Supplementary Information

Homopolymerization and copolymerization of ε-caprolactone and L-lactide organocatalyzed by carboxylic acids with mono-, di-, and tri-functionality

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Table S1. Thermic properties of α-hydroxyl-ω-docosyl-PCL with different organocatalysts [a].

Organocatalyst	$M_{n(NMR)}$[b]	Conv.(%)[b]	T_m (°C)[c]	ΔH_m (J/g)[c]	ΔH_{mPCL} (J/g)[d]	x_i (%)[e]
1	650	45	45	116	57	42
2	1090	88	45	114	80	59
3	1080	85	45	112	78	57
4	1380	>98	46	111	83	61
5	1230	>98	46	114	84	62
6	1260	>98	48	114	85	63
7	1320	>98	47	113	85	63

[a]ROP of ε-CL with 1-docosanol as initiator at 150°C, ratio $[M]_0/[I]_0/[Cat]_0$ = 100 : 10 : 1 (mmolar ratio= 10 : 1 : 0.1).
[b]Obtained by ^{1}H NMR analysis.
[c]Obtained by DSC analysis, second heating.
[d]Obtained by the equation $\Delta H_{mPC}L=(\Delta H_m)\bullet$(weight fraction of PCL).
[e]Using the value of 135.3 J/g for a PCL 100% crystalline, the crystallinity of PCL (x_{PCL}) was calculated.

Table S2. Thermic properties of PCL and copolymers PCL-*co*-PLLA using citric acid **7** as organocatalyst [a].

Entry	Composition (%)		T_m (°C)[b]	ΔH_m (J/g)[b]	ΔH_{mPCL} (J/g)[c]	x_i (%)[d]
	CL	L-LA				
1	100	0	46	113	113	83
2	97	3	46	97	94	69
3	95	5	40	85	80	59
4	89	11	40	83	73	54
5	82	18	42	70	57	42
6	72	28	43	62	44	32
7	63	37	44	56	35	25

[a]ROP in bulk. $[M]_0/[I]_0/[Cat]_0$= 100/10/1. $[M]_0$= 10 mmol, T= 150 °C, t= 24 h.

[b]Obtained by DSC analysis, second heating.

[c]Obtained by the equation $\Delta H_{mPC}L=(\Delta H_m)\bullet$(weight fraction of PCL).

[d]Using the value of 135.3 J/g for a PCL 100% crystalline, the crystallinity of PCL (x_{PCL}) was calculated.

Figure S1. ^{13}C NMR spectrum (125 MHz) of α-hydroxyl-ω-docosyl-PCL (citric acid as organocatalyst, 100 min, 150 °C) in $CDCl_3$ at room temperature.

