Supporting Information for

Waste not, want not: CO_2 (Re)cycling in Block Polymer Synthesis

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Experimental Section

Materials and Methods

Lithium-L-lactate, triphosgene, and diphosgene were purchased from Acros Organics and used as received. Cyclohexene oxide (CHO) was purchased from Acros Organics and dried, over CaH_2, distilled, degassed through freeze-pump-thaw cycles and stored under inert atmosphere (vinyl-cyclohexene oxide was also purified in the same way). L-Phenyllactic acid was purchased from Sigma Aldrich and used without further purification. Standard procedures were followed to dry THF, toluene, dichloromethane, and chloroform-d[1]. The catalyst $[LZn_2(OAc)_2]$,[1] L-lactide *O*-carboxyanhydride (LLAOCA),[2] and L-phenyllactide *O*-carboxyanhydride (LPheLAOCA)[3] were synthesized by the previously published methods.

NMR spectra were recorded on a Bruker AV-400 or on a Bruker AV-500 instrument. All spectra were processed using MestreNova or Topspin software. Elemental analyses were performed by Mr Stephen Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7. SEC analysis was carried out on a Shimadzu LC-20AD instrument, equipped with a Refractive Index (RI) detector and two PSS SDV 5 μm linear M columns. HPLC grade THF was used the eluent at 1.0 mL/min at 30 °C. Samples were passed through 0.2 μm PTFE filters prior to analysis. Monodisperse polystyrene standards were used for calibration. Narrow MW polystyrene standards were used to calibrate the instrument. All the DSC analyses were carried out in a Mettler Toledo instrument, with a heating-cooling rate of 10 °C per minute, from -40 to 200 °C. MALDI ToF analyses were performed in a MALDI Micro MX spectrometer, with dithranol as matrix (10 mg/mL) and sodium trifluoroacetic acid (10 mg/mL) as an additive. The polymer (ca. 10 mg/mL), the matrix and the additive were mixed in a ratio of 1/4/1 (v/v) in THF and 5 μL were spotted on the MALDI plate. All the analysis was performed in positive reflectron mode.

Synthesis of L-lactic acid *O*-carboxyanhydride (LLAOCA)[2]

A 250 mL three necked round bottom flask fitted with a dropping funnel charged with L-lactic acid lithium salt (3.50 g, 36.45 mmol) and anhydrous THF (50 mL). The resulting suspension was cooled to 0 °C. To this solution, triphosgene (3.97 g, 13.36 mmol) in anhydrous THF (15 mL) was slowly added, using a dropping funnel. The reaction mixture was allowed to stir for 3 h at room temperature. After the completion of the reaction the suspension became a clear solution. The THF was then removed to an additional solvent trap connected to Schenk line under reduced pressure. The remaining white solid was then redissolved in dichloromethane (20 mL) and filtered to another Schlenk flask using a cannula. The solution containing LLAOCA was precipitated from anhydrous pentane (100 mL). The solvent was then

removed using a cannula filtration. The product was crystallized from a dichloromethane/pentane binary mixture and sublimed before being used for polymerisation.

*****CAUTION**: Due to extremely high toxicity of phosgene, all reactions were conducted in an inert atmosphere and in a well-ventilatted fume cupboard. The residual solvent and all contaminated glassware was carefully quenched using an aq.NH_3/ethanol (1:1) solution. This procedure was followed for all other syntheses involving phosgene.

Isolated yield = 1.80 g, 44%

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.16 (q, 1H, C*H*), 1.76 (d, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 148.1, 76.2, 16.6. HRMS (m/z): Calcd $C_4H_4O_4$ requires 116.01 (M), found 117.0186 $(M+H)^+$.

Synthesis of L-phenyllactide *O*-carboxyanhydride (LPheLAOCA)[3]

To a slurry of L-phenyl lactic acid (5.00 g, 30.10 mmol) and activated charcoal (0.25 g) in anhydrous THF (30 mL), diphosgene (4.36 mL, 36.12 mmol) was added in portions. The resulting mixture was then allowed to stir at room temperature for 8 hours. This solution was then filtered to a Schlenk flask, through a plug of celite. The resulting clear solution was concentrated to ~10 mL and layered with pentane (50 mL) resulting in the precipitation of LPheLAOCA as a white solid. The OCA was crystallised from a THF/pentane mixture (v/v 5/50 mL). The isolated product was sublimed before polymerisation. Isolated yield 3.75 g, 65%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.20-7.42 (m, 5H, Ar-*H*), 5.30 (t, 1H, C*H*, *J* = 5 Hz), 3.20-3.42 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 148.1, 76.2, 16.6. ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz): 166.4, 147.9, 131.6, 129.8, 129.3, 128.5, 80, 36.5. HRMS (m/z): Calcd $C_{10}H_8O_4$ requires 192.04 (M), found 193.0502 $(M+H)^+$.

Representative polymerisation procedure for L-lactide-*O*-carboxyanhydride (LLAOCA) in tetrahydrofuran (THF)

[$LZn_2(OAc)_2$] (0.004 g, 0.005 mmol), LLAOCA (0.29 g, 2.50 mmol) were weighed to a 15 mL Schlenk tube, equipped with a magnetic stirring bar, and then tightly closed. The reaction mixture was then vigorously stirred, at 80 °C, for 16 h. At the end of the reaction an aliquot was taken for ^{1}H NMR spectroscopy to estimate the conversion and the product distribution. The remaining crude polymer solution was diluted with dichloromethane (2 mL) and then precipitated using cold pentane, the precipitate was filtered and the product dried under vacuum at 40 °C for 48 h.

Representative polymerisation procedure of L-lactide-*O*-carboxyanhydride (LLAOCA) in cyclohexeneoxide (CHO)

$[LZn_2(OAc)_2]$ (0.004 g, 0.005 mmol), LLAOCA (0.29 g, 2.50 mmol), and cyclohexene oxide (1.97 g, 19.47 mmol) were weighed to a 15 mL Schlenk tube, equipped with a magnetic stirring bar, and then tightly closed. The reaction mixture was then vigorously stirred at 80 °C for 16 h. At the end of the reaction an aliquot was taken for ^{1}H NMR spectroscopy to estimate the conversion and the product distribution. The remaining crude polymer solution was diluted with dichloromethane (2 mL) and the polymer by adding excess cold pentane. The solution was filtered and the product dried under vacuum at 40 °C for 48 h.

Online reaction monitoring of LLAOCA/CHO polymerisation using ATR IR spectroscopy

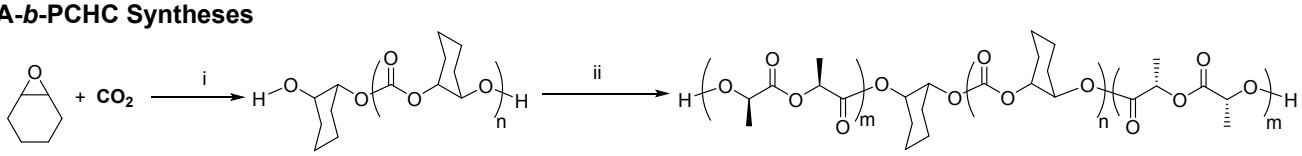
A 50 mL three necked Schlenk tube was equipped with a Mettler-Toledo ReactIR 4000 spectrometer, with a MCT detector, and a silver halide DiComp probe. To a pre-connected and vacuum dried three necked flask, LLAOCA (0.90 g, 7.76 mmol), $[LZn_2(OAc)_2]$ (0.012 g, 0.016 mmol) and CHO (6.20 mL, 61.42 mmol). The reaction mixture was immediately immersed in a in a pre-heated oil bath at 80 °C. The polymerisation was then monitored for 54 h. IR resonances corresponding to LLAOCA, PLLA, PCHC and CO_2 were monitored.

***In situ* reaction monitoring of LLAOCA/CHO polymerisation using ^{1}H NMR spectroscopy**

$[LZn_2(OAc)_2]$ (0.0025 g, 0.0031 mmol), LLAOCA (0.18 g, 1.57 mmol), cyclohexene oxide (0.67 mL, 6.90 mmol), THF-d_8 (0.51 mL) and mesitylene (0.044 mL) were weighed to a vial and immediately transferred in to a 1 mL J Young NMR tube and tightly sealed. The tube was then inserted to a previously shimmed and heated NMR instrument (Bruker 500 MHz). The first ^{1}H NMR spectrum of this reaction mixture was recorded after 2 minutes at 80 °C. The polymerisation was monitored by measuring ^{1}H NMR spectra at regular time intervals over 53 h. The conversion was determined by comparison of resonances assigned to LLAOCA (1.76 ppm), PLLA (1.56 ppm), PCHC (4.92–4.18 ppm), and *trans*-CHC (4.02 ppm). Mesitylene (6.57 ppm) was used as an internal standard.

PLA-*b*-PCHC Syntheses

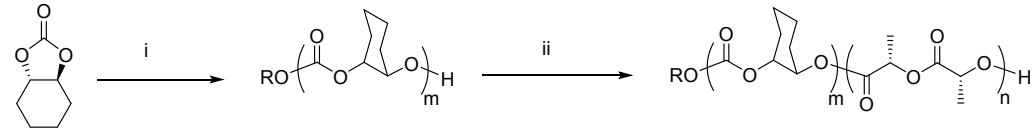
A.



Conditions: i) **1**, CO_2 = 1 bar; ii) **2**, L-lactide

Poly(L-lactide-*b*-cyclohexene carbonate-*b*-L-lactide)

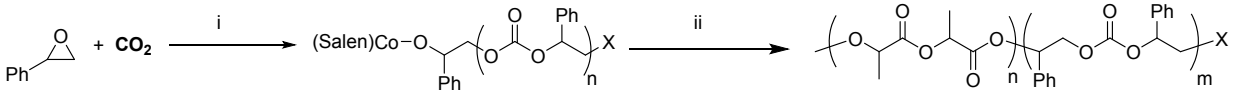
B.



Conditions: i) 3/BnOH; ii) **3**/BnOH, L-lactide

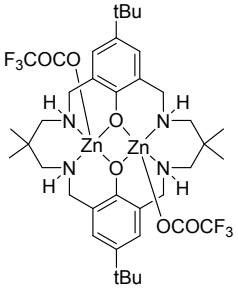
Poly(cyclohexene carbonate-*b*-L-lactide)

C.



Conditions: i) **4** ; ii) **5**, H_2O, Lactide

Poly(styrene carbonate-*b*-lactide)



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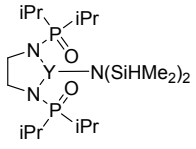

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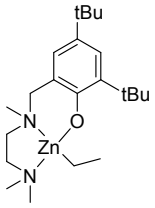

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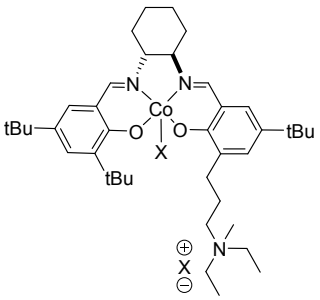

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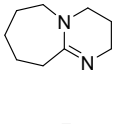
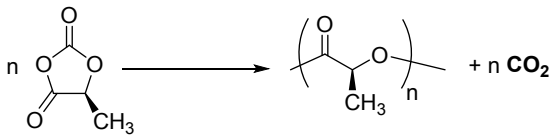


5

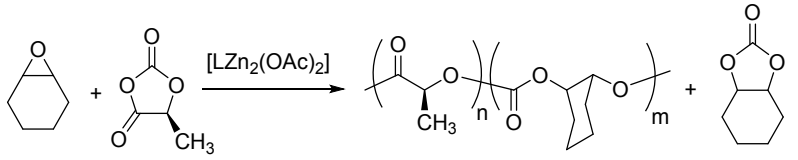
Scheme S1: Previously reported methods to prepare poly(ester-*b*-carbonate) AB or ABA type block copolymers.[4-6]



LLAOCA PLLA

Scheme S2: Ring opening polymerisation of LLAOCA using $[LZn_2(OAc)_2]$.

