Electronic Supplementary Material (ESI) for Polymer Chemistry.

Understanding the ring-opening polymerisation of 1,3-dioxolan-4-ones

Supporting information

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Materials and instruments

Commercial reagents were purchased from Acros Organics, Alfa Aesar, Fisher, VWR or Sigma Aldrich and used as received unless otherwise stated. Benzyl alcohol and 1,3-dioxolane-4-one (DOX) monomers and diphenyl ether were purified by stirring over CaH_2 followed by distillation under an inert atmosphere. Toluene, 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. All of the catalysts were synthesized according to the reported methods and the spectra were identical as reported.[1-11] All ^{1}H, ^{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). The dn/dc value of PMA was experimentally determined to be 0.11.[12] Mass spectrometry was performed on a Bruker UltraflexExtreme MALDI-TOF mass spectrometer. MALDI-TOF samples were prepared using the following matrices dithranol for poly(mandelic acid) and sodium or potassium trifluroacetic acid was used as the ionization source. Differential scanning calorimetry (DSC) was carried out on a DSC 2500 TA instrument using a heat (25-220 °C) /cool (220-25 °C) / heat (25-220 °C) cycle at a rate of 10 °C min^{-1} (otherwise specified). Values of T_g and T_m were obtained from the second heating scan.

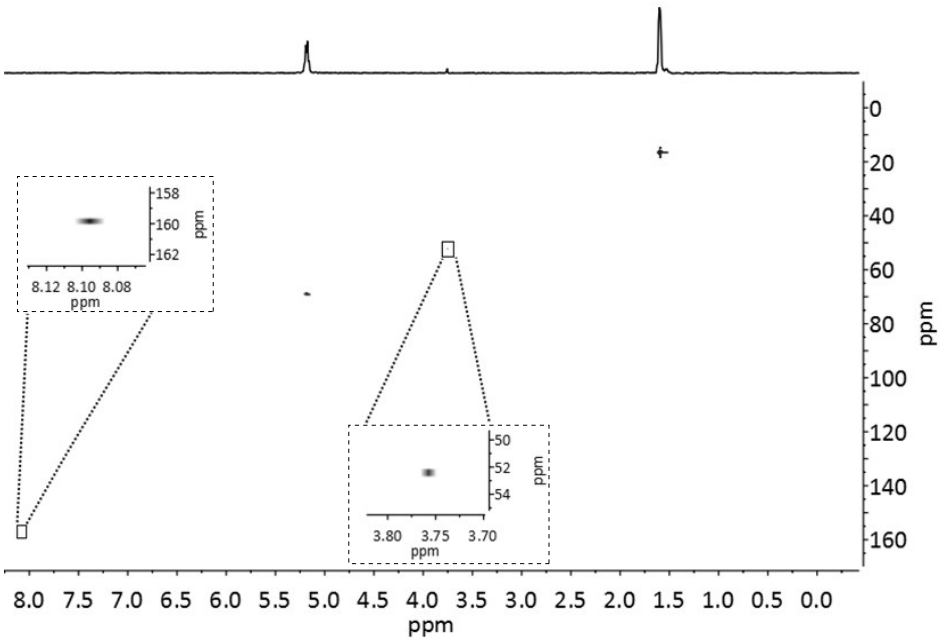


Figure S1 HSQC 2D NMR spectrum of PLA synthesized from 5-MeDOX and SA2

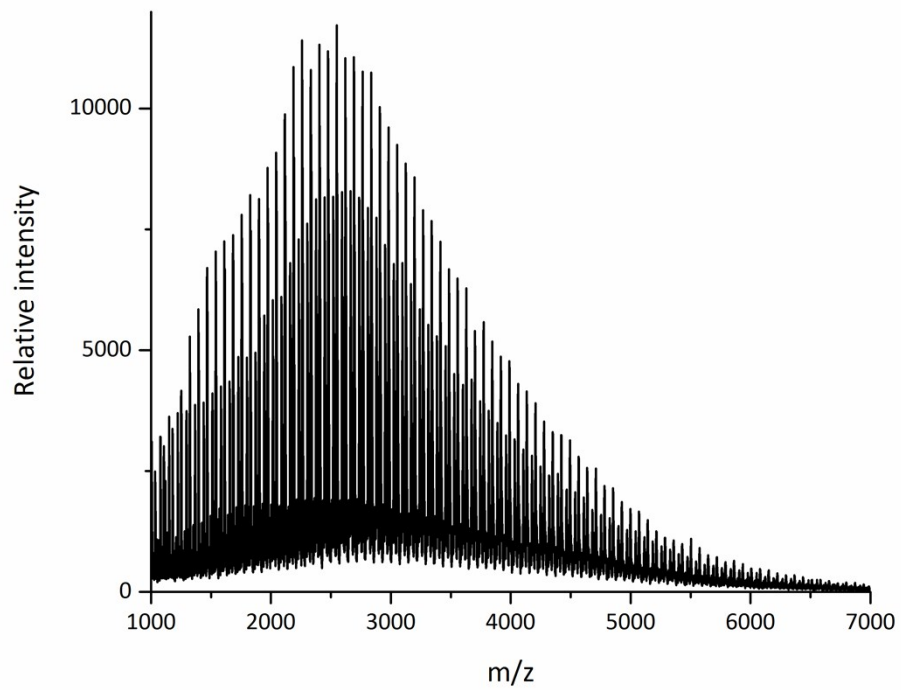


Figure S2 MALDI-ToF mass spectrum of PLA containing unidentified NMR peaks synthesized from 5-MeDOX

