Supporting Information for

A broad scope of aliphatic polyesters prepared by elimination of small molecules from sustainable 1,3-dioxolan-4-ones

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Materials

Commercial reagents were purchased from Acros Organics, Alfa Aesar, Fisher, VWR or Sigma Aldrich and used as received unless otherwise stated. Rac-lactide and L-lactide were provided by Corbion and were purified by three vacuum sublimations prior to polymerizations. Benzyl alcohol, β-butyrolactone, ε-caprolactone, d_5-pyridine, and d-chloroform were purified by stirring over CaH_2 followed by distillation under an inert atmosphere. d_6-Benzene and d_8-toluene were dried over Na/benzophenone and subsequently distilled under an inert atmosphere. Toluene, dichloromethane, THF, hexanes and diethyl ether were dried using an Innovative Technologies purification system consisting of alumina and copper catalyst. The solvents were degassed by three freeze-pump-thaw cycles prior to use. MeAl(salen)^{tbu,tbu,pr} was synthesised by following established protocols.

General considerations

General methods: All air-sensitive manipulations were performed in an MBraun LABmaster sp glovebox equipped with a -35°C freezer (with [O_2] and [H_2O] at 0.1ppm according to built-in analysers) or on a dual manifold Schlenk line using standard Schlenk techniques.

Characterization: All ^1H, ^{13}C NMR spectra were obtained on Bruker Avance III 400 and 500 MHz spectrometers or on a Bruker Avance I 600 MHz spectrometer. All spectra were obtained at ambient temperature. The chemical shifts (δ) and coupling constants (J) were recorded in parts per million (ppm) and Hertz (Hz). Gel permeation chromatography (GPC) was carried out in THF at a flow rate of 1 mL min^{-1} at 35 °C on a Malvern Instruments Viscotek 270 GPC Max triple detection system with 2 mixed-bed styrene/DVB columns (300 × 7.5 mm). PLA, PHB and PCL dn/dc values used were 0.050,[1] 0.065,[2] and 0.072ml/g.[3] The dn/dc value of PMA was experimentally determined to be 0.11. For other polymers molecular weights were left uncorrected versus polystyrene standards. Mass spectrometry was performed on a Bruker UltraflexExtreme MALDI-TOF spectrometer. MALDI-TOF samples were prepared using the following matrices; 2,5-dihydroxybenzoic acid for poly(lactic acid) and poly(hexahydromandelic acid), dithranol for poly(mandelic acid) and sodium or potassium trifluroacetic acid was used as the ionization source. Differential scanning calorimetry (DSC) was carried out using a DSC 404 *F3 Pegasus*® DSC instrument using a heat (25-200 °C) / cool (200-25 °C) / heat (25-500 °C) cycle at a rate of 10 °C min^{-1}. Values of T_g and T_m were obtained from the second heating scan.

Monomer syntheses

Two general monomer synthesis procedures followed below:

Procedure 1.

The parent α-hydroxy acid (7.53mmol), paraformaldehyde (0.36g, 12mmol) and p-toluenesulfonic acid monohydrate (0.13g, 0.75mmol) were dissolved in benzene (50mL) and refluxed at 110 °C in a Deans-Stark apparatus to periodically remove water over 6h. The reaction mixture was cooled and washed with sodium bicarbonate aq. (10%), water and sodium chloride aq. (sat.). The organic layer was dried with magnesium sulphate and the solvent was removed from the organic layer in vacuo. The crude product was stirred over calcium hydride for 16h before being purified by vacuum distillation.

1,3-Dioxolan-4-one (DOX): Colourless oil, 26% yield. ^{1}H NMR (500MHz, $CDCl_3$) *δ* 5.50 (s, 2H, OC**H**$_2$O), 4.20 (s, 2H, CC**H**$_2$O) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.20, 96.10, 62.45ppm.

5-Methyl-1,3-dioxolan-4-one (MeDOX): Colourless oil, 75% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.50 (s, 1H, OC**H**$_2$O), 5.38 (s, 1H, OC**H**$_2$O), 4.27 (q, *J* = 6.8 Hz, 1H, OCC**H**O), 1.47 (d, *J* = 6.8 Hz, 3H, CC**H**$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 121.97, 42.36, 42.34, 18.32, -35.26.

5-Phenyl-1,3-dioxolan-4-one (PhDOX): Colourless oil, 96% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 – 7.37 (m, 5H, Ar), 5.67 (s, 1H, OC**H**$_2$O), 5.58 (s, 1H, OC**H**$_2$O), 5.23 (s, 1H, CCC**H**O) ppm. ^{13}C NMR (126 MHz, Chloroform-d) δ 171.38, 133.30, 129.24, 128.90, 126.52, 94.57, 74.49 ppm.

5-Isopropyl-1,3-dioxolan-4-one (iPrDOX): Colourless oil, 90% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 5.51 (s, 1H, OC**H**$_2$O), 5.42 (d, J = 0.9 Hz, 1H, OC**H**$_2$O), 4.04 (dt, J = 4.4, 0.7 Hz, 1H, OCC**H**O), 2.18 (heptd, J = 6.8, 4.2 Hz, 1H), 1.09 (d, J = 6.9 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 172.35, 94.48, 29.88, 18.26, 16.65.

5-Cyclohexyl-1,3-dioxolan-4-one (CyDOX): Colourless oil, 86% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 5.50 (s, 1H, OC**H**$_2$O), 5.42 (s, 1H, OC**H**$_2$O), 4.03 (d, J = 4.0 Hz, 1H, OCC**H**O), 1.91 – 1.73 (m, 3H), 1.72 – 1.58 (m, 2H), 1.34 – 1.09 (m, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 172.59, 94.74, 39.43, 28.93, 26.92, 26.08, 26.02, 25.87.

5-nButyl-1,3-dioxolan-4-one (nBuDOX): Colourless oil, 60% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 5.48 (s, 1H, OC**H**$_2$O), 5.38 (s, 1H, OC**H**$_2$O), 4.16 (m, 1H, OCC**H**O), 1.85 (m, 1H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 1.77 –h 1.65 (m, 1H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 1.52 – 1.27 (m, 4H,

C**H$_2$**C**H$_2$**CH$_3$), 0.89 (t, J = 7.2 Hz, 3H, C**H$_3$**). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.98, 94.03, 73.02, 29.92, 26.88, 22.12, 13.66.

