Benzoic Acid-Organocatalyzed Ring-Opening (co)Polymerization (ORO(c)P) of L-Lactide and Ɛ-Caprolactone Under Solvent-free Conditions: from Simplicity to Recyclability.

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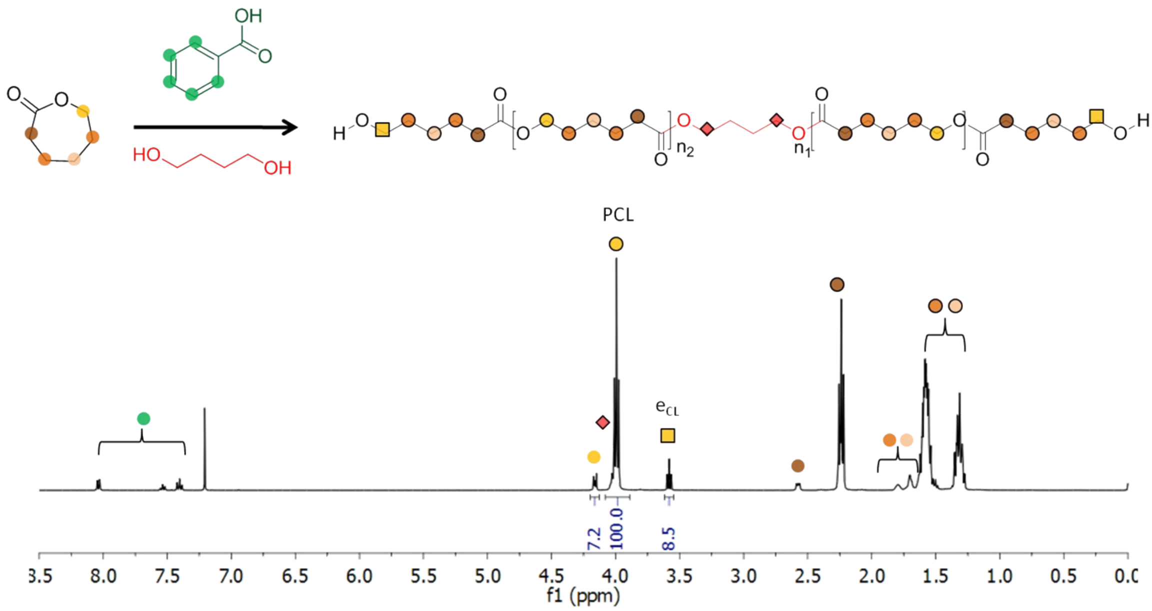
A. BA-OROP of CL

Figure S1: **^{1}H NMR spectrum of crude PCL obtained by BA-OROP of CL initiated by BD in bulk at 155°C [CL/BA/BD = 25/1.25/1] (entry 3, Table 1)($CDCl_3$, 400 MHz)**



The conversion is determined by

$$C_{CL} = \frac{\left({}^{I_{PCL}}/_{2} - {}^{I_{eCL}}/_{4}\right)}{\left({}^{I_{PCL}}/_{2} - {}^{I_{eCL}}/_{4}\right) + {}^{I_{CL}}/_{2}}$$

The degree of polymerization calculated from the chain end

$$DP,e = \frac{{}^{I_{PCL}}/_{2} - {}^{I_{eCL}}/_{4}}{{}^{I_{eCL}}/_{4}}.$$

Figure S2: **DSC spectra of the PCL initiated from BD (entries 3-5-6, Table 1)**

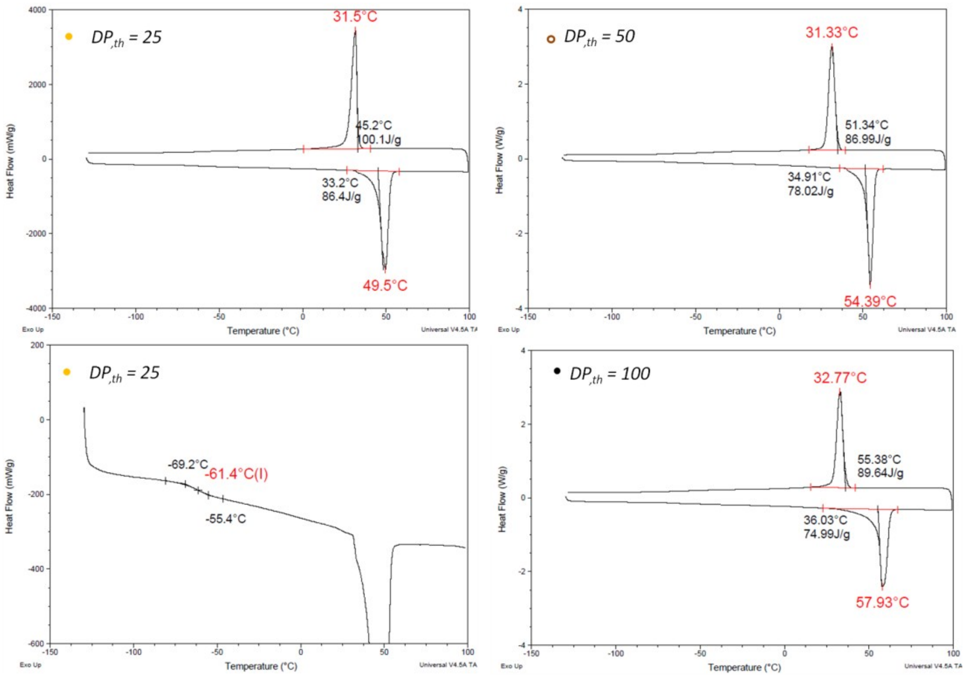


Figure S3: **SEC traces of PCLs obtained by BA-OROP of CL initiated by BD in bulk at 155°C (entries5&6, Table 1) THF as eluent at 313 K.**

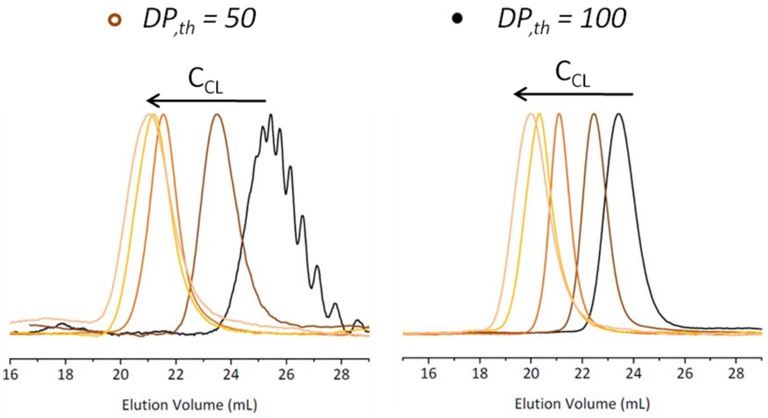


Table S1: Chain extension experiment for BA-OROP of CL[a]

Entry	M	I	Cat (%)	$[M]_0/[I]_0$	T (°C)	Time (h)	Conv (%)	Mn,SEC ($g.mol^{-1}$)	Đ
20	CL	BD	5	25	155	2	91	3930	1.11
21	CL	PCL-entry 20	5	25	155	2	n.a	7590	1.17

[a] Reactions were performed in bulk under argon atmosphere with reaction conditions: m_{CL} = 200 mg using 5mol % catalyst *vs* monomers.