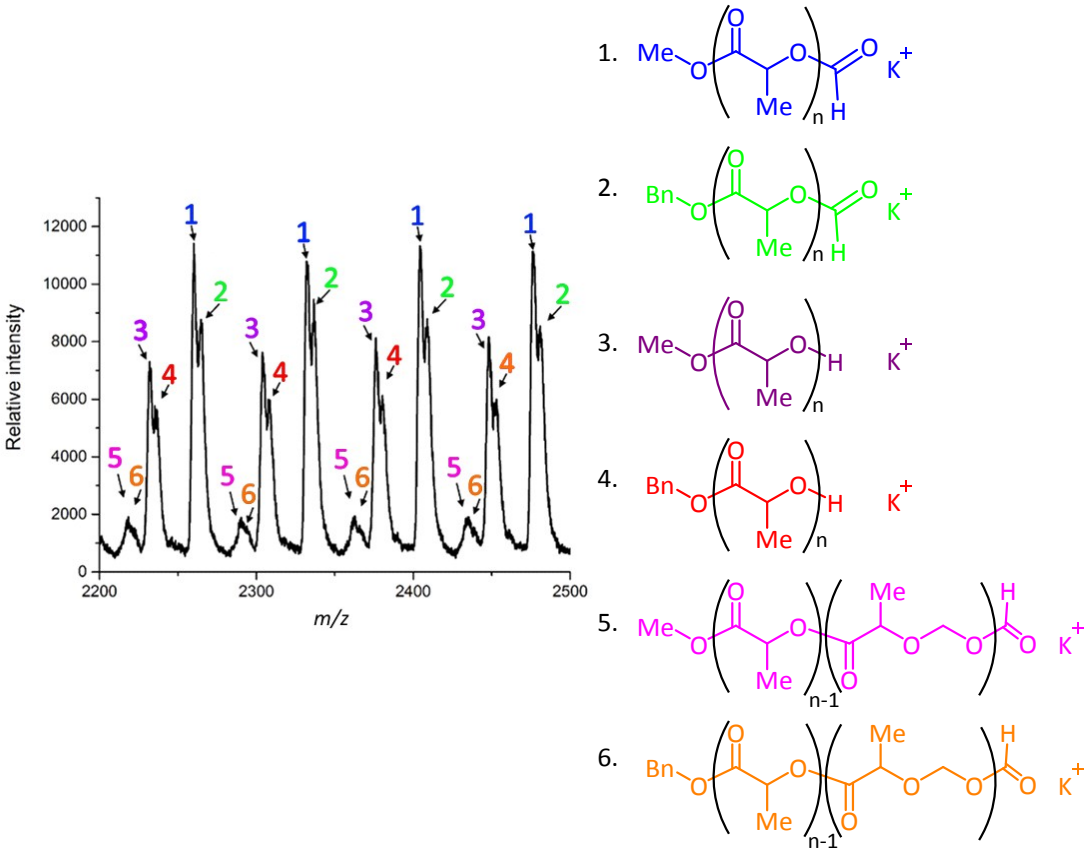


Figure S3 MALDI-ToF of PLA synthesised from the polymerisation of 5-MeDOX catalysed by SA1 and initiated by BnOH. The mass spectrum is plotted from 2200-2500 g/mol to illustrate defined peak shapes. Each repeating series is labelled to the identified series on the right

Table S1 Polymerisation of 5-MeDOX stopped at various time points and incorporating data from the generated additional methoxy initiators

Time	Conv (%)[a]	$M_{n,th}$ (g mol^{-1})[b]	M_n (g mol^{-1}) [c]	$Đ$[c]	$M_n/M_{n,th}$	# MeO[d]	$M_{n,th}$ (g mol^{-1})
0.75	12	1800	/	/	/	2.72	500
2	32	4700	1100	1.17	0.23	3.37	1100
5	63	9200	2100	1.16	0.23	4.31	1700
7	68	9900	1900	1.37	0.19	4.40	1800
17	84	12200	1900	1.39	0.16	6.20	1700
97	99	14400	1200	1.25	0.08	9.51	1400

5-MeDOX:SA1:BnOH = 200:1:1. Monomer concentration = 2 M in toluene. The reaction was conducted at 100 °C. Conv. = Monomer conversion. [a] monomer conversion determined from crude ^{1}H NMR spectrum. [b] Mn,th (g/mol) = (M:BnOH) × MW(monomer) × (conv (%)) + MW(end group). [c] Đ and M_n (g/mol) determined by gel permeation chromatography. [d]determined by comparing the relative integrations of the methoxy CH_3 and the PLA CH.

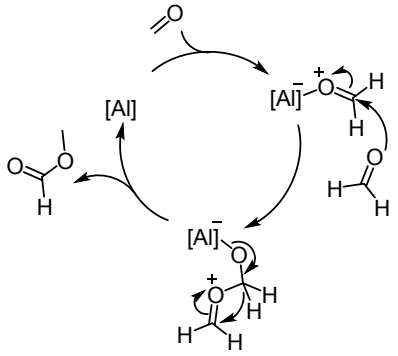
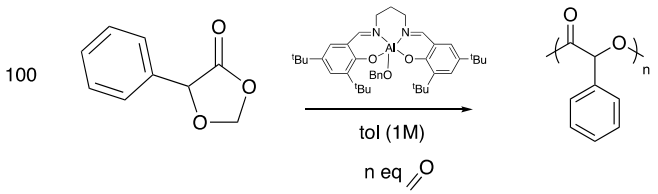


Figure S4 Mechanism of Tishchenko reaction catalysed by [Al]

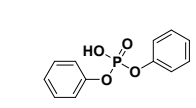
Table S2 Polymerisation data for reactions conducted with exogenous paraformaldehyde

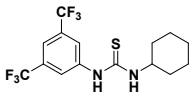


CH_2O (mol %)	Conversion (%)	$M_{n,th}$ (g mol^{-1})
0	45.3	6,070
5	41.5	5,561
7.5	26.5	3,551
15	16.0	2,144
20	<5	-

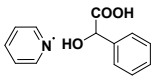
Reactions conducted using *S*-PhDOX for 18 h at 120 °C in sealed ampoules under a static atmosphere of N_2. Conversion determined by ^{1}H NMR spectroscopy of crude samples. Paraformaldehyde used as the CH_2O source.