5-iButyl-1,3-dioxolan-4-one (iBuDOX): Colourless oil, 60%. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.50 (s, 1H), 5.39 (s, 1H), 4.20 (ddd, *J* = 9.3, 3.9, 0.9 Hz, 1H, OCC**H**O), 1.87 (dh, *J* = 8.1, 6.6 Hz, 1H, CH_2C**H**(CH_3)), 1.75 – 1.59 (m, 2H, C**H$_2$**CH(CH_3)), 0.96 (dd, *J* = 6.8, 5.5 Hz, 6H, C**H$_3$**). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.43, 93.93, 77.25, 77.00, 76.75, 71.83, 38.95, 25.03, 22.79, 21.63.

Procedure 2.

The parent α-hydroxy acid (7.53mmol), and p-toluenesulfonic acid (0.13g, 0.75mmol) were dissolved in a mixture of acetone and benzene (1:1) (50mL) and refluxed in a Deans-Stark apparatus, periodically removing water formed over 6h. The reaction mixture was cooled and washed with sodium bicarbonate aq. (10%), water and sodium chloride aq. (sat.). The organic layer was dried with magnesium sulphate and the solvent was removed from the organic layer *in vacuo.* The crude product was then stirred over calcium hydride for 16h before being purified by vacuum distillation or toluene recrystallization to obtain pure products.

2,2,5-trimethyl-1,3-dioxolan-4-one (Me_3DOX): Colourless oil, 60% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.43 (q, *J* = 6.8 Hz, 1H, C**H**CH_3), 1.56 (s, 3H, OOCC**H$_3$**), 1.49 (s, 3H, OOCC**H$_3$**), 1.42 (d, *J* = 6.8 Hz, 3H, CHC**H$_3$**). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.78, 110.36, 110.29, 110.06, 70.40, 27.41, 25.56, 17.36.

2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-one (Me_2PhDOX): White crystalline solid, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.46 (m, 2H, Ar), 7.48 – 7.36 (m, 4H, Ar), 5.42 (s, 1H, OOCC**H**), 1.75 (s, 3H, OOCC**H$_3$**), 1.70 (s, 3H, OOCC**H$_3$**). ^{13}C NMR (126 MHz, CDCl3) δ 171.42, 134.45, 128.95, 128.73, 126.42, 110.94, 75.89, 27.26, 26.19.

Representative Polymerizations

MeAl[salen]$^{tBuBu\text{-}Pr}$ (5.5 mg, 0.01 mmol), BnOH (1 μL, 0.01 mmol) and MeDOX (88 mg, 1.0 mmol) in toluene (1 mL) was added to an oven dried ampoule. The ampoule was then sealed and heated to 120 °C for 24 h. The reaction was then quenched by addition of two drops of MeOH and samples were taken for crude ^{1}H NMR. The remainder was added dropwise to cold methanol and upon cooling to −35 °C for two days a white solid was precipitated. The white solid was filtered, dried to constant weight and used for GPC analysis.

Toxicity of Phosgene Gases and Paraformaldehyde

Paraformaldehyde: LCt50 = 810 ppm/4h (dust, rat) (Sigma Aldrich MSDS)

Diphosgene: LCt50 = 1.25ppm/4h (human) (by Haber's law)[4]

LCt50 = 1.7 ppm/4h (rat)[5]

Monomer pricing (1 kg)

PhDOX: 90% yield

PhDOX (90% yield):

$$\frac{1000\ (g)}{164.16(gmol^{-1})} = 6.092\ (mol)$$

Mandelic acid:

$$6.092\ (mol) \div 0.9 = \ 6.769\ (mol)$$

$$6.769\ (mol) \times 152.15\ (gmol^{-1}) = 1.029\ (kg)$$

$$1.029\ (kg) \times 128.38\ (\$kg^{-1}) = \ 132.10\ (\$)$$

https://us.vwr.com/store/

Paraformaldehyde:

$$6.769\ (mol) \times \frac{12\ (mol)}{7.53\ (mol)} = 10.79\ (mol)$$

$$10.79\ (mol) \times 30.03\ (gmol^{-1}) = \ 0.324\ (kg)$$

$$0.324\ (kg) \times 50.54\ (\$kg^{-1}) = 16.38\ (\$)$$

Paratoluensulfonic acid monohydrate:

$$0.677\ (mol) \times 190.22\ (gmol^{-1}) = 0.1288\ (kg)$$

$$0.1288\ (kg) \times 61.42\ (\$kg^{-1}) = 7.91\ (\$)$$

1 kg PhDOX = $ 156.39

Ph(OCA): 75% yield

Ph(OCA) (75% yield):

$$\frac{1000\ (g)}{178.14(gmol^{-1})} = 5.614\ (mol)$$

Mandelic acid:

$$5.614\ (mol) \div 0.75 = \ 7.485\ (mol)$$

$$7.485\ (mol) \times 152.15\ (gmol^{-1}) = 1.139\ (kg)$$

$$1.139\ (kg) \times 128.38\ (\$kg^{-1}) = \ 146.20\ (\$)$$

Diphosgene (Trichloromethyl chloroformate):

$$7.485\ (mol) \times 197.82\ (gmol^{-1}) = 1.481\ (kg)$$

$$1.481\ (kg) \times 478.80(\$0.25kg^{-1}) = \ 2836.41\ (\$)$$

1 kg Ph(OCA) = $2982.61

All chemical pricings obtained from https://us.vwr.com/store/

Degradation of poly(mandelic acid) with proteinase K

Poly(mandelic acid) (PMA) (0.5g) was dissolved in 5 mL of $CHCl_3$ and placed in a PTFE evaporation dish. The solvent was slowly evaporated to from a 1 mm thick plastic film. 25.92 mg of PMA film was incubated for 24 hours at 37 ^{o}C in a 1 mL buffer solution (H_2O, 30 mM TrisHCl (pH 8), 10 mM $CaCl_2$) containing proteinase K (10 mg, from tritirachium album). The PMA film was rinsed with deionized water three times and dried to a constant weight of 23.21 mg (12% weight loss).

Recycling Recovered Paraformaldehyde

After a polymerization of MeDOX, paraformaldehyde was recovered from the walls of an ampoule and subsequently dried *in vacuo* to constant weight. The recovered paraformaldehyde (11.7 mg), mandelic acid (40 mg) and *p*-toluenesulfonic acid (10mg) was dissolved in 30 mL of benzene. The solution was added to a round bottom equipped with a stir bar and refluxed in a Dean-Stark apparatus for 6h. An aliquot was removed from the reaction mixture, dried *in vacuo* and dissolved in DMSO-*d6* for ^{1}H NMR spectroscopy. The rest of the reaction mixture was purified as previously described. By ^{1}H NMR analysis, 100% conversion was obtained, matching production of PhDOX from new paraformaldehyde.