Figure S4: **BA-OROP of CL initiated by BnOH in bulk at 155 °C [CL/BA/BD = 25/1.25/1] (entry 7, Table 1). Evolution of the uncorrected $M_{n,SEC}$ of the crude polymers (•), and dispersity Đ (x) with monomer conversion.**

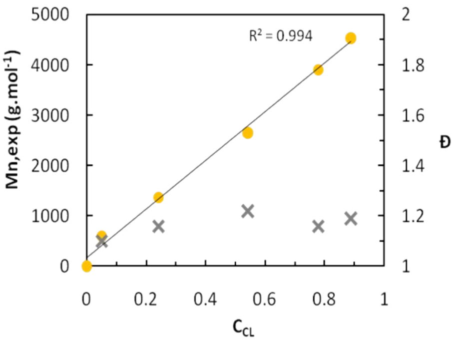

R² = 0.994
Mn,exp (g.mol⁻¹)
5000
4000
3000
2000
1000
0
Đ
2
1.8
1.6
1.4
1.2
1
0
0.2
0.4
0.6
0.8
1
C_CL

Figure S5: **SEC traces of PCLs obtained by BA-OROP of CL initiated by BnOH in bulk at 155°C (entry 7, Table 1). THF/NEt$_3$ (2w%) as eluent, 308K.**

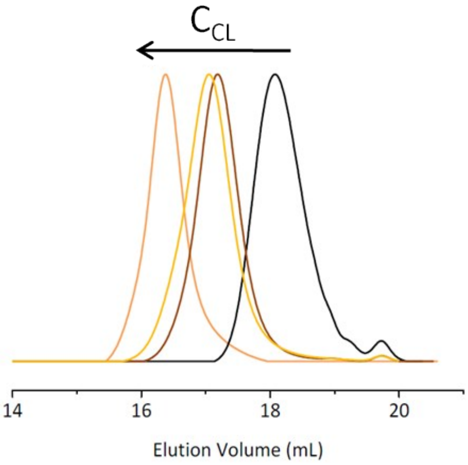
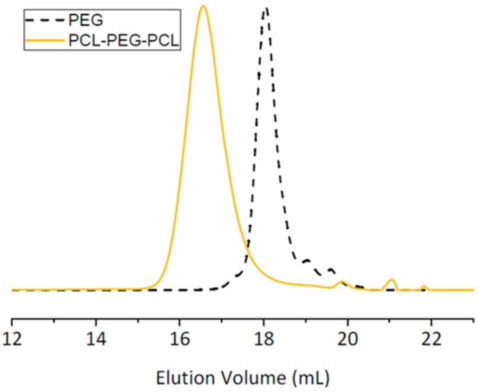
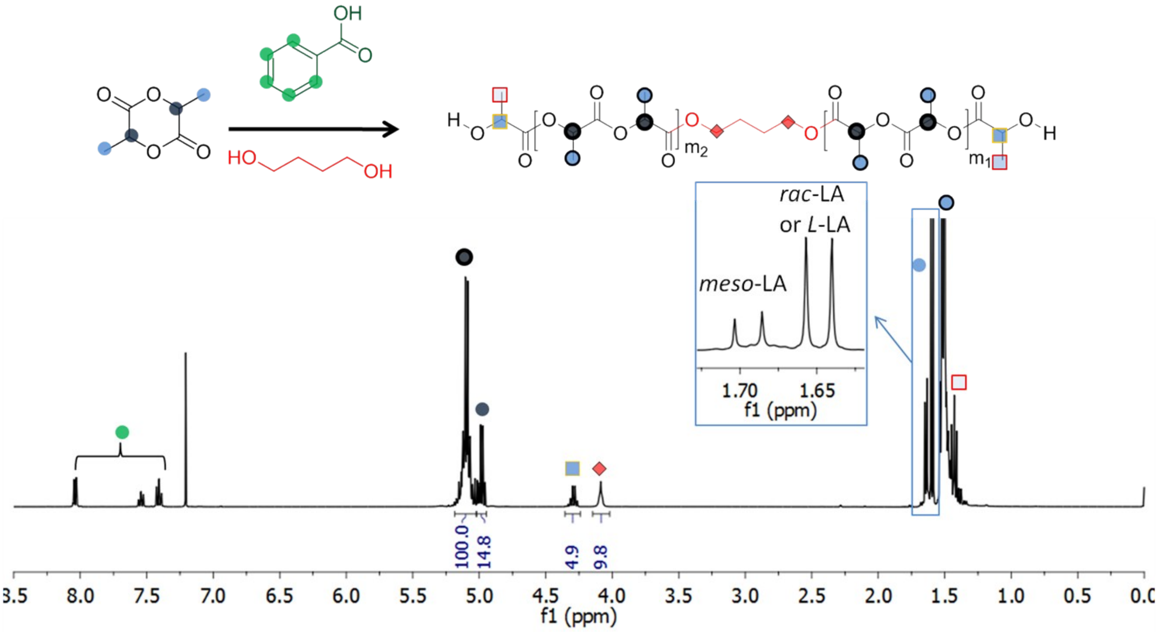


Figure S6: **SEC traces of PEG$_{1000}$ (dashed line) and crude PCL initiated from PEG$_{1000}$ (entry 8, Table 1, solid line) THF/NEt$_3$ (2w%) as eluent, 308K.**



B. BA-OROP of L-LA

Figure S7: ^{1}H NMR spectrum of crude PLA obtained by BA-OROP of LLA initiated by BD in bulk at 155°C [LLA/BA/BD = 25/1.25/1](Entry 11, Table 2) [$CDCl_3$, 400 MHz].



The conversion is determined by

$$C_{LA} = \frac{{}^{I_{PLA}}\!/_{2}}{{}^{I_{PLA}}\!/_{2} + {}^{I_{LA}}\!/_{2}}$$

The degree of polymerization calculated from the initiator

$$DP,I = \frac{{}^{I_{PLA}}\!/_{2}}{{}^{I_{BD}}\!/_{4}} .$$

The degree of polymerization calculated from the end chain

$$DP,e = \frac{{}^{I_{PLA}}\!/_{2}}{{}^{I_{e}}\!/_{2}} .$$

Figure S8: Semi-logarithmic kinetic plot (left) for the BA-OROP of LA with BD as initiator in bulk at 180°C [LLA/BA/BD = 25/1.25/1] (entry 13, Table 2). Evolution of the uncorrected $M_{n,SEC}$ of the crude polymers (•), and dispersity *Đ* (x) with monomer conversion compared to the same polymerization conducted at 155°C (entry 11, Table 2).

