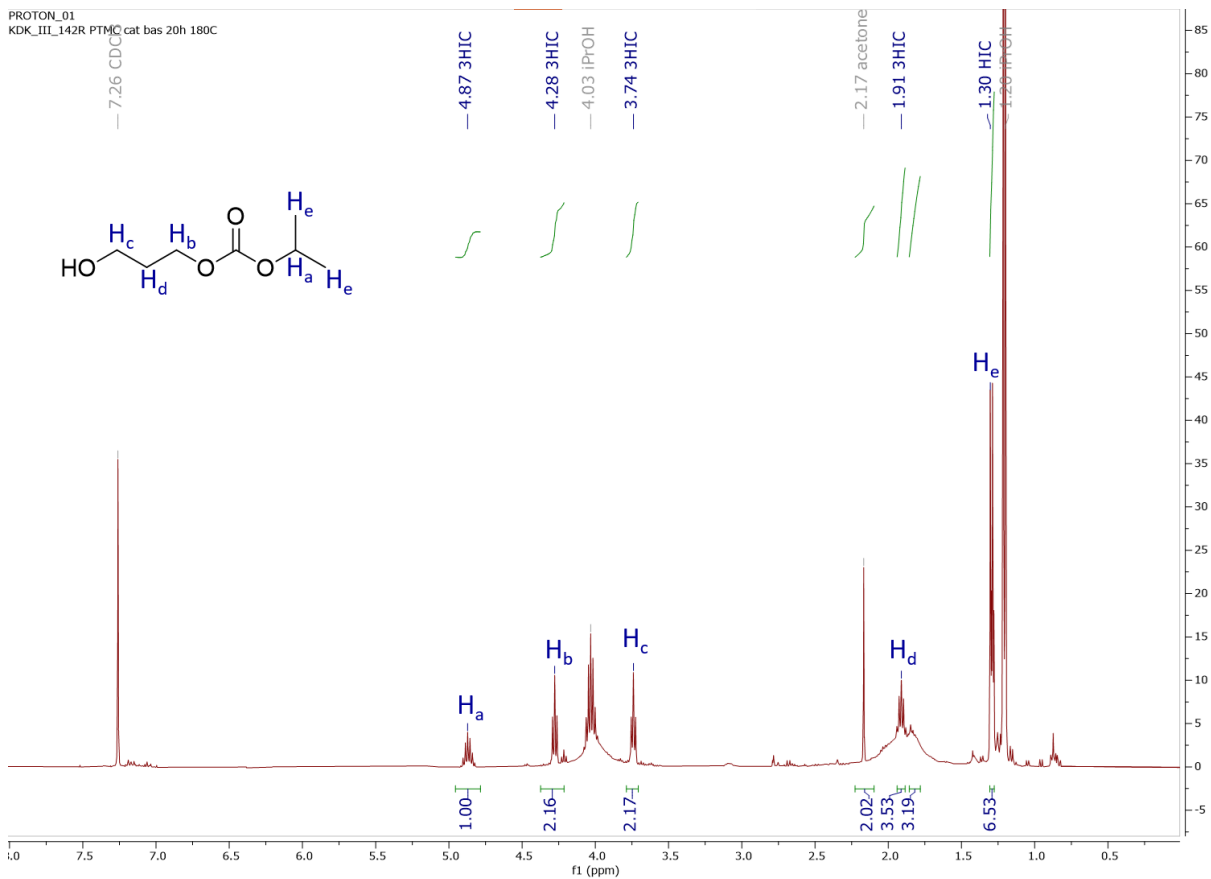


Figure S30. ¹H NMR characterization of solvolysis of PTMC to 3-hydroxypropyl isopropyl carbonate (**5b**).

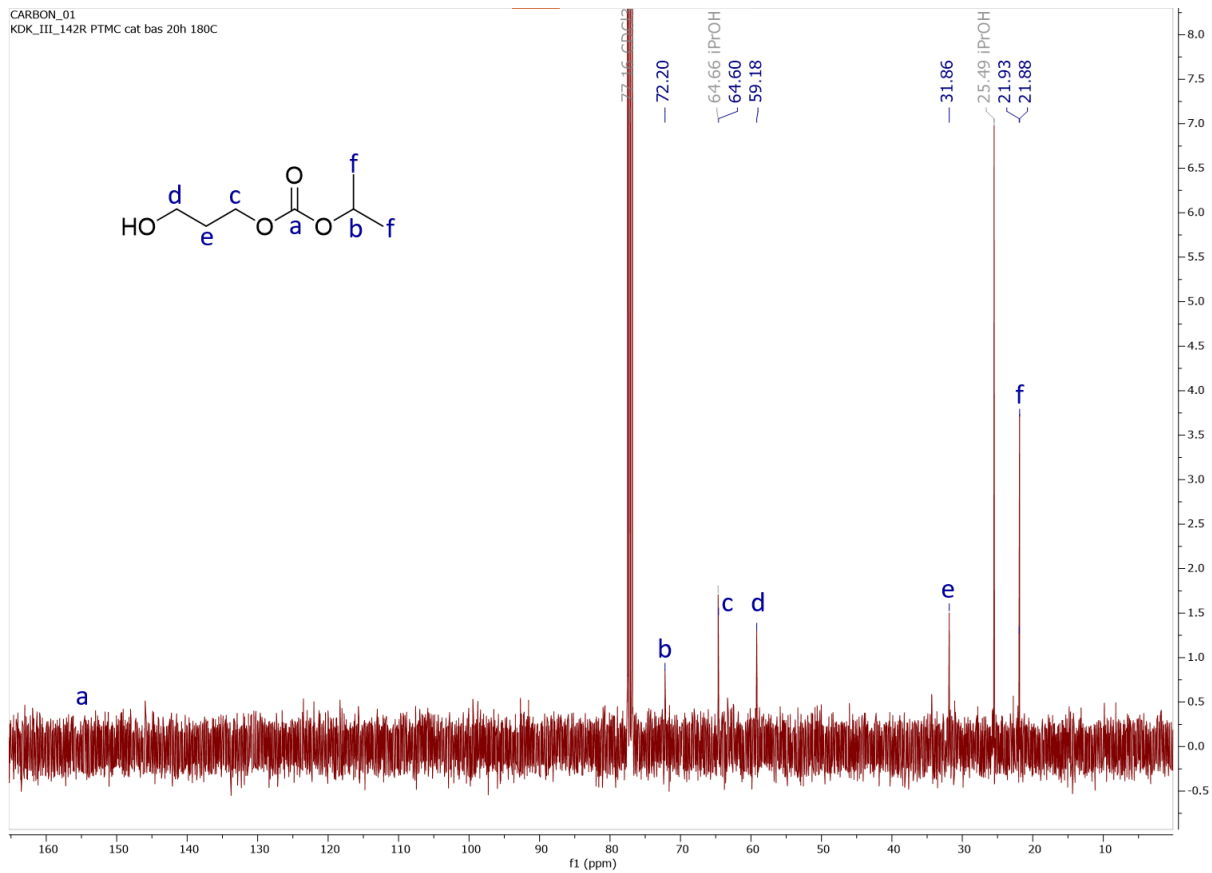


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of solvolysis of PTMC to 3-hydroxypropyl isopropyl carbonate (**5b**).

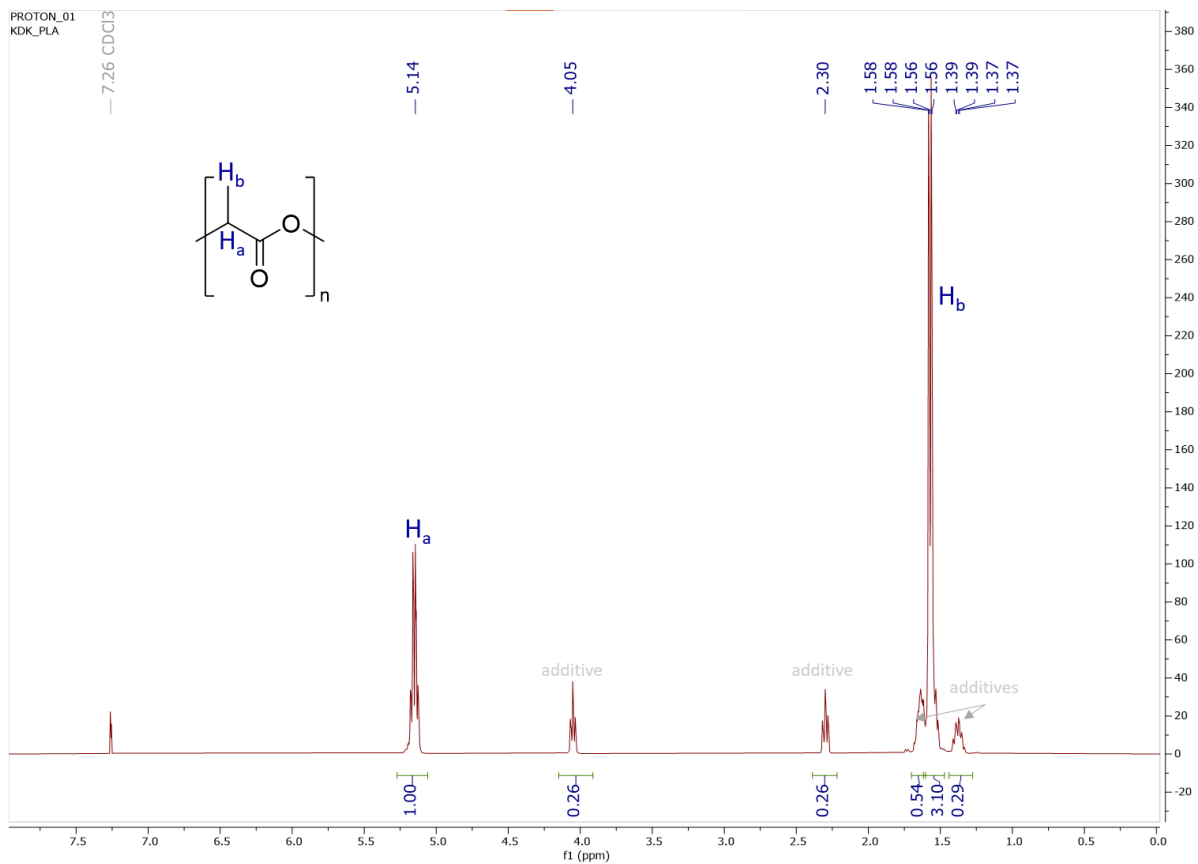
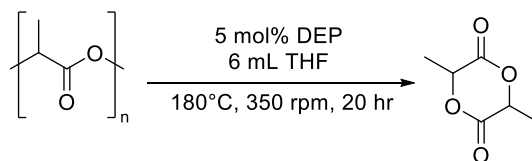


Figure S32. ¹H NMR of poly(lactic acid) (PLA) straw with some additive impurities.



