Supplementary Information

Well-Controlled Synthesis of Biodegradable Polyesters using Edible Catalysts

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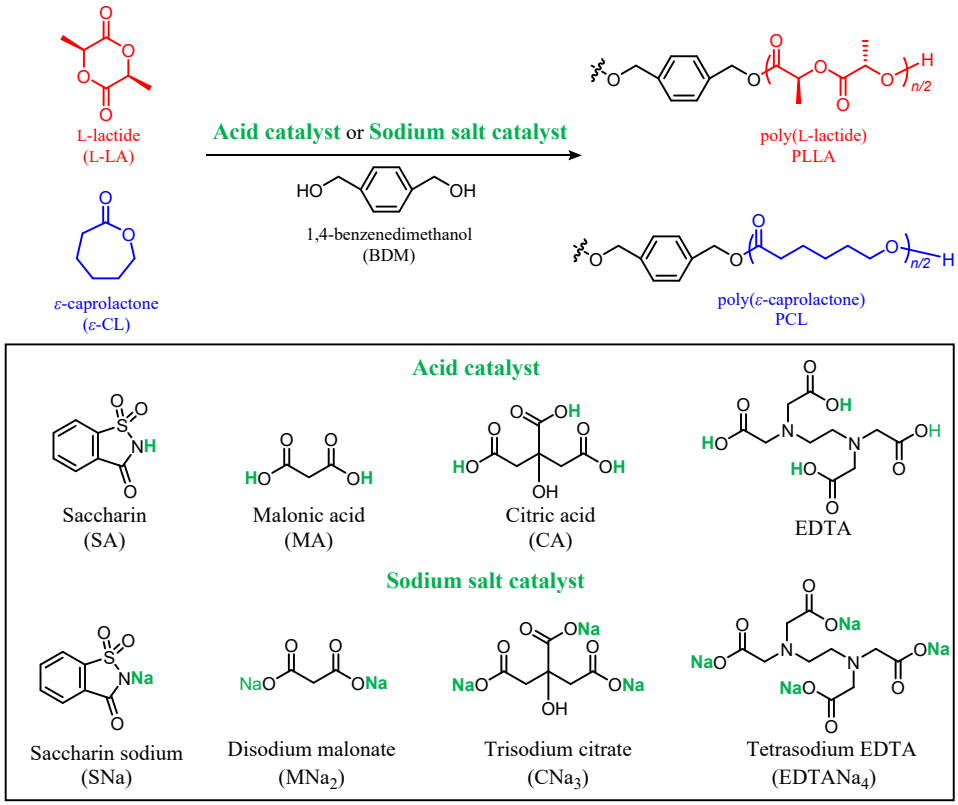


Table S1 Ring-opening polymerization of L-LA and ε-CL using various catalysts [a]

run	monomer	catalyst	conv. (%) [b]	$M_{n,th.}$ (g mol^{-1}) [b]	$M_{n,NMR}$ (g mol^{-1}) [c]	$M_{n,SEC}$ (g mol^{-1}) [d]	$Đ$ [d]
1	L-LA	SA	4.8	830	n.d. [e]	n.d. [e]	n.d. [e]
2		MA	8.9	1420	n.d. [e]	n.d. [e]	n.d. [e]
3		CA	9.2	1460	n.d. [e]	n.d. [e]	n.d. [e]
4		EDTA	7.2	1180	n.d. [e]	n.d. [e]	n.d. [e]
5		SNa	34.1	5050	n.d. [e]	3900	1.12
6		MNa_2	88.2	12,900	7060	7800	1.15
7		CNa_3	64.9	9490	6620	5800	1.14
8		$EDTANa_4$	96.2	14,000	16,400	8900	1.21
9	ε-CL	SA	82.3	9530	8930	15,200	1.13
10		MA	25.6	3060	n.d. [e]	4400	1.16
11		CA	97.9	11,300	13,300	9500	1.81
12		EDTA	<3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]
13		SNa	<3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]
14		MNa_2	<3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]
15		CNa_3	<3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]
16		$EDTANa_4$	<3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]

[a] Polymerization conditions: atmosphere, Ar; initiator, BDM; $[monomer]_0/[BDM]_0/[catalyst]$ = 100/1/5; temperature, 100 ºC; reaction time, 24 h. [b] Determined by ^{1}H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Calculated from $[monomer]_0/[BDM]_0$ × conv. × (M.W. of monomer) + (M.W. of BDM). [d] Determined by SEC in THF using polystyrene standard. [e] Not determined.

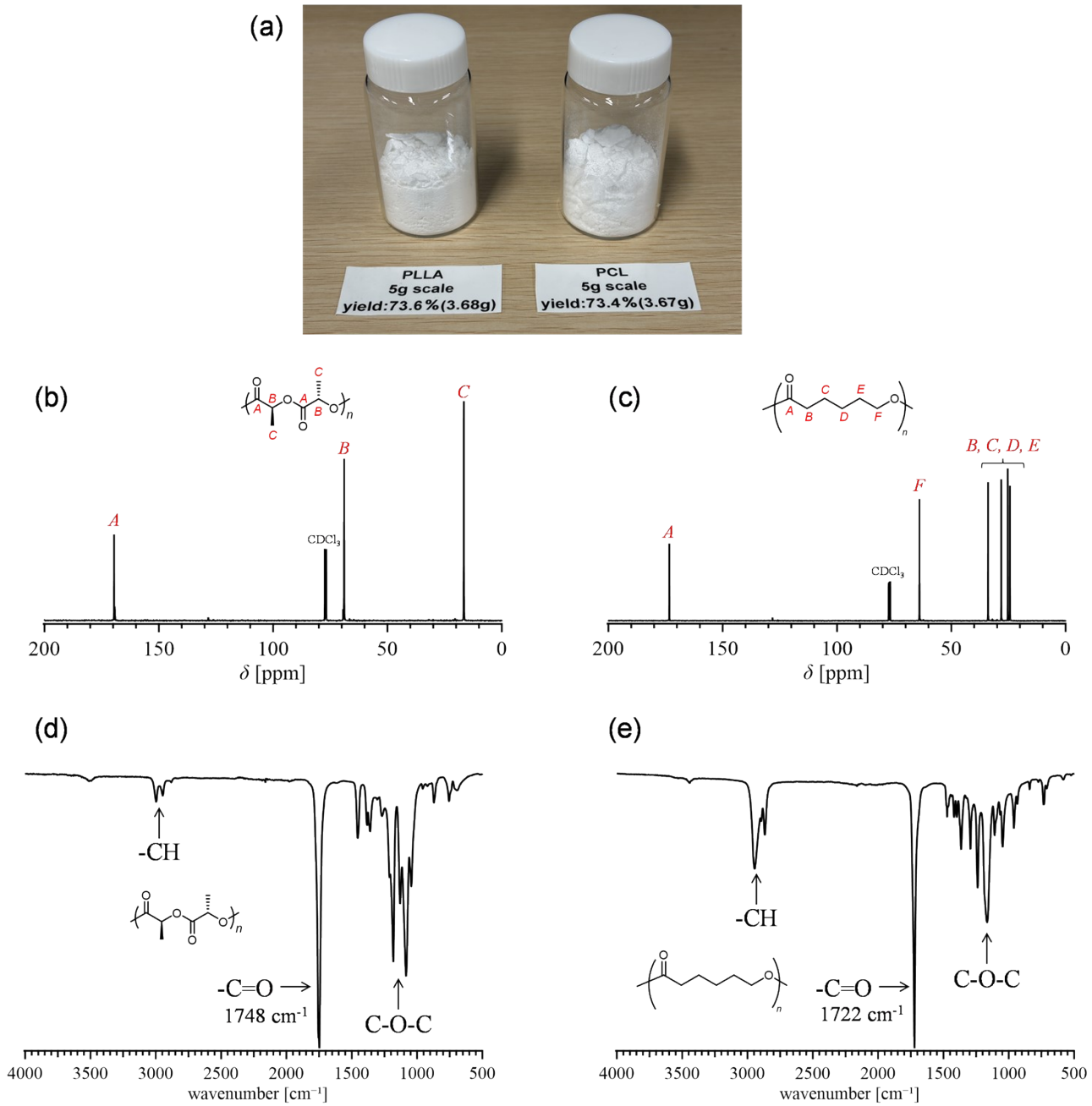


Fig. S1. **(a)** Photographs of PLLA and PCL synthesized on a larger scale. (runs 5 and 8 in **Table 1**). **(b)** ^{13}C NMR spectrum of the PLLA obtained from run 5 in **Table 1** (solvent, $CDCl_3$; 100 MHz). **(c)** ^{13}C NMR spectrum of the PCL obtained from run 8 in **Table 1** (solvent, $CDCl_3$; 100 MHz). **(d)** FT-IR spectrum of of the PLLA obtained from run 5 in **Table 1**. **(e)** FT-IR spectrum of of the PCL obtained from run 8 in **Table 3**.