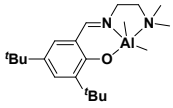
Table S3 Polymerisation data of 5-PhDOX with various catalyst systems

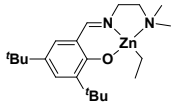

Diphenylphosphoric acid (DPP)

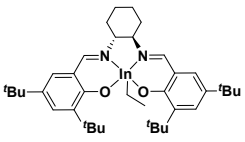

Thiourea

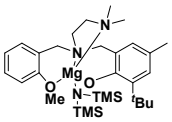

DBU

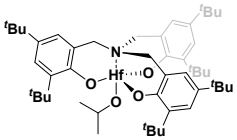

Pyridine/mandelic acid adduct

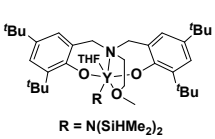

Phenimine [Al]

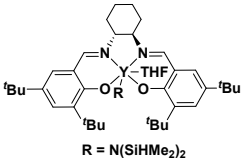

Phenimine [Zn]


[In]


[Mg]


[Hf]


R = N(SiHMe$_2$)$_2$
[Y]-1


R = N(SiHMe$_2$)$_2$
[Y]-2

Entry	Catalyst	M:C:I	Temp (°C)	Time (h)	Conv (%)[a]	$M_{n,th}$ (kg mol^{-1})[b]	$M_{n,exp}$ (kg mol^{-1})[c]	Đ[c]	Tacticity[d]
1	DPP	100:1:1	120	18	<5	/	/	/	/
2[e]	Thiourea	100:3:1	120	40	78	10.5	/	/	atactic
3[f]	DBU	100:1:1	120	18	--	/	/	/	atactic
4	PY-MA	200:1:0	120	48	<5	/	/	/	/
5	Phenimine [Al]	200:1:2	120	18	<5	/	/	/	/
6	Phenimine [Zn]	100:1:1	120	24	15	2.1	/	/	atactic
7[f]	[In]	100:1:1	120	40	--	/	/	/	atactic
8[f]	[Mg]	100:1:1	120	18	--	/	/	/	atactic
9	[Hf]	100:1:0	120	44	34	4.7	3.4	1.25	isotactic
10[f]	[Y]-1	100:1:1	120	18	--	/	/	/	atactic
11[f]	[Y]-2	100:1:1	120	18	--	/	/	/	atactic
12	SnOct	50:1:1	120	4	65	4.5	3.4	2.15	atactic

S-PhDOX were used, monomer concentration = 1 M in toluene (except for entry 9, concentration = 5 M). Conv. = Monomer conversion. [a] monomer conversion% was determined by crude sample ^{1}H NMR spectroscopy. [b] $M_{n,th}$ (g/mol) = ([M]/[BnOH]) ×MW(monomer) × (% conv.) + MW(end group). [c] Đ and M_n (g/mol) determined by gel permeation chromatography.[d] Determined from the ^{1}H NMR spectrum's methine region. [e] KOMe was used as an initiator. [f] Convention is unavailable due to the bad product selectivity.

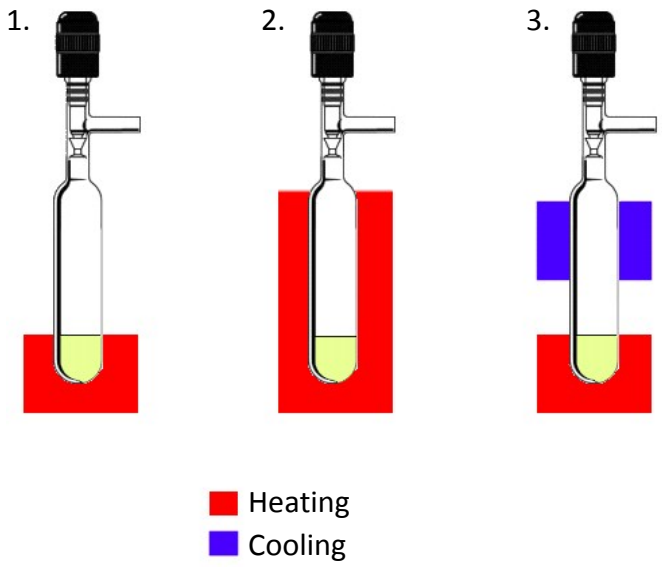


Figure S5 Three reaction setups tested for the polymerisation of 5-MeDOX

Table S4 Variations in the reaction setup for the polymerisation of 5-MeDOX as shown in Figure S