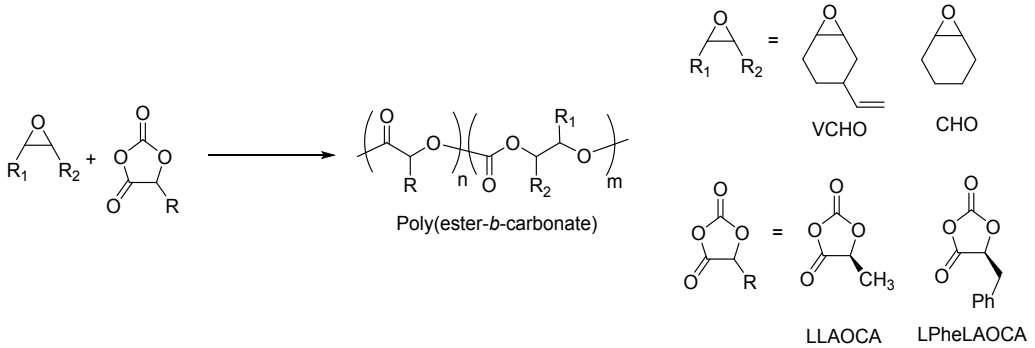
Table S1: Selective polymerisation of LLAOCA and CHO to produce PLLA-*b*-PCHC [a]



Entry	Time (h)	LLAOCA Conv (%) [b]	PCHC (%) [c]	*trans*-CHC (%) [d]	Polymer	$M_{n,exp}$ ($M_{n,calc}$) g mol^{-1} [e]	Đ [e]	*DP* [f] PLLA/PCHC
1 [g]	16	97	-	-	PLLA	4300 (17,500)	1.15	101/-
2 [h]	16	>99	0	0	PLLA	4100 (18,000)	1.98	97/-
3	0.16	23	0	0	PLLA	2800 (4100)	1.66	38/0
4	1	>99	8	0	PLLA-*b*-PCHC	4600	1.33	56/6
5	8	>99	17	1	PLLA-*b*-PCHC	7600	1.30	78/14
6	16	>99	53	1	PLLA-*b*-PCHC	8400	1.24	76/20
7	24	>99	71	2	PLLA-*b*-PCHC	11000	1.54	88/33
8	48	>99	91	9	PLLA-*b*-PCHC	13600	1.45	90/35

[a] All the polymerisations were conducted in a 15 mL Schlenk tube in THF, THF-CHO mixture or in neat CHO, [LLAOCA] = 1.25 M, [$LZn_2(OAc)_2$] = 2.5 mM. [b] Determined by ^{1}H NMR spectroscopy from the normalized integrals for resonance from LLAOCA (1.76 ppm) and PLLA (1.56 ppm). [c] Determined by ^{1}H NMR spectroscopy of crude polymerisation sample from the normalized integrals for resonance from PLLA (1.56 ppm) and PCHC (4.92 – 4.18 ppm). [d] *trans*-CHC = cyclohexene carbonate, determined by ^{1}H NMR spectroscopy from the normalized integrals for resonance from PLLA (1.56 ppm) and *trans*-CHC (4.02 ppm). [e] Determined by SEC in THF, calibrated with narrow polydisperse polystyrene standards. $M_{n,calc}$ values are reported only for PLLA using $M_{n,calc}$ = [Degree of Polymerisation x 72]/2. Note equivalent calculations for block polymers are not considered informative since it is not possible to properly compare experimental and calculated values as the block polymer composition changes with conversion. [f] DP is degree of polymerisation and is determined using ^{1}H NMR spectroscopy by comparing the relative intensity of integrals from PLLA (1.56 ppm) and PCHC (4.92 – 4.18 ppm) (using the isolated polymer sample). [g] Polymerisation conducted in THF, [$LZn_2(OAc)_2$]/[LLAOCA] = 500, [LLAOCA] = 1.25 M. [h] Polymerisation conducted in THF-CHO mixture with [$LZn_2(OAc)_2$]/[LLAOCA]/[CHO] = 1/500/500, [LLAOCA] = 1.25 M in THF-CHO mixture.

Table S2: Polymerisation of other OCAs and epoxides [a]



Entry	Epoxide	OCA	OCA Conv (%) [b]	PC (%) [c]	CC (%) [d]	Polymer	$M_{n,exp}$ g mol^{-1} [e]	Đ [e]
1	VCHO	LLA	>99	>99	0	PLLA-*b*-PVCHC	6100	2.18
2	CHO	LPheLLA	>99	68	13	PLPheLA-*b*-PCHC	2500	1.31

[a] All the polymerisations were conducted in a 15 mL Schlenk tube, neat epoxide, [OCA] = 1.25 M, 48 h. VCHO = 4-vinyl 1,2-cyclohexene oxide. [b] Determined by ^{1}H NMR spectroscopy from the normalized integrals for resonance from LLAOCA (1.76 ppm) and PLLA (1.56 ppm). [c] PC = polycarbonate, determined by ^{1}H NMR spectroscopy from the normalized integrals for resonance from PLLA (1.56 ppm) and PCHC (4.92–4.18 ppm). [d] CC = cyclic carbonate, determined by ^{1}H NMR spectroscopy from the normalized integrals for resonance from PLLA (1.56 ppm) and *trans*-CHC (4.02 ppm). [e] Determined by SEC, in THF, calibrated with narrow dispersity polystyrene standards.

Table S3: DSC analysis of polymer samples

Entry	Polymer	$M_{n,exp}$ g mol^{-1} [a]	Đ[a]	$T_{g,\,exp}$ °C [b]	$T_{g,\,calc}$ °C [c]	*Ester (W_1)/Carbonate (W_2) Wt %* [d]
1	PLLA	4300	1.15	57	57	100/0
2	PLLA-*b*-PCHC	7600	1.30	61	66	74/26
3	PLLA-*b*-PCHC	8400	1.26	69	69	66/34
4	PLLA-*b*-PCHC	11000	1.54	73	72	60/40
5	PLLA-*b*-PCHC	13500	1.45	78	77	52/48
6 [e]	PLLA-*b*-PVCHC	6100	2.18	74	-	-
7	PLPheLA	4000	1.13	33	33	100/0
8	PLPheLA-*b*-PCHC	2500	1.31	32	45	62/38

[a] Determined by SEC in THF, calibrated with narrow dispersity polystyrene standards. [b] Determined by DSC at a heating rate of 10 °C per minute, from -40 to 200 °C. [c] Calculated $T_{g,\,calc}$ determined using the Fox-Flory equation $(1/T_g) = (W_1/T_{g,1}) + (W_2/T_{g,2})$, where W_1 and W_2 are the weight fractions of ester and carbonate blocks, $T_{g,1}$ and $T_{g,2}$ are the glass transition temperatures of PLLA (57 °C) and PCHC (122 °C). [d] Determined by ^{1}H NMR spectroscopy. [e] The sample could not be characterised due to the overlap of methine resonances attributed to PLLA and PVCHC.

Characterisation of compounds

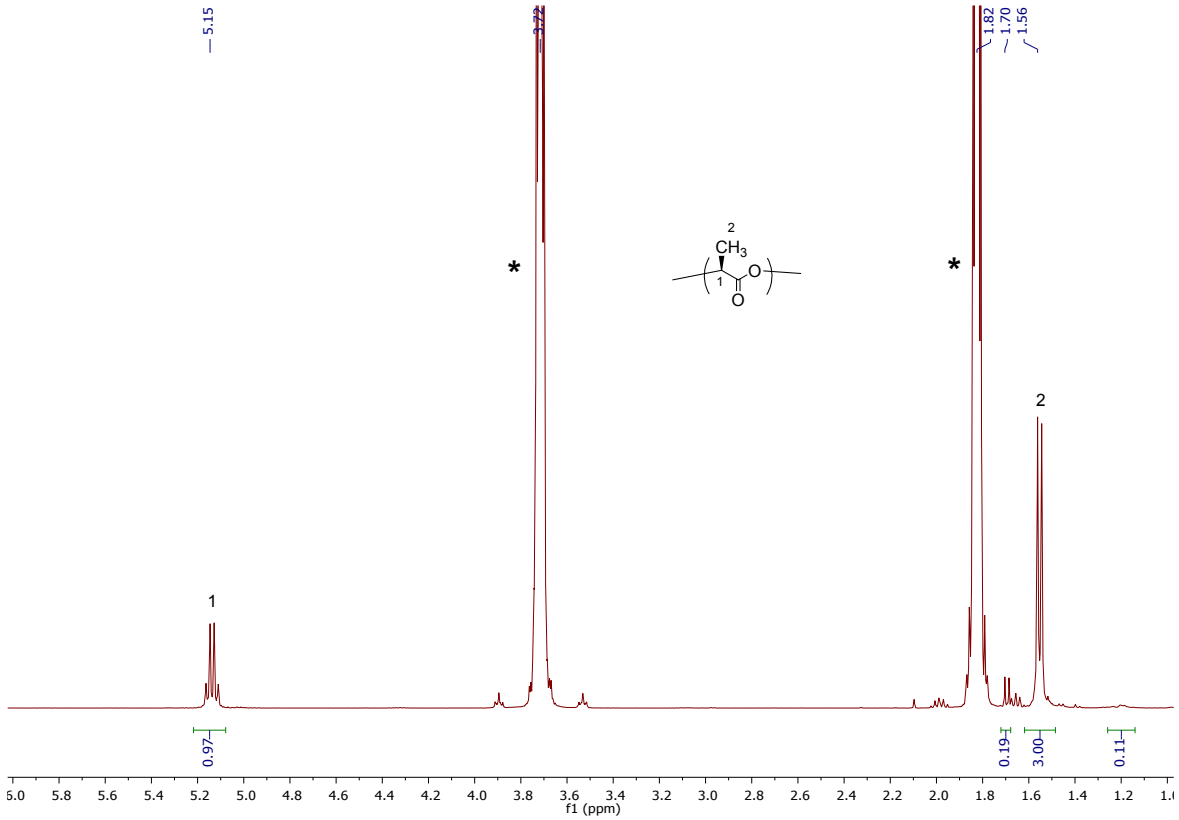


Figure S1: ^{1}H NMR spectrum of the crude product from the ROP of LLAOCA using [$LZn_2(OAc)_2$] in THF ($CDCl_3$, 400 MHz). * THF.

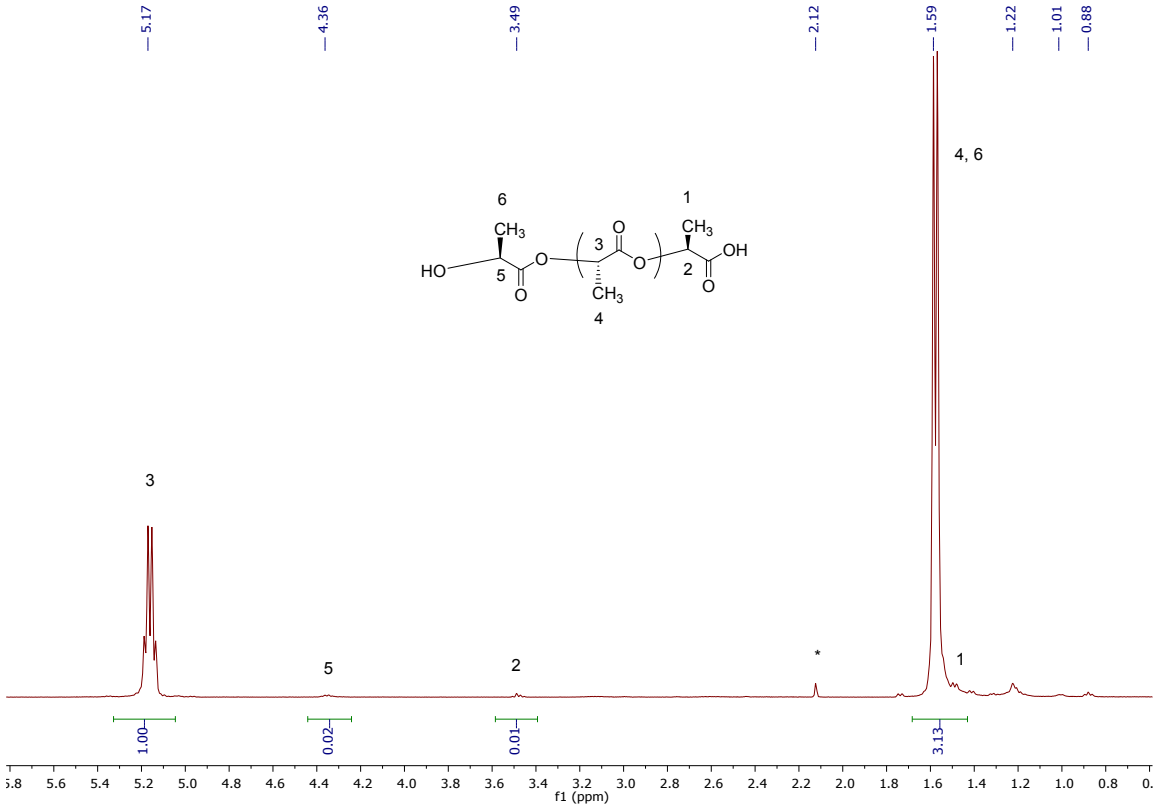


Figure S2: ^{1}H NMR spectrum of the isolated PLLA obtained from the ROP of LLAOCA using [$LZn_2(OAc)_2$] in THF (Table 1, Entry 1) ($CDCl_3$, 400 MHz). * Solvent.