Scheme S10. General reaction conditions for the cyclodepolymerization of PLA with DEP.

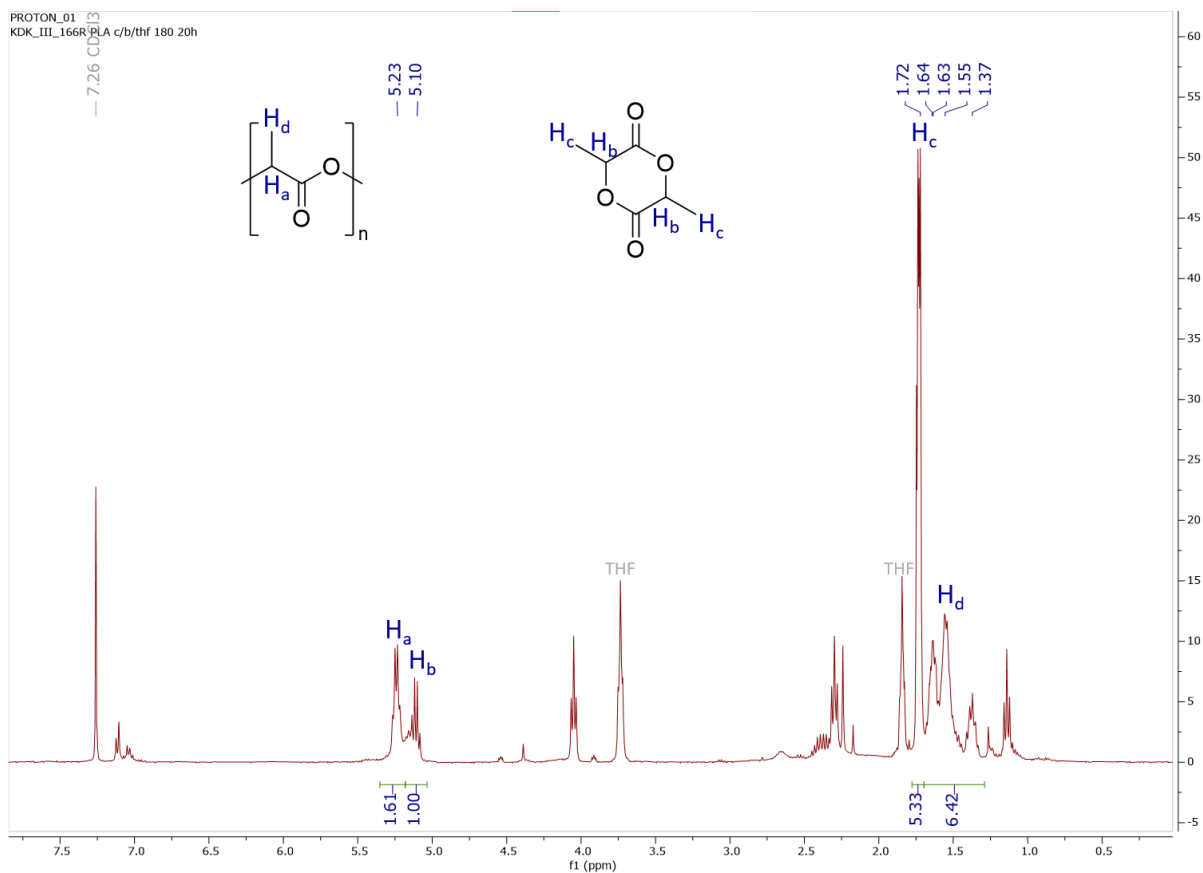
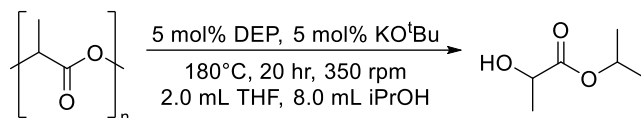


Figure S34. ^1H NMR of depolymerization product of PLA to D,L-lactide (**6a**) with DEP in 38% yield with solvent impurities.



Scheme S11. Reaction conditions for the solvolysis of poly(lactic acid) (**PLA**) to isopropyl 2-hydroxypropanoate (**6b**) with DEP.

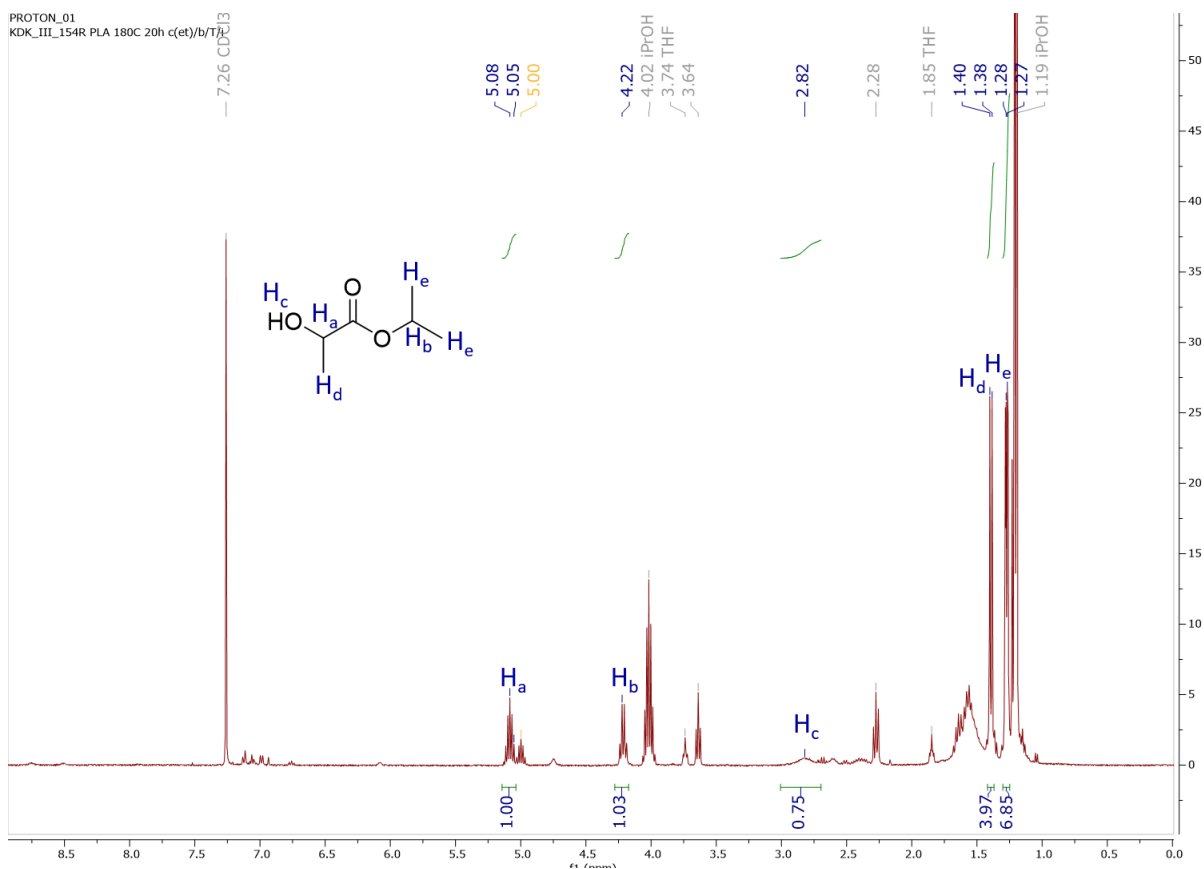


Figure S35. ¹H NMR characterization of solvolysis of poly(lactic acid) (**PLA**) to isopropyl 2-hydroxypropanoate (**6b**).