Setup	Conv.[a] (%)	$M_{n,\,th}$ (g mol^{-1})[b]	M_n (g mol^{-1})[c]	$Đ$[c]
1. Heating the glass contacting reaction mixture	93	3456	3000	1.35
2. Heating the entirety of the vessel	99	3672	/	/
3. Heating the glass contacting reaction mixture & cooling above[d]	93	3456	4600	1.52

5-MeDOX:SA1:BnOH = 50:1:1. Conducted *at 120 °C in toluene 2M for 24h. Conv. = Monomer conversion. [a] monomer conversion% determined from crude ^{1}H NMR spectrum. [b] $M_{n,th}$ (g/mol) = ([M]/[BnOH]) × MW(monomer) × (% conv.) + MW(end group). [c] Đ and M_n (g/mol) determined by gel permeation chromatography. Đ=dispersity=M_w/M_n. [d] conducted using a carousel reactor.*

Table S5 Addition of molecular sieves to the polymerisation of 5-MeDOX

Pore size	MS (W/V%)	Time (h)	Poly(lactic acid) (%)	Lactide (%)
None	/	7	84	12
3 Å	10	7	65	20
5 Å	10	7	67	26
10 Å	10	7	55	13
None	/	15	89	9
3 Å	10	15	75	11
5 Å	10	15	51	8
10 Å	10	15	79	13
None	/	13	88	7
3 Å	20	13	75	15
5 Å	20	13	71	15
10 Å	20	13	61	8

5-MeDOX:SA1:BnOH = 100:1:1. Conducted *at 120 °C in toluene under an atmosphere of static N_2*