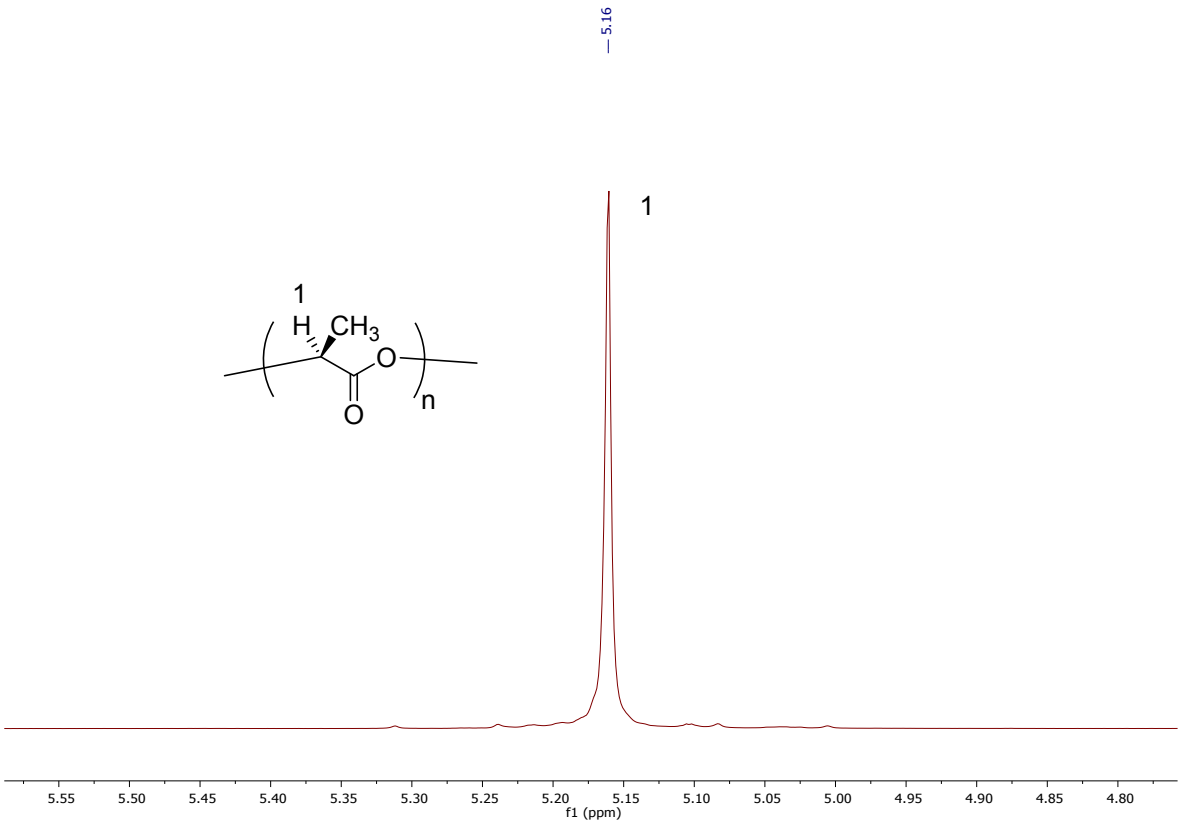


Figure S3: $^{1}H\{^{1}H\}$ NMR spectrum of the isolated PLLA, obtained from the ROP of LLAOCA using $[LZn_2(OAc)_2]$ in THF (Table 1, Entry 1) ($CDCl_3$, 500 MHz).

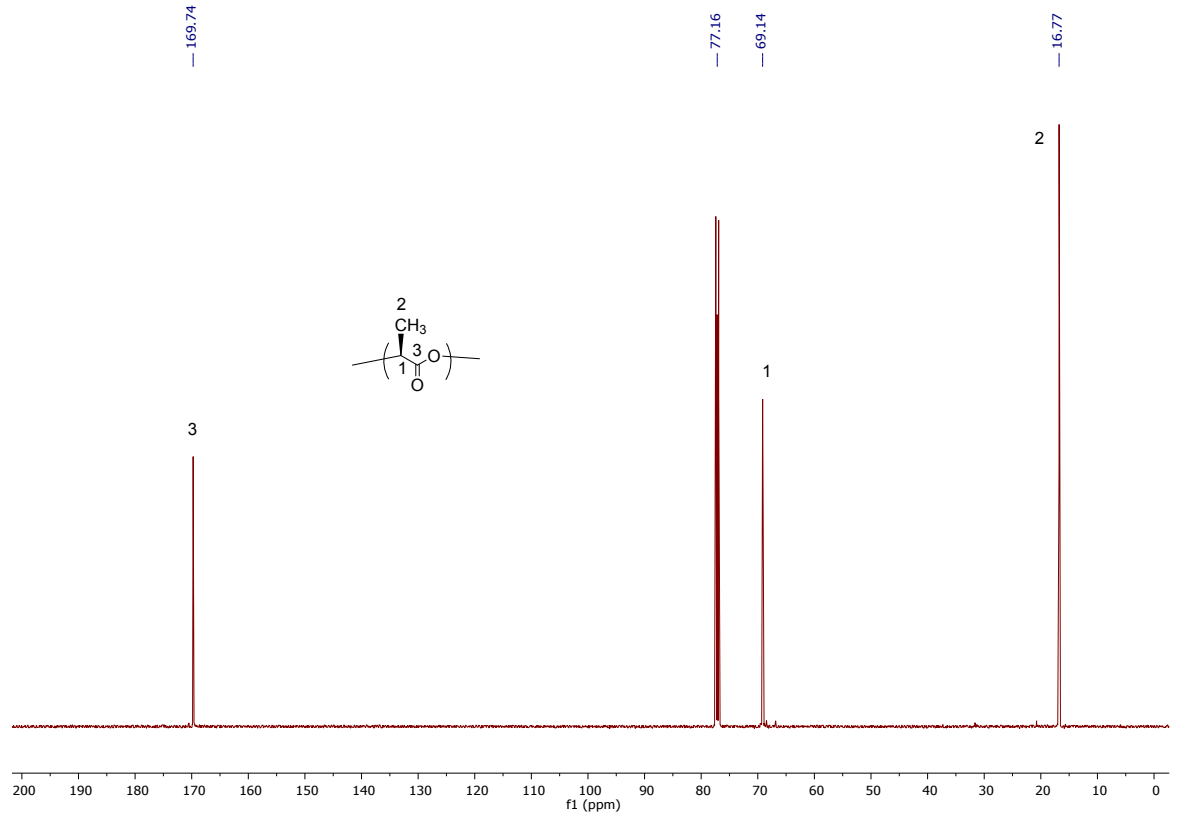


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of the isolated PLLA, obtained from the ROP of LLAOCA using $[LZn_2(OAc)_2]$ in THF (Table1, Entry 1) ($CDCl_3$, 125 MHz).

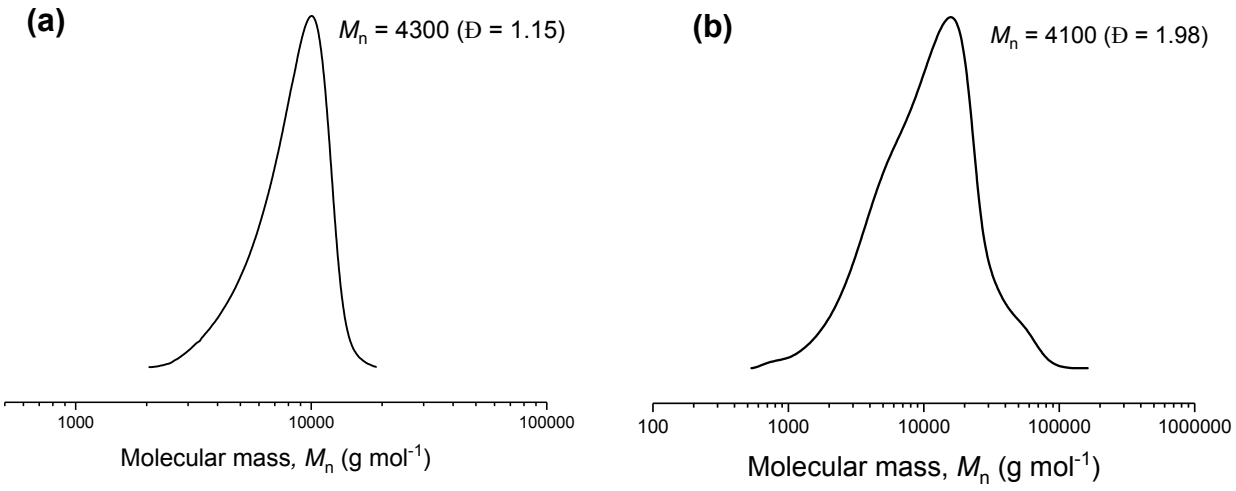


Figure S5: SEC analysis of polymers (a) PLLA from LLAOCA ROP in THF (Table 1, Entry 1); (b) PLLA from LLAOCA ROP in THF and CHO (Table 1, Entry 2).

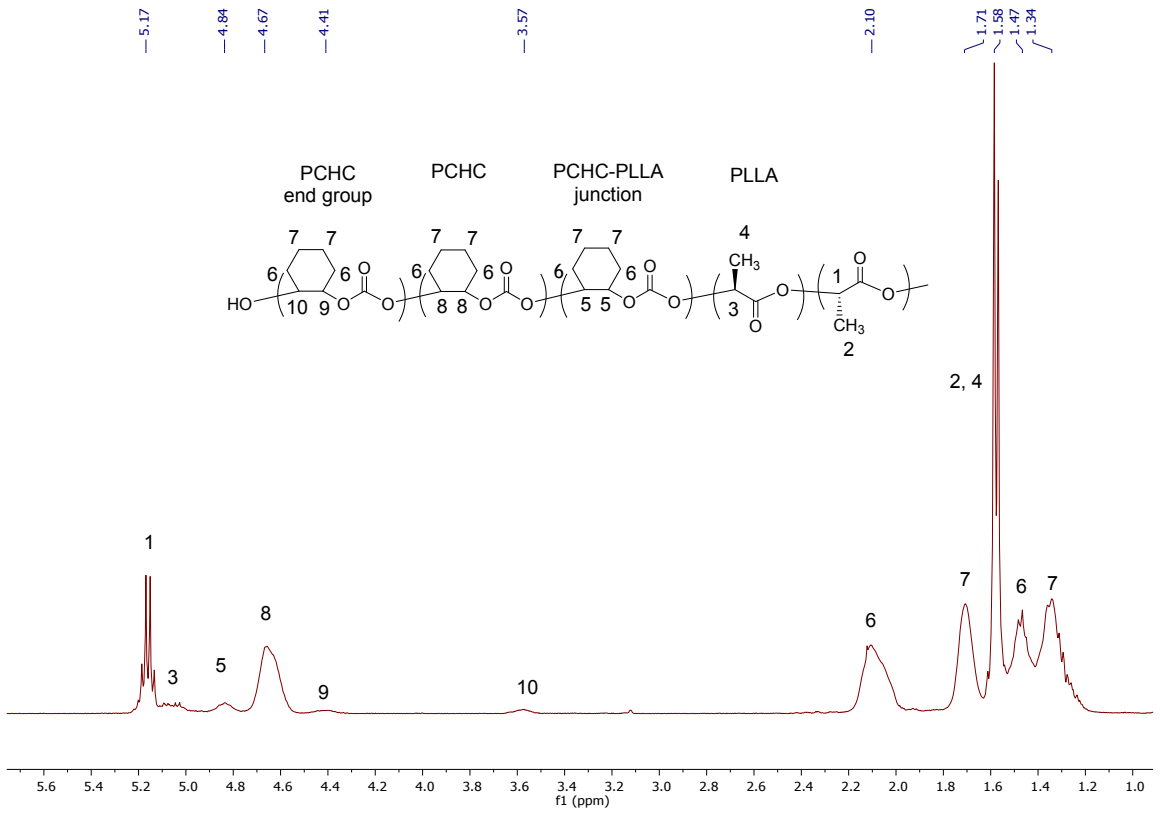


Figure S6: ^{1}H NMR spectrum of the isolated polymer PCHC-*b*-PLLA. (Table 1, Entry 7) ($CDCl_3$, 500 MHz).

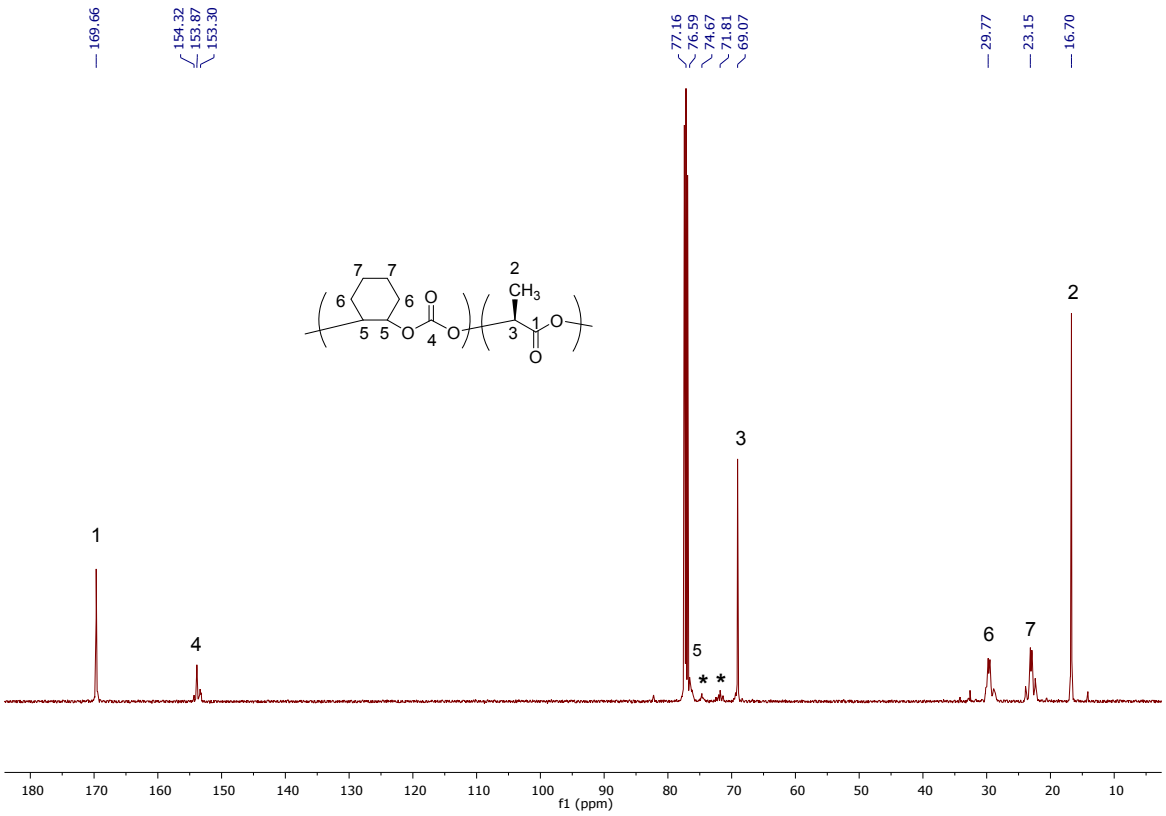


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of the isolated polymer PCHC-*b*-PLLA, (Table 1, Entry 7) ($CDCl_3$, 125MHz). * PLLA-*b*-PCHC junction units.