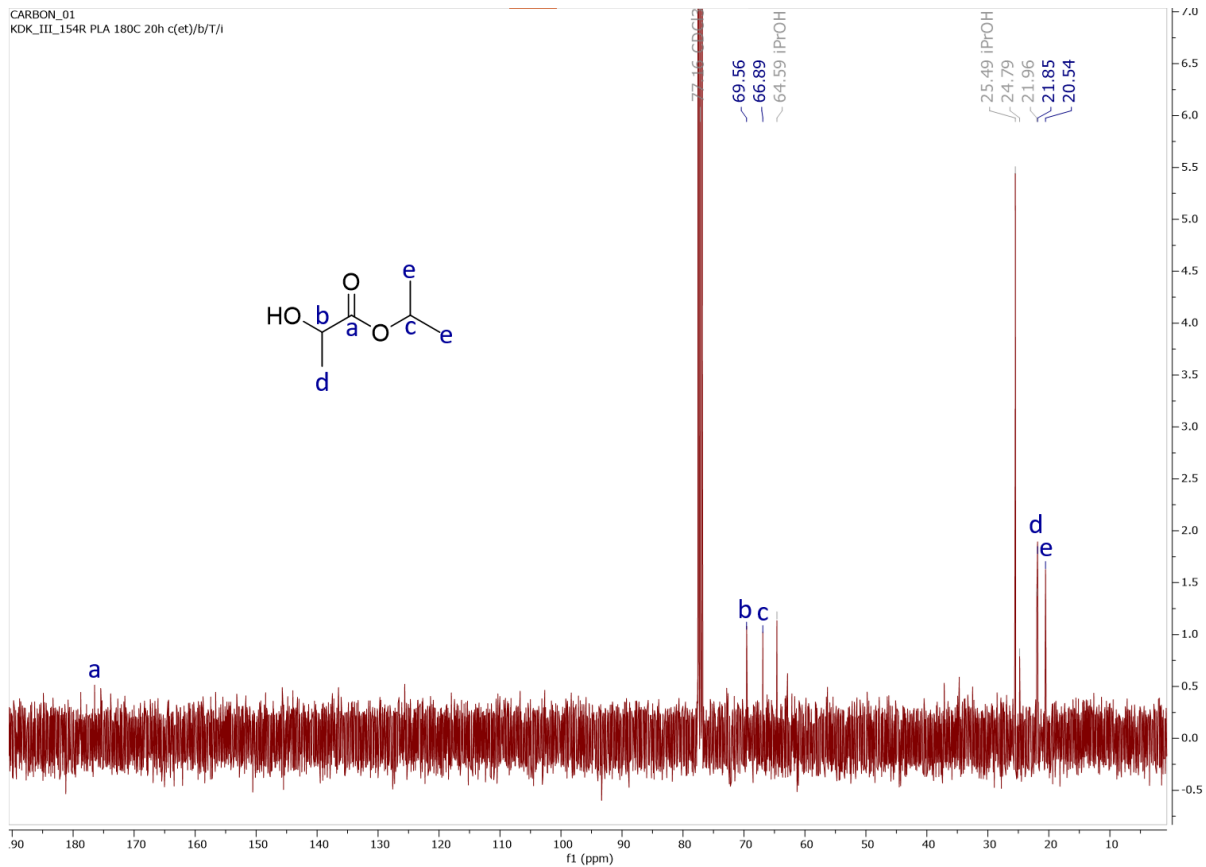


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of solvolysis of poly(lactic acid) (PLA) to isopropyl 2-hydroxypropanoate (**6b**).

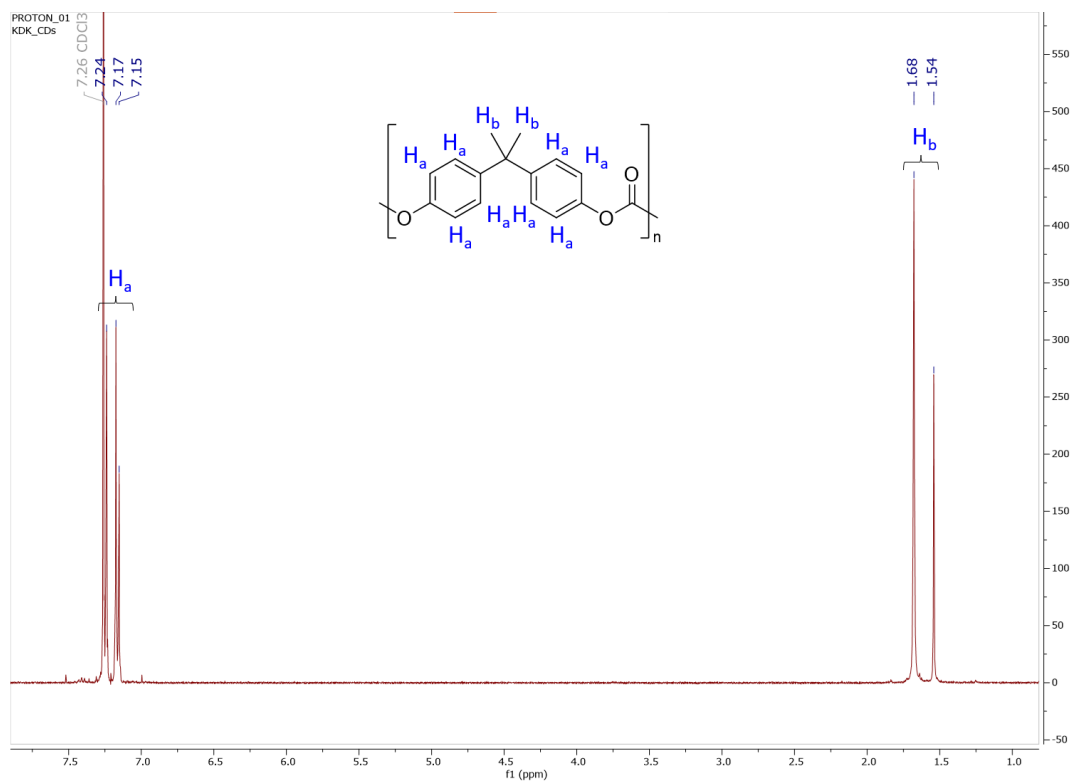


Figure S37. ^1H NMR characterization of CD's made of poly(bisphenol-A carbonate) (PBPA).

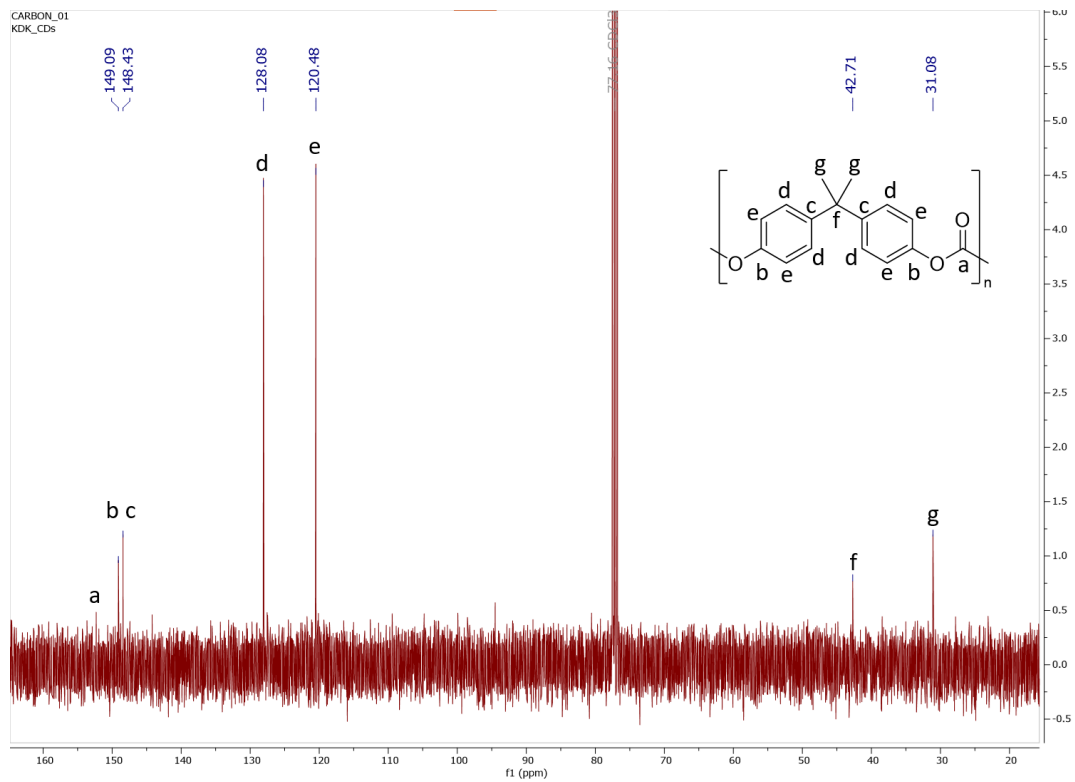
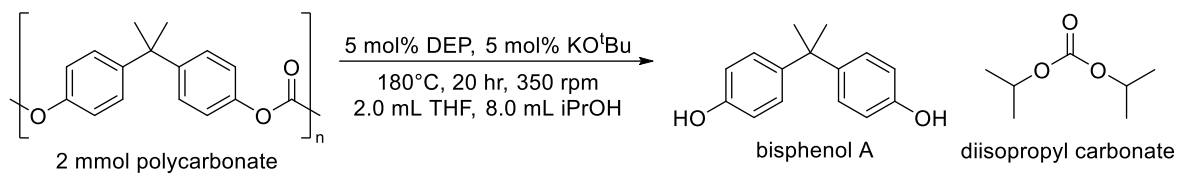


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of CD's made of poly(bisphenol-A carbonate) (PBPA).



Scheme S12. Reaction conditions for the solvolysis of poly(bisphenol-A carbonate) (PBPA) to bisphenol A (BPA) and diisopropyl carbonate (DIPC) (**8**) with DEP.