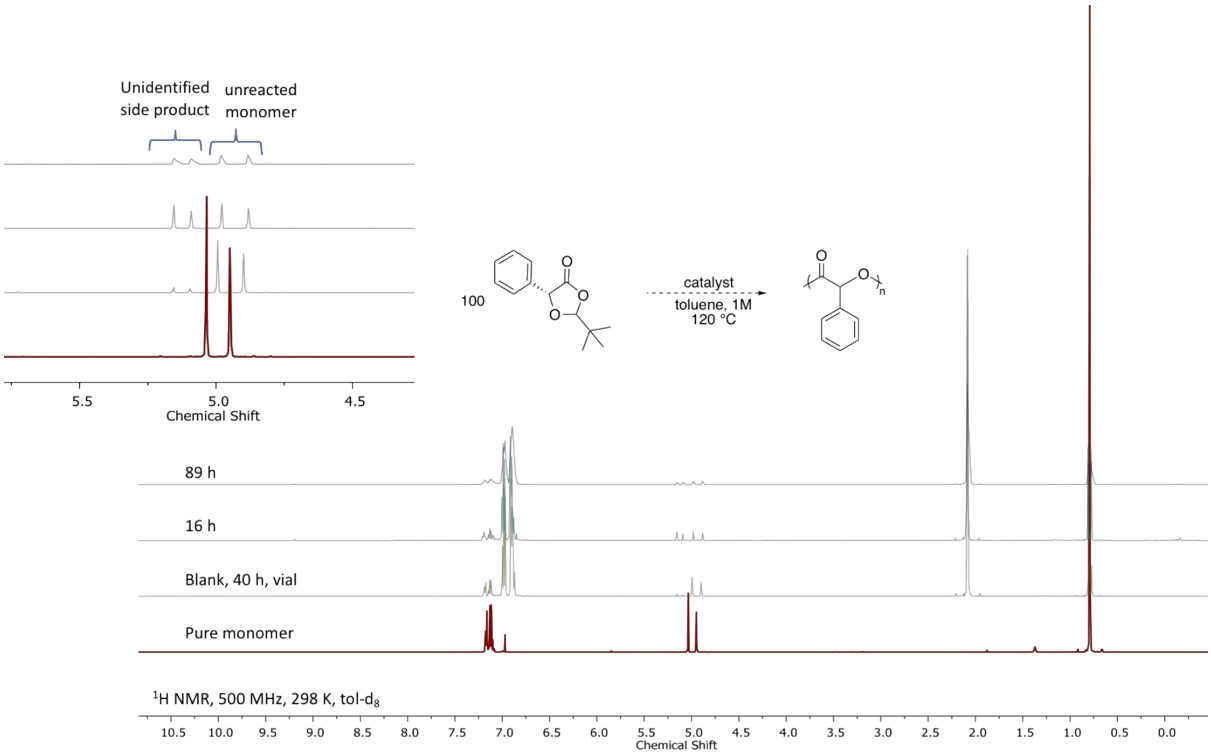


Figure S6 ^{1}H NMR spectral overlay of crude samples of reactions conducted using zinc bis(diketiminate) catalyst and initiated by benzyl alcohol. Unidentifiable product peaks are evident at ca. 5.1 ppm and 2.1 ppm. Blank reaction conduced in a 7 mL scintillation vial and sealed prior to heating in a preheated oil bath.