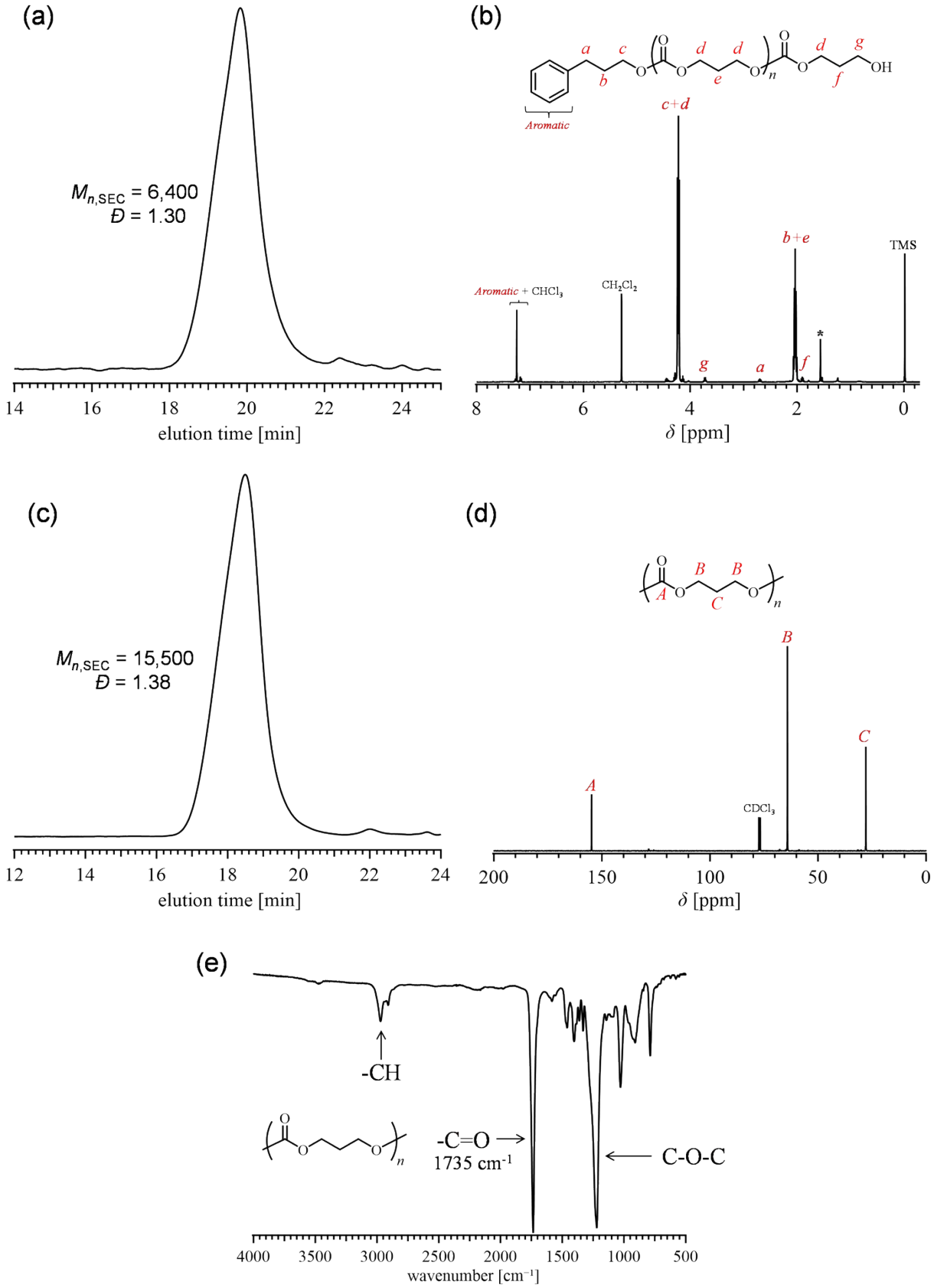


Fig. S2 (a) SEC trace of the PTMC obtained from run 2 in **Table 2** (eluent, THF; flow rate, 1.0 mL min^{-1}). **(b)** ^{1}H NMR spectrum of the PTMC obtained from run 2 in **Table 2** (solvent, $CDCl_3$; 400 MHz). **(c)** SEC trace of the PTMC obtained from run 3 in **Table 2** (eluent, THF; flow rate, 1.0 mL min^{-1}). **(d)** ^{13}C NMR spectrum of the PTMC obtained from run 3 in **Table 2** (solvent, $CDCl_3$; 100 MHz). **(e)** FT-IR spectrum of of the PTMC obtained from run 3 in **Table 2**.