DOX copolymerization data

NMR data

Poly(lactic-co-glycolic acid): ^{1}H NMR (601 MHz, Chloroform-*d*) δ 5.16 (q, *J* = 7.1 Hz, 1H), 4.90 – 4.57 (m, 2H), 1.58 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.58, 166.49, 69.01, 60.79, 16.64.

Poly(3-hyroxybutyrate-co-glycolic acid): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.47 – 5.26 (m, 2H), 4.83 – 4.49 (m, 2H), 2.82 – 2.47 (m, 1H), 1.41 – 1.18 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, Chloroform-d) δ 169.30, 169.22, 167.14, 166.91, 166.47, 128.78, 128.72, 128.50, 68.88, 68.66, 61.35, 61.00, 60.96, 60.94, 60.84, 60.59, 40.54, 40.26, 19.94, 19.92, 19.86, 19.82.

Poly(caprolactone-co-glycolic acid): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.82 – 4.54 (m, 2H), 4.20– 4.00 (m, 2H), 2.44– 2.24 (m, 2H), 1.73 – 1.58 (m, 4H), 1.47 – 1.30 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.42, 172.74, 172.69, 172.57, 167.85, 167.33, 167.08, 65.32, 65.12, 65.08, 64.09, 61.05, 60.55, 60.19, 34.03, 33.59, 33.54, 33.52, 28.28, 28.18, 28.15, 28.13, 28.10, 25.39, 25.35, 25.22, 25.19, 24.47, 24.40, 24.34, 24.29.

Table S01. ε-Caprolactone and DOX copolymerizations.

M1:M2	Time (h)	[a]M1 (%)	conv	[a]M2 (%)	conv	[b]$M_{n,th}$ (Da)	[c]M_n (Da)	[c]M_w (Da)	[d]Đ	Mn, nmr
90:10	3	90		100		9920	7000	9600	1.4	/
80:20	7	100		100		10390	6800	9600	1.4	9770
70:30	7	73		100		7670	5400	6800	1.3	5430
60:40	7	79		97		7760	2900	3700	1.3	7120
50:50	7	78		97		7370	2700	3400	1.3	5730

40:60	7	46	88	5270	1700	2500	1.5	2400
40:60	17	83	94	7160	2800	4800	1.7	5730
30:70	17	58	92	5830	1300	2300	1.8	5380

M1 = ε-caprolactone, M2 = DOX, C = MeAl(salen)^{tbu,tbu,pr}, I = BnOH. M:C:I = 100:1:1. Monomer concentration = 1M .[a] monomer conversion % determined by crude sample ^{1}H NMR spectroscopy. [b]$M_{n,th}$ = (M:BnOH) × MW(monomer) × (conv (%)) + MW(end group). [c]determined by gel permeation chromatography. [d] Đ=dispersity=M_w/M_n.

Table S02. β-Butyrolactone and DOX copolymerizations.

M1:M2	Time (h)	[a]M1 conv (%)	[a]M2 conv (%)	[b]$M_{n,th}$ (Da)	[c]M_n (Da)	[c]M_w (Da)	[d]Đ	Mn, nmr
90:10	17 h	52	100	4710	6000	7000	1.2	
80:20	24 h	92	99	7590	4600	5700	1.3	7000
70:30	24 h	90	98	7230	3400	4000	1.2	6700
60:40	24 h	86	93	6700	1500	2400	1.6	5800

M1 = β-butyrolactone, M2 = DOX, C = MeAl(salen)^{tbu,tbu,pr}, I = BnOH. M:C:I = 100:1:1. Monomer concentration = 1M .[a] monomer conversion %determined by crude sample ^{1}H NMR spectroscopy. [b]$M_{n,th}$ = (M:BnOH) × MW(monomer) × (conv (%)) + MW(end group). [c]determined by gel permeation chromatography. [d] Đ=dispersity=M_w/M_n.

Substituted RDOX homopolymerizations

R = Methyl, Poly(lactic acid): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.16 (q, *J* = 7.1 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.59, 77.26, 77.01, 76.75, 69.01, 16.65.

R = Phenyl, Poly(mandelic acid): ^{1}H NMR (601 MHz, Chloroform-*d*) δ 7.48 – 7.01 (m, 5H), 6.15 – 5.92 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.76, 132.33, 129.34, 128.64, 127.80, 74.75.

R = Cyclohexyl, Poly(hexahydromandelic acid): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.05 – 4.87 (m, 1H), 2.32 – 0.68 (m, 11H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.70, 39.51, 28.69, 27.18, 25.89.

R = iPropyl, Poly(vandelic acid): ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 4.9 (m, 55.7H), 4.1 (d, 2H), 2.3 (b, 59.2H) 1.39 (s, 9H), 1.1 (m, 350.6H). (CDCl3, 125 MHz) δ: 168.6, 125, 128,

R = nButyl, Poly(2-nButylhexanoic acid): ^{1}H NMR (601 MHz, Chloroform-*d*) δ 5.21 – 5.03 (m, 1H), 2.03 – 1.85 (m, 2H), 1.45 – 1.30 (m, 5H), 0.98 – 0.82 (m, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ169.17, 72.49, 33.66, 27.03, 22.36, 13.78.

R = iButyl, Poly(2-iButylhexanoic acid): ^{1}H NMR (601 MHz, Chloroform-*d*) δ 5.09 (dd, *J* = 9.4, 4.2 Hz, 1H), 1.85 – 1.73 (m, 4H), 0.94 (dd, *J* = 20.2, 6.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.70, 71.34, 39.31, 24.50, 22.96, 21.41.

Table S03. MeDOX Polymerizations

Catalyst	Solvent	Conc (M)	Temp (°C)	Time (h)	[a]Conv (%)	[b]$M_{n,th}$ (Da)	[c]M_n (Da)	[c]M_w (Da)	[d]Đ
MeAl(salen)	Tol	1	85	72	86	6,300	290	430	1.46
MeAl(salen)	Tol	1	110	24	81	5,940	8,290	9,630	1.16
$Sn(Oct)_2$	Tol	1	110	24	28	2,124	/	/	/
$Sn(Oct)_2$	Bulk	Bulk	120	1.5	59	4,356	2,300	3,980	1.73
$ZnEt_2$	THF	1	75	48	88	6,444	4,320	6,270	1.45
$ZnEt_2$	THF	1	75	192	99	7,306	3,862	5,548	1.44

I = BnOH. M:C:I = 100:1:1. Solution polymerizations completed in toluene. [a] monomer conversion % determined by crude sample ^{1}H NMR spectroscopy. [b]$M_{n,th}$ = (M:BnOH) × MW(monomer) × (conv (%)) + MW(end group). [c]Determined by gel permeation chromatography. [d] Đ=dispersity=M_w/M_n.