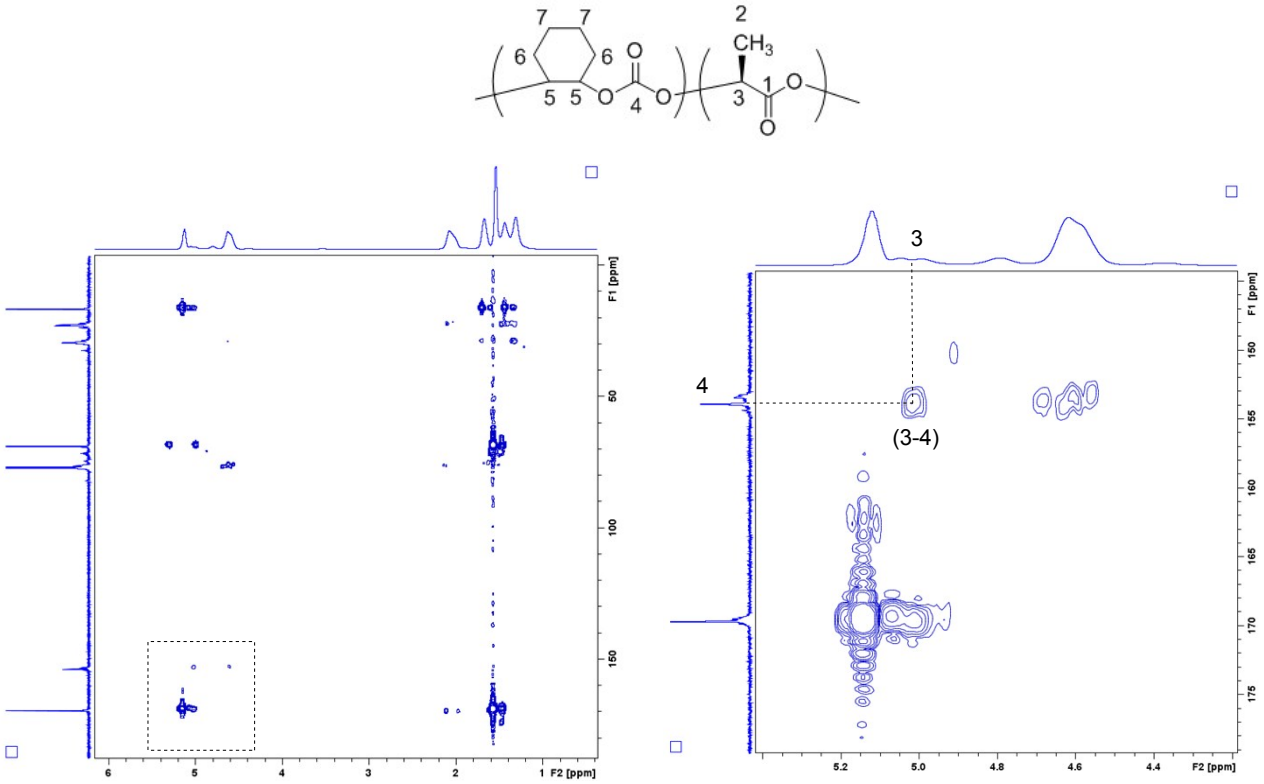


Figure S8: HMBC spectrum of PLLA-*b*-PCHC (Table 1, Entry 7).

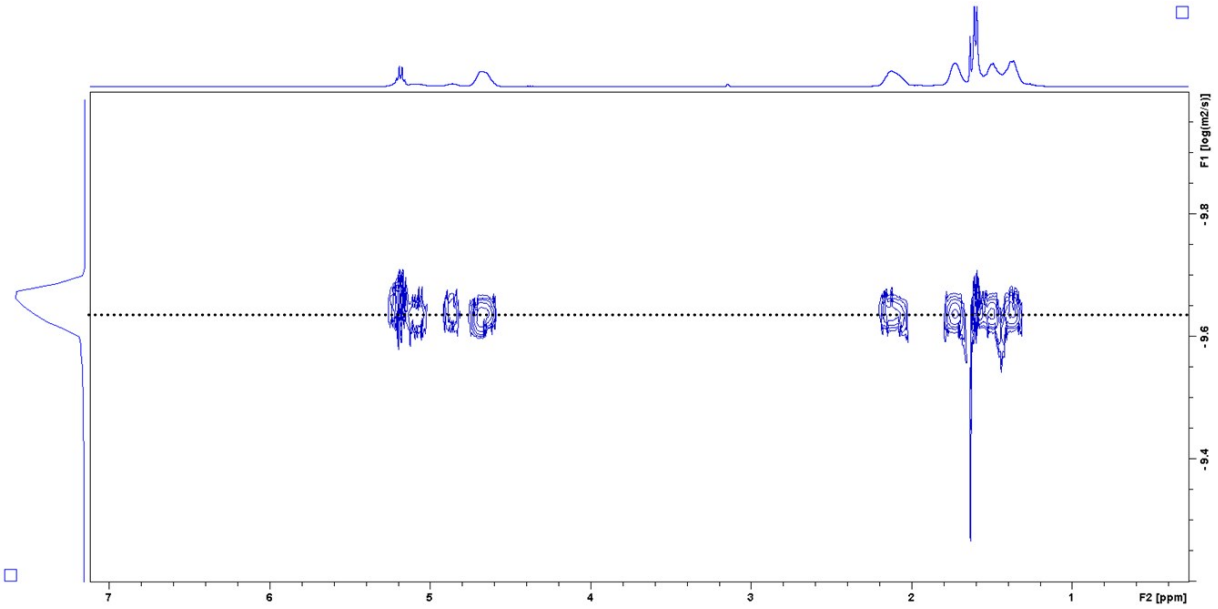


Figure S9: ^{1}H DOSY NMR spectrum of PLLA-*b*-PCHC (Table 1, Entry 7).

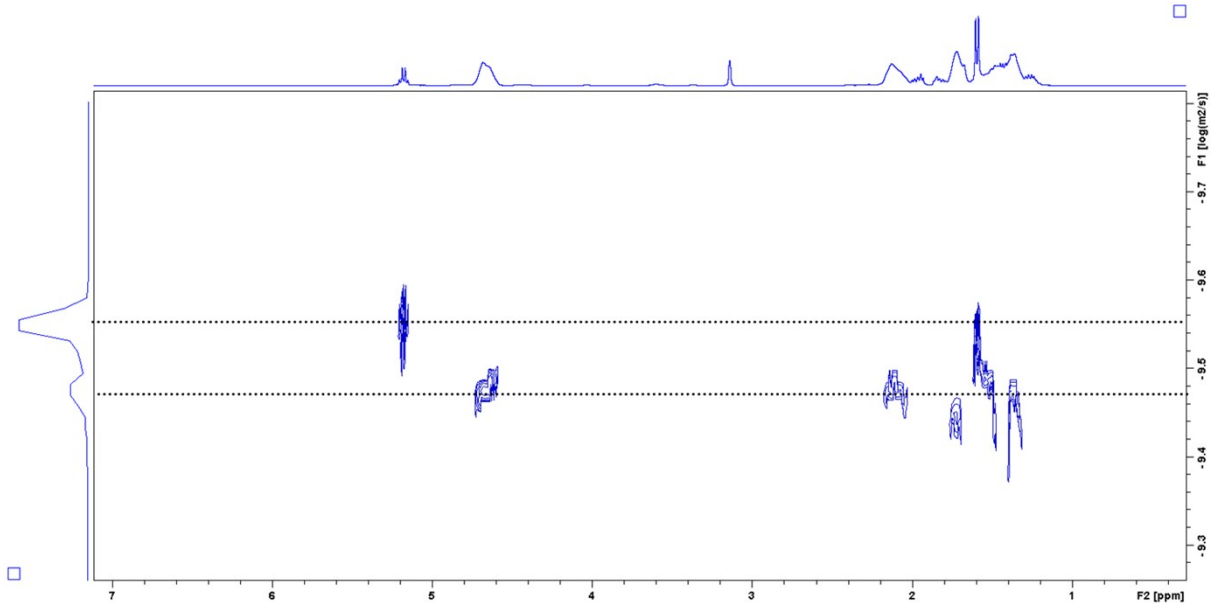


Figure S10: ^{1}H DOSY NMR spectrum of a physical mixtures of PLLA (M_n = 7000 g mol^{-1}) and PCHC (M_n = 4000 g mol^{-1}) ($CDCl_3$, 400 MHz).

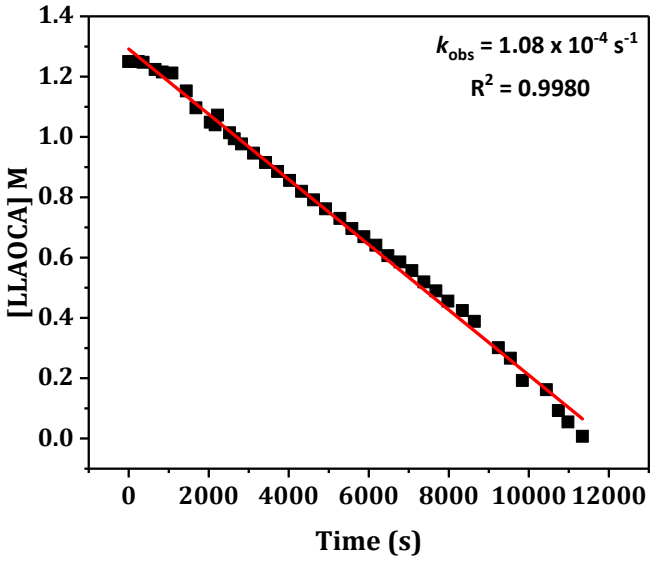


Figure S11: Plot of [LLAOCA] vs time. Reaction conditions: $[LLAOCA]_0$ = 1.25 M, $[CHO]_0$ = 5.5 M, $[LZn_2(OAc)_2]$/[LLAOCA]= 1/500, 80 °C. The linear fit indicates zero order reaction in [LLAOCA].

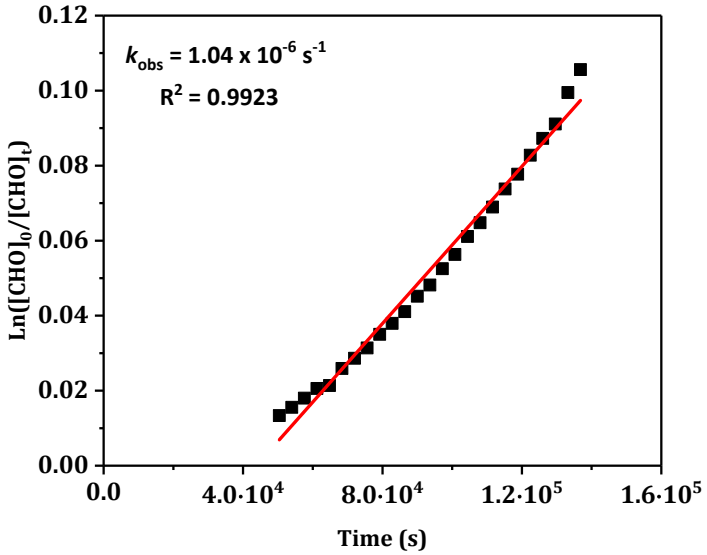


Figure S12: Plot of Ln{$[CHO]_0/[CHO]_t$} vs time. $[LLAOCA]_0$ = 1.25 M, $[CHO]_0$ = 5.5 M, $[LZn_2(OAc)_2]$/[LLAOCA]= 1/500, 80 °C. The linear fit indicates a first order dependence in [CHO], with a k_{obs} = 1.04 x 10^{-6} s^{-1}. Note that the curvature indicates relatively slow initiation.