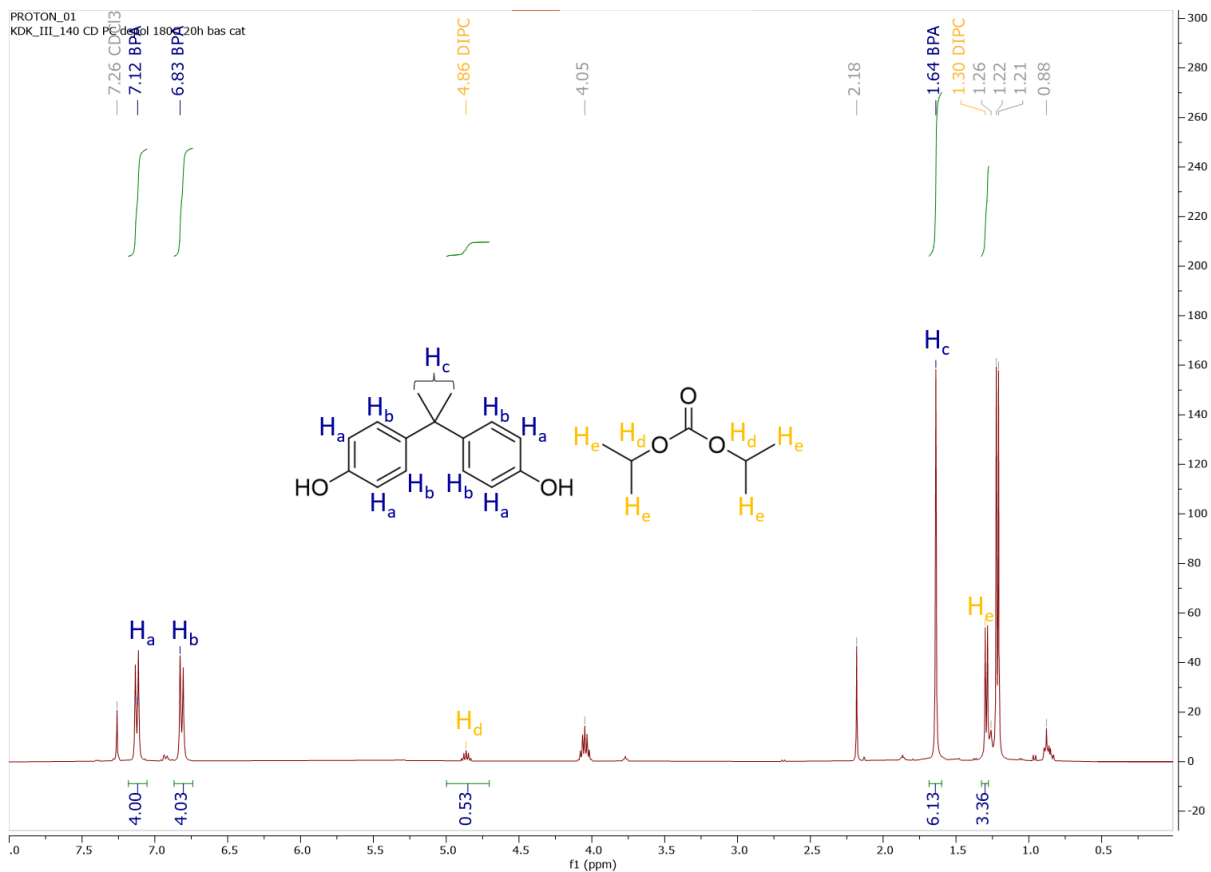


Figure S39. ¹H NMR characterization of bisphenol A and diisopropyl carbonate (**8**) from solvolysis of PBPA.

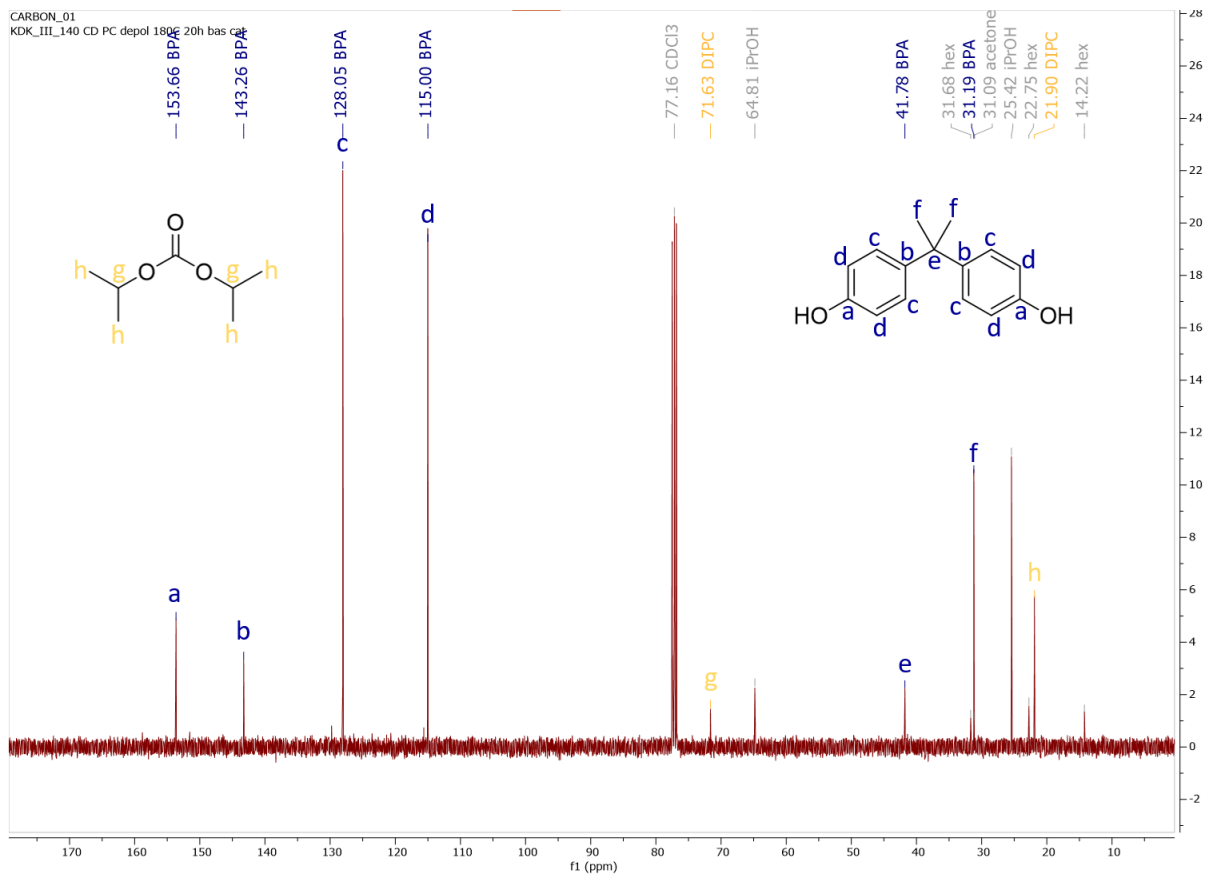
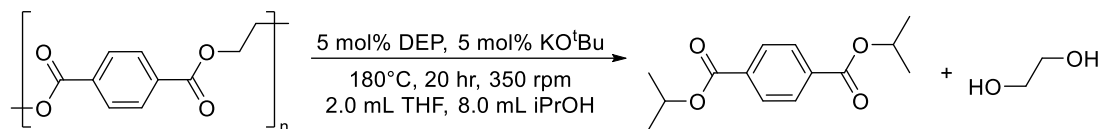


Figure S40. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of bisphenol A and diisopropyl carbonate (**8**) from solvolysis of PBPA.



Scheme S13. Reaction conditions for the solvolysis of poly(ethylene terephthalate) (**PET**) to diisopropoxy terephthalate and ethylene glycol (**9**) with DEP.

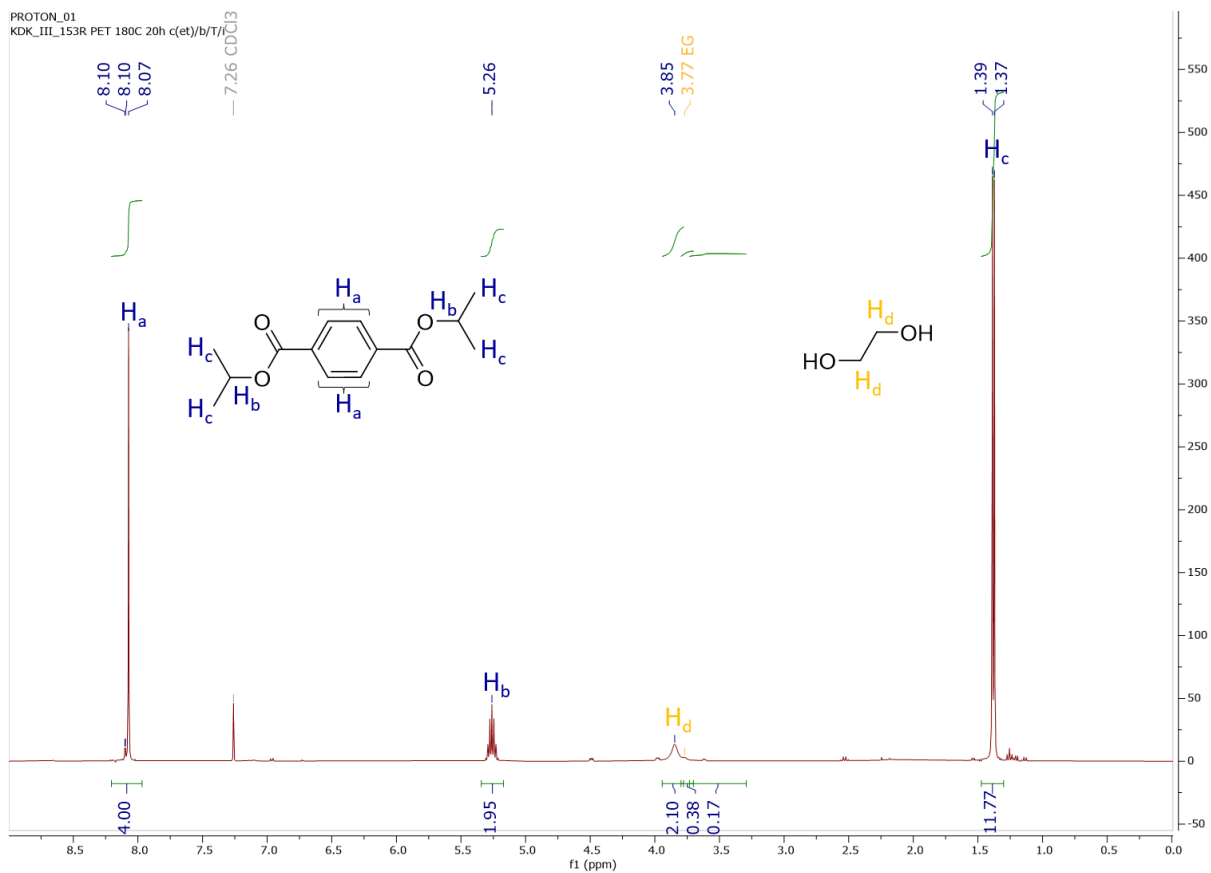


Figure S41. ¹H NMR characterization of solvolysis of PET to diisopropoxy terephthalate and ethylene glycol (**9**).