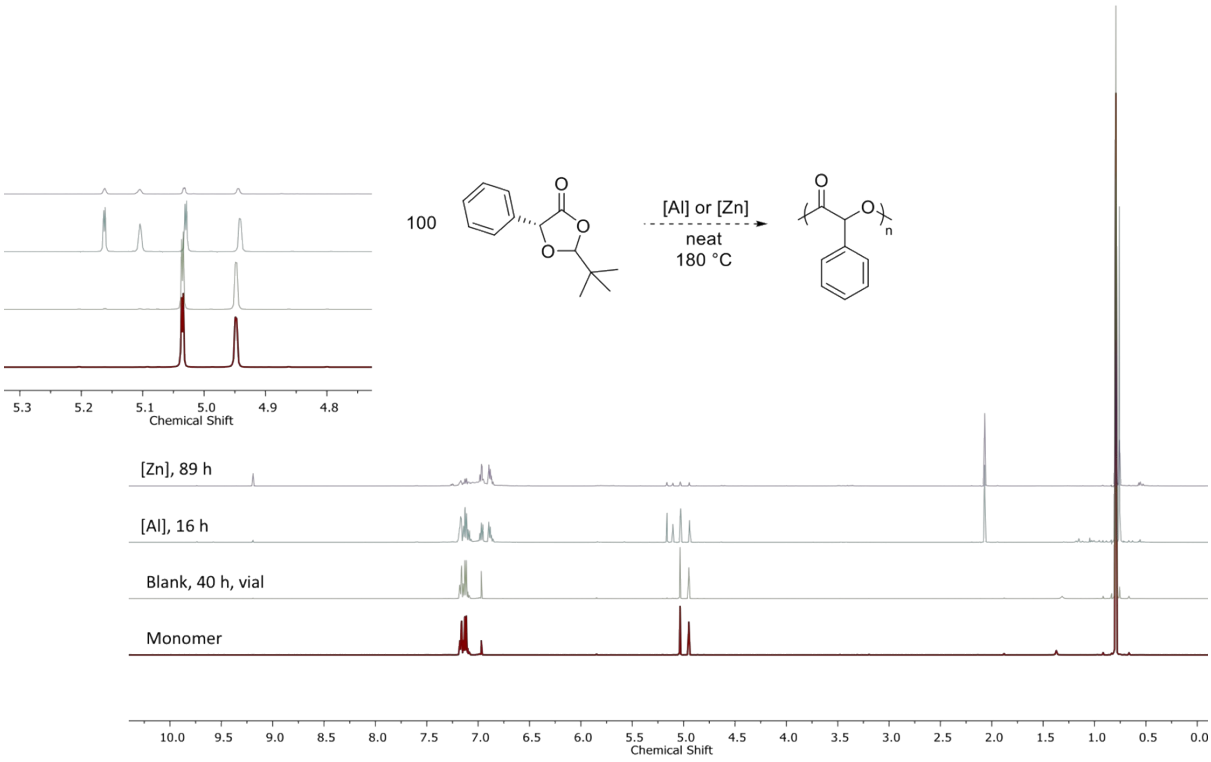


Figure S7 ^{1}H NMR spectral overlay of crude samples of reactions conducted using zinc bis(diketiminate) catalysts or aluminum salen catalyst SA2, initiated by