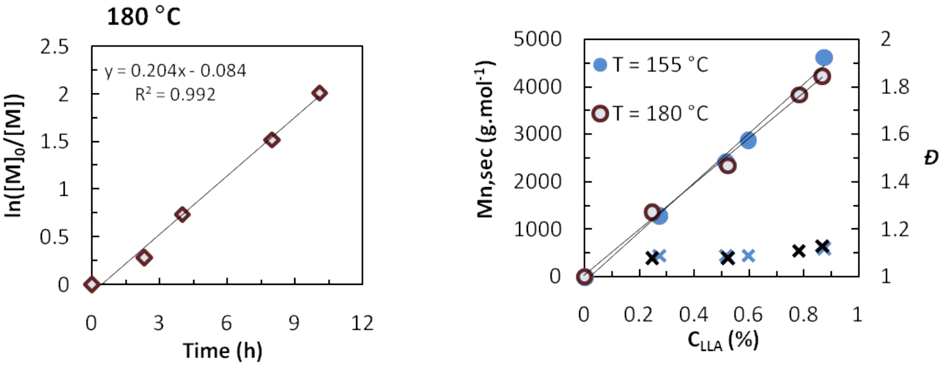


Figure S9: SEC traces of PLA obtained by BA-OROP of LA initiated by BD in bulk at 155°C (entry 14-15 Table 2) THF as eluent at 313 K.

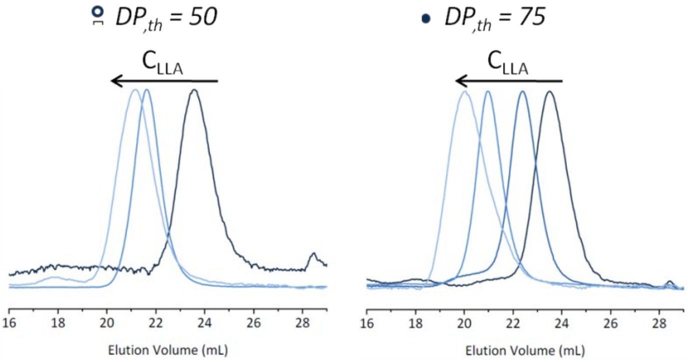


Figure S10: MALDI-ToF MS spectrum of PLA (entry 11, Table 2) with M_{LLA}= 144 g.mol^{-1}, $M_{LA/2}$ = 72 g.mol^{-1}.

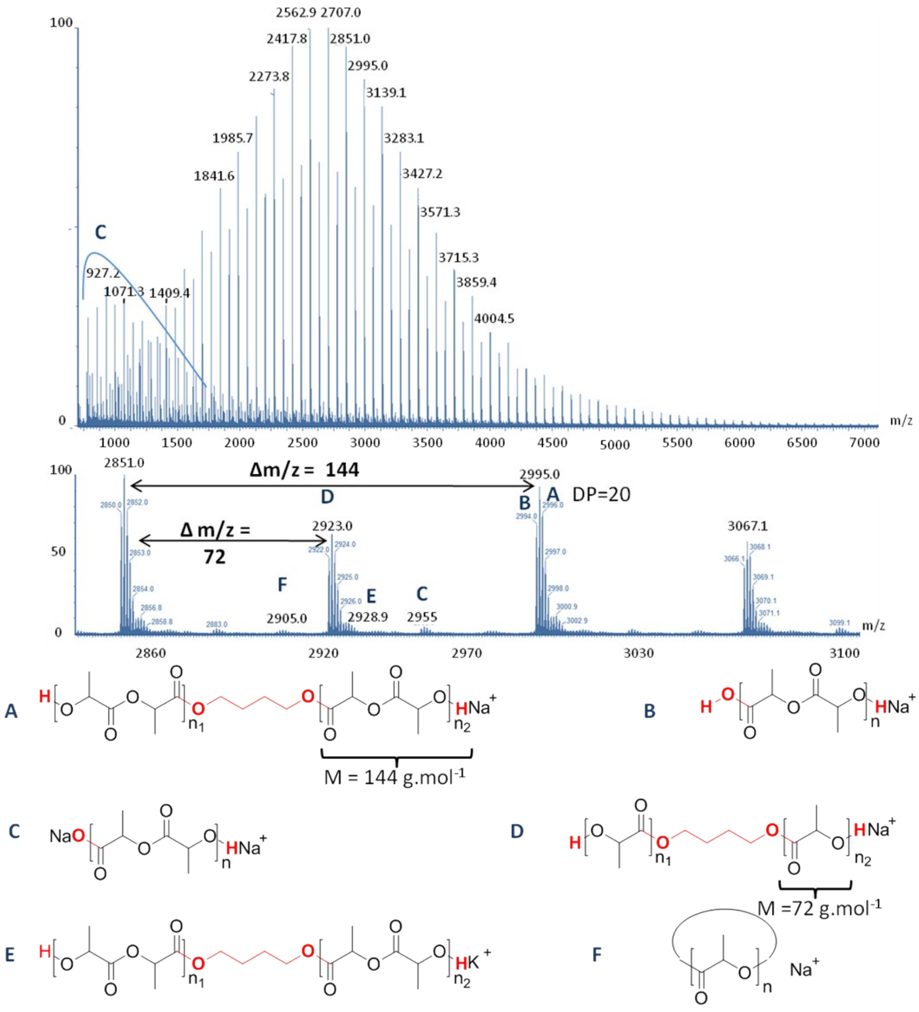


Figure S11: DSC spectrum of the PLA initiated from BD (entry 11-14-15, Table 2)

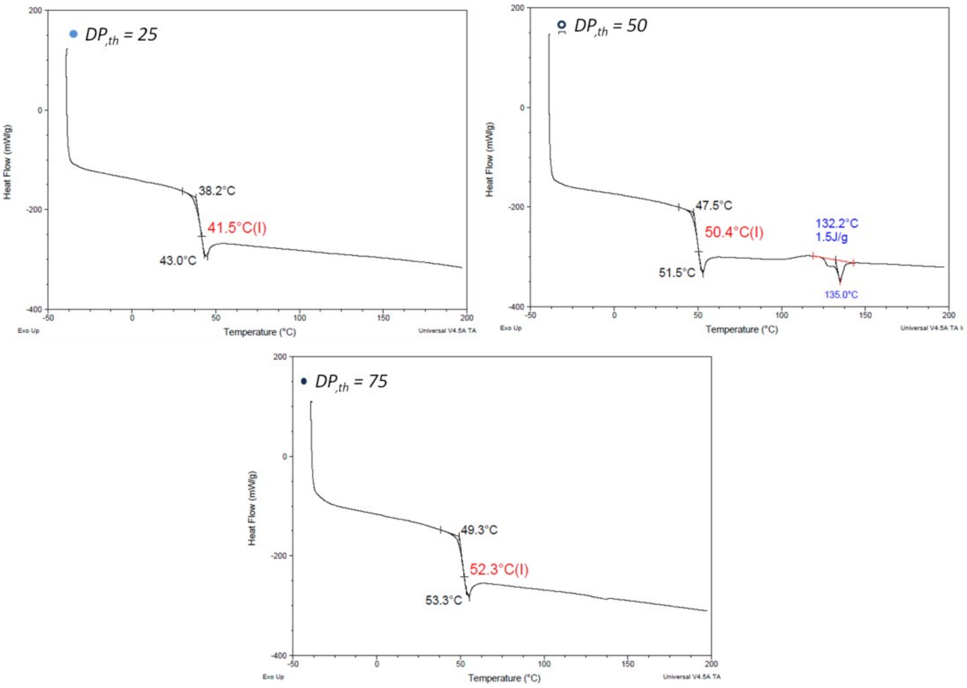
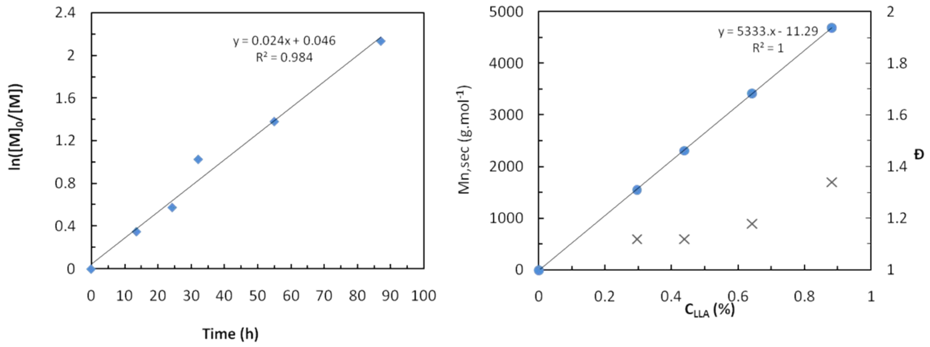