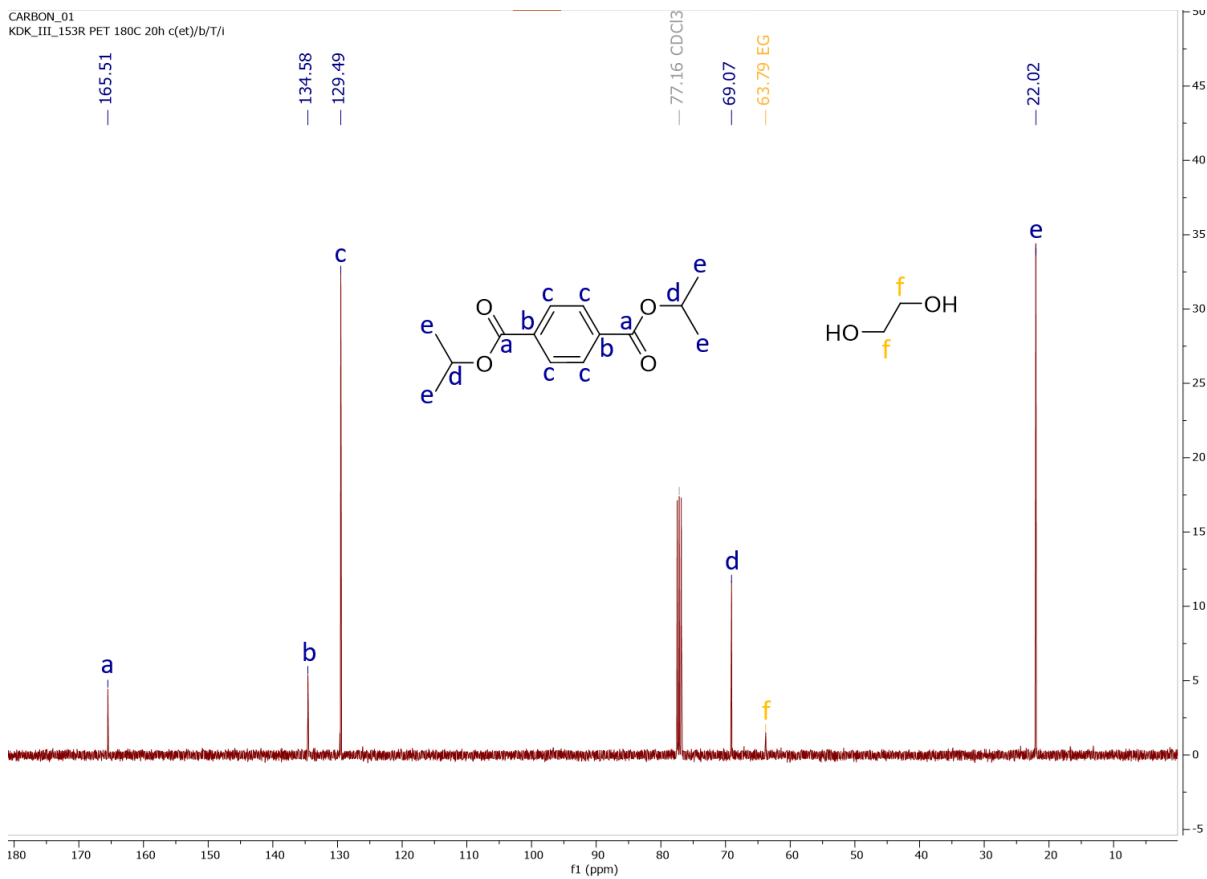
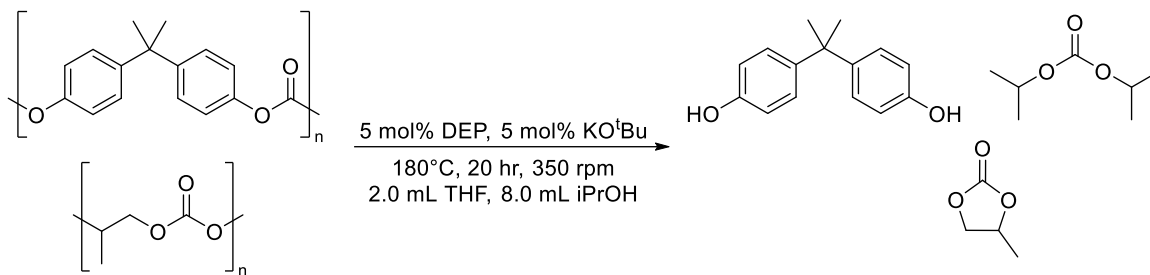


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of solvolysis of PET to diisopropoxy terephthalate and ethylene glycol (**9**).



Scheme S14. Reaction conditions for the combination of PBPAC and PPC with DEP.

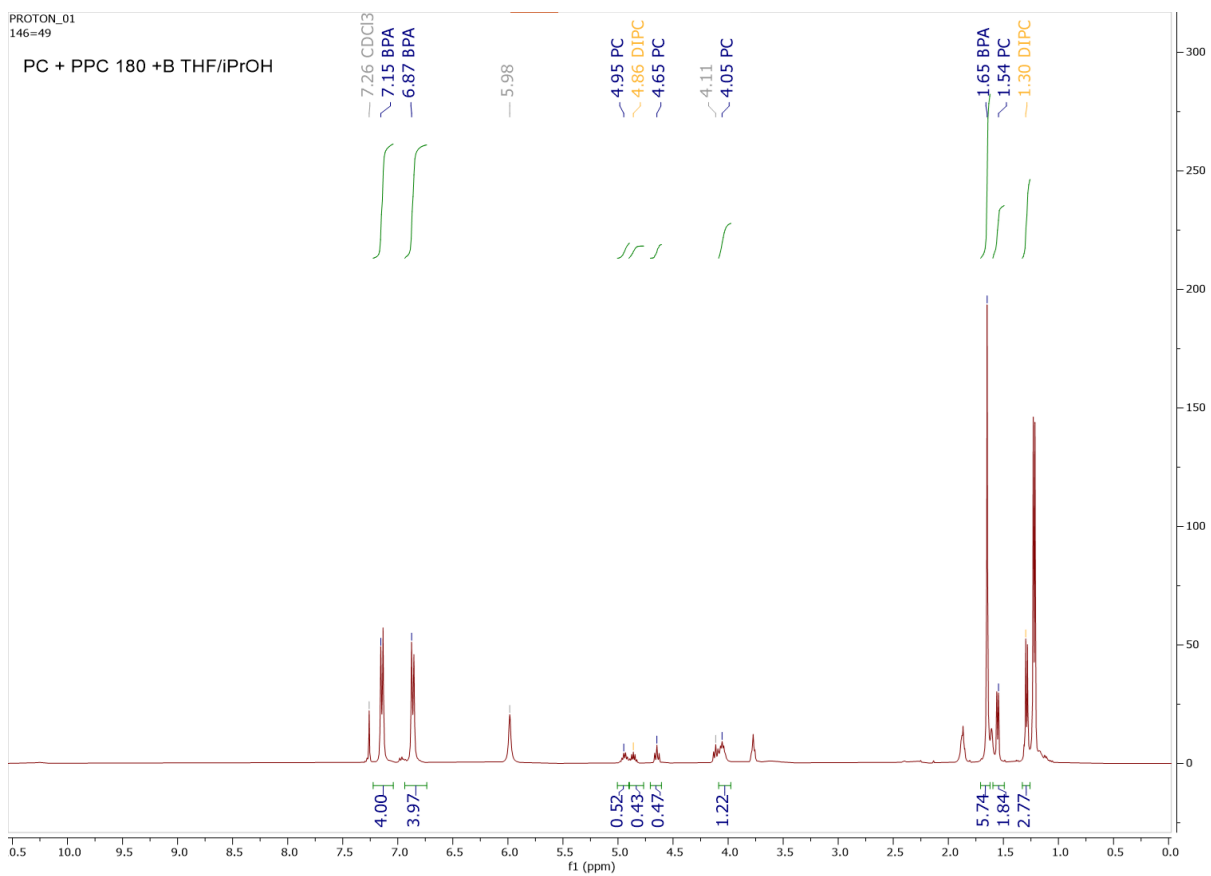


Figure S43. ¹H NMR characterization of products of PBPAC and PPC outlined reaction conditions.

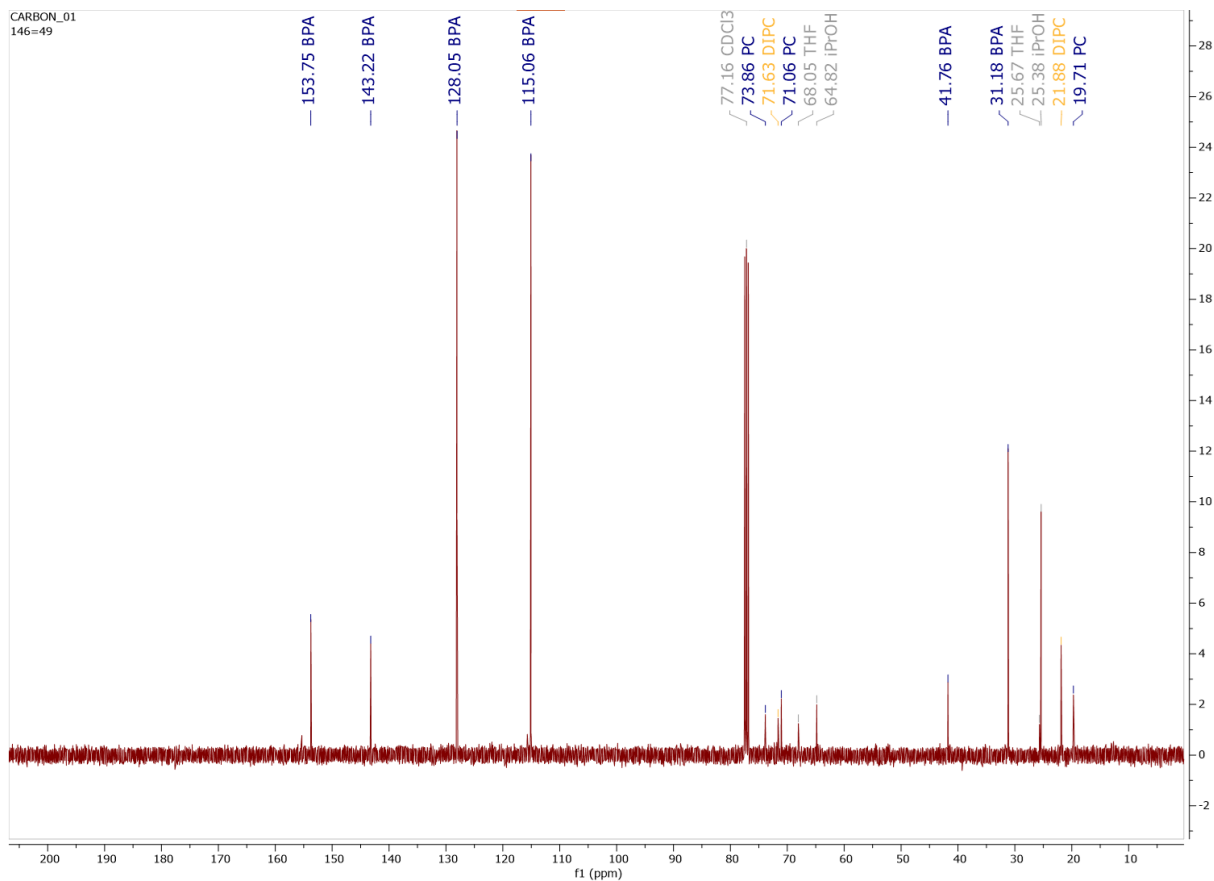


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR characterization of products of PBPAC and PPC outlined reaction conditions.