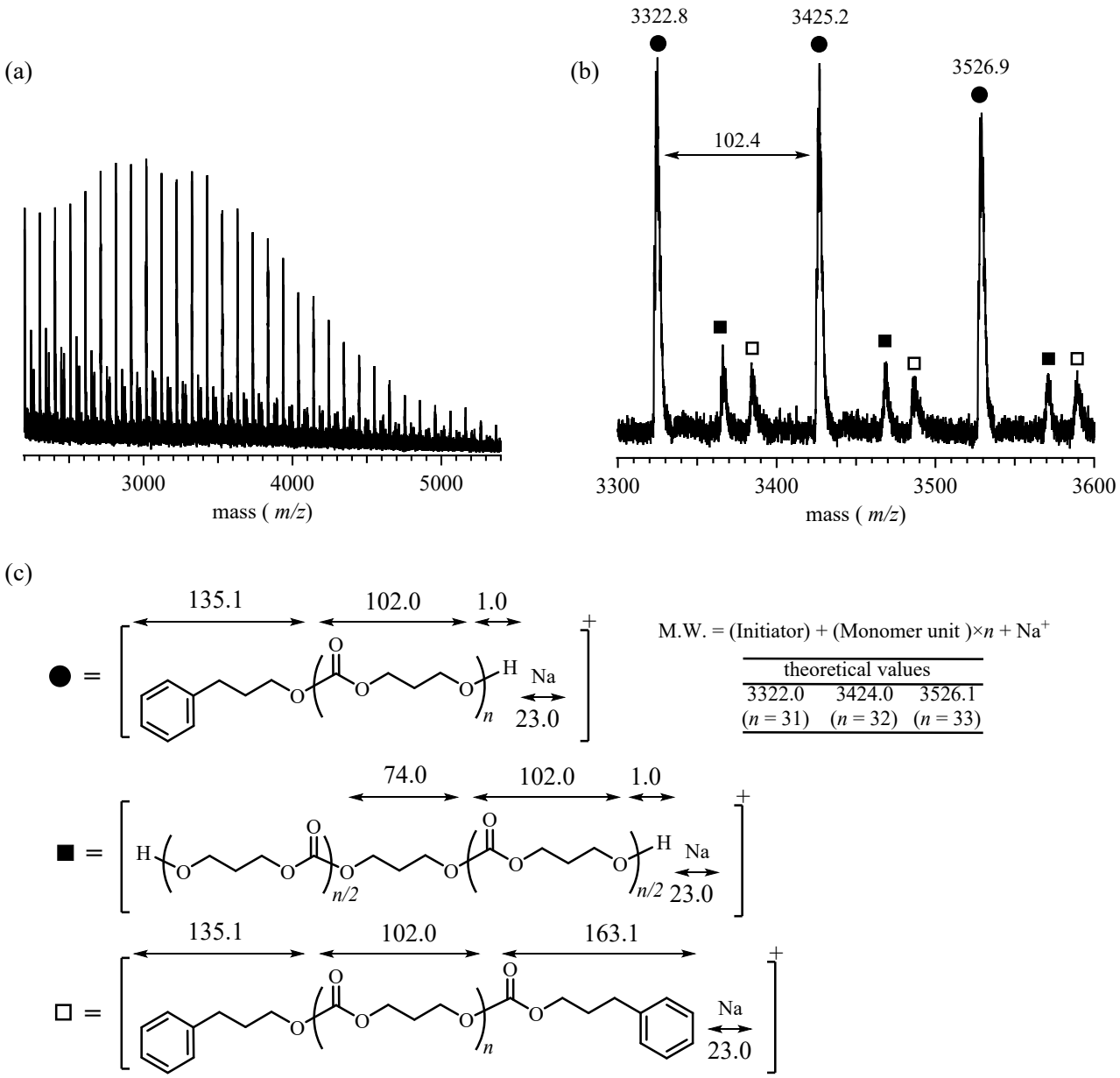


Fig. S3 (a) MALDI-TOF mass spectrum of PTMC (run 2 in **Table 2**), (b) expanded spectrum (ranging from 3300 to 3600), and (c) theoretical values.

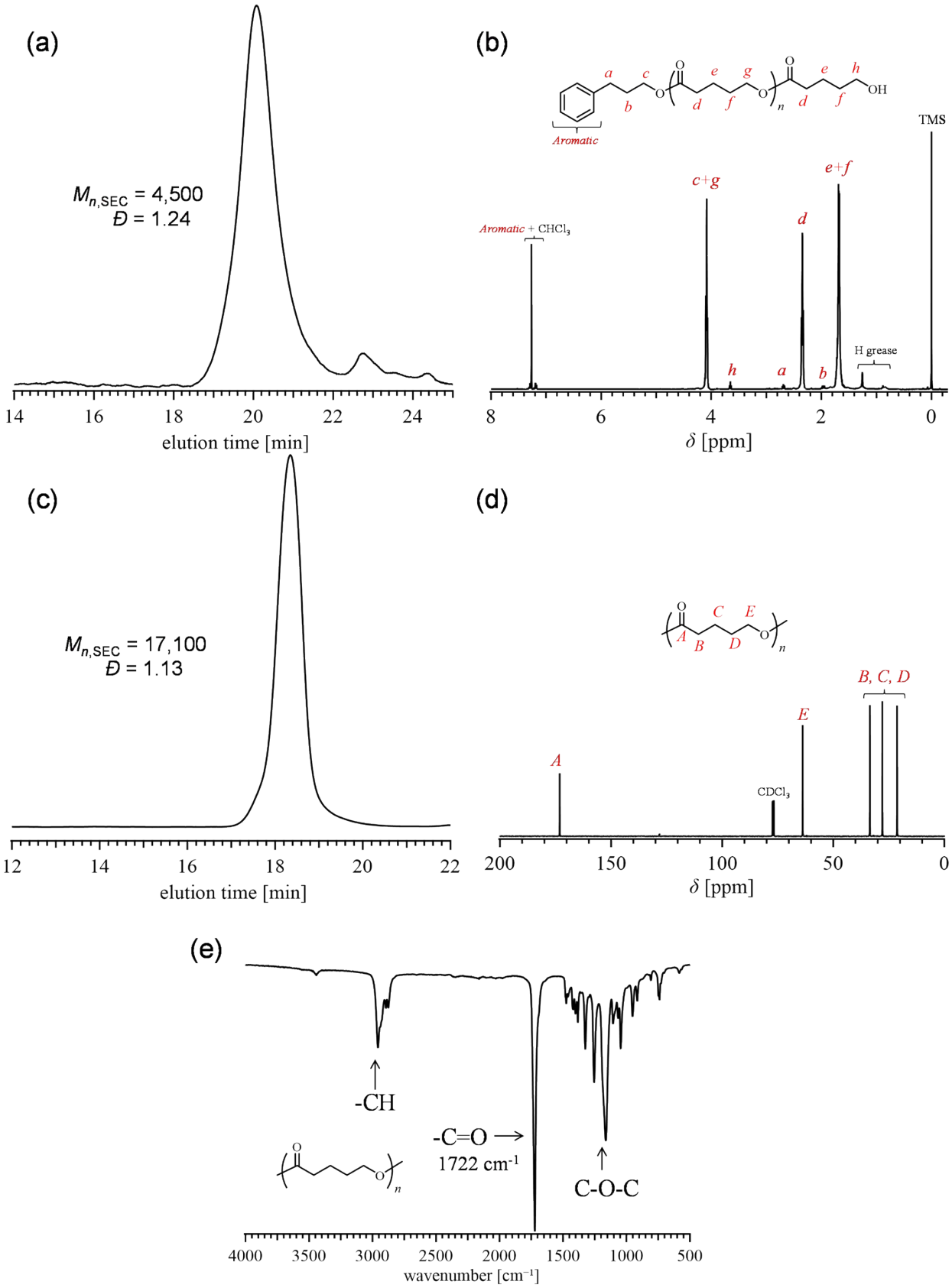


Fig. S4 (a) SEC trace of the PVL obtained from run 4 in **Table 2** (eluent, THF; flow rate, 1.0 mL min^{-1}). **(b)** ^{1}H NMR spectrum of the PVL obtained from run 4 in **Table 2** (solvent, $CDCl_3$; 400 MHz). **(c)** SEC trace of the PVL obtained from run 6 in **Table 2** (eluent, THF; flow rate, 1.0 mL min^{-1}). **(d)** ^{13}C NMR spectrum of the PVL obtained from run 6 in **Table 2** (solvent, $CDCl_3$; 100 MHz). **(e)** FT-IR spectrum of of the PVL obtained from run 6 in **Table 2**