Table S2: Chain extension experimentfor BA-OROP of LA (entry 16, Table 2)[a]

Entry	M	I	Cat (%)	$[M]_0/[I]_0$	T (°C)	Time (h)	Conv (%)	$M_{n,sec}$ ($g.mol^{-1}$)	*Đ*
16	LA	PPA	5	25	155	87	88	4690	1.34
16ce	LA	PLA-entry 16	5	25	155	55	62	7170	1.32

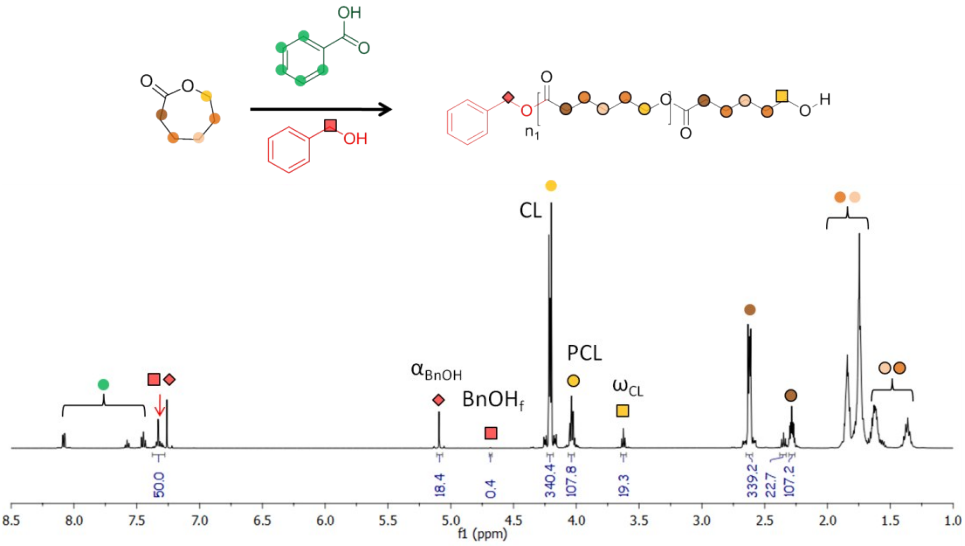
[a]Reactions were performed in bulk under argon atmosphere with reaction conditions: m_{LA} = 200 mg using 5mol % catalyst *vs* monomers.

Figure S12: Semi-logarithmic kinetic plot (left) for BA-OROP of LA with PPA as initiator in bulk at 155 °C for a targeted degree of polymerization of 25 (entry 16, Table 2). Evolution of the uncorrected $M_{n,SEC}$ of the crude polymers (•), and dispersity *Đ* (x) with monomer conversion.



C. Kinetic & mechanistic aspect

Figure S13: **^{1}H NMR spectrum of crude PCL obtained by BA-OROP of CL initiated by BnOH in bulk at 155°C [CL/BA/BD = 25/1.25/1] (entry 2, Table S3) ($CDCl_3$, 400 MHz)**



The conversion is determined by

$$C_{CL} = \frac{I_{PCL}/2}{I_{PCL}/2 + I_{CL}/2}$$

The degree of polymerization calculated from the ω-chain end

$$DP,\omega = \frac{I_{PCL}/2}{I_{\omega CL}/2}.$$

The degree of polymerization calculated from the ω-chain end

$$DP,\alpha = \frac{I_{PCL}/2}{I_{\alpha BnOH}/2}.$$

Fraction of BnOH which initiated the ROP of CL

$$F_{BnOH} = \frac{I_{BnOHf}}{I_{BnOHf} + I_{\alpha BnOH}}$$

Figure S14: **Semi-logarithmic kinetic plot BA-OROP of CL initiated by BnOH in bulk at 155 °C [CL/BA/BnOH = 25/1.25/1] (entry 7, Table 1).**

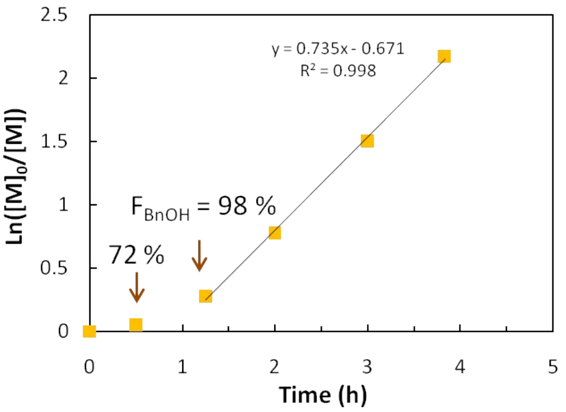


Table S3: **Results and conditions of the BA-OROP of CL with BnOH as initiator at 155 °C.**[a]

Run	$[M]_0$ $/[I]_0$	Time (h)	C_{CL}[b] (%)	$M_{n,SEC}$[c] $(g.mol^{-1})$	$Đ$[c]	F_{BnOH}[d] (%)	DP,α[e]	DPc[f]	DP,ω[g]
1	25	0.5	5	600	1.1	72	1.7	1.3	1.6
2	25	1.25	24	1370	1.16	98	5.9	6	5.6
3	25	2	54	2660	1.16	100	13.4	13.4	12.5
4	25	3	78	3910	1.19	100	19.2	19.4	18.5
5	25	3.83	89	4540	1.25	100	22	22.2	21.4

[a] Reactions were performed in bulk at 155°C under argon atmosphere with reaction conditions: m_{CL} = 200 mg and ($[CL]_0/[BA]_0/[BnOH]_0$ = 25/1.25/1). [b] CL conversions were determined by ^1H NMR analysis. [c] Average molar mass and dispersities ($Đ$) of crude copolymers determined by SEC chromatography (polystyrene standards), at 308 K and THF/NEt_3 (2w%) as eluent. [d] F_{BnOH} BnOH conversion. [e] Degree of polymerization calculated from the α-chain ends determined by ^1H NMR. [f] Theoritical degree of polymerization $DP,c = \frac{[CL]_0}{[I]_0} \times C_{CL}$. [g] Degree of polymerization calculated from the ω-chain ends determined by ^1H NMR.