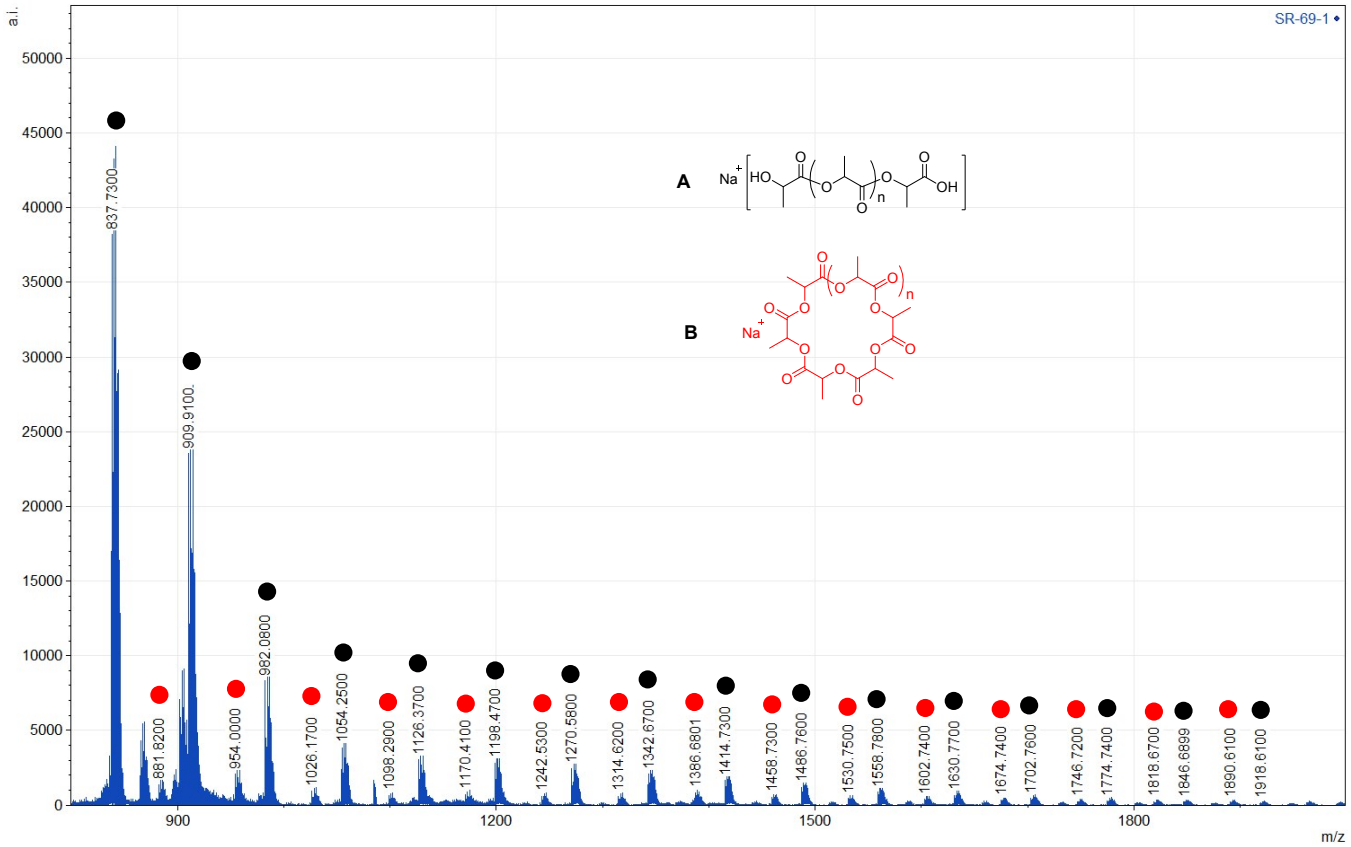


Figure S13: MALDI-ToF spectrum of the isolated PLLA. Reaction conditions: $[LLAOCA]_0$ = 1.25 M, $[LZn_2(OAc)_2]/[LLAOCA]$= 1/500, 80 °C (Table 1, Entry 1). Series A has a repeat unit m/z = 90.02 (lactic acid + $(72)_n$ (PLLA) + 22.98 (Na^+), where n = 11-25. Series B follows m/z = $(72)_n$ (PLLA) + 22.98 (Na^+), where n = 12-26.

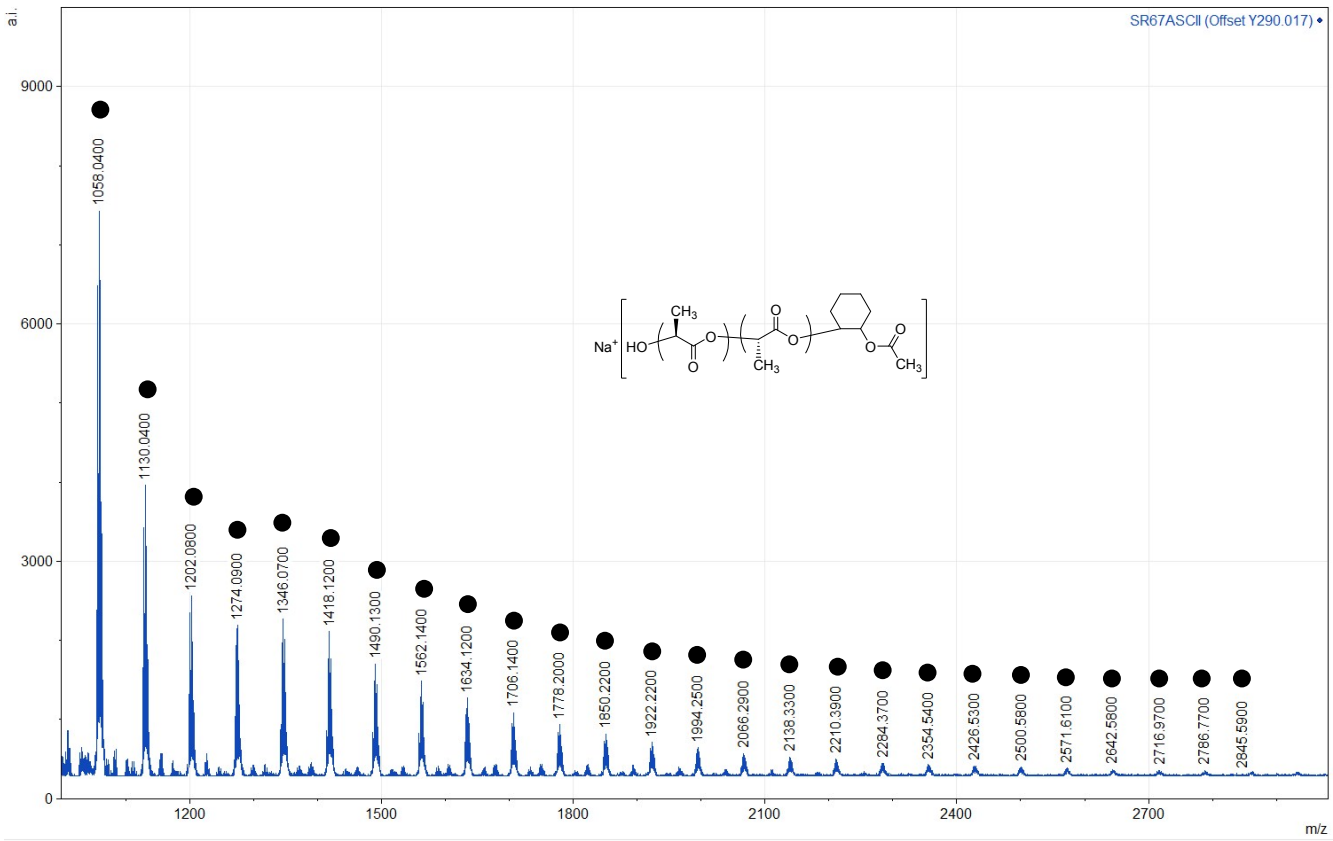


Figure S14: MALDI-ToF spectrum of PLLA with a cyclohexyl acetate end group. Reaction conditions: $[LLAOCA]_0$ = 1.25 M, $[LZn_2(OAc)_2]/[LLAOCA]$ = 1/500, 80 °C, 10 min (Table 1, Entry 3). The series follows m/z = 157.01 (cyclohexyl acetate) + $(72)_n$ (PLLA) + 22.98 (Na^+), where n = 9-37.

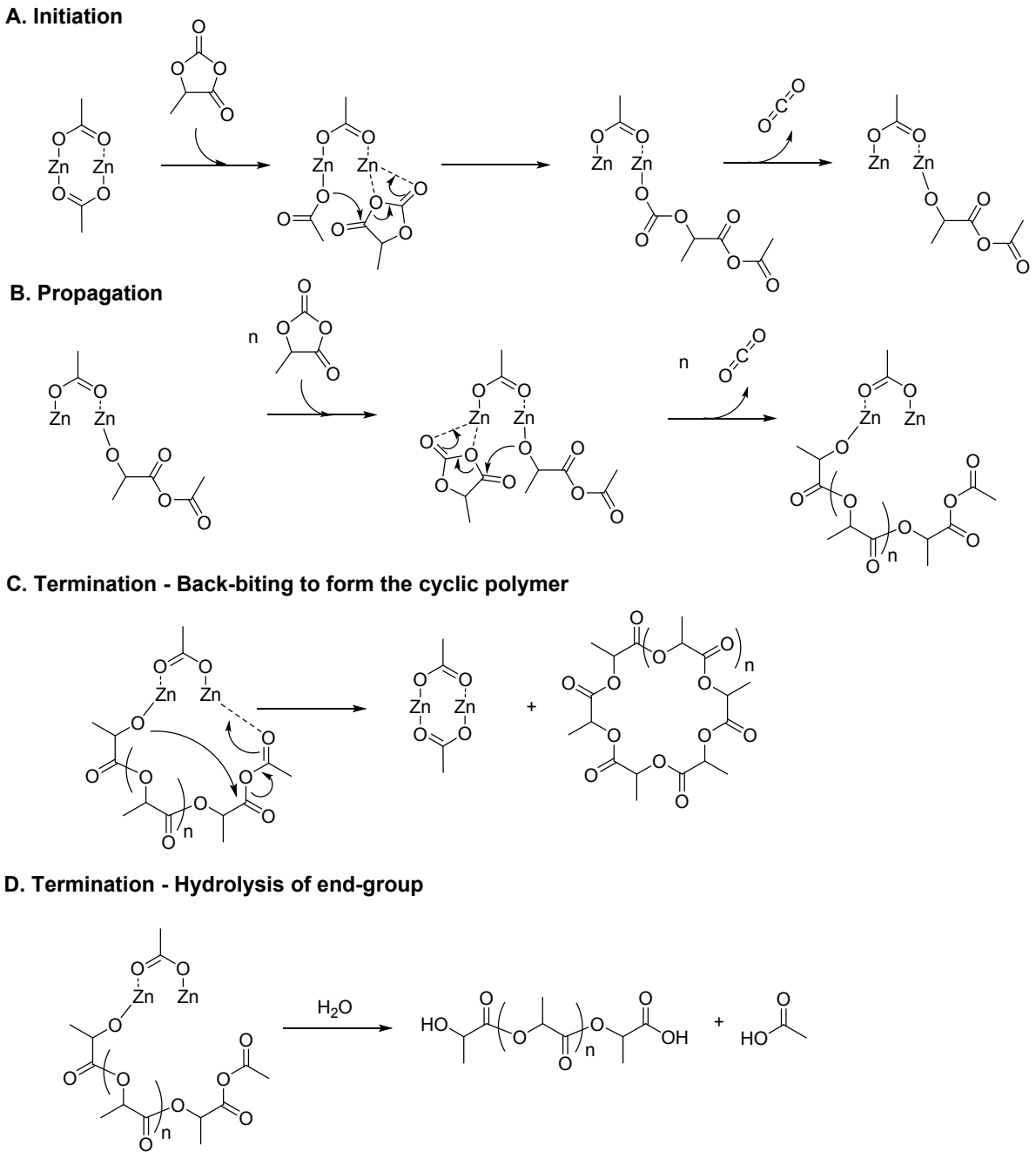


Figure S15: Illustrates the proposed initiation, propogation and termination pathways of LLAOCA polymerisation in THF using $[LZn_2(OAc)_2]$ to produce cyclic and linear PLLA. Note that for clarity the ligand is not shown.