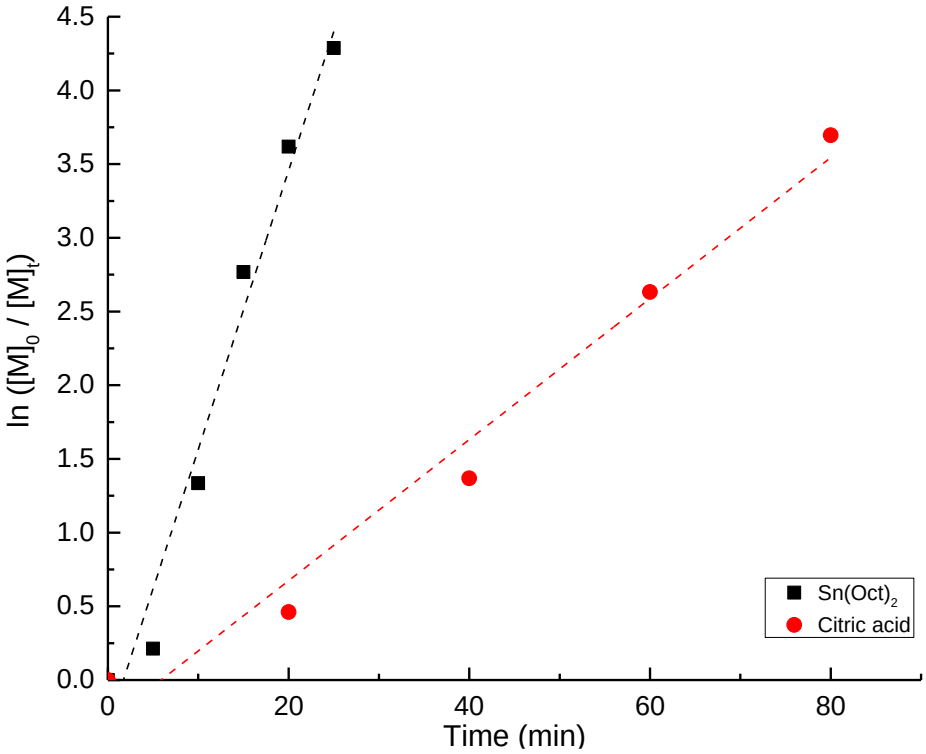


Figure S2. Semi-logarithmic plot of the first-order behavior for the ROP reaction of CL, $Sn(Oct)_2$ (black line), and **7** (red line).