Figure S15: **^{13}C NMR spectra of the carbonyl region of an equimolar mixture of(a) BA and CLin $CDCl_3$; (b) BA and LLA in $CDCl_3$; (c) ^1H NMR spectra of a mixture of BA and BD (1/2), (d) Chemical shifts of the H_{ae} proton in the ^1H NMR spectrum observed when BD is mixed with BA in $CDCl_3$with different n_{BA}/n_{BD} ratios.**

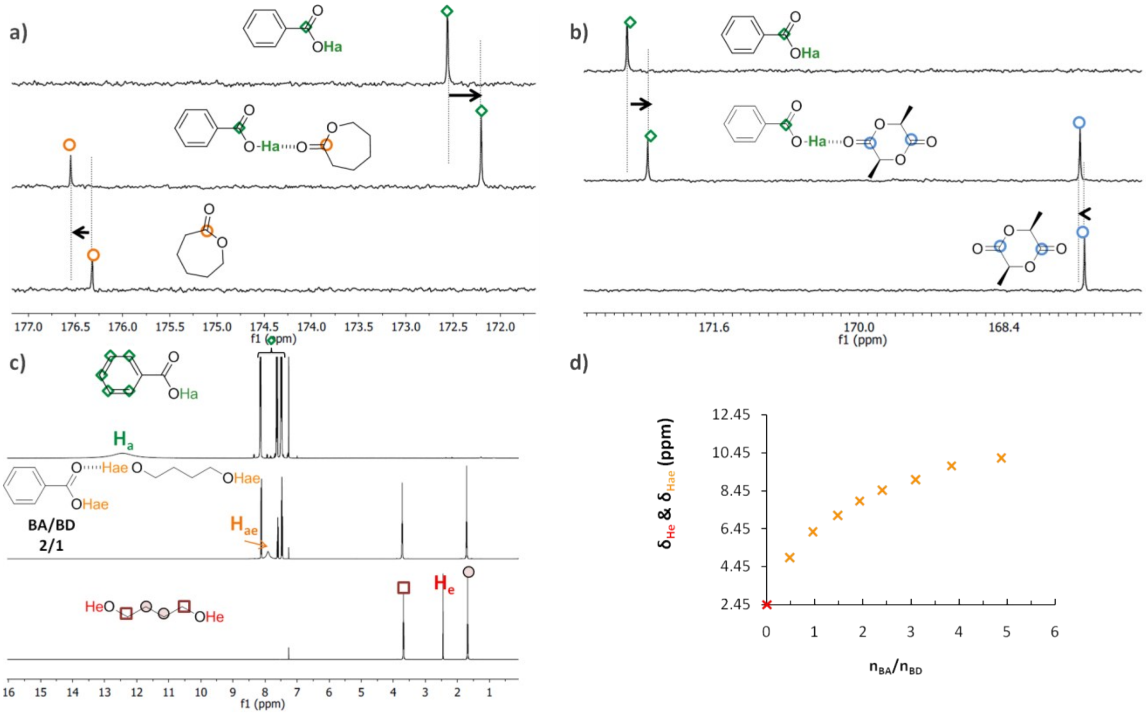

a)
OHa
O-Ha····O
177.0
176.5
176.0
175.5
175.0
174.5
174.0
173.5
173.0
172.5
172.0
f1 (ppm)
b)
OHa
O-Ha····O
171.6
170.0
168.4
f1 (ppm)
c)
OHa
Ha
O····Hae
OHae
OHae
BA/BD
2/1
Hae
HeO
OHe
He
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
f1 (ppm)
d)
δHe & δHae (ppm)
12.45
10.45
8.45
6.45
4.45
2.45
0
1
2
3
4
5
6
nBA/nBD

Figure S16: Semi-logarithmic kinetic plot for BA-OROP of CL initiated by BD in bulk at 155°C, 5*mol%* catalyst *rel. to CL* for different targeted degrees of polymerization (entry 3, 5&6 Table 1).

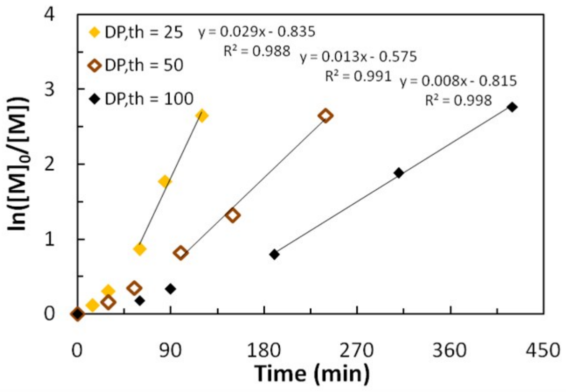


Figure S17: ln(kapp) = β ln([I]$_0$) + ln(kp) with β the kinetic order relative to the initiator for BA-OROP of CL initiated by BD (entries3,5 and 6 Table 1).

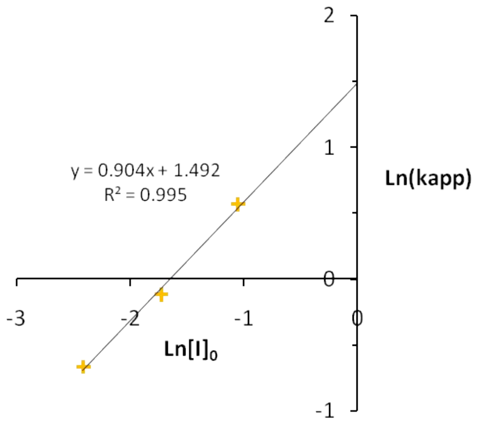


Table S4: Calculation of β the kinetic order relative to the initiator for CL ROP.

kapp	ln kapp	[I]$_0$	ln[I]$_0$
1.76291134	0.56696661	0.3498043	-1.05038142
0.889	-0.11765804	0.17764736	-1.72795484
0.51414331	-0.66525324	0.08952627	-2.41322323

Entries 3,5 and 6 Table 1

Figure S18: Semi-logarithmic kinetic plot BA-OROP of LLA initiated by BD in bulk at 155°C, 5mol% catalyst *vs* monomer, for different targeted degrees of polymerization (entry 11, 14&15 Table 2).

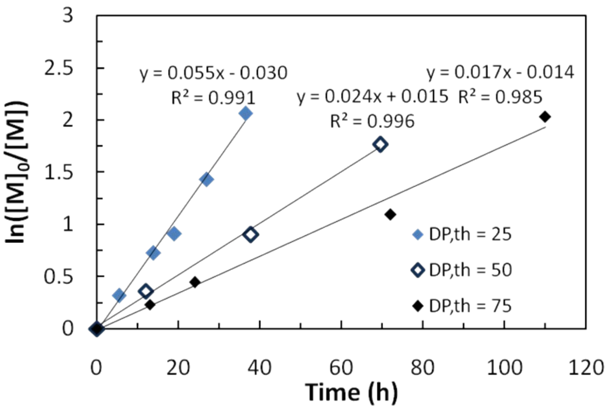


Figure S19: $\ln(kapp) = \beta \ln([I]_0) + \ln(kp)$ with β the kinetic order relative to the initiator for LLA ROP (entries 11, 14 and15 Table 2).