benzyl alcohol. Blank reaction conduced in a 7 mL scintillation vial and sealed prior to heating in a preheated oil bath.

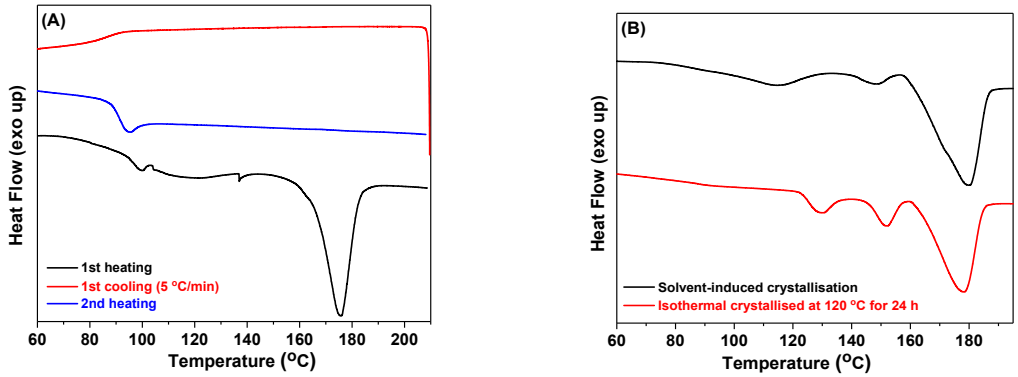
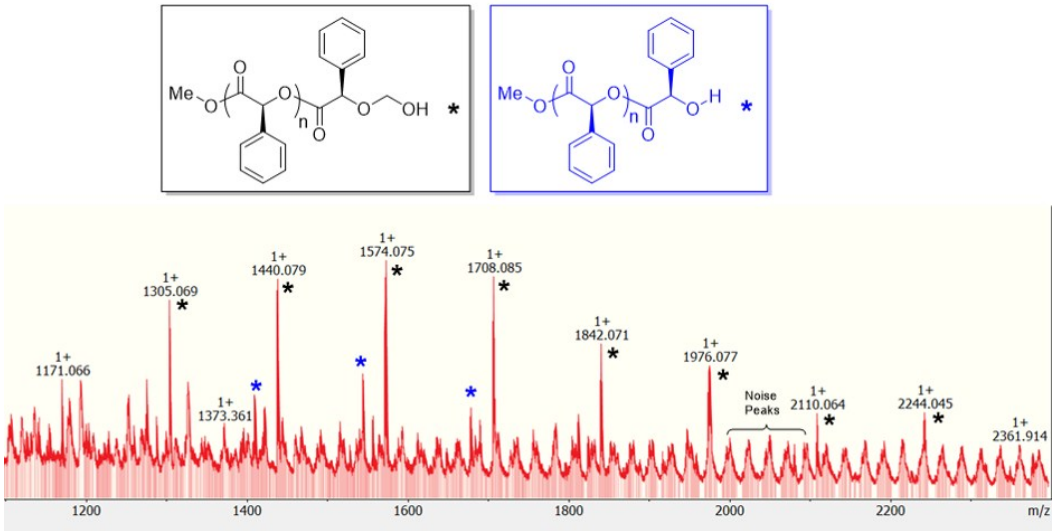