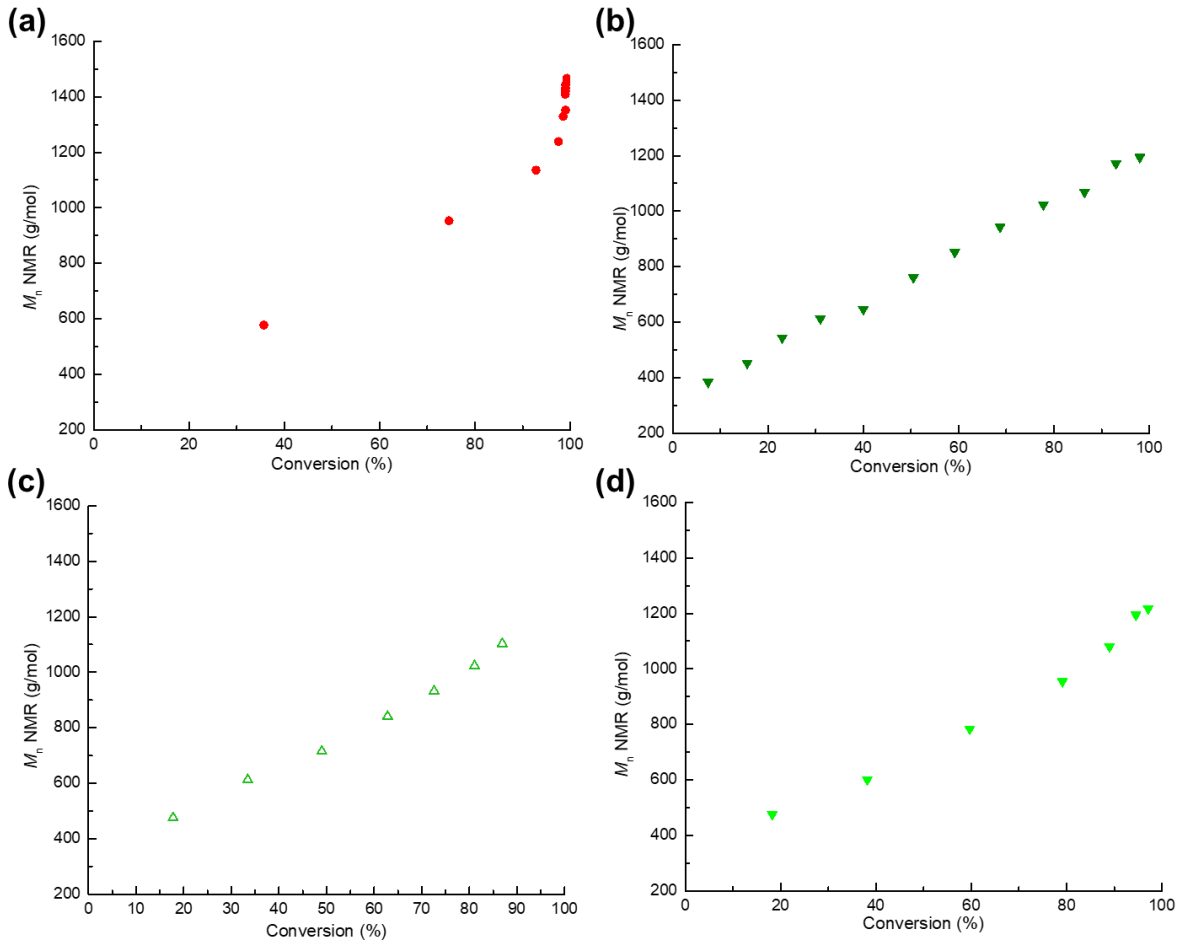


Figure S3. Graphs of the dependence of M_n on the conversion percentage for the four most active organocatalysts: (a) citric acid **7**, (b) fumaric acid **5**, (c) malic acid **6**, and (d) succinic acid **4**.

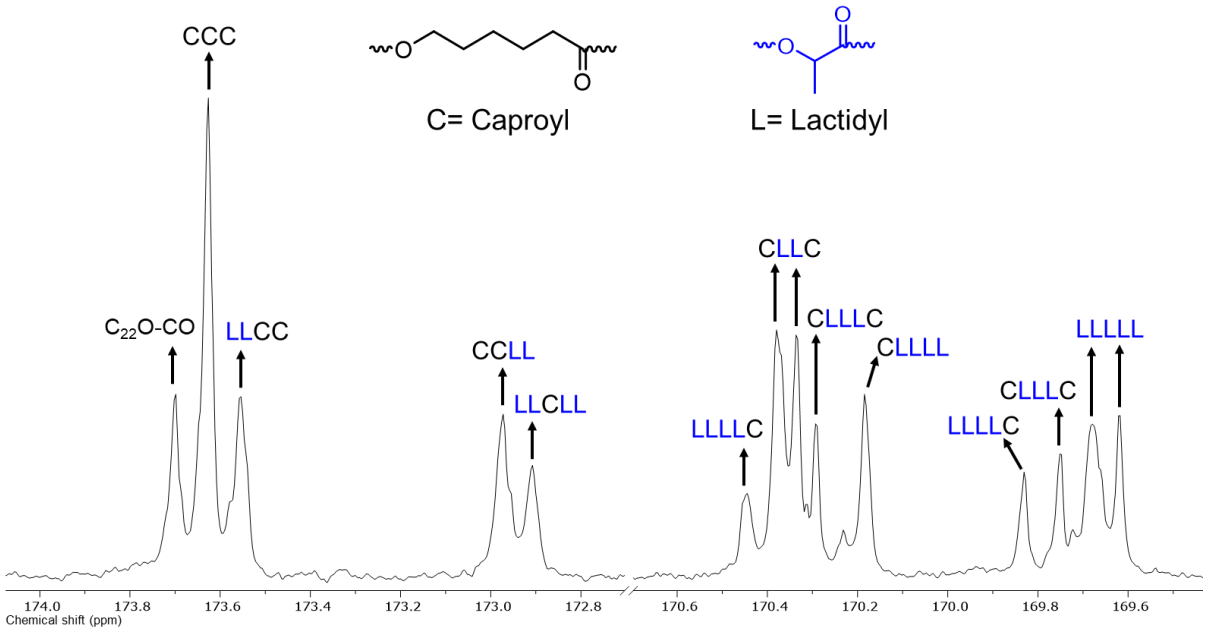


Figure S4. Expansion of the ^{13}C NMR spectrum (125 MHz) in the carbonyl carbon region of the PCL-*co*-PLLA copolymer (Table 3, Entry 6) and the triad assignments (acquisition time=18 h).