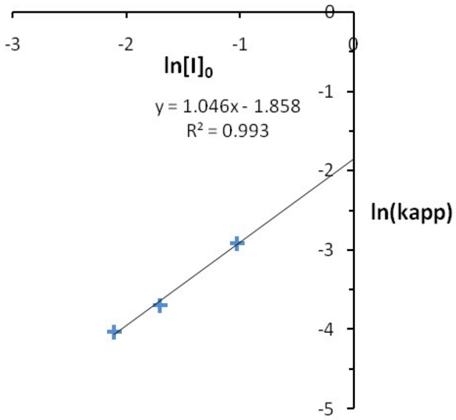


Table S5: Calculation of β the kinetic order relative to the initiator for LLA ROP.

kapp	ln kapp	$[I]_0$	$\ln[A]_0$
0.0542	2.91507437	0.3575	1.02861992
0.0248	3.69691163	0.1816	1.70594881
0.0178	4.02855682	0.1217	2.10619628

Entries 11, 14 and 15 Table 2

D. Recyclability by vacuum treatment

Figure S20: **SEC traces of PCL before and after vacuum treatment (VT) initiated by hexane-1,6-diol of run 1.**

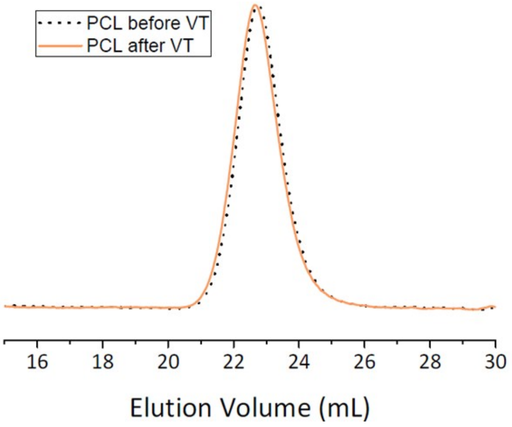
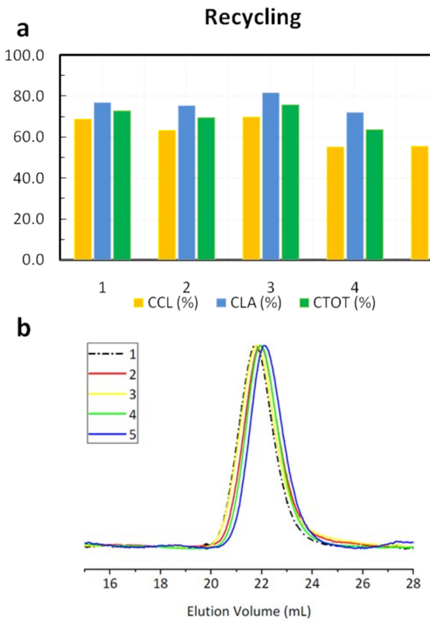


Figure S21: **a) Bar graph showing the conversion of CL and of LA and the total conversion at the end of the copolymerization initiated by BD for each cycle and b) normalized SEC traces from RI detector of pure copolymers (THF, 313 K, 1mL.min^{-1}).**



E. BA-OROcP: Triblock copolymer synthesis

Table S6: Results and conditions of the LA and CL triblock synthesis.[a]

Entry	M1	$[M]_0/[I]_0$	Time (h)	C_1[b] (%)	Mn,sec[c] (g.mol^{-1})	Đ[c]	M2	$[M]_0/[I]_0$	Time (h)	C_2[b] (%)	Mn,sec[c] (g.mol^{-1})	Đ[c]
1	CL	25	2	93	4240	1.12	LA	25	26	75	7730	1.14
2	LA	25	36	90	4200	1.15	CL	25	2	27	n.d	n.d

[a] Reactions were performed in bulk at 155°C under argon atmosphere with reaction conditions: m_{CL} = 200 mgm_{LLA}= 253 mg using 5mol% catalyst *vs* monomers and targeted DP of 25 for each monomer.[b]CL and LA conversions were determined by ^{1}H NMR analysis.[c] Average molar mass and dispersity (*Đ*) of crude copolymers determined by SEC chromatography (polystyrene standards), at 40°C and THF as eluent.

Figure S22: Thermogravimetric analysis (TGA) of the triblock copolymer (from 20°C to 600 °C with 10 °C/min)

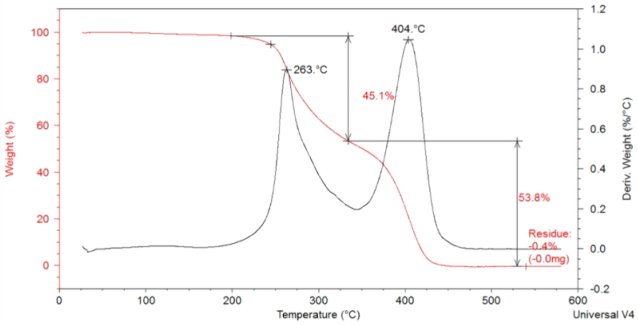


Figure S23: (a) The two modes of transesterification reactions, ^{13}C NMR spectra, comparison between (a) the PCL macroinitiator,(b) the as-obtained PLA-*b*-PCL-*b*-PLA triblock and (c) a PLA.(LL and L refer to lactidyl and lactoyl units, respectively)