Table S04. PhDOX Polymerizations

M	M:C:I	Catalyst	Time (h)	[a]Conv (%)	[b]$M_{n,th}$ (Da)	[c]M_n (Da)	[c]M_w (Da)	[d]Đ	[e]Tacticity
rac-PhDOX	100:1:1	$Sn(Oct)_2$	19	38	5210	800	1100	1.4	atactic
S-PhDOX	50:1:1	ZnEt2	4	27	3700	2000	2300	1.2	atactic
S-PhDOX	50:1:1	$Sn(Oct)_2$	4	65	4470	3400	7400	2.2	isotactic
Rac-PhDOX	100:1:1	MeAl(salen)[f]	72	92	12450	4000	5600	1.2	atactic
R-PhDOX	100:1:1	MeAl(salen)[f]	72	98	13250	4800	6300	1.3	isotactic
S-PhDOX	100:1:1	MeAl(salen)[f]	72	96	12990	4900	6000	1.2	isotactic
S-PhDOX	50:1:1	MeAl(salen)[f]	4	89	6080	3700	4800	1.3	isotactic
S-PhDOX	50:1:1	MeAl(salen)[g]	4	59	4070	3900	4100	1.1	atactic
S-PhDOX	50:1:1	MeAl(salan)	4	43	2990	1000	3800	3.7	isotactic
S-PhDOX	200:1:1	MeAl(salen)[f]	120	83	22370	8400	9600	1.1	isotactic
R-PhDOX	200:1:1	MeAl(salen)[g]	120	96	25860	7700	11300	1.5	isotactic

Monomer concentration = 1M. I = Benzyl alcohol .[a] monomer conversion % determined by crude sample ^{1}H NMR spectroscopy. [b]$M_{n,th}$ = (M:BnOH) × MW(monomer) × (conv (%)) + MW(end group). [c]determined by gel permeation chromatography. [d] Đ=dispersity=M_w/M_n. [e]Determined from methine peak in ^{1}H NMR spectrum. [f]Salen ligand substituted with tBu at the 2,4 positions. [g]Salen ligand substituted with Cl at the 2,4 positions.

Table S05. Other alkyl substituted DOX polymerizations.

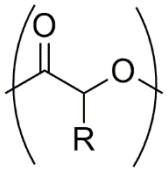
Monomer	Conc (1M)	Temp. (^{o}C)	Time (h)	[a]Conv (%)	$M_{n,th}$ (Da)	M_n (Da)	M_w (Da)	Đ
tMDOX	1	120	168	95	6950	4600	6800	1.5
dMPhDOX	1	120	168	6	/	/	/	/
dMPhDOX	bulk	180	20	91	13000	12800	15800	1.2
nBuDOX	1	120	72	97	11160	1800	2500	1.4
iBuDOX	1	120	72	99	11390	7500	8900	1.1
CyDOX	1	120	72	65	9200	1500	1800	1.3
iPrDOX	1	120	20	33	3400	3800	5600	1.5

Monomer:MeAl(salen):BnOH = 100:1:1. Solution polymerizations were completed in toluene. [a]monomer conversion %determined by crude sample ^{1}H NMR spectroscopy. [b]Mn,th = ([M]/[BnOH]) ×MW(monomer) ×(% conv.) + MW(end group). [c]determined by gel permeation chromatography. Đ=dispersity=M_w/M_n.

Table S06 Glass Transition Temperatures.

Below is a list of the various PAHAs synthesised and their relevant glass transition temperatures.

R	Glass Transition Temperature T_g (°C)
R-Me	59
rac-Ph	100
R-Ph	115
iPr	41
Cy	98
iBu	22



For original measurement and report of these glass transition temperatures see:
G. L. Baker, E. B. Vogel and M. R. S. III, *Polym. Rev.*, 2008; M. Yin, G. L. Baker, *Macromolecules,* 1999, **32**, 7711; F. Jing, M. R. Smith, G. L. Baker, *Macromolecules,* 2007, **40**, 9304.