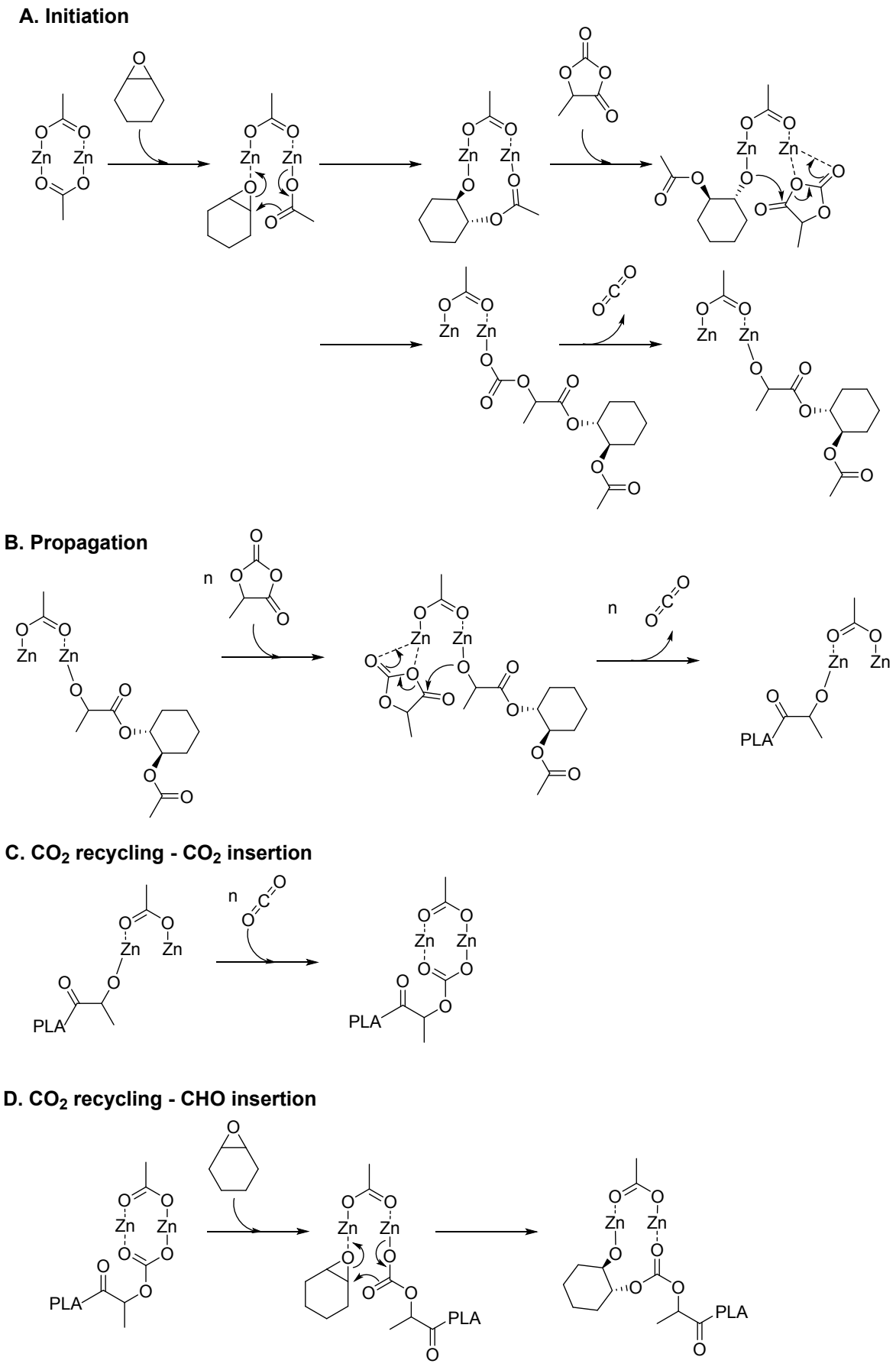


Figure S16: Illustrates the proposed initiation, propogation and CO_2 recycling pathways of LLAOCA-CHO selective polymerisation to produce PLLA-*b*-PCHC.

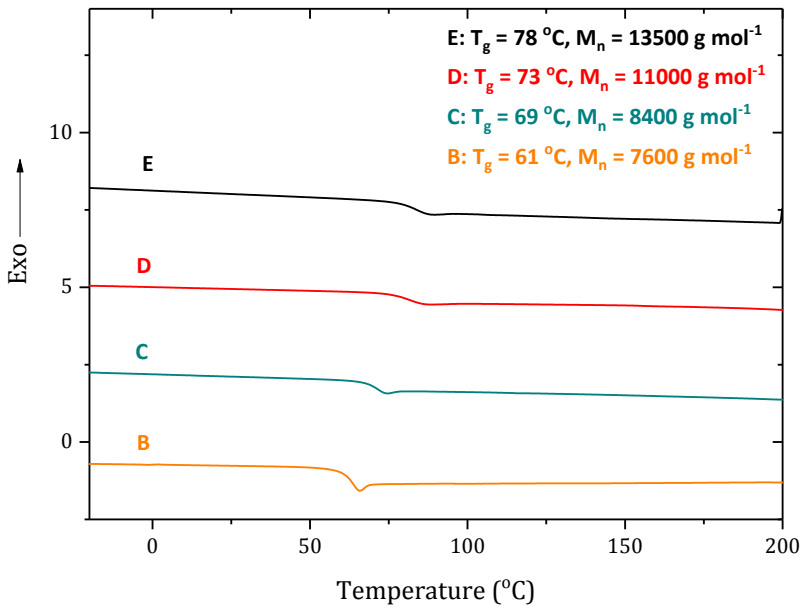


Figure S17: DSC thermograms of PLLA-*b*-PCHC with different molar masses (Table S3).

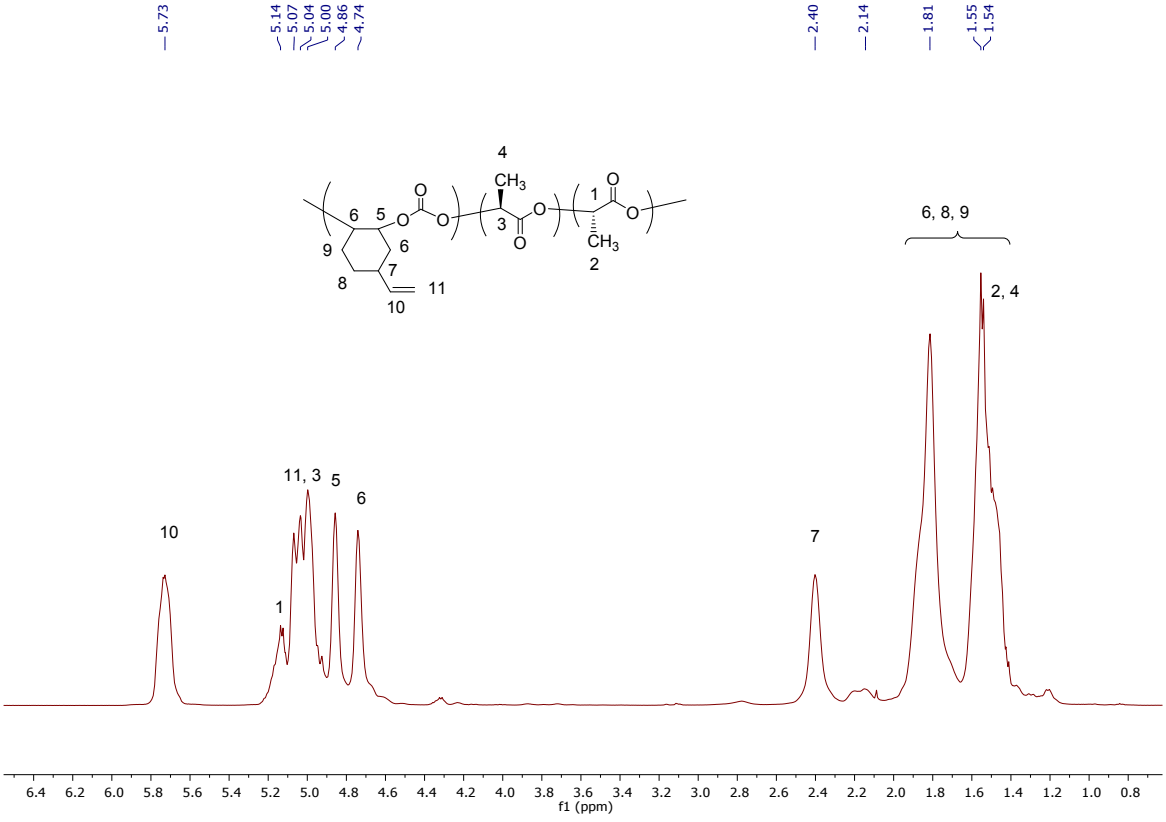


Figure S18: ^{1}H NMR spectrum of isolated PLLA-*b*-PVCHC, with M_n = 6100 g mol^{-1} ($CDCl_3$, 500 MHz).

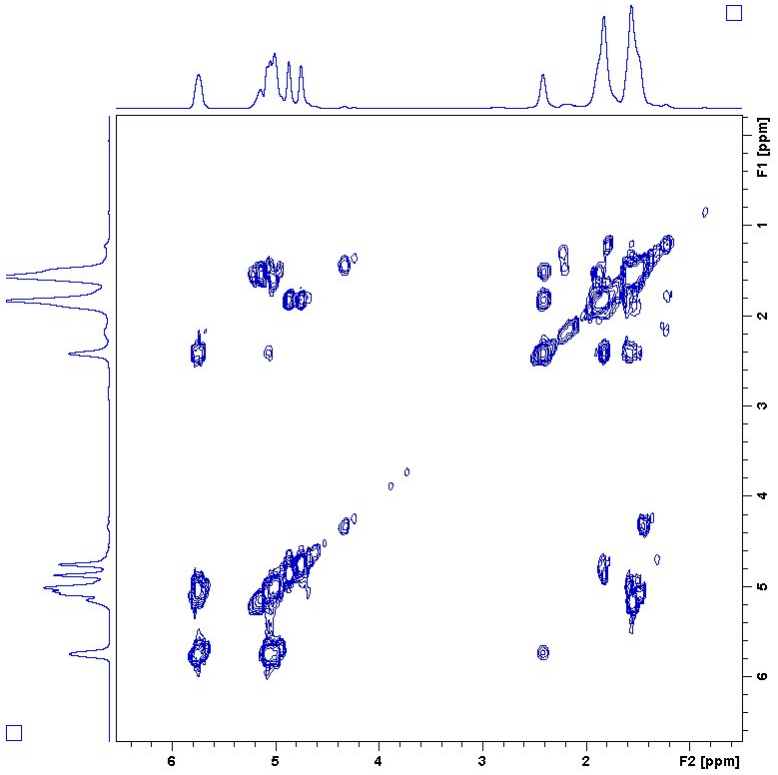


Figure S19: COSY NMR spectrum of PLLA-*b*-PVCHC, with M_n = 6100 g mol^{-1} ($CDCl_3$, 500 MHz).

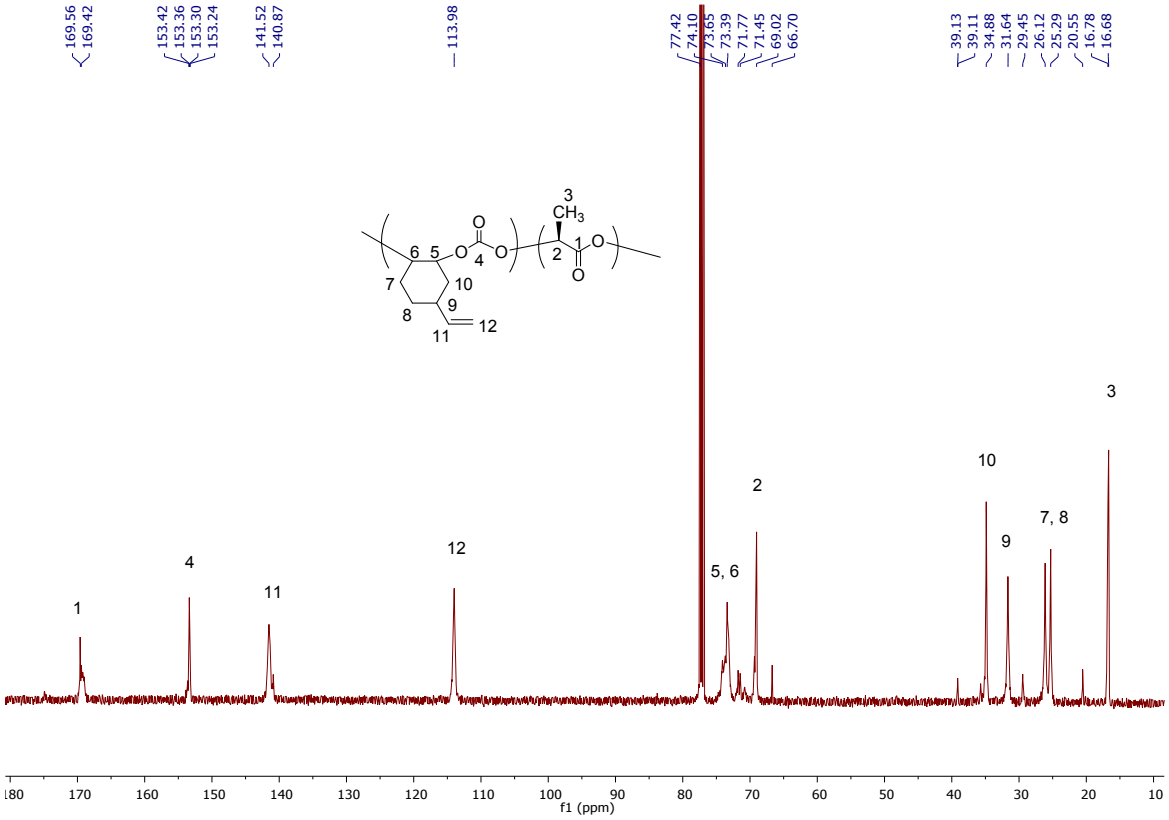


Figure S20: $^{13}C\{^1H\}$ NMR spectrum of PLLA-*b*-PVCHC, with M_n = 6100 g mol^{-1} ($CDCl_3$, 125 MHz).