5.2 SEC Characterizations

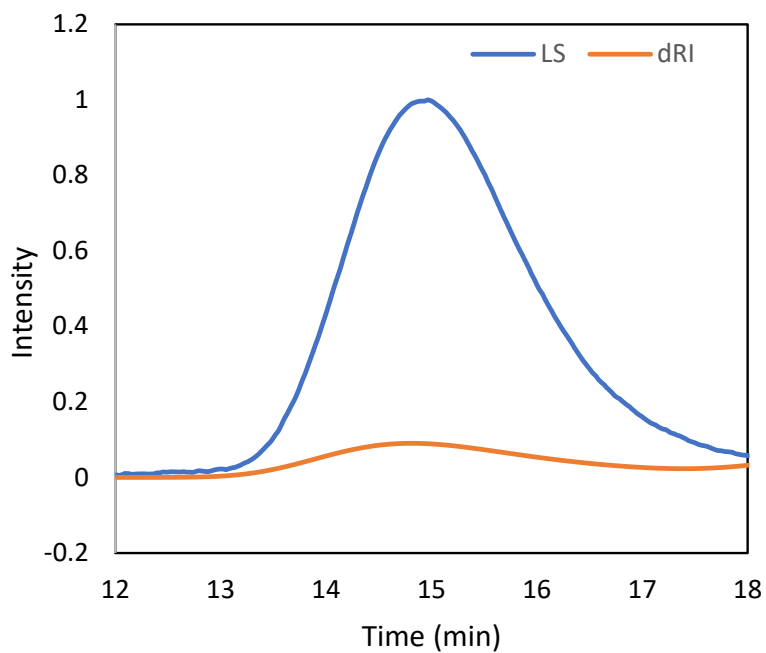


Figure S42. SEC of Entry 1, **Table S3**: depolymerization of PPC with DEP and KO^tBu 2h.

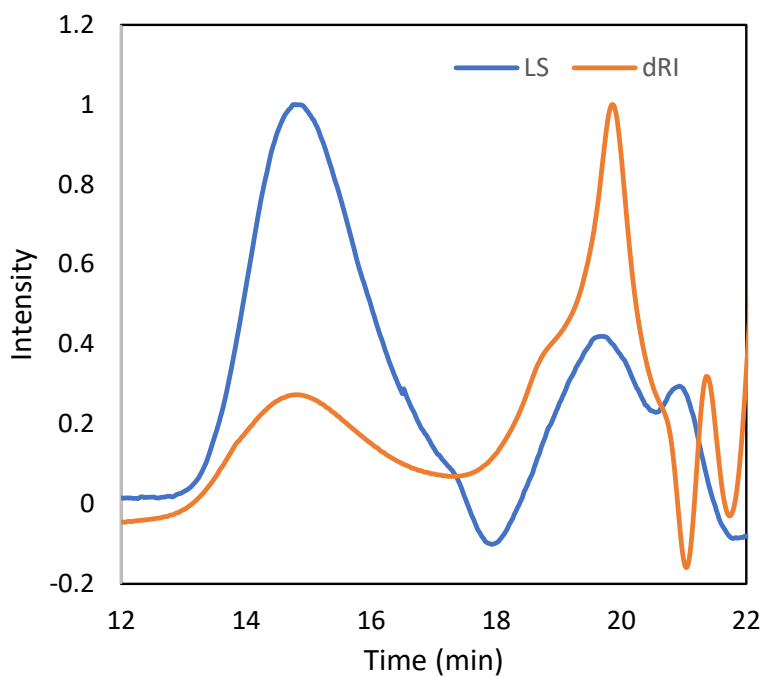


Figure S43. SEC of Entry 2, **Table S3**: depolymerization of PPC with DEP and KO^tBu 4h.

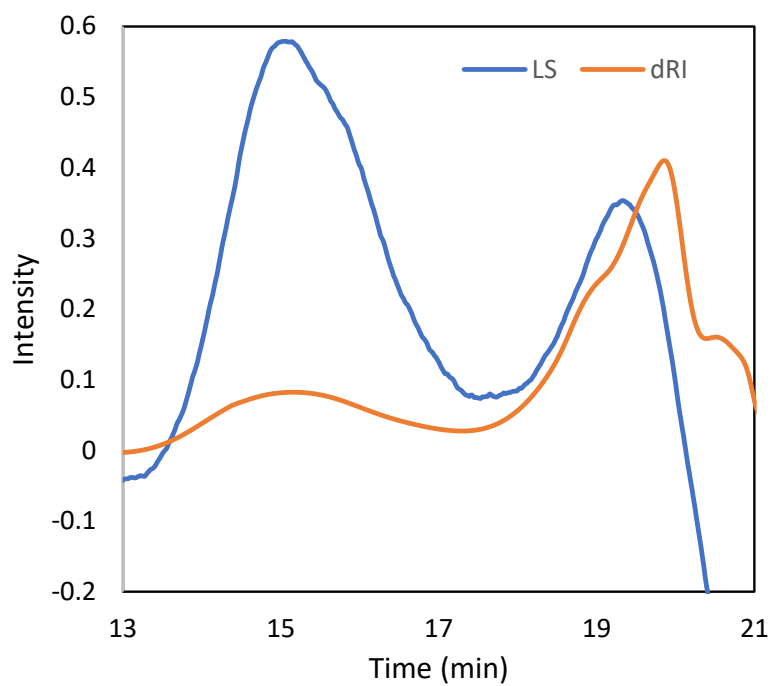


Figure S44. SEC of Entry 3, **Table S3**: depolymerization of PPC with DEP and KO^tBu 6h.

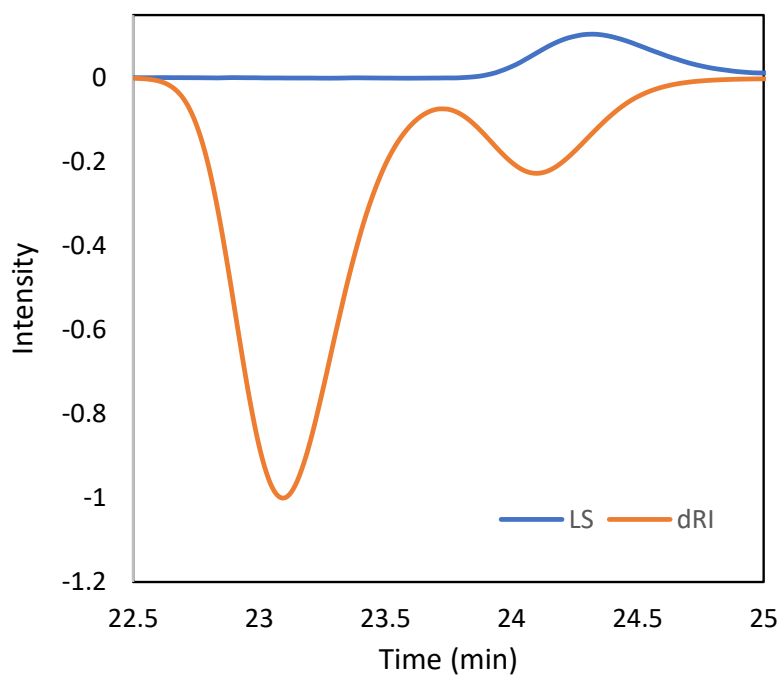


Figure S45. SEC of Entry 4, **Table S3**: depolymerization of PPC with DEP and KO^tBu 8h.

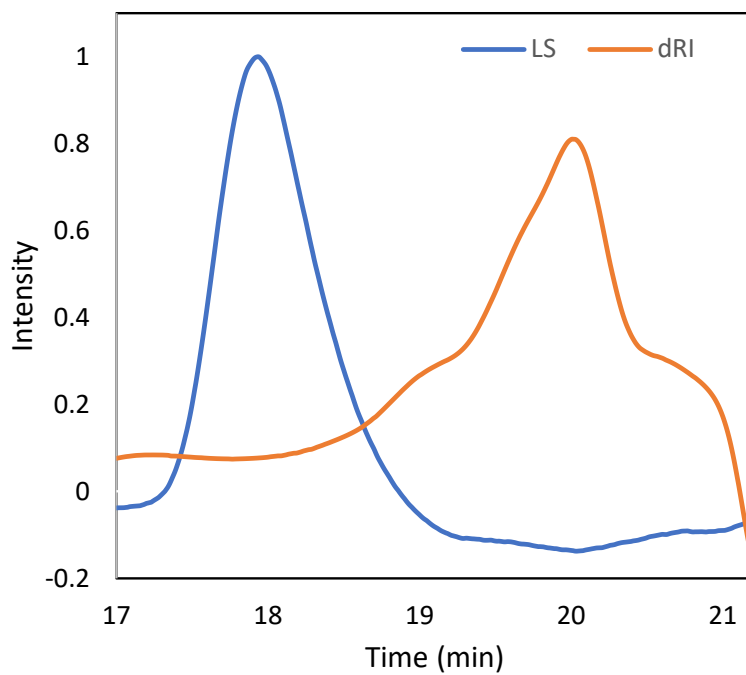


Figure S46. SEC of Entry 5, **Table S3**: depolymerization of PPC with DEP and KO'Bu 10h.