Figures

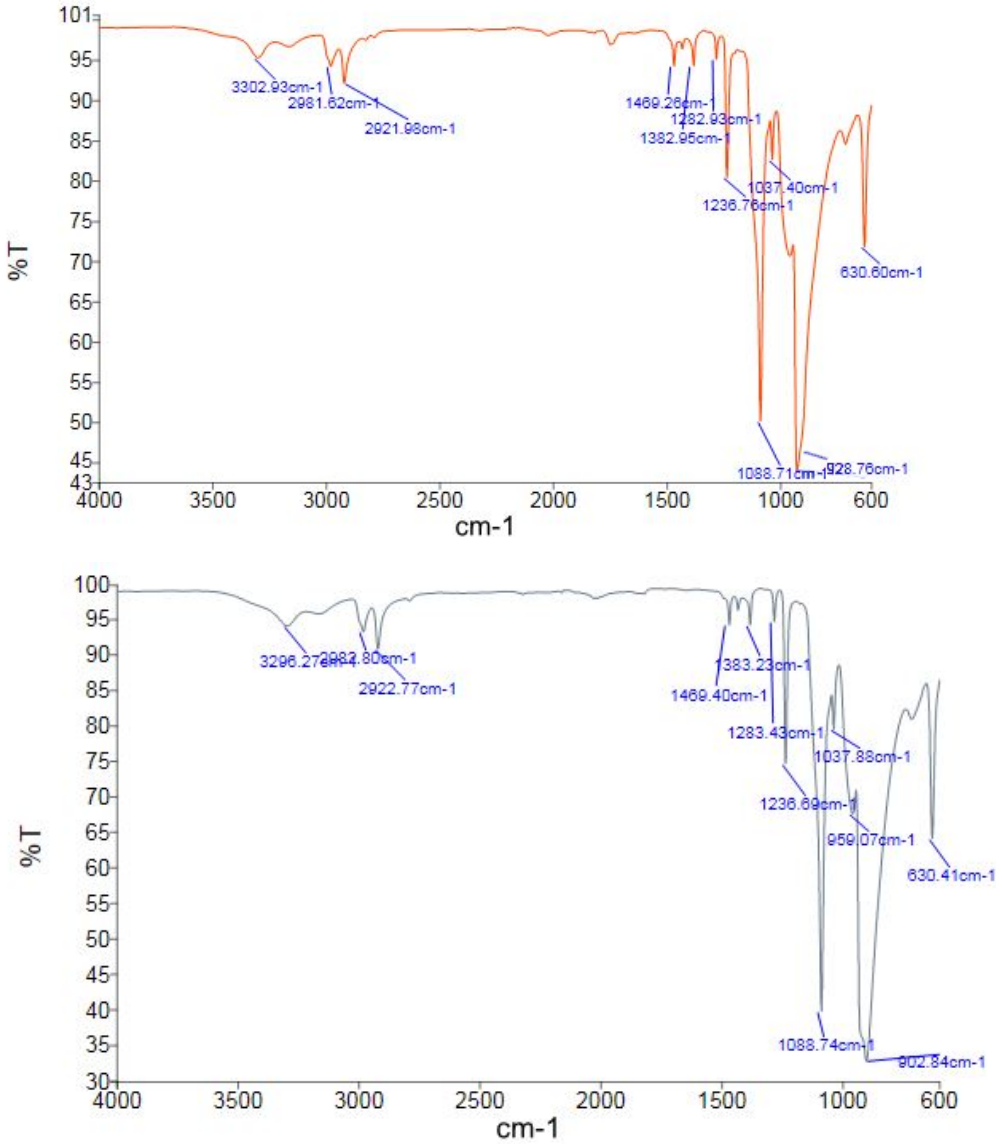


Figure S1. IR spectrum of white solid sublimed from reaction (above) and comparative paraformaldehyde spectrum (below).