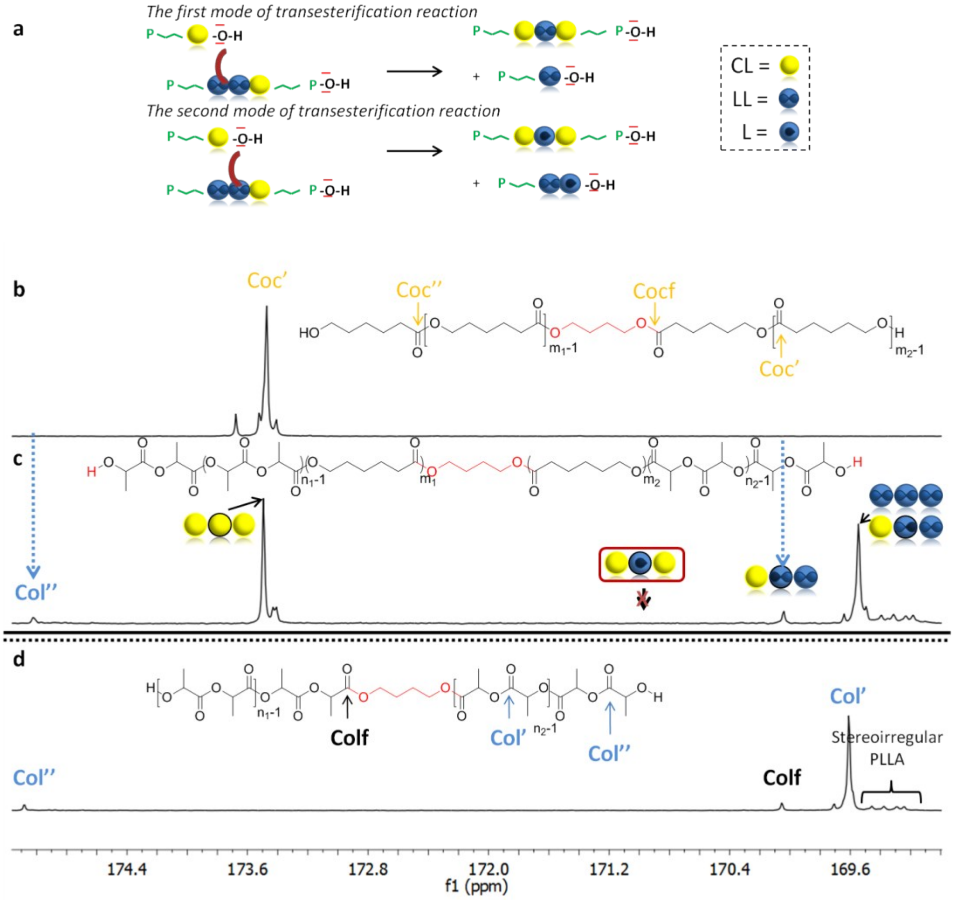


Figure S24: ^1H NMR spectra comparison between the PLA macroinitiator (a) and the as-obtained crude PCL-*b*-PLA-*b*-PCL triblock [$CDCl_3$, 400MHz]. * NMR peaks of CL monomer

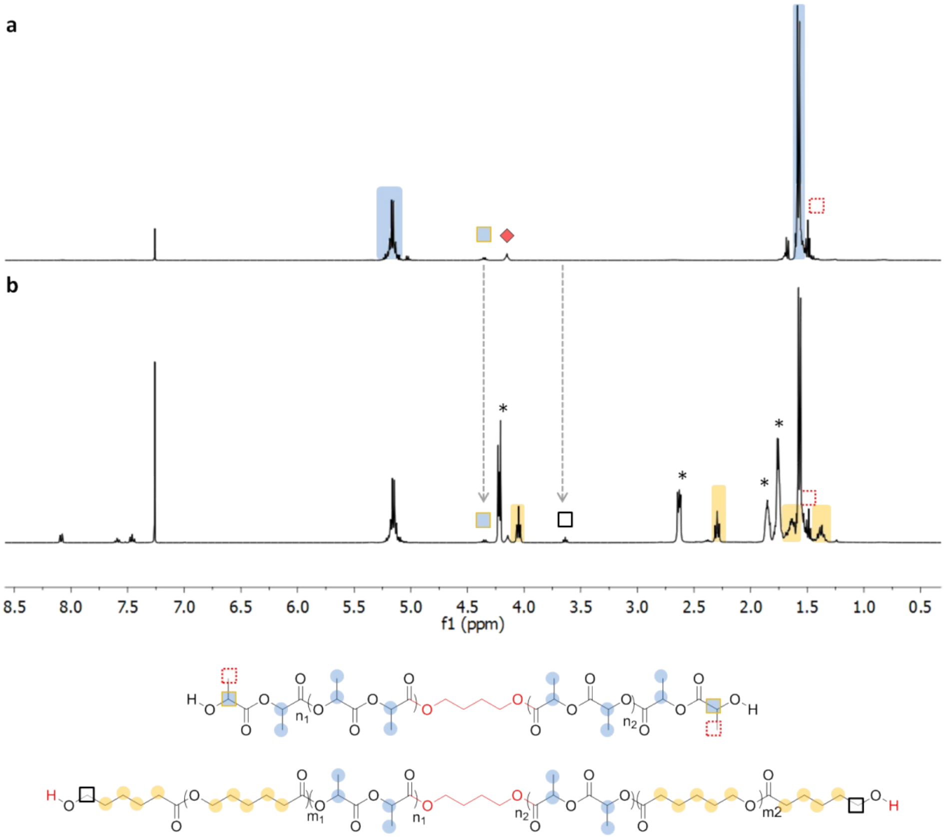
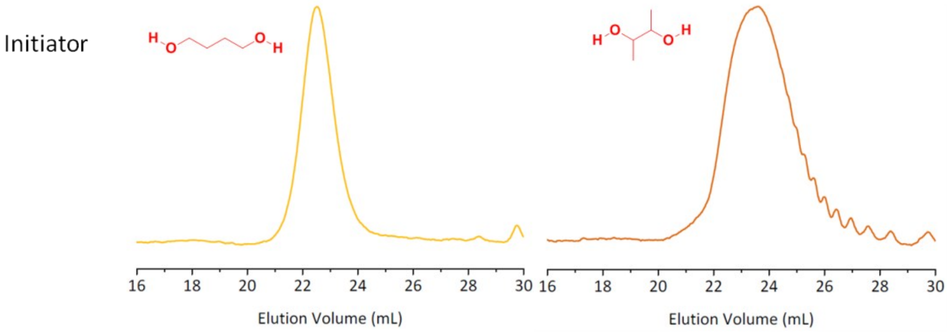


Table S7: BA-OROP of CL initiated by a primary and a secondary alcohol initiators in bulk at 155°C

Entry	I	Cat (%)^b	$[M]_0/[I]_0$	Time (h)	C_M (%)^c	$M_{n,SEC}$ ($g.mol^{-1}$)^d	$Đ^d$	$DP_{th}{}^e$	$DP_{exp}{}^f$
1	BD	5	30	1.7	78	4360	1.09	23.5	22.3
2	2,3-BD	5	30	1.7	36	2460	1.31	10.9	17.9

Figure S25. SEC traces of PCL initiated from BD (left) and from 2,3-BD (right)



F. BA-OROcP: Random copolymer synthesis

Table S8: **Results and conditions for the BA-ROcP of LA and CL.**[a]

Entry	$[M]_0/[I]_0$	Time (h)	C_{LA}[b] (%)	C_{CL}[b] (%)	f_{CL}[c] (%)	F_{CL}[d] (%)	DP,c[e]	DP,e[f]	Mn,sec[g] (g.mol^{-1})	Đ[g]
1	25&25	38	88	88	51.4	51.5	44.1	41	7870	1.16

[a]Reactions were performed in bulk at 155°C under argon atmosphere with reaction conditions: nCL= nLA = 1.4 mmol using 5mol% catalyst *vs* monomers. [b]CL and LA conversions were determined by ^{1}H NMR analysis. [c] CL fraction in the initial feed.[d] CL fraction in the pure copolymer. [e]Theoritical degree of polymerization

$$DP,c = \frac{[LLA]_0}{[I]_0} \times C_{LLA} + \frac{[CL]_0}{[I]_0} \times C_{CL}$$

. [f]Degree of polymerization calculated from the chain ends determined by ^{1}H NMR. [g]Average molar mass and dispersity (Đ) of crude copolymers determined by SEC chromatography (polystyrene standards), at 40°C and THF as eluent.