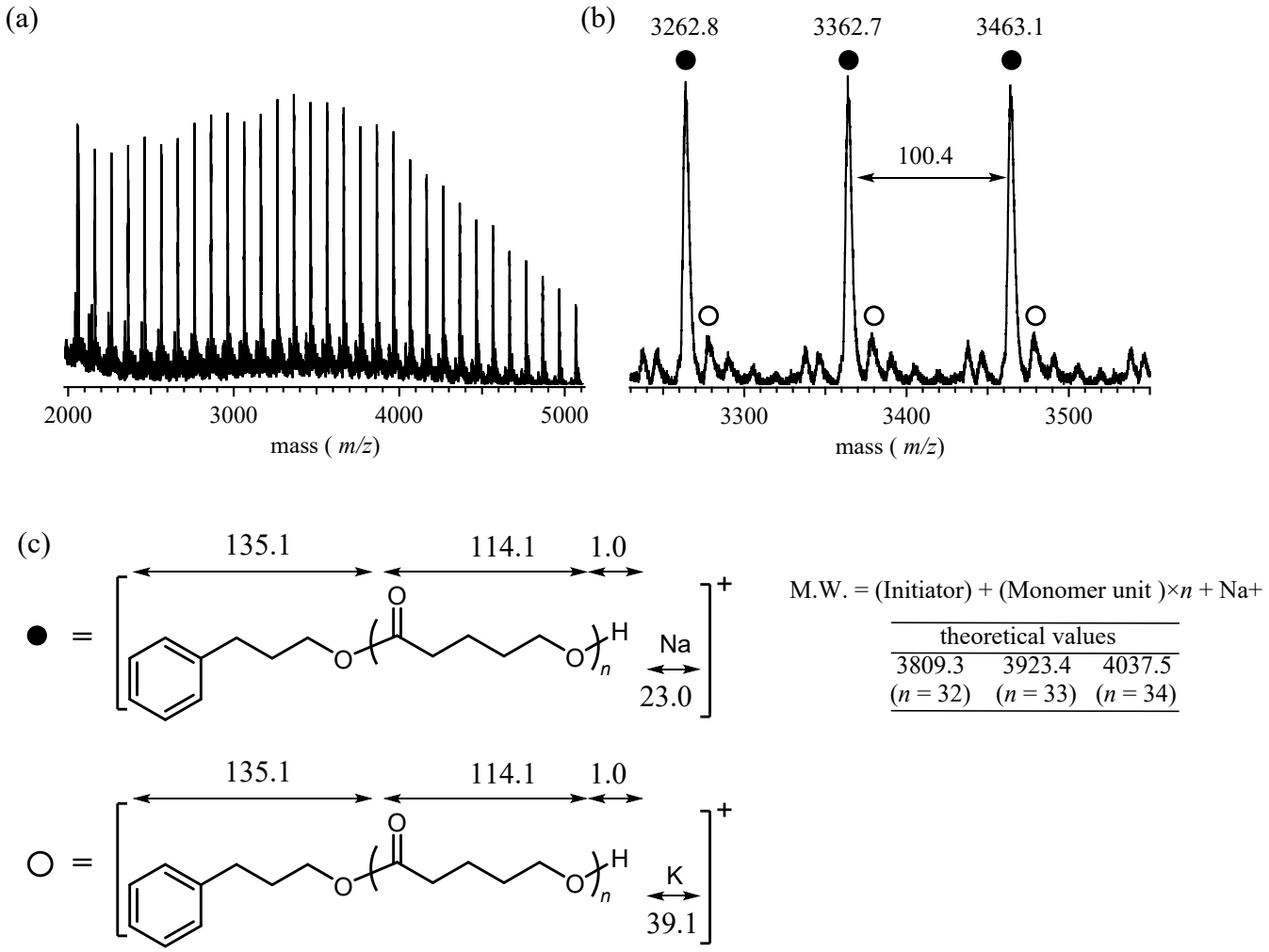


Fig. S5 (a) MALDI-TOF mass spectrum of PVL (run 4 in **Table 2**), (b) expanded spectrum (ranging from 3230 to 3550), and (c) theoretical values.

Scheme S1 Ring-opening polymerization of L-LA and ε-CL catalyzed by various citrates

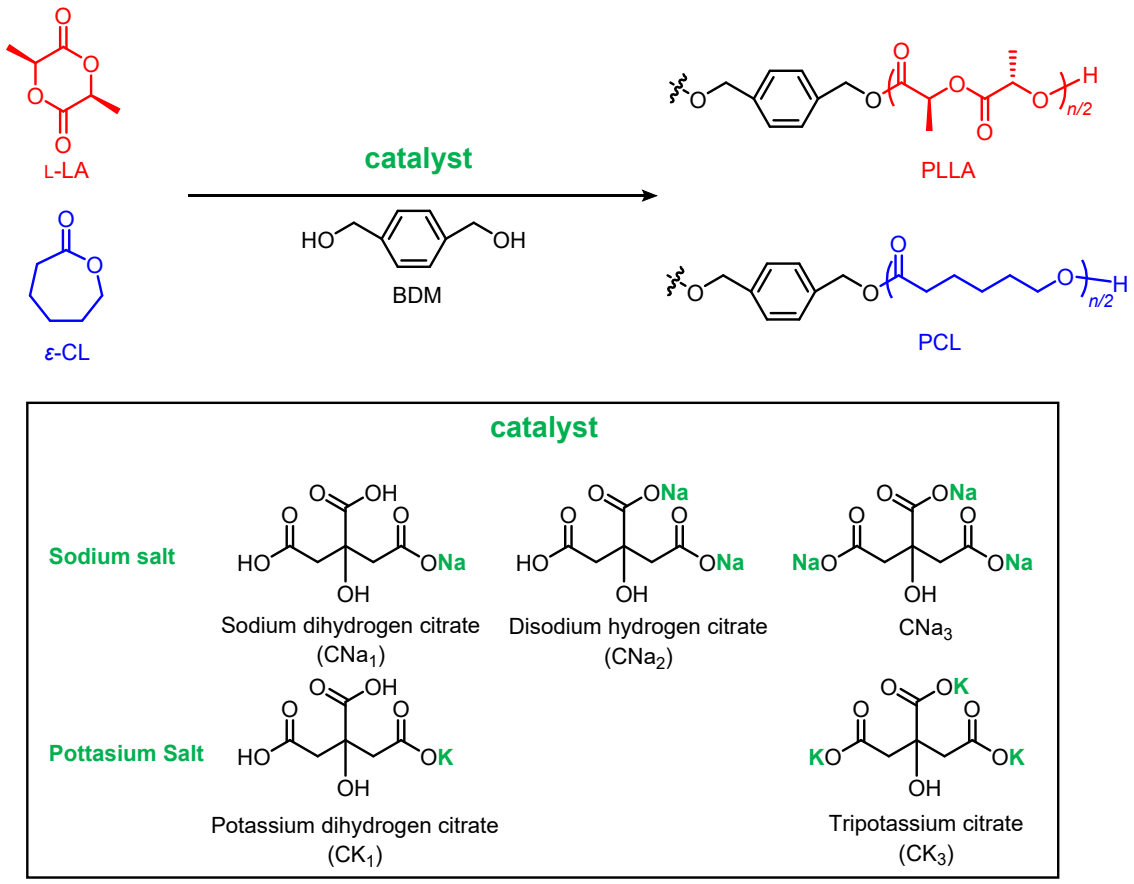


Table S2 Ring-opening polymerization of L-LA and ε-CL catalyzed by various citrates [a]

run	monomer	Catalyst	conv. (%) [b]	$M_{n,th.}$ (g mol^{-1}) [c]	$M_{n,NMR}$ (g mol^{-1}) [b]	$M_{n,SEC}$ (g mol^{-1}) [d]	$Đ$ [d]
1	L-LA	CA	9.2	1460	n.d. [e]	n.d. [e]	n.d. [e]
2		CNa_1	9.6	1520	n.d. [e]	n.d. [e]	n.d. [e]
3		CNa_2	17.1	2600	n.d. [e]	n.d. [e]	n.d. [e]
4		CNa_3	64.9	9490	6620	5800	1.14
5		CK_1	21.1	3180	n.d. [e]	n.d. [e]	n.d. [e]
6		CK_3	97.8	14,200	7780	10,500	1.09
7	ε-CL	CA	97.9	11,300	11,900	9500	1.81
8		CNa_1	96.9	11,200	11,900	8300	1.44
9		CNa_2	15.4	1900	n.d. [e]	n.d. [e]	n.d. [e]
10		CNa_3	< 3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]
11		CK_1	< 3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]
12		CK_3	< 3.0	n.d. [e]	n.d. [e]	n.d. [e]	n.d. [e]

[a] Polymerization conditions: atmosphere, Ar; initiator, BDM; $[monomer]_0/[BDM]_0/[catalyst]$ = 100/1/5; temperature, 100 ºC; reaction time, 24 h. [b] Determined by ^{1}H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Calculated from $[monomer]_0/[BDM]_0$ × conv. × (M.W. of monomer) + (M.W. of BDM). [d] Determined by SEC in THF using polystyrene standard. [e] Not determined.

In general, once the monomer is nearly fully consumed, side reactions such as intra- and intermolecular transesterification may occur, leading to an increase in dispersity (*Đ*), as observed in run 7 of **Table S2**. However, in run 6 of **Table S2**, a narrow dispersity was obtained even though the L-LA monomer reached nearly complete conversion.

To elucidate the dependence of dispersity (*Đ*) on the progression of polymerization during the ROP of L-LA, kinetic monitoring was conducted under the same polymerization conditions as those used in run 6 of **Table S2**. The polymerization was carried out in a single batch, and aliquots were withdrawn at predetermined time intervals. The resulting crude samples were analyzed by ^{1}H NMR and SEC to evaluate monomer conversion, $M_{n,SEC}$, and *Đ*. The results are summarized in **Table S3** and **Fig. S6**.

Although the results were not identical to those obtained in run 6 of **Table S2**, the kinetic study showed that the conversion of L-LA reached near completion between 12 and 24 h. With further extension of the reaction time, the dispersity gradually increased. Nevertheless, even after 72 h, the final dispersity (*Đ* = 1.45) remained significantly lower than that observed for the ROP of *ε*-CL catalyzed by CA (*Đ* = 1.81, run 7 in **Table S2**).