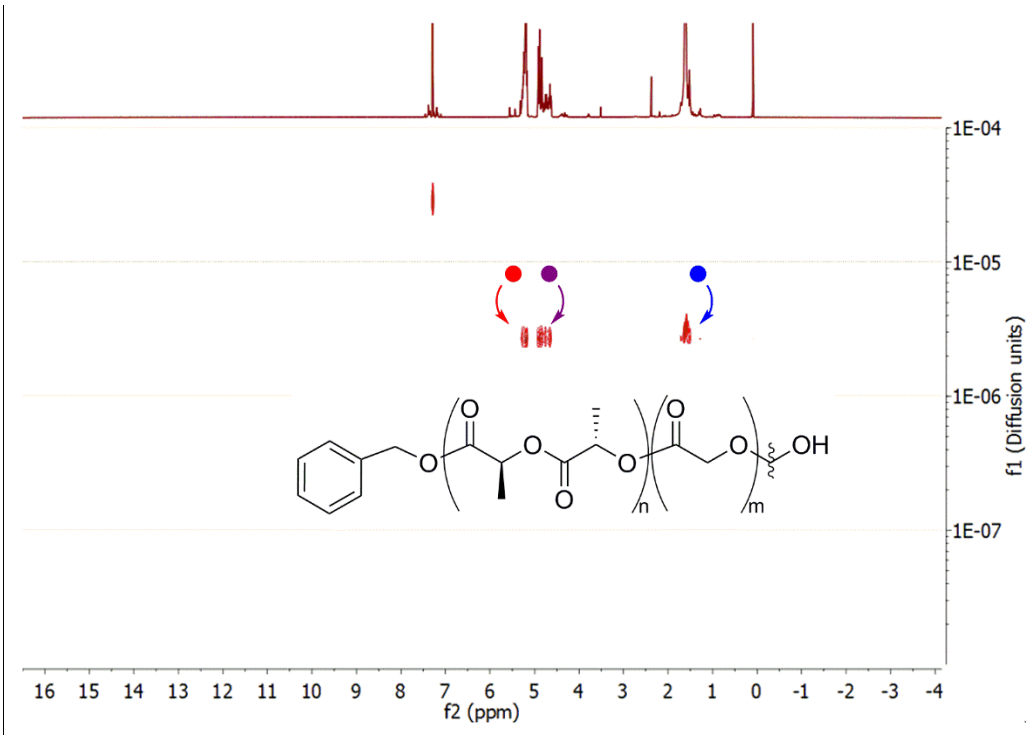


Figure S2 DOSY NMR spectrum of PLA-PGA copolymer in $CDCl_3$

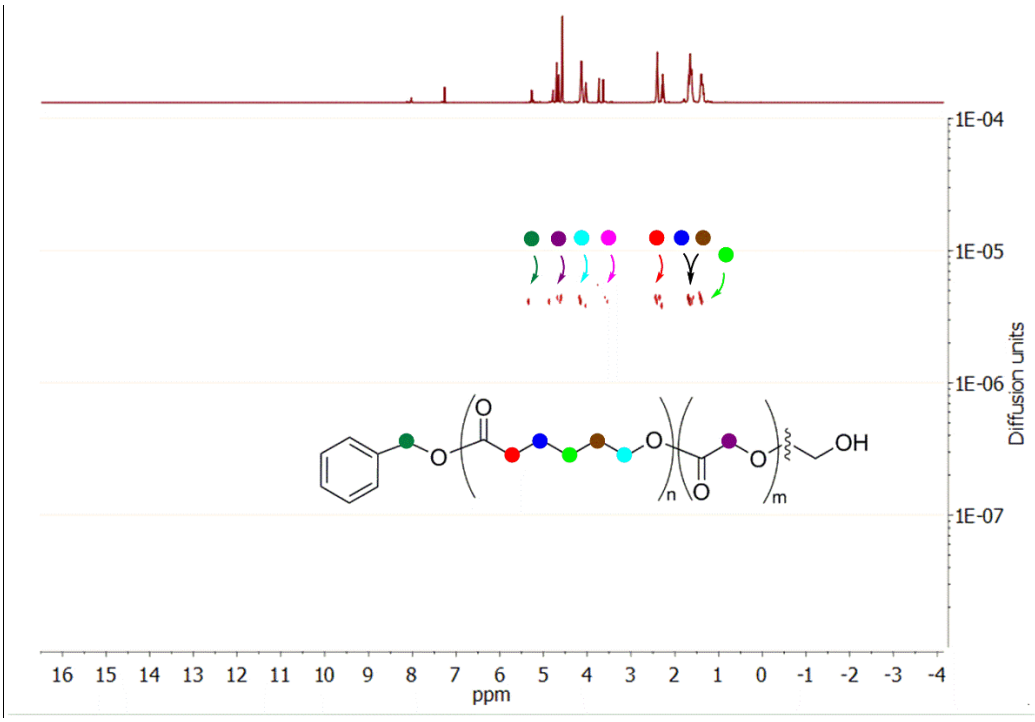


Figure S3 DOSY NMR spectrum of crude PCL-PGA copolymer in $CDCl_3$

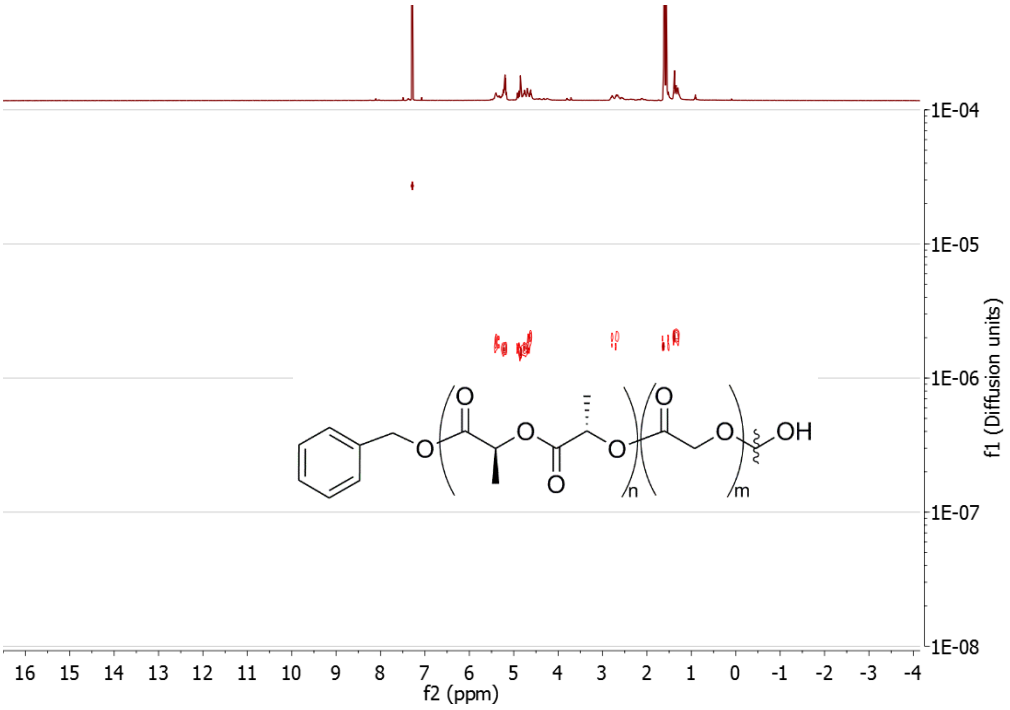


Figure S4 DOSY NMR spectrum of crude PLA-PGA copolymer in $CDCl_3$

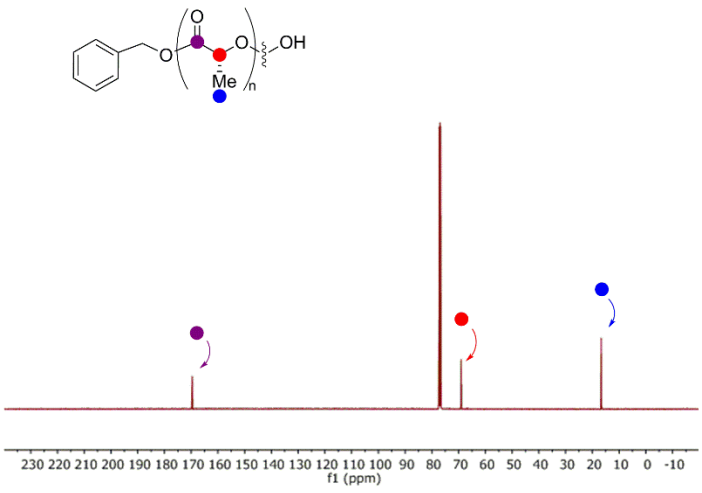


Figure S5 PLA $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)

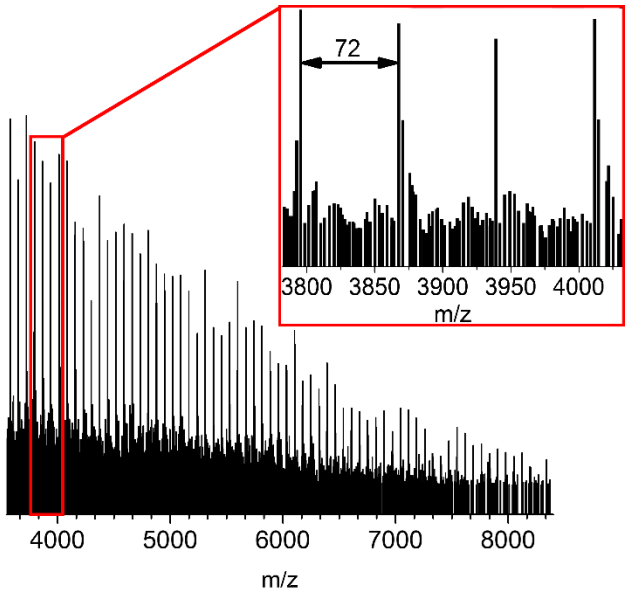


Figure S6. MALDI-ToF spectrum of PLA from the polymerization of MeDOX.