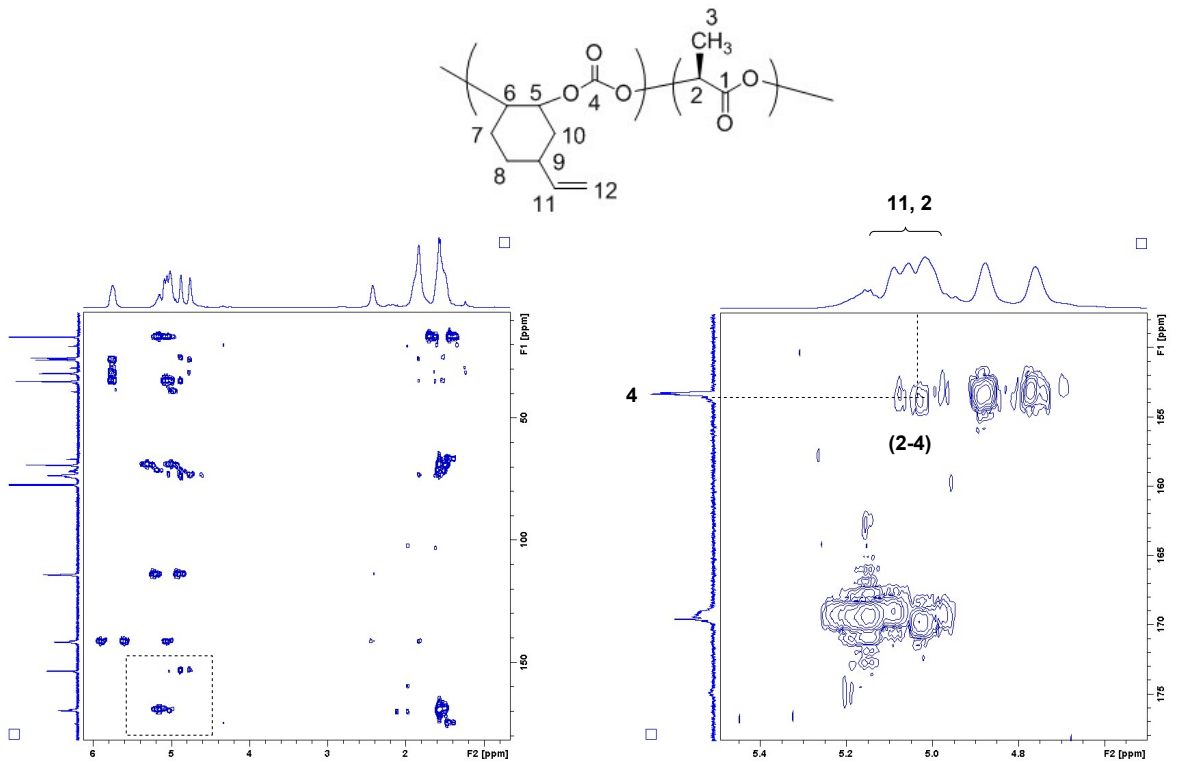


Figure S21: HMBC spectrum of PLLA-*b*-PVCHC, with M_n = 6100 g mol^{-1} ($CDCl_3$, 500 MHz).

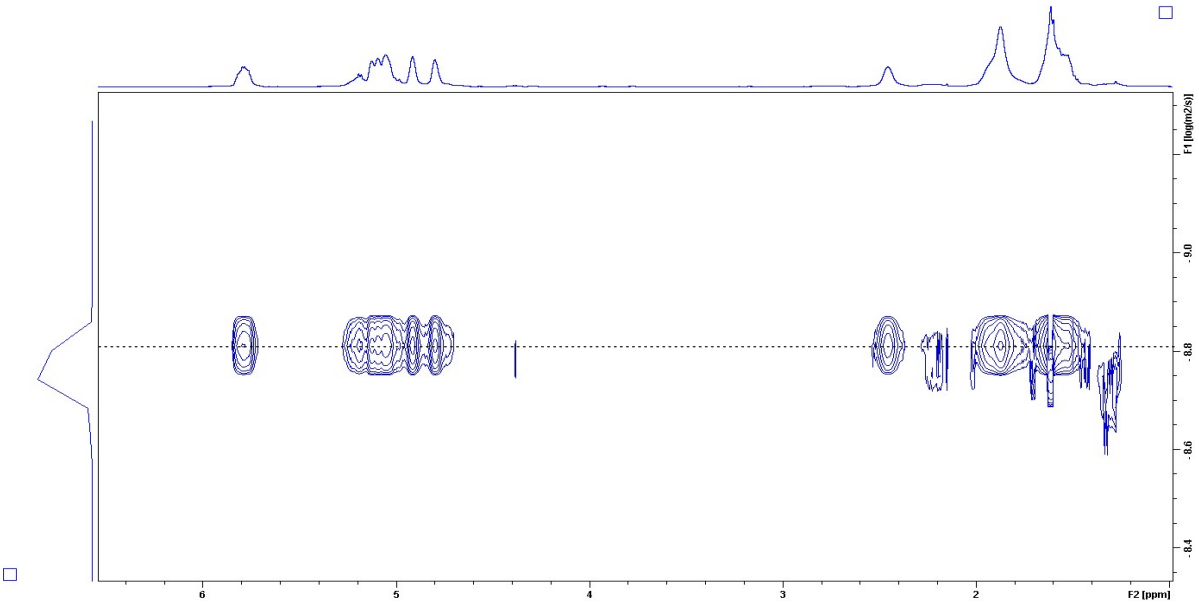


Figure S22: ^{1}H DOSY NMR spectrum of PLLA-*b*-PVCHC with M_n = 6100 g mol^{-1} ($CDCl_3$, 500 MHz).

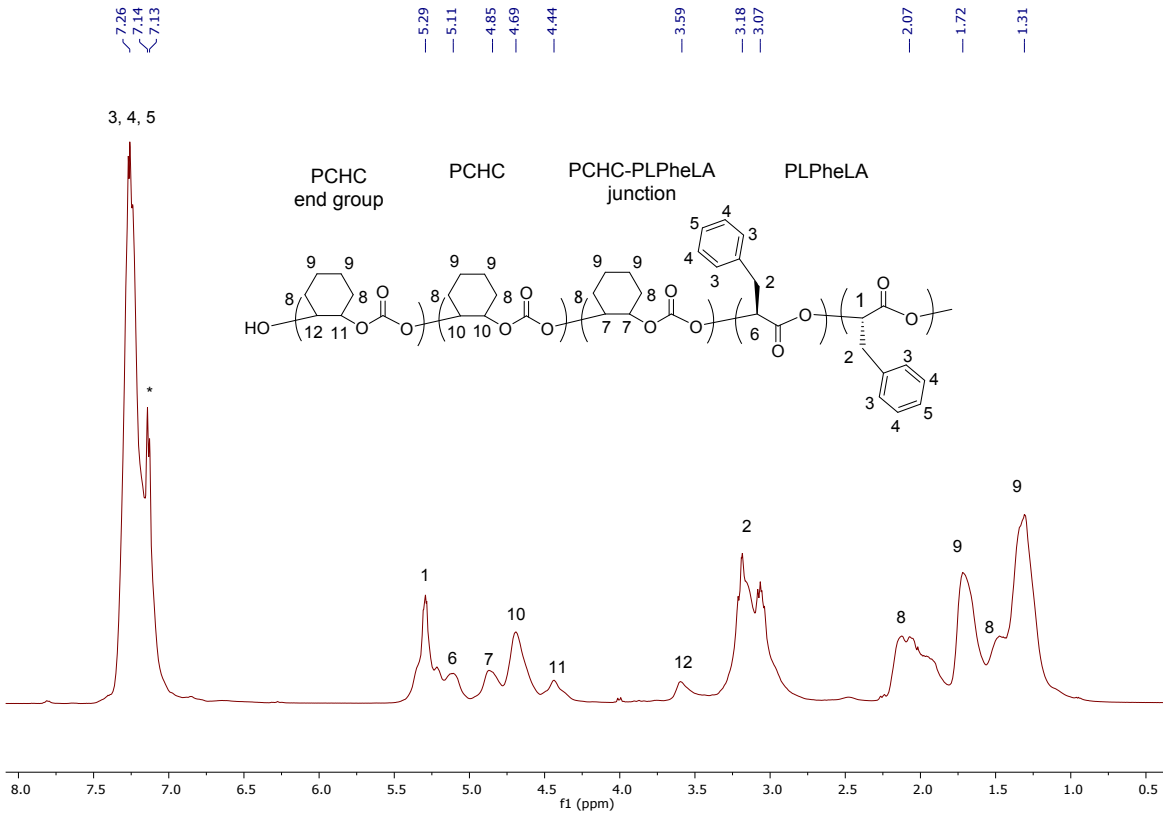


Figure S23: ^{1}H NMR spectrum of PLPheLA-*b*-PCHC with M_n = 2500 g mol^{-1} ($CDCl_3$, 500 MHz).

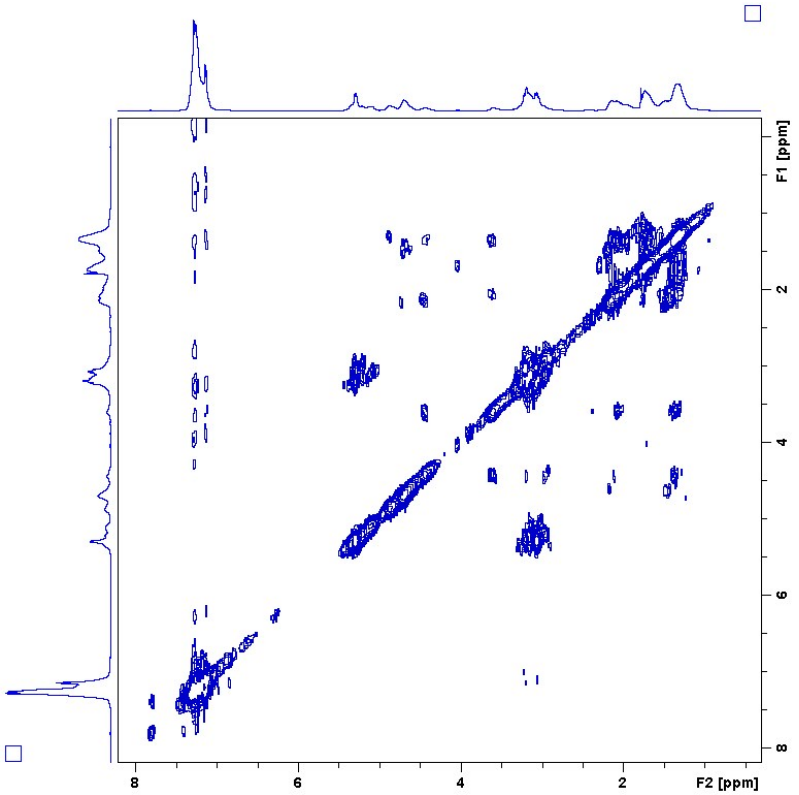


Figure S24: COSY NMR spectrum of PLPheLA-*b*-PCHC) with M_n = 2500 g mol^{-1}($CDCl_3$, 125 MHz).

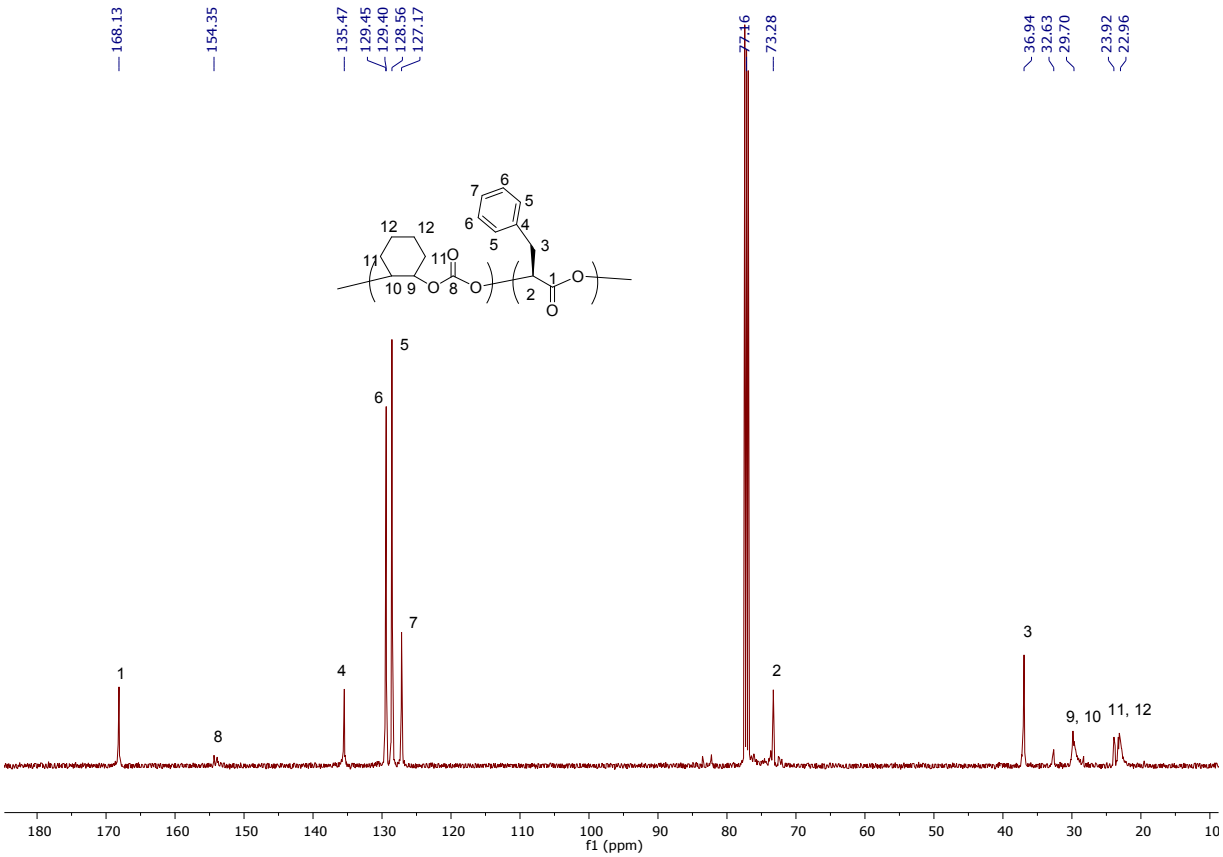


Figure S25: $^{13}C\{^{1}H\}$ NMR of PLPheLA-*b*-PCHC with M_n = 2500 g mol^{-1} ($CDCl_3$, 125 MHz).