Therefore, the "inconsistency" between the polymerizations catalyzed by CA and CK_3 can be reasonably attributed to their different activities in promoting transesterification after the monomer conversion reaches a high level.

Table S3 Kinetic study of the Ring-opening polymerization of L-LA catalyzed by CK_3 [a]

time (h)	conv. (%) [b]	$M_{n,SEC}$ (g mol^{-1}) [c]	*Đ* [c]
5.5	60.0	6100	1.22
12.0	88.0	8700	1.24
24.0	99.6	9000	1.32
48.0	99.6	9100	1.37
72.0	99.7	8600	1.45

[a] Polymerization conditions: atmosphere, Ar; initiator, BDM; $[L\text{-LA}]_0/[BDM]_0/[CK_3] = 100/1/5$; temperature, 100 ºC. [b] Determined by ^{1}H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Determined by SEC in THF using polystyrene standard.

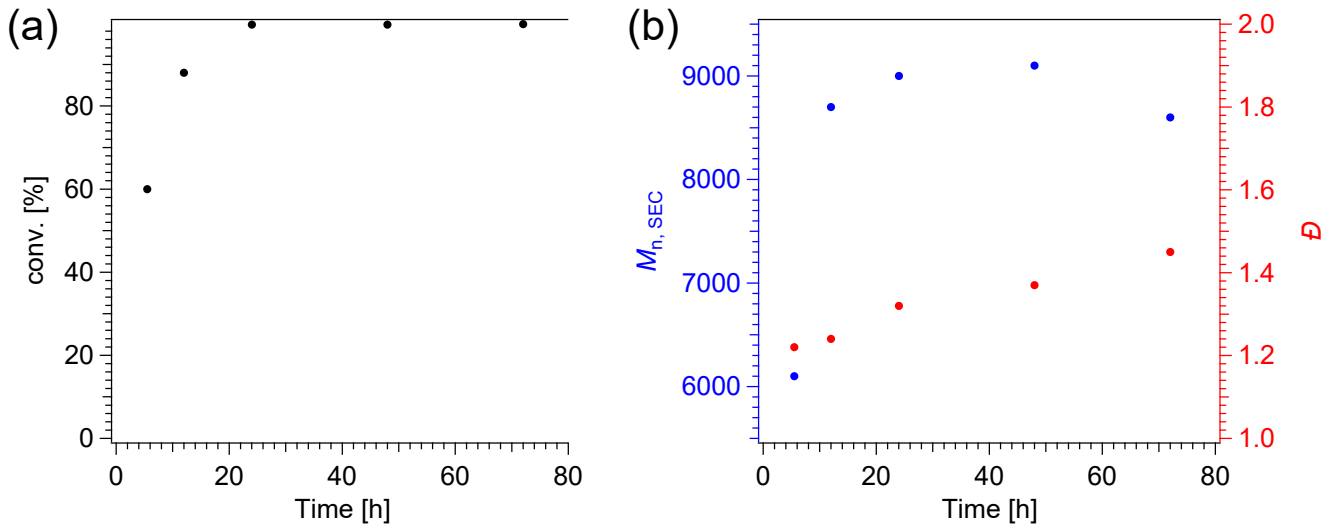
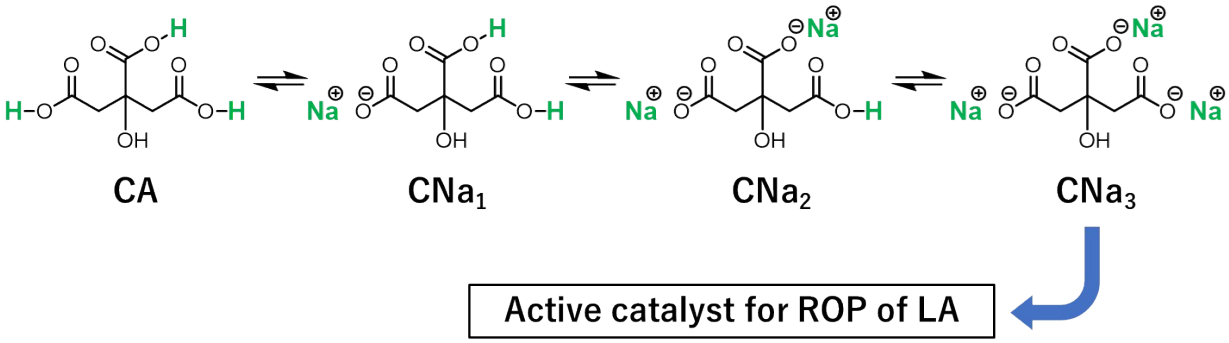


Fig. S6 (a) Time−conversion plot, (b) Time−$M_{n,SEC}$/*Đ* plot of **Table S3**.



Scheme S2 Equilibrium and possible active catalyst for ROP of LA when using CNa_1 and CNa_2 as the catalysts (runs 1–4 in **Table 3** and **Table S2**).

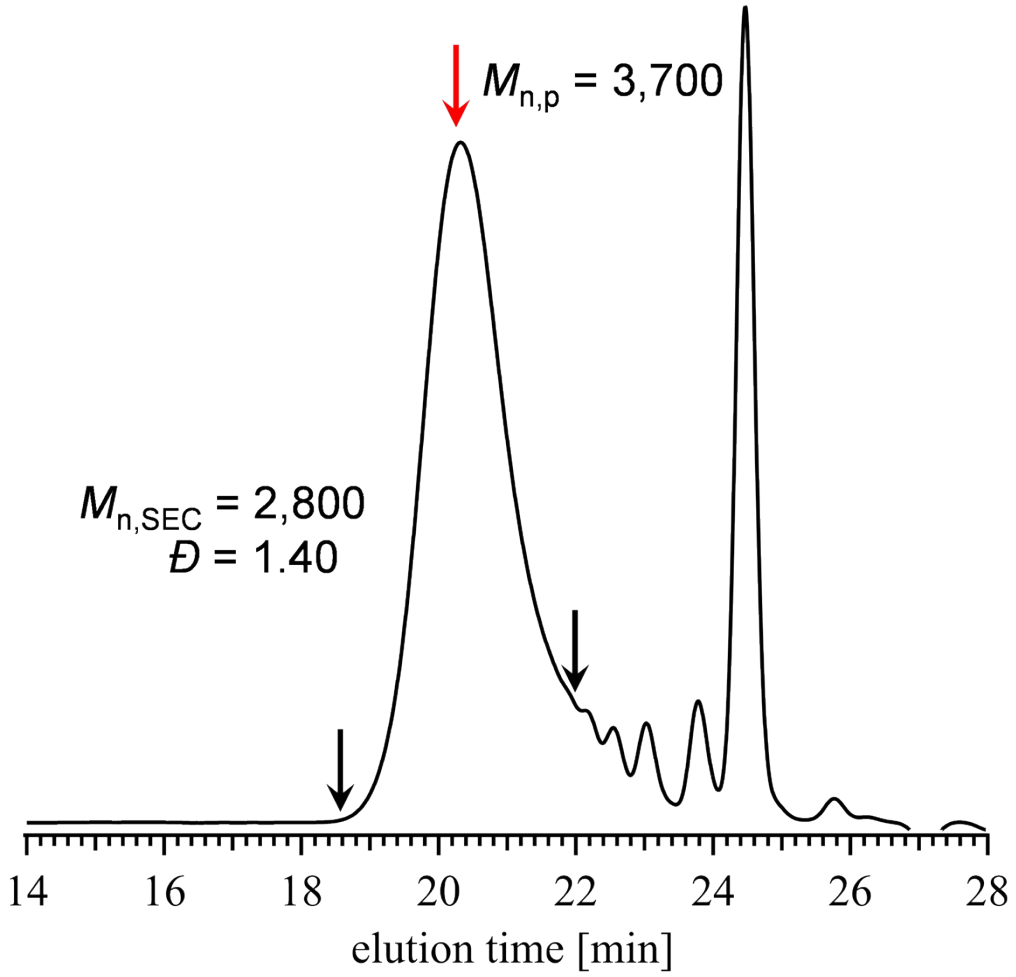


Fig. S7 SEC traces of the PLLA-*stat*-PCL using CA as a catalyst obtained from run 1 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1}). $M_{n,SEC}$ was determined from the elution range between the two black arrows.