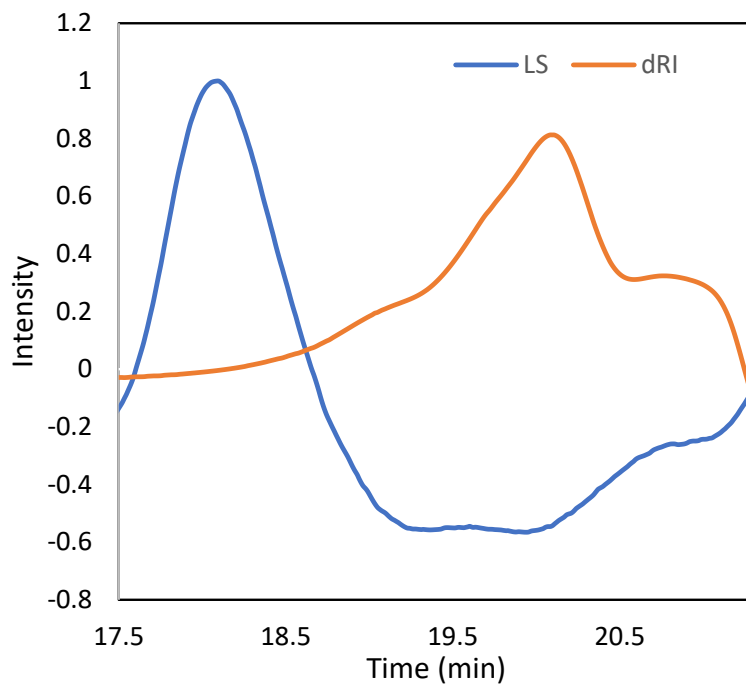


Figure S47. SEC of Entry 6, **Table S3**: depolymerization of PPC with DEP and KO'Bu 12h.

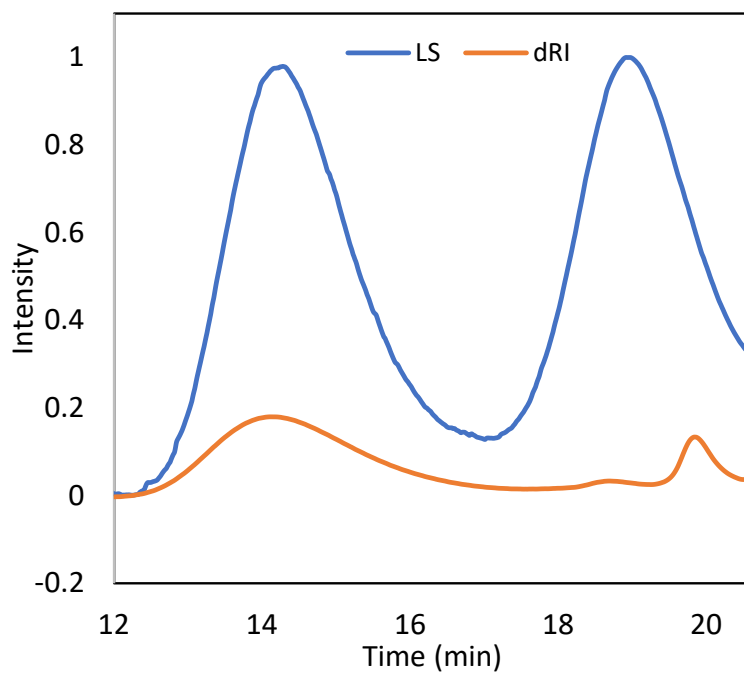


Figure S48. SEC of Entry 7, **Table S3**: depolymerization of PPC with DEP and NaO'Bu 2h.

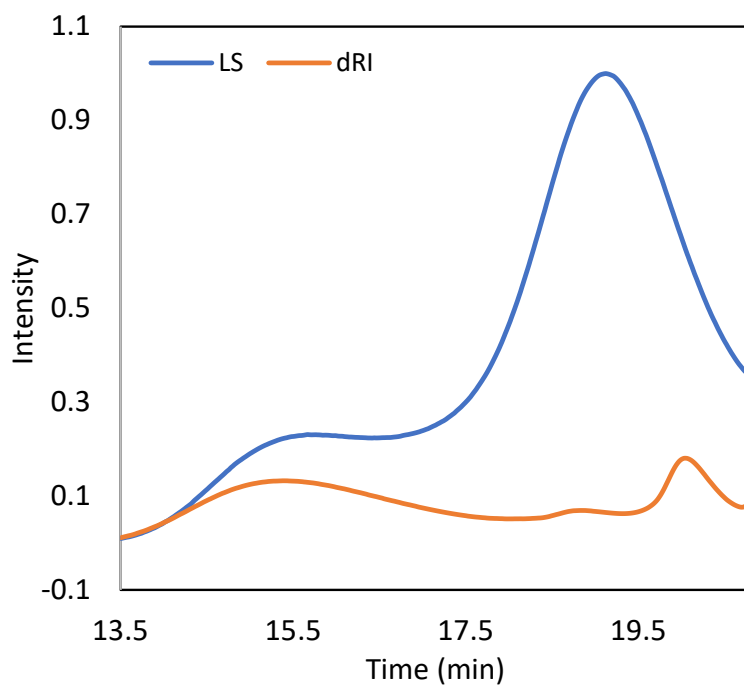


Figure S49. SEC of Entry 8, **Table S3**: depolymerization of PPC with DEP and NaO'Bu 4h.

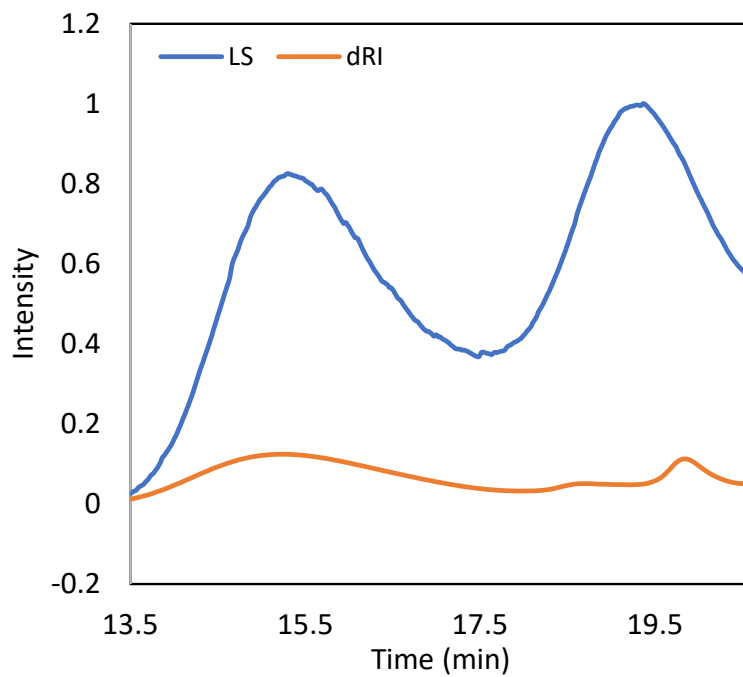


Figure S52. SEC of Entry 11, **Table S3:** depolymerization of PPC with DEP and NaO'Bu 6h.

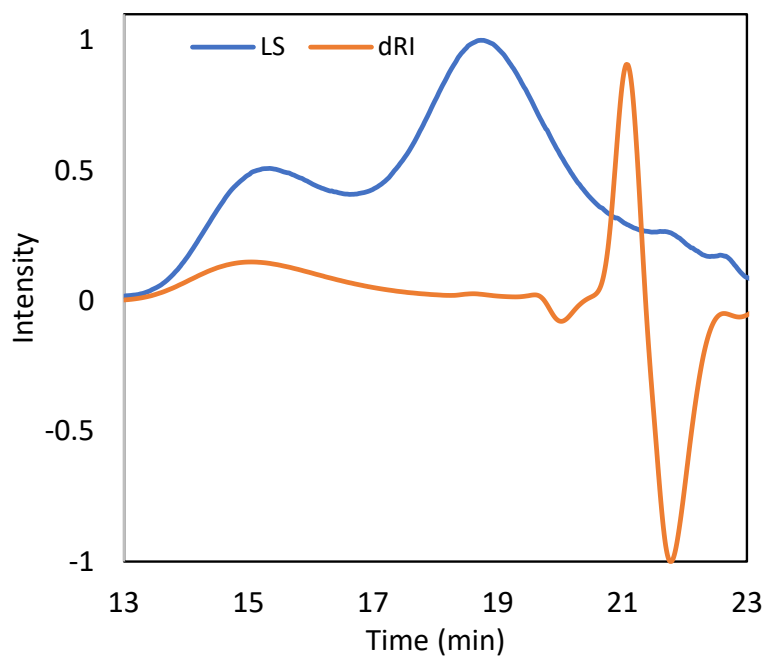


Figure S53. SEC of Entry 12, **Table S3:** depolymerization of PPC with DEP and NaO'Bu 8h.