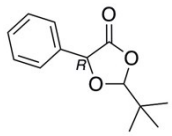
Figure S8 DSC curves of 5 °C/min slow-cooling process (A) and solvent-induced crystallisation / isothermal crystallisation PMAs (B)

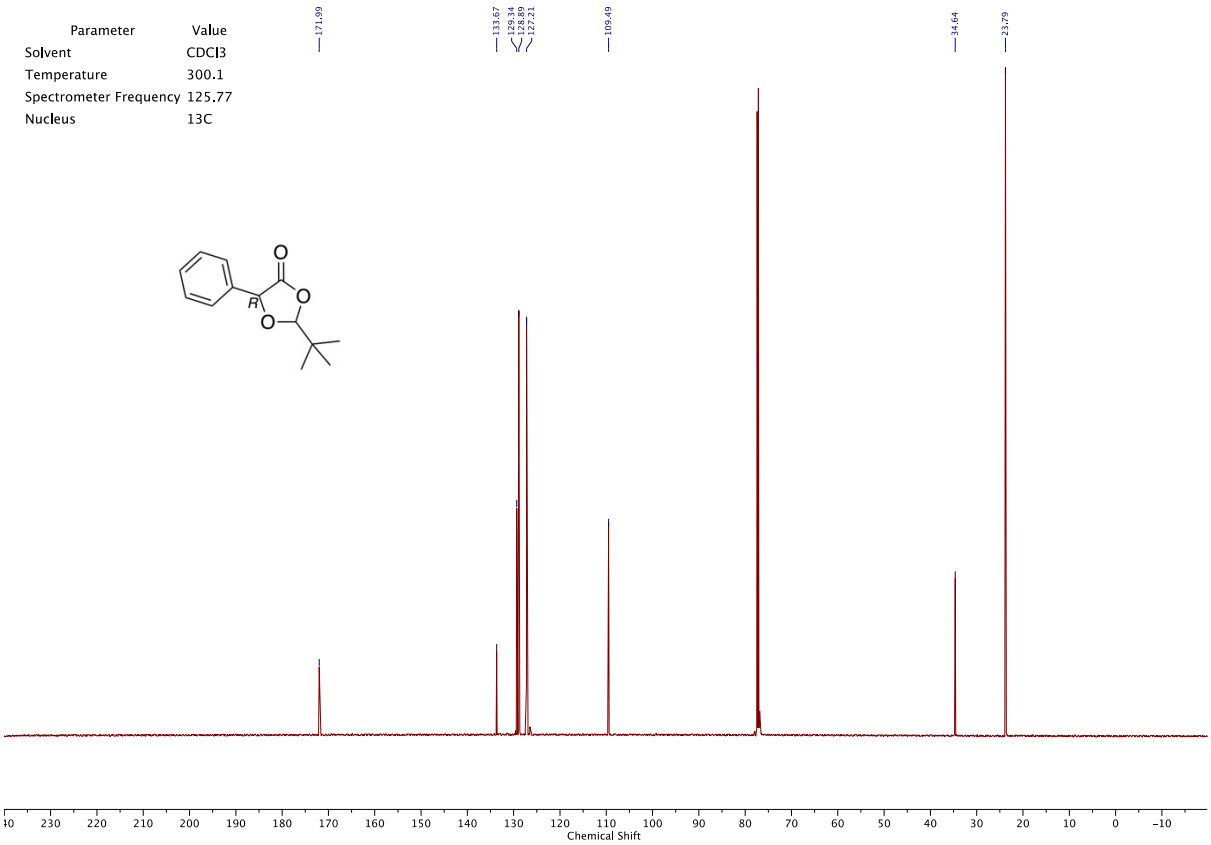
Figure S9 MALDI-ToF spectrum of PMA sample prepared under dynamic vacuum conditions. Note: the peaks between the major resonances are the noise peaks due to the low responses of the major peaks.



Selected spectra:

Parameter	Value
Solvent	CDCl3
Temperature	300.1
Spectrometer Frequency	500.12
Nucleus	1H





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