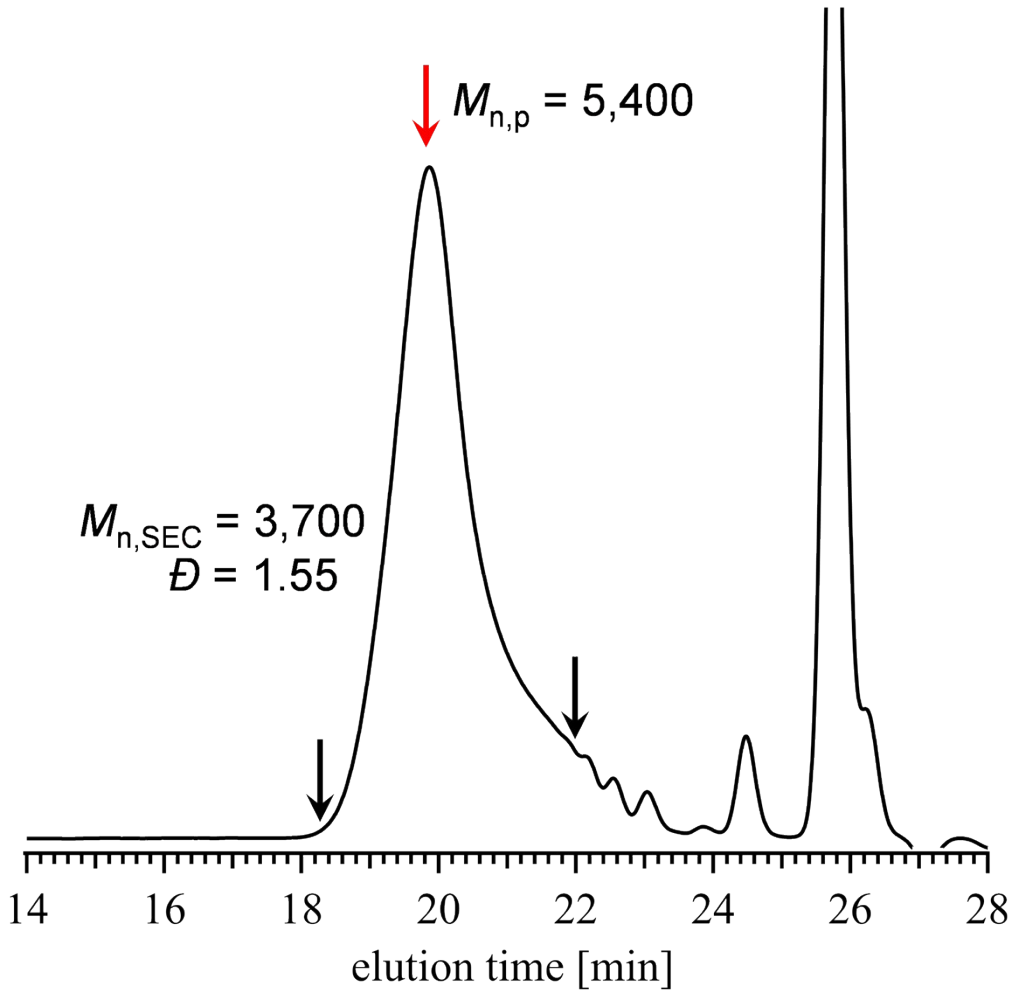


Fig. S8 SEC traces of the PLLA-*stat*-PCL using CNa_3 as a catalyst obtained from run 2 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1}). $M_{n,SEC}$ was determined from the elution range between the two black arrows.

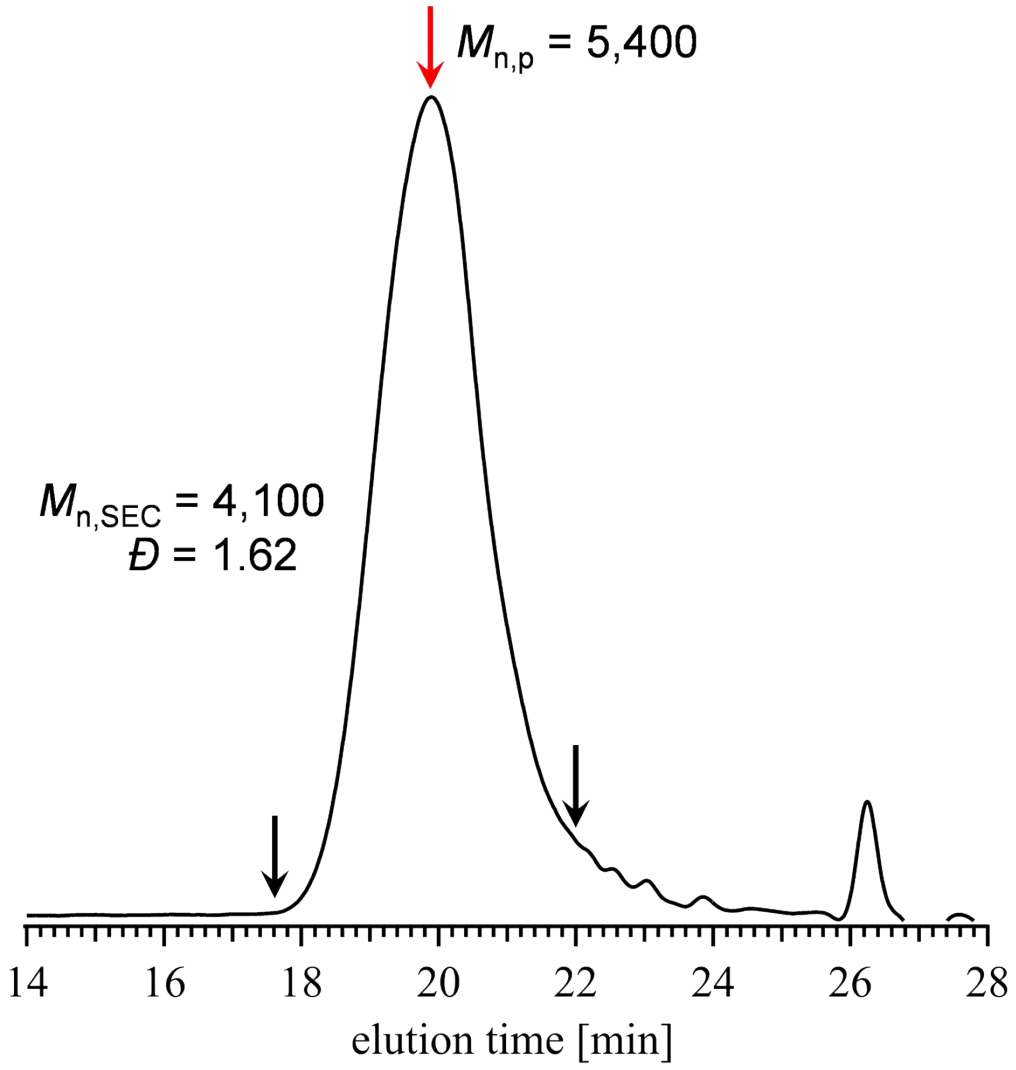


Fig. S9 SEC traces of the PLLA-*stat*-PCL using CNa_1 as a catalyst obtained from run 3 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1}). $M_{n,SEC}$ was determined from the elution range between the two black arrows.