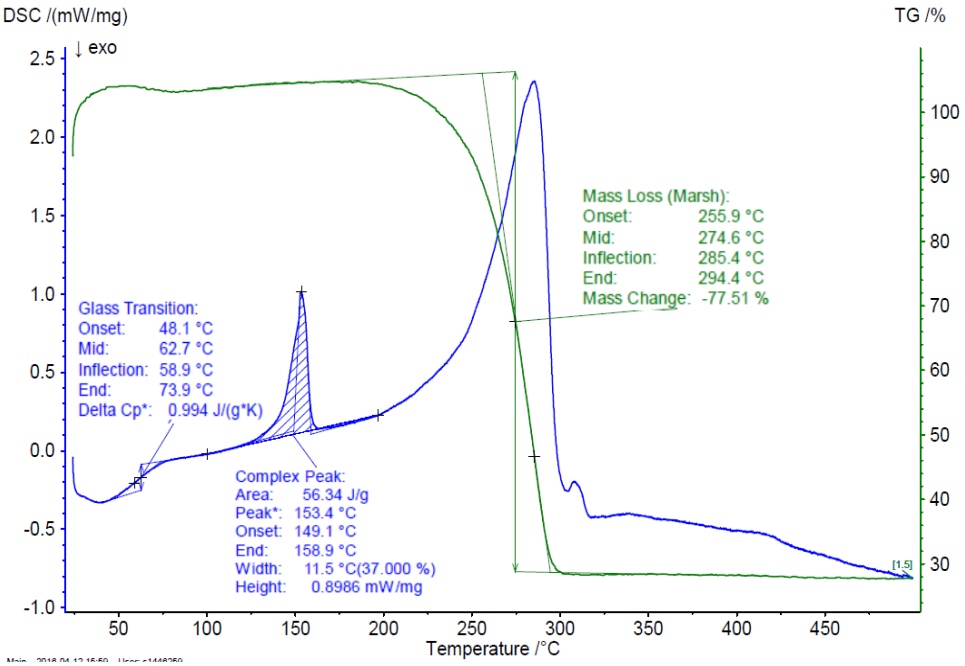


Figure S7. DSC(blue) and TGA(green) of PLA from MeDOX

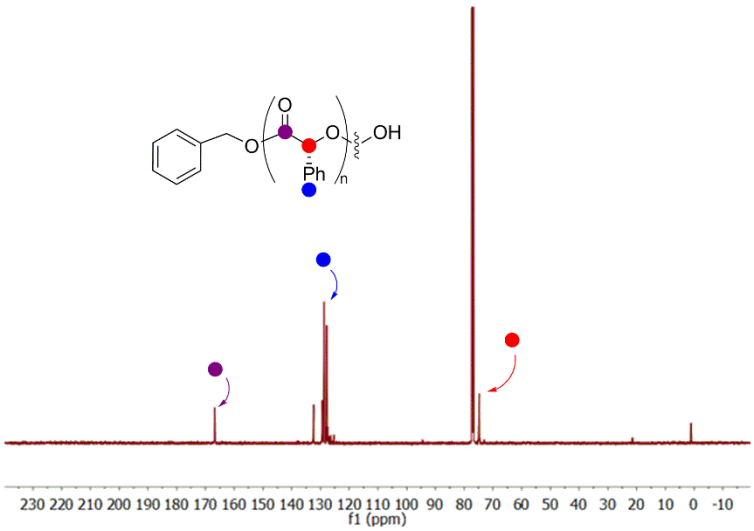


Figure S8 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of PMA

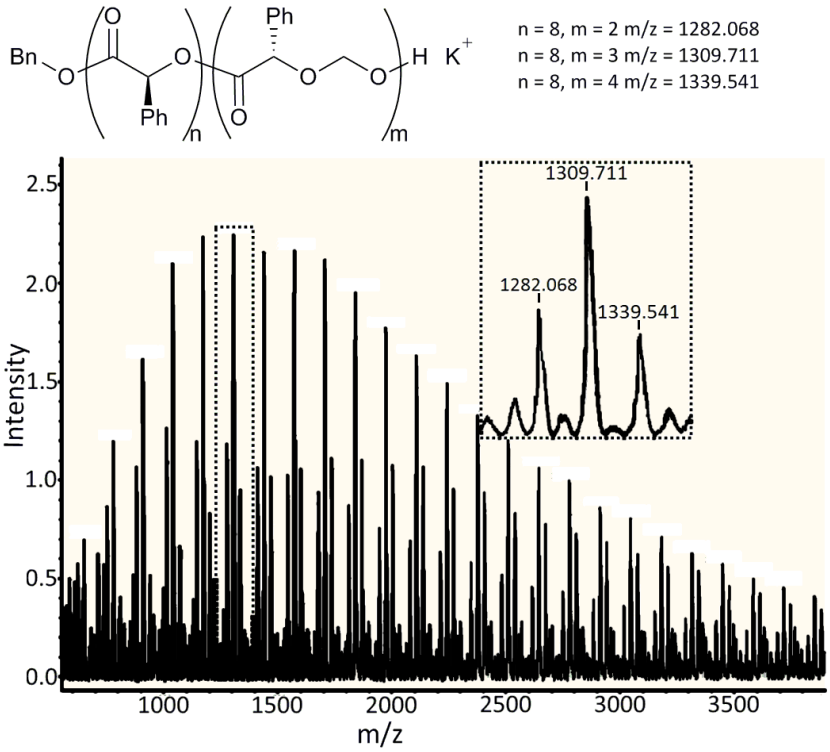


Figure S9 MALDI-ToF spectrum of poly(mandelic acid), showing the mandelic acid repeat unit (peak difference of m/z = 134) and three series correlating with retained acetal linkages, each initiated by a benzyl alcohol unit. This sample is representative of short polymer chains suitable for MALDI analysis and thus may not be representative of polymer samples at higher conversions and longer chains.