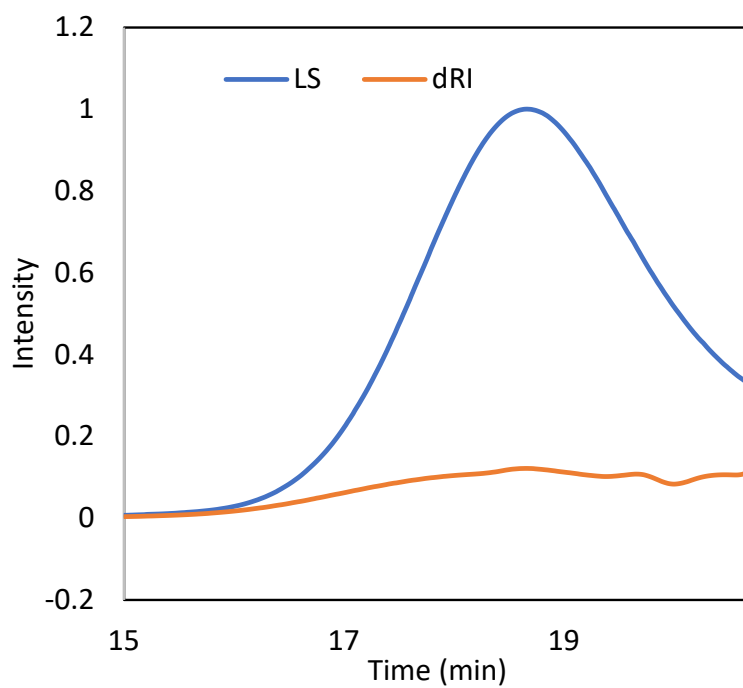


Figure S52. SEC of Entry 11, **Table S3:** depolymerization of PPC with DEP and NaO'Bu 10h.

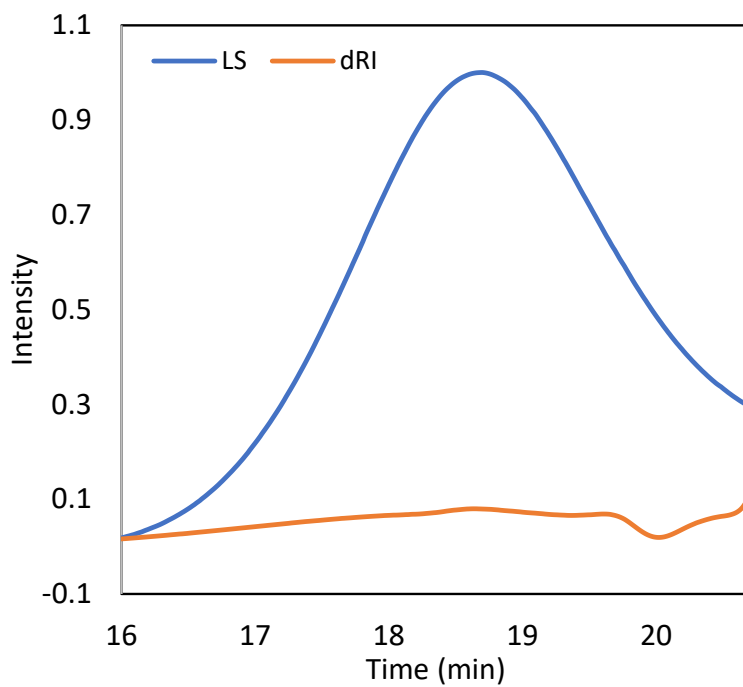


Figure S53. SEC of Entry 12, **Table S3:** depolymerization of PPC with DEP and NaO'Bu 12h.

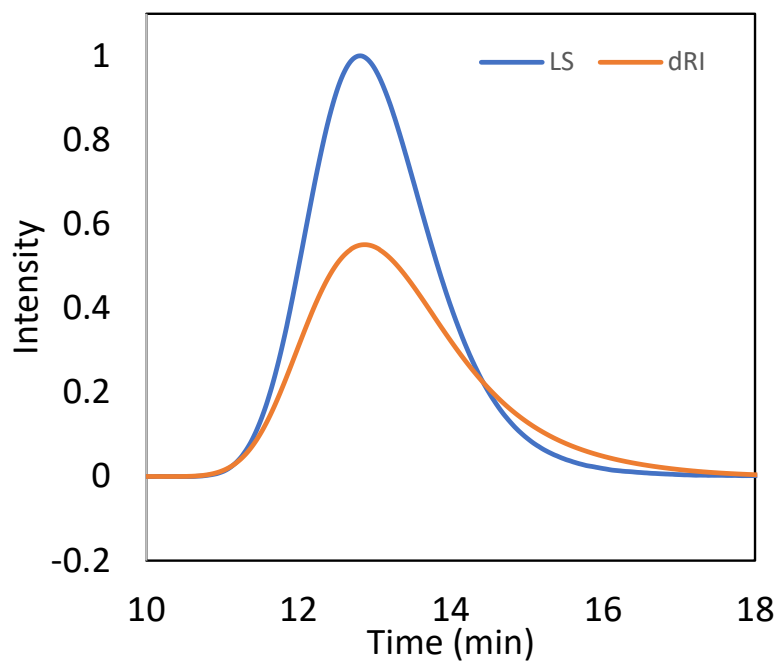


Figure S54. SEC of Entry 13, **Table S3**: depolymerization of PPC with 2.5% DEP for 2h.

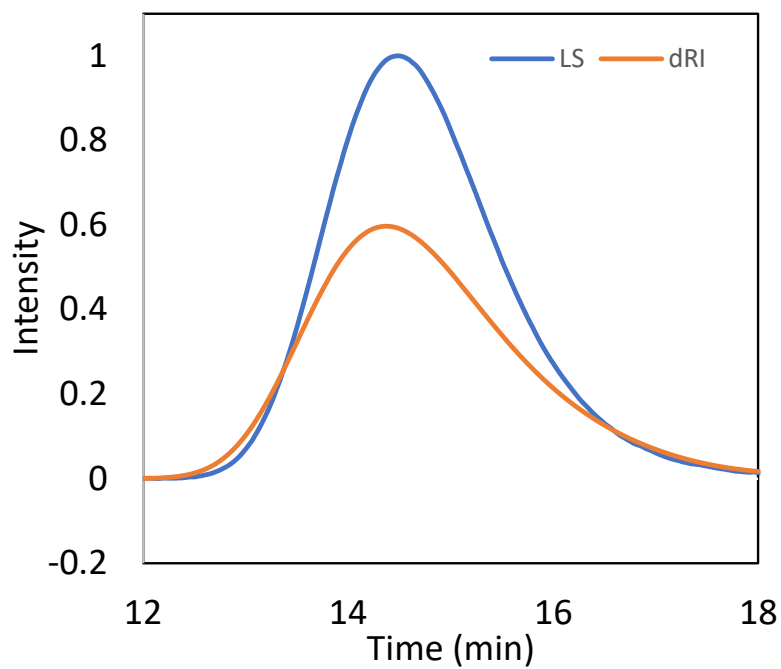


Figure S55. SEC of Entry 14, **Table S3**: depolymerization of PPC with 2.5% DEP for 6h.

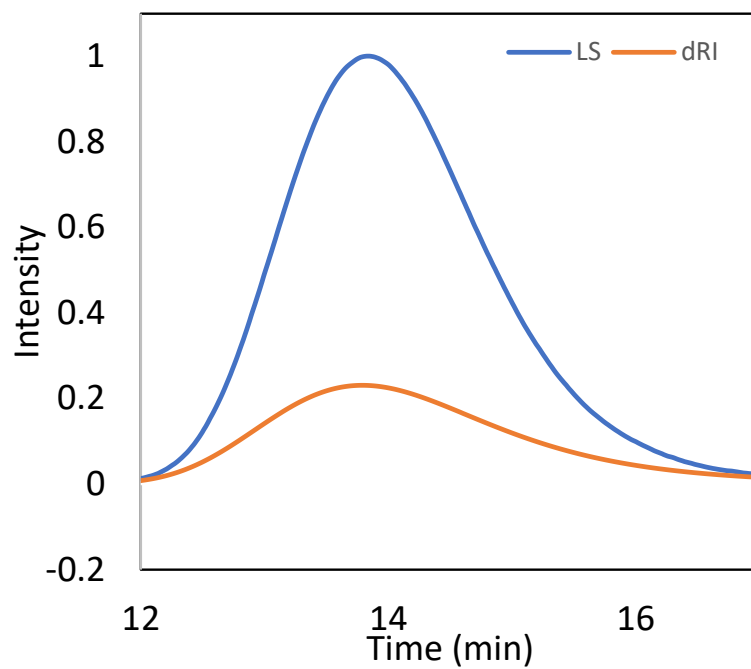


Figure S56. SEC of Entry 15, **Table S3**: depolymerization of PPC with 7.5% DEP for 2h.

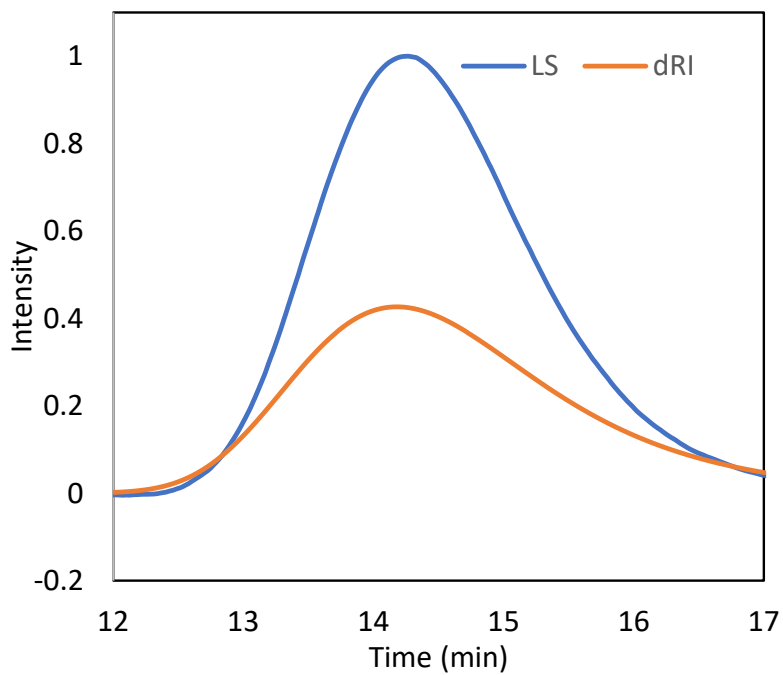


Figure S57. SEC of Entry 16, **Table S3**: depolymerization of PPC with 7.5% DEP for 6h.

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