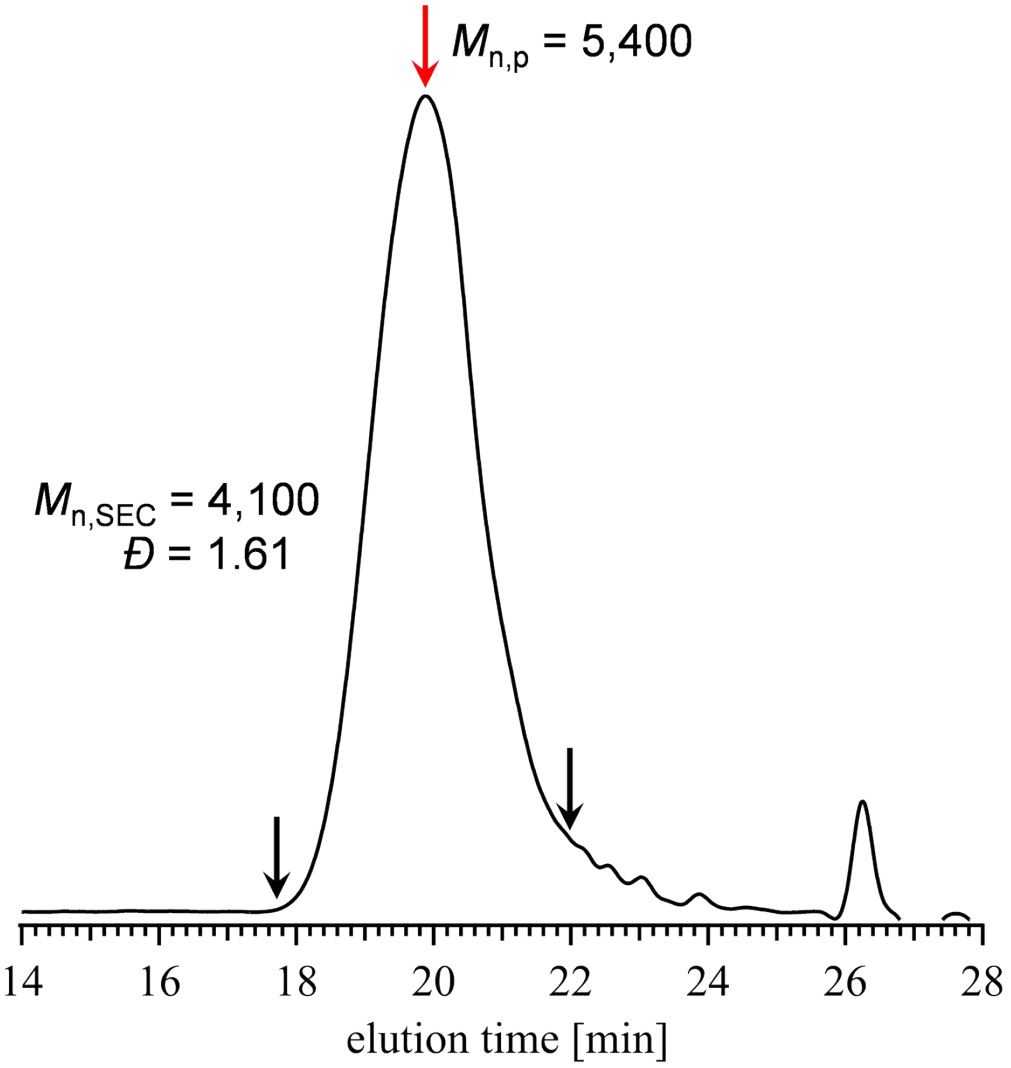


Fig. S10 SEC traces of the PLLA-*stat*-PCL using CNa_2 as a catalyst obtained from run 4 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1}). $M_{n,SEC}$ was determined from the elution range between the two black arrows.

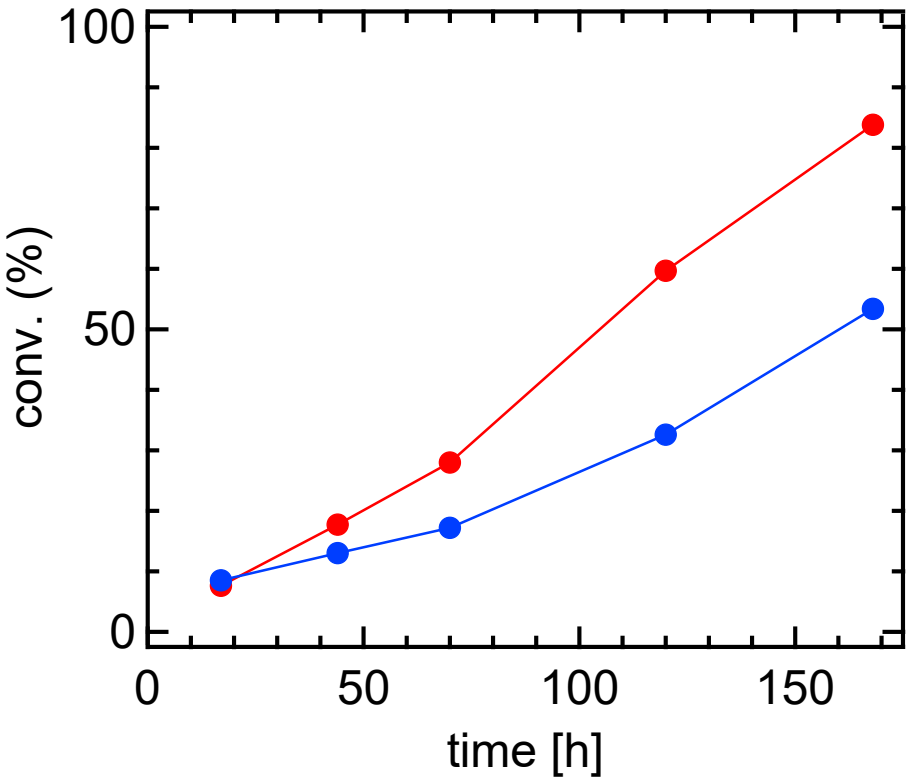


Fig. S11 Plot of monomer conversion vs. time (run 7 in **Table 3**).