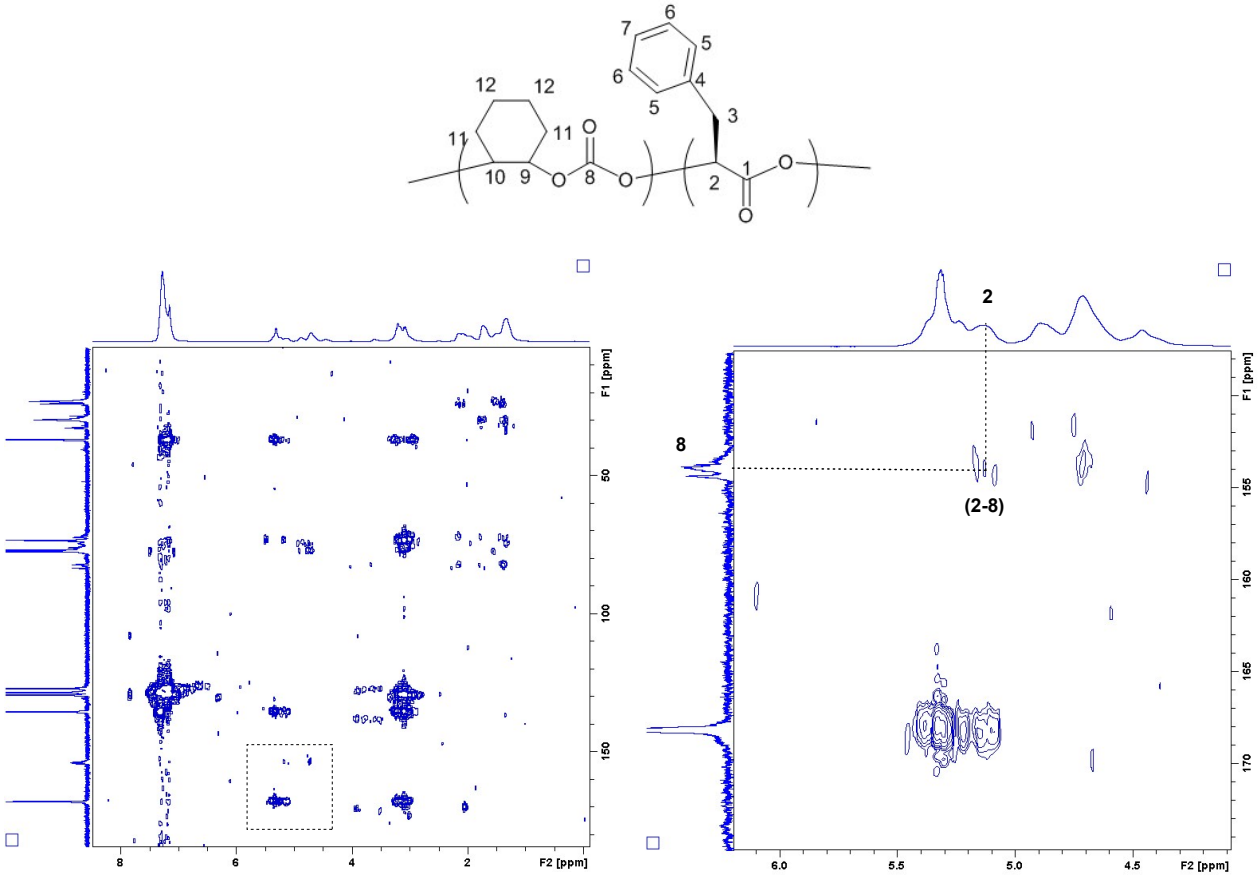


Figure S26: HMBC NMR spectrum of PLPheLA-*b*-PCHC with M_n = 2500 g mol^{-1} ($CDCl_3$, 500 MHz).

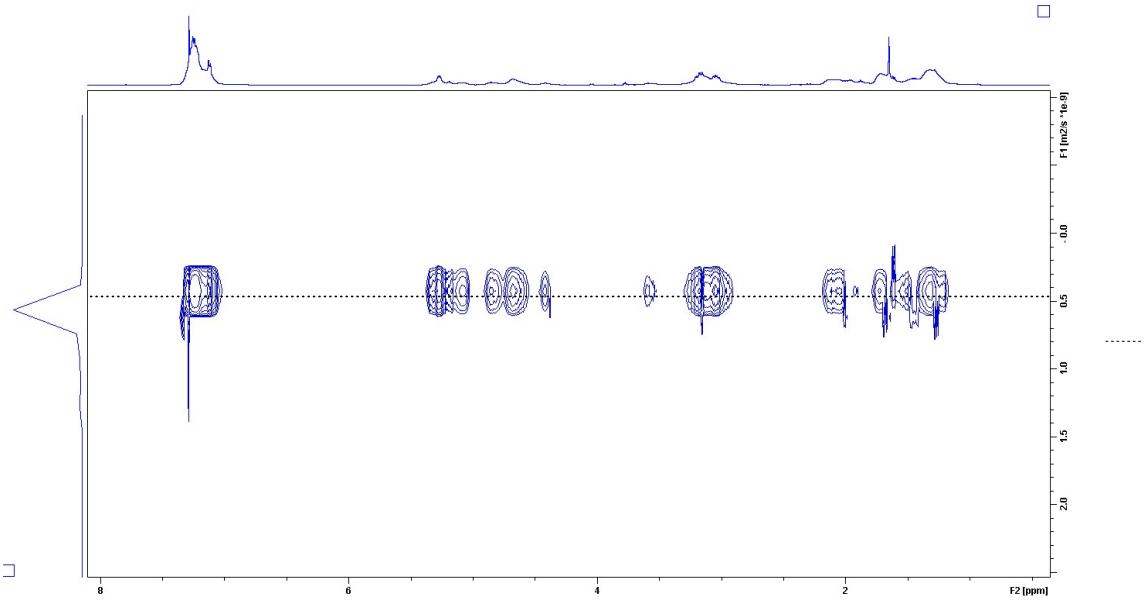


Figure S27: ^{1}H DOSY spectrum of PLPheLA-*b*-PCHC with M_n = 2500 g mol^{-1}(CDCl$_3$, 500 MHz).

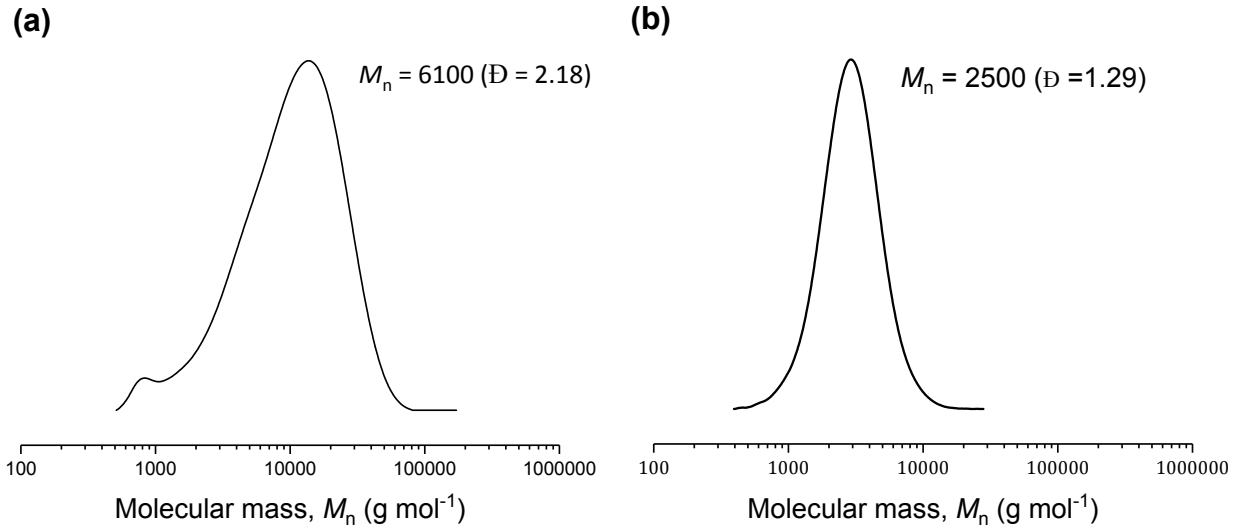


Figure S28: SEC plots of polymers (a) PLLA-*b*-PVCHC obtained by the reaction of LLAOCA and VCHO (Table S2, Entry 1); (b) PLPheLA-*b*-PCHC obtained by the reaction of LPhLAOCA and CHO (Table S2, Entry 2).

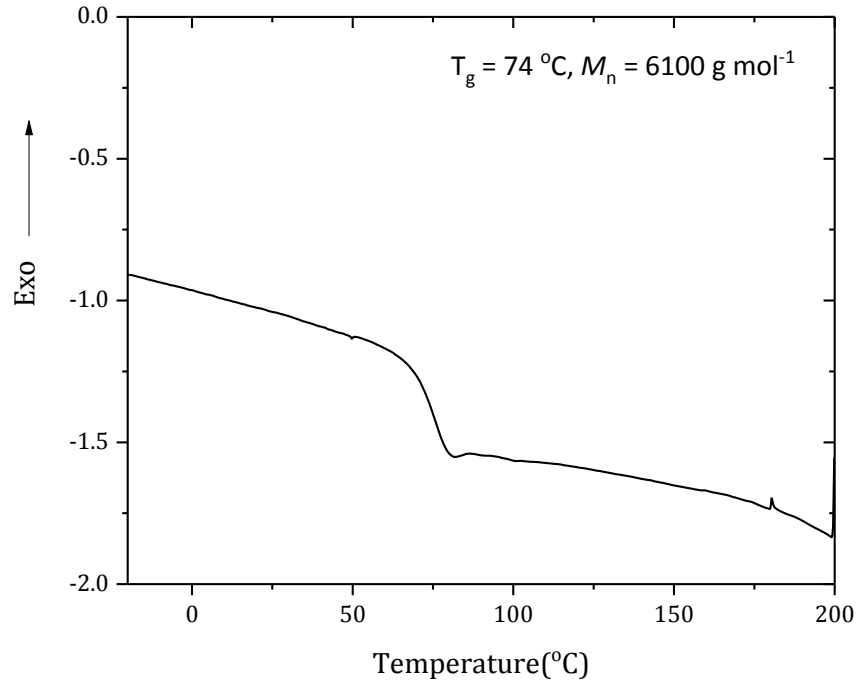


Figure S29: DSC thermogram of PLLA-*b*-PVCHC with M_n = 6100 g mol^{-1} (Table S3, Entry 1).

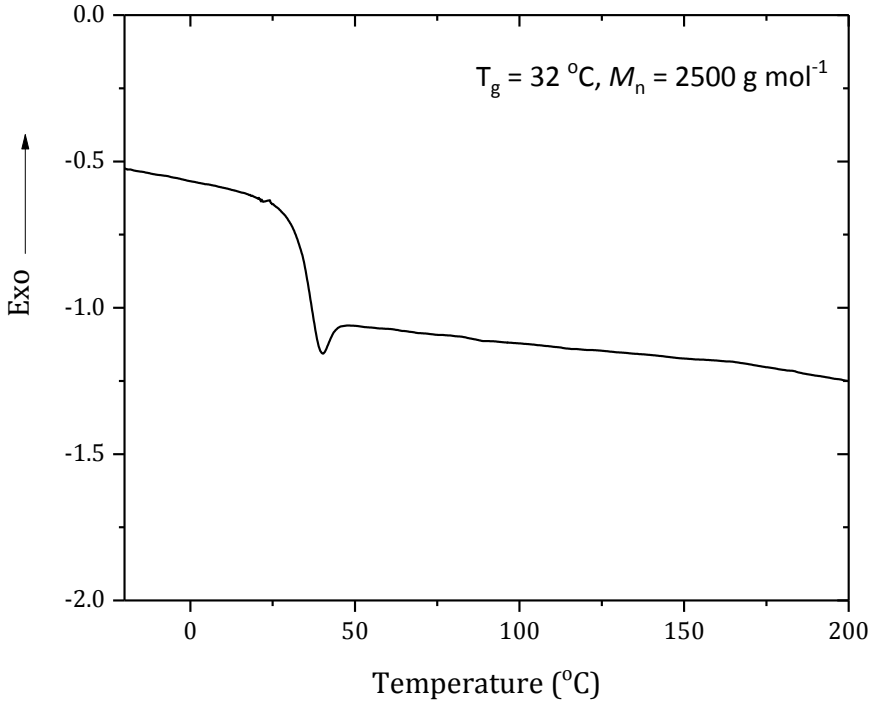


Figure S30: DSC thermogram of PLPheLA-*b*-PCHC (Table S3, Entry 2).

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