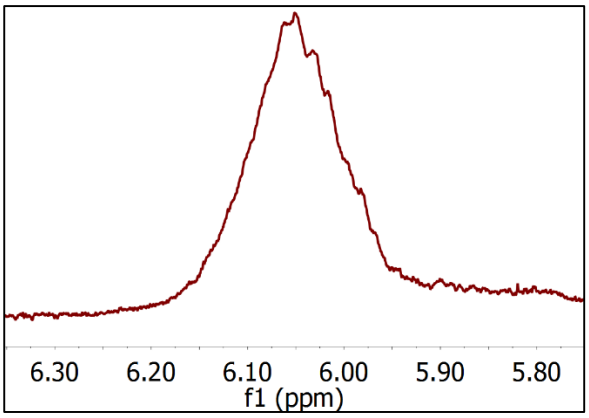


Figure S10. ^{1}H NMR spectrum of methine region of atactic PMA

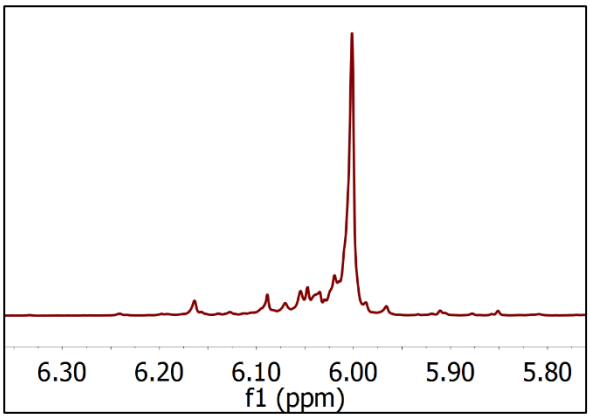


Figure S11. ^{1}H NMR spectrum of methine region of isotactic PMA

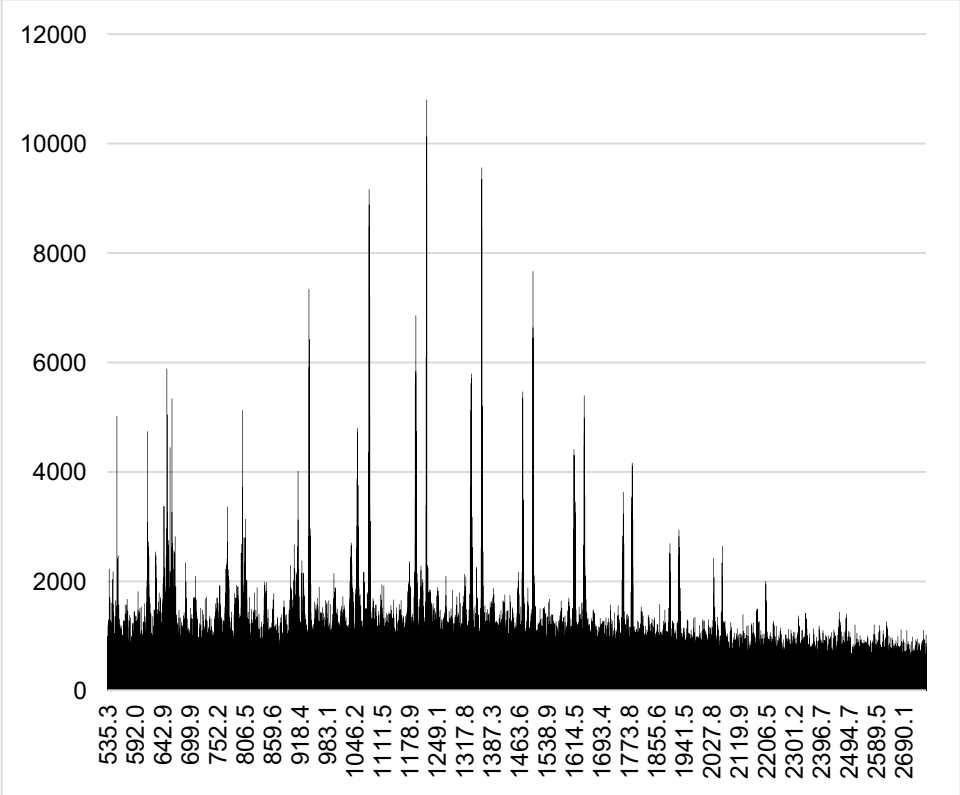


Figure S12. MALDI-ToF spectrum of low molecular weight poly(hexahydromandelic acid) (PHHMA)

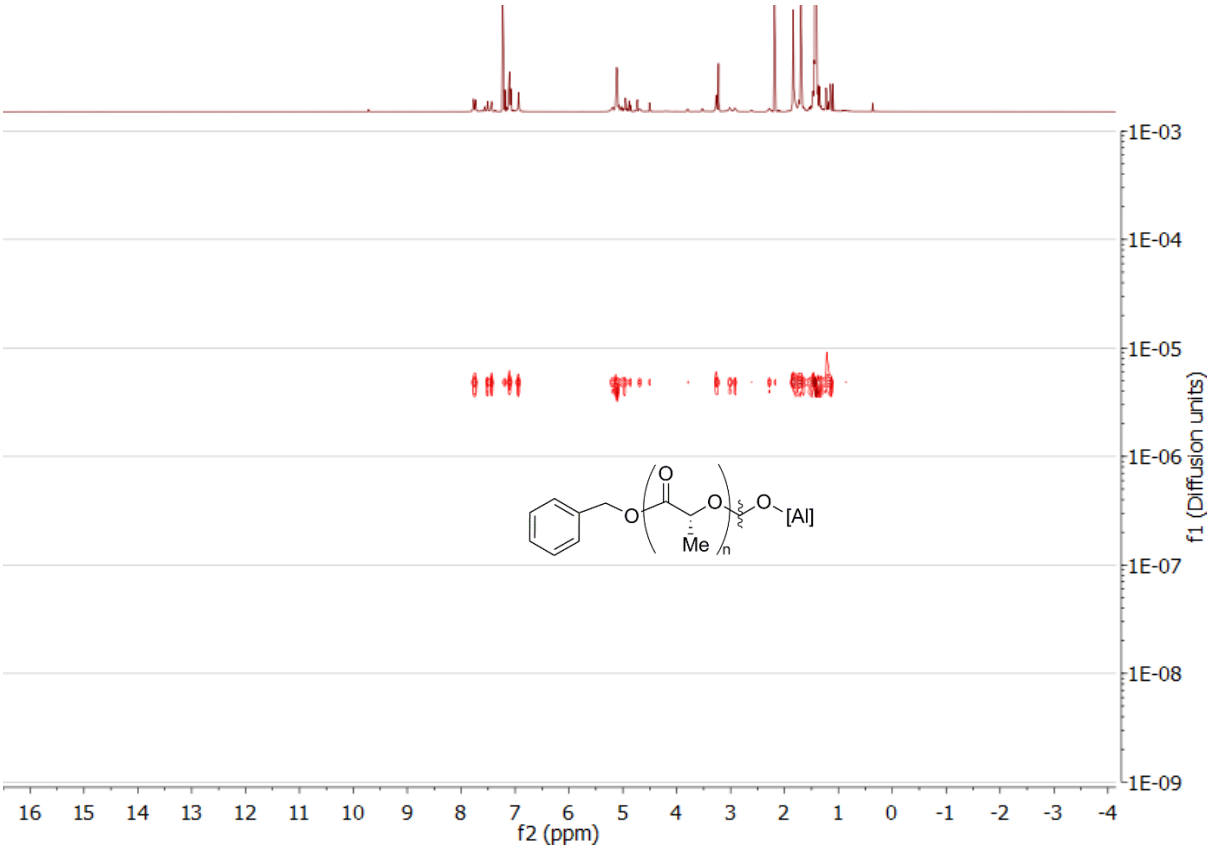


Figure S13. DOSY NMR spectrum of active polymer chain using monomer:catalyst:initiator ratio of 20:1:1 in toluene (110 °C, 2h).

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