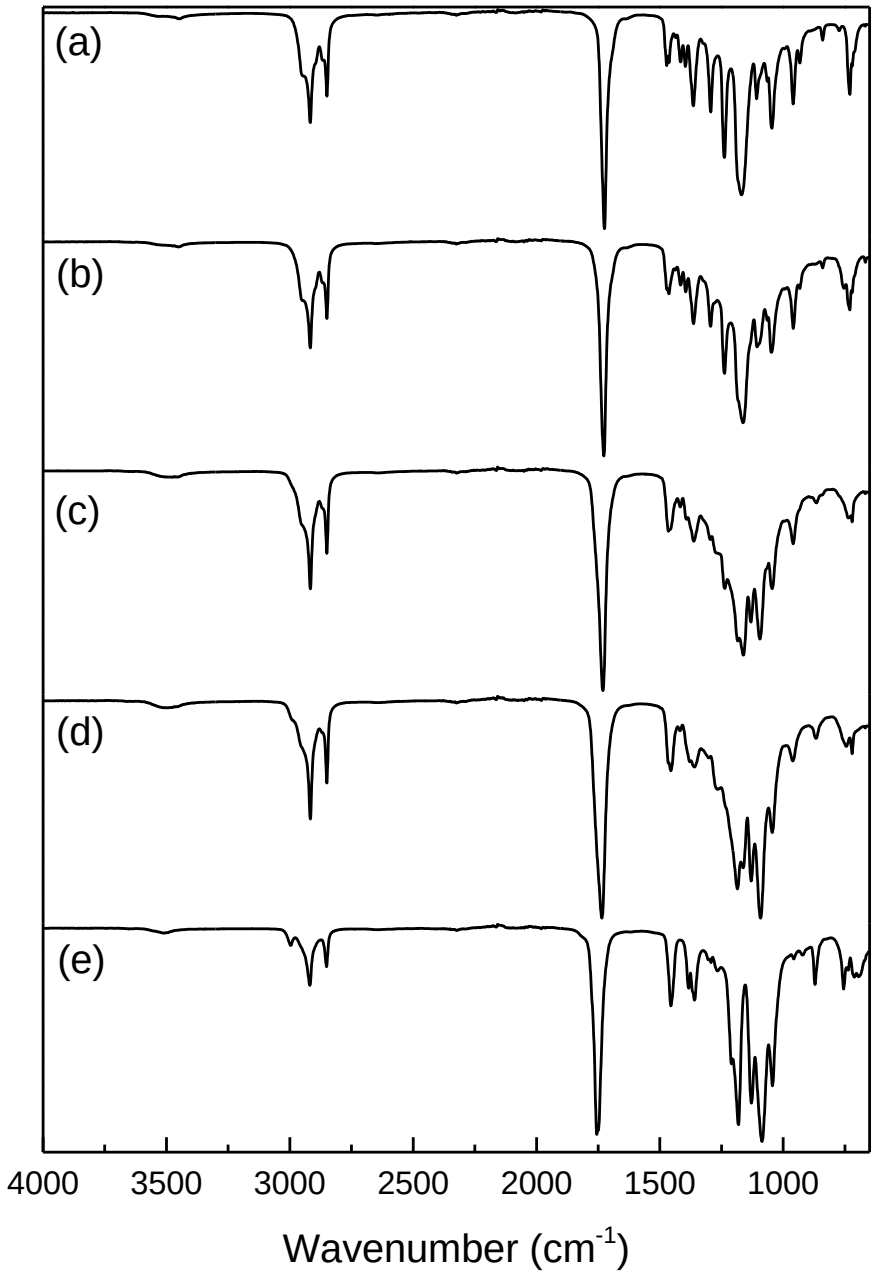
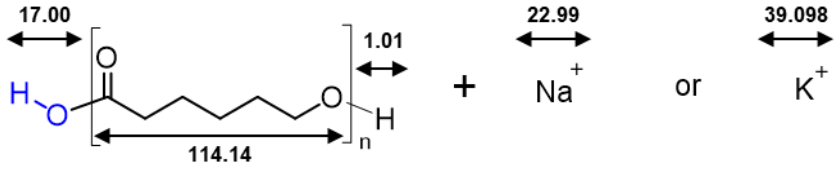
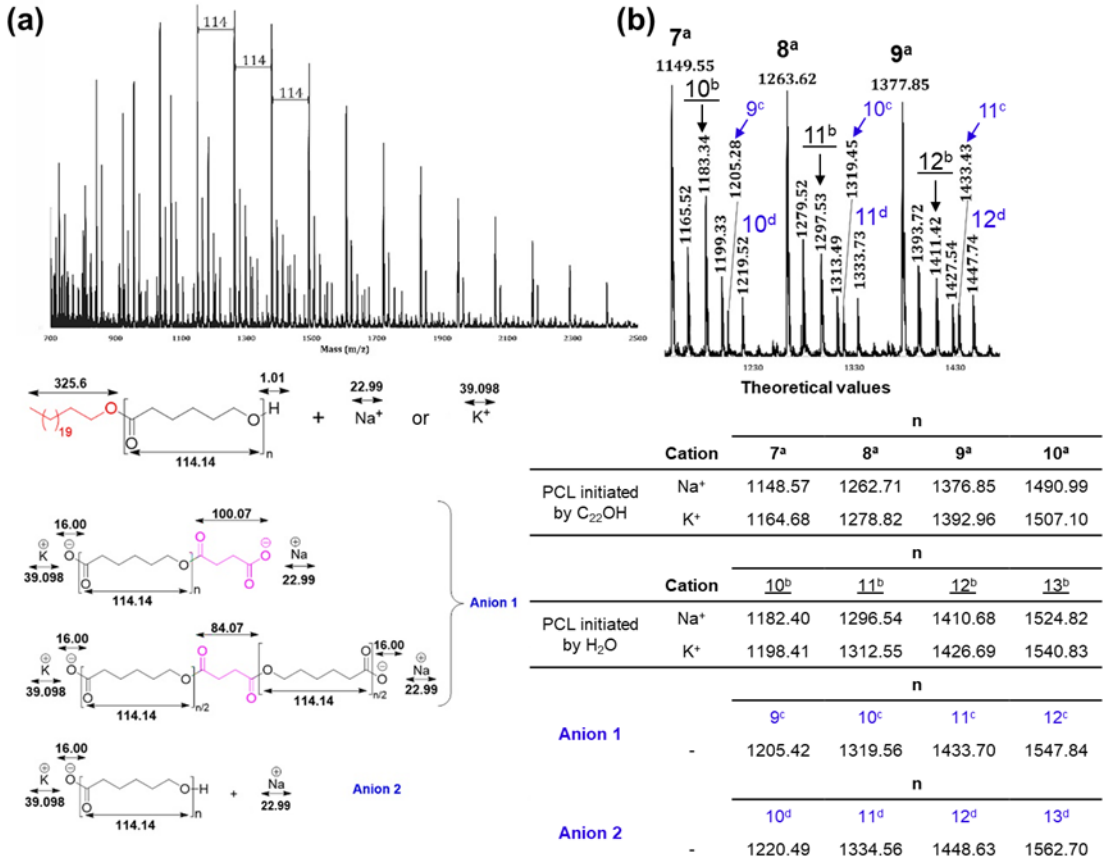


Figure S5. FT-IR spectra of a) PCL, PCL-co-PLLA with CL/L-LA feed b) (90-10), c) (70-30), d) (50-50) and e) PLLA.



Scheme S1. Chemical structure of PCL initiated by H_2O and detected by MALDI-TOF.



		n			
	Cation	7^a	8^a	9^a	10^a
PCL initiated by $C_{22}OH$	Na^+	1148.57	1262.71	1376.85	1490.99
	K^+	1164.68	1278.82	1392.96	1507.10

		n			
	Cation	10^b	11^b	12^b	13^b
PCL initiated by H_2O	Na^+	1182.40	1296.54	1410.68	1524.82
	K^+	1198.41	1312.55	1426.69	1540.83

		n			
		9^c	10^c	11^c	12^c
Anion 1	-	1205.42	1319.56	1433.70	1547.84

		n			
		10^d	11^d	12^d	13^d
Anion 2	-	1220.49	1334.56	1448.63	1562.70