Figure S26: **Stack of ^{1}HNMR spectra of the crude copolymers [$CDCl_3$, 400MHz, r.t] [LLA/CL/BA/BD = 25/25/2.5/1].**

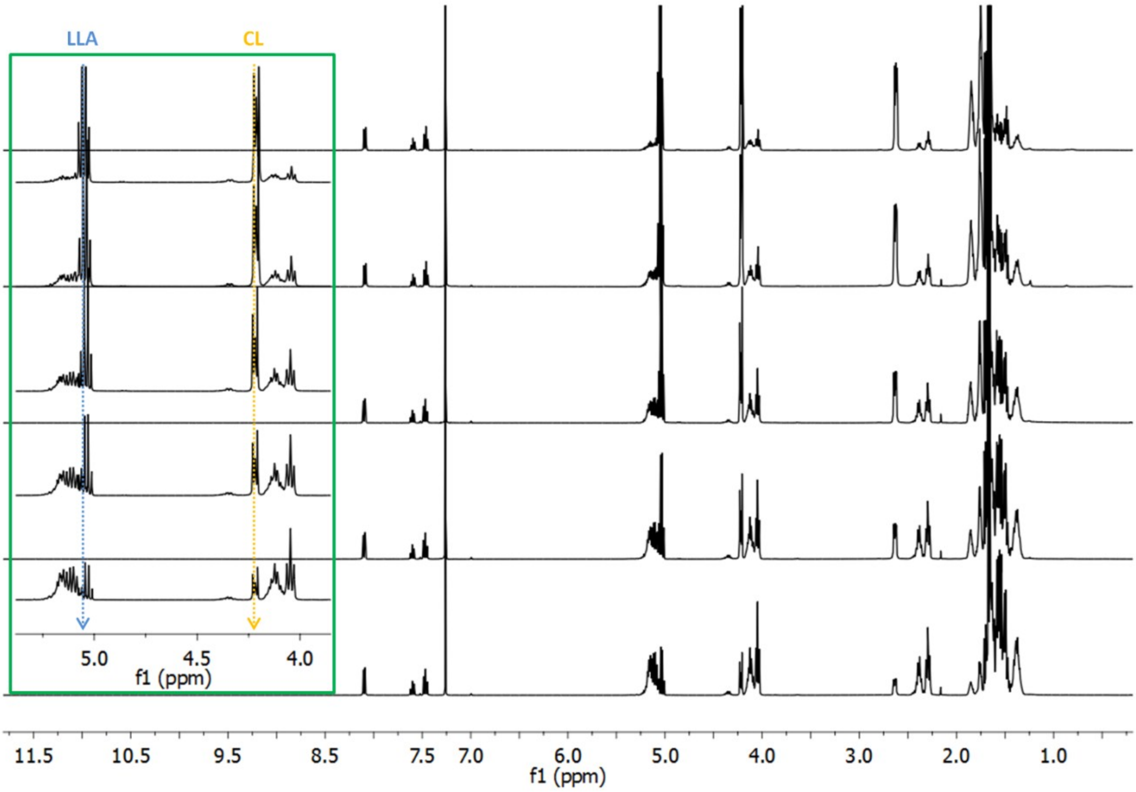
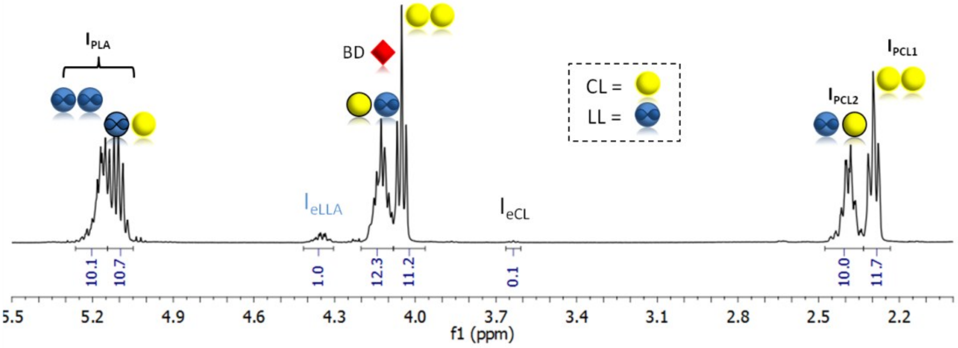


Figure S27: ^{1}H NMR spectrum of pure P(LA-*co*-CL) initiated by BD (entry 1, Table S7) [$CDCl_3$, r.t, 400 MHz]. with I_{eLLA} and I_{eCL} the chain ends representing a LLA or a CL unit respectively.



$$I_{PCL} = I_{PCL1} + I_{PCL2}$$

The degree of polymerization calculated from the chain end:

$$DP,e = \frac{\frac{I_{PLA} + I_{PCL}}{2}}{\frac{I_{eLLA}}{2} + \frac{I_{eCL}}{4}}$$

Determination of the composition in the copolymers:

$$F_{CL} = \frac{I_{PCL}}{I_{PLA} + I_{PCL}}$$

Figure S28: Evolution of the uncorrected $M_{n,SEC}$(•), and of the dispersity *Đ* (x) of the crude copolymers with monomer conversion.

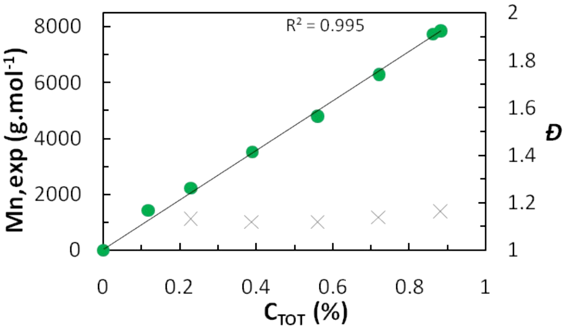
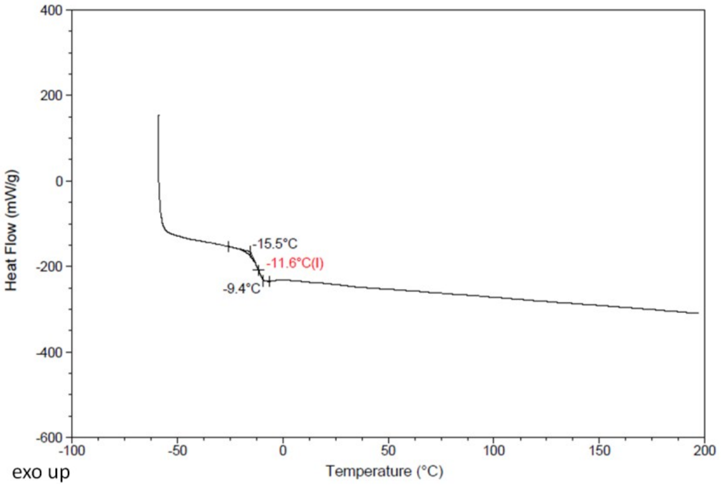


Figure S29: DSC spectrum of the pure P(LA-*co*-CL) initiated by BD (entry 1, Table S8).


400
200
0
-200
-400
-600
Heat Flow (mW/g)
-100
-50
0
50
100
150
200
Temperature (°C)
exo up
-15.5°C
-11.6°C(I)
-9.4°C