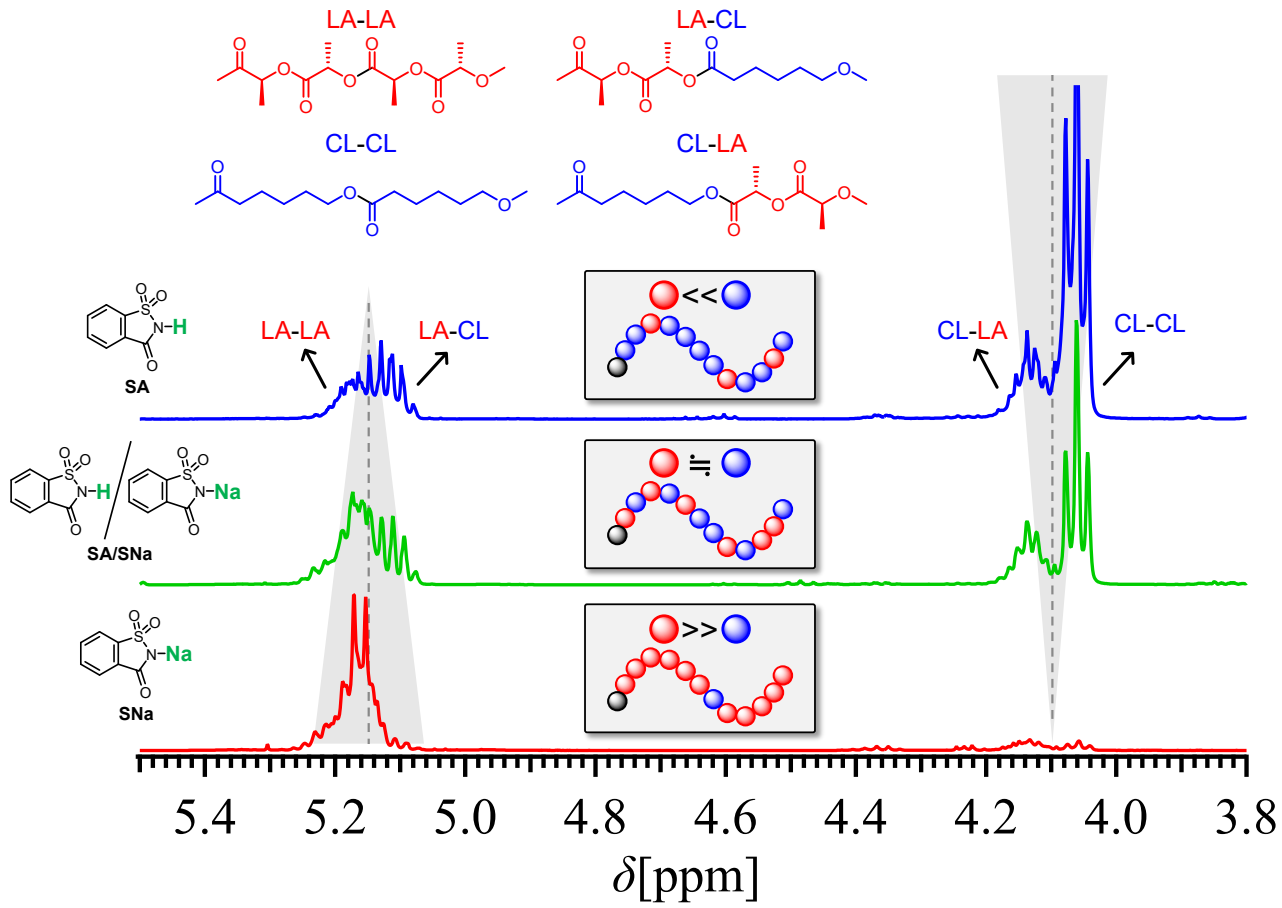


Fig. S12 ^{1}H NMR spectra of the PLLA-*stat*-PCL obtained from runs 5, 6 and 8 in **Table 3** (solvent, $CDCl_3$; 400 MHz). (expanded spectrum ranging from 3.8 ppm to 5.5 ppm.)

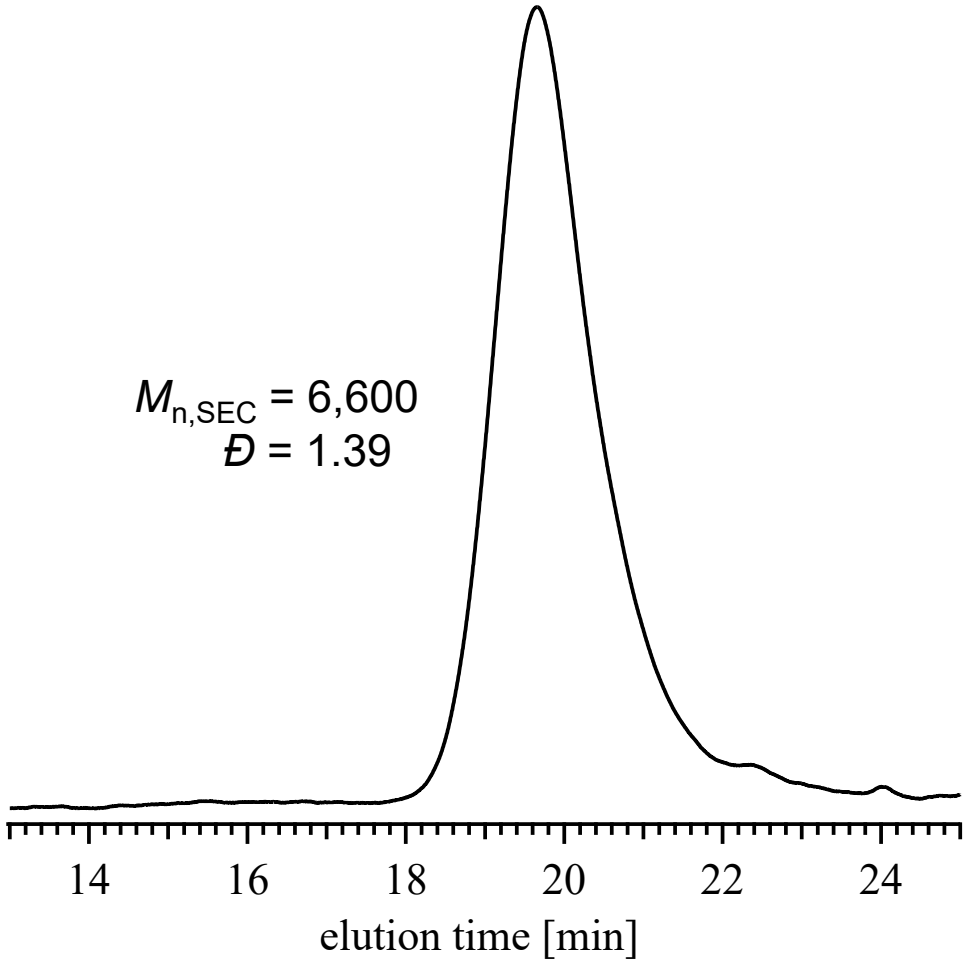


Fig. S13 SEC trace of the PLLA-*stat*-PCL using SA as a catalyst obtained from run 5 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1})

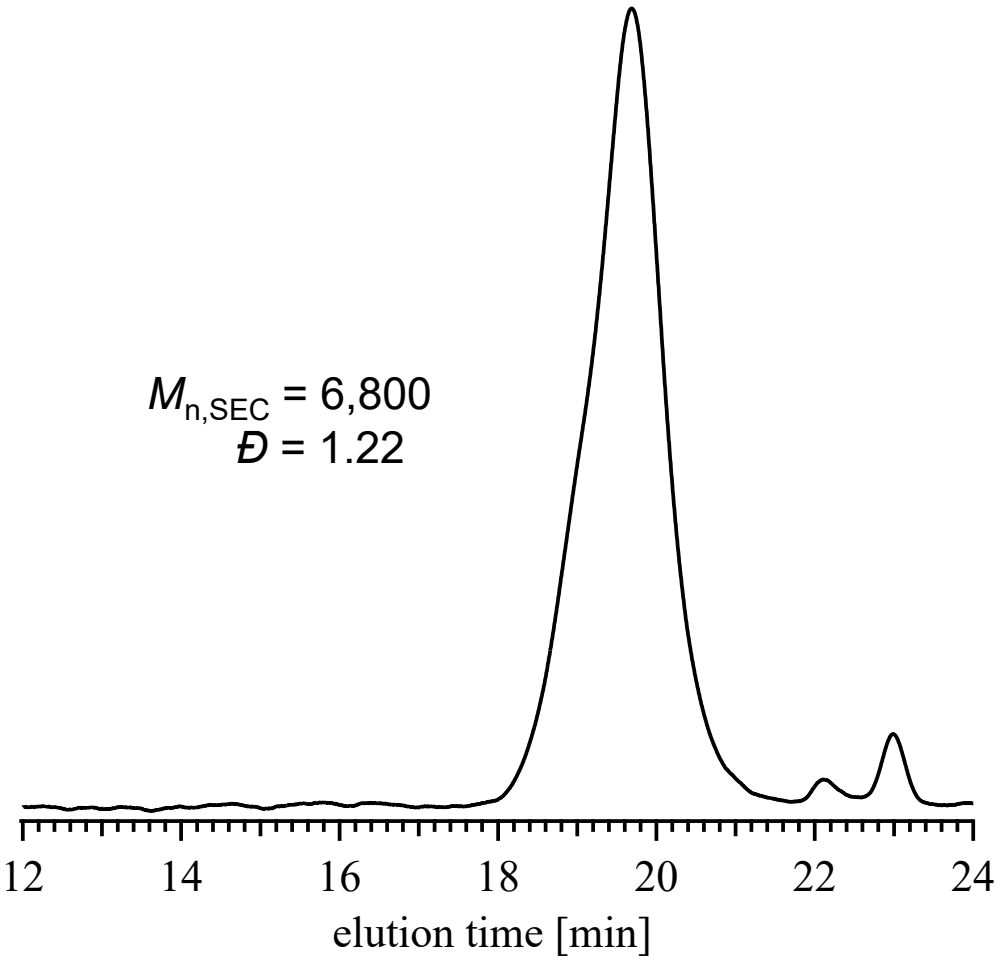


Fig. S14 SEC trace of the PLLA-*stat*-PCL using SNa as a catalyst obtained from run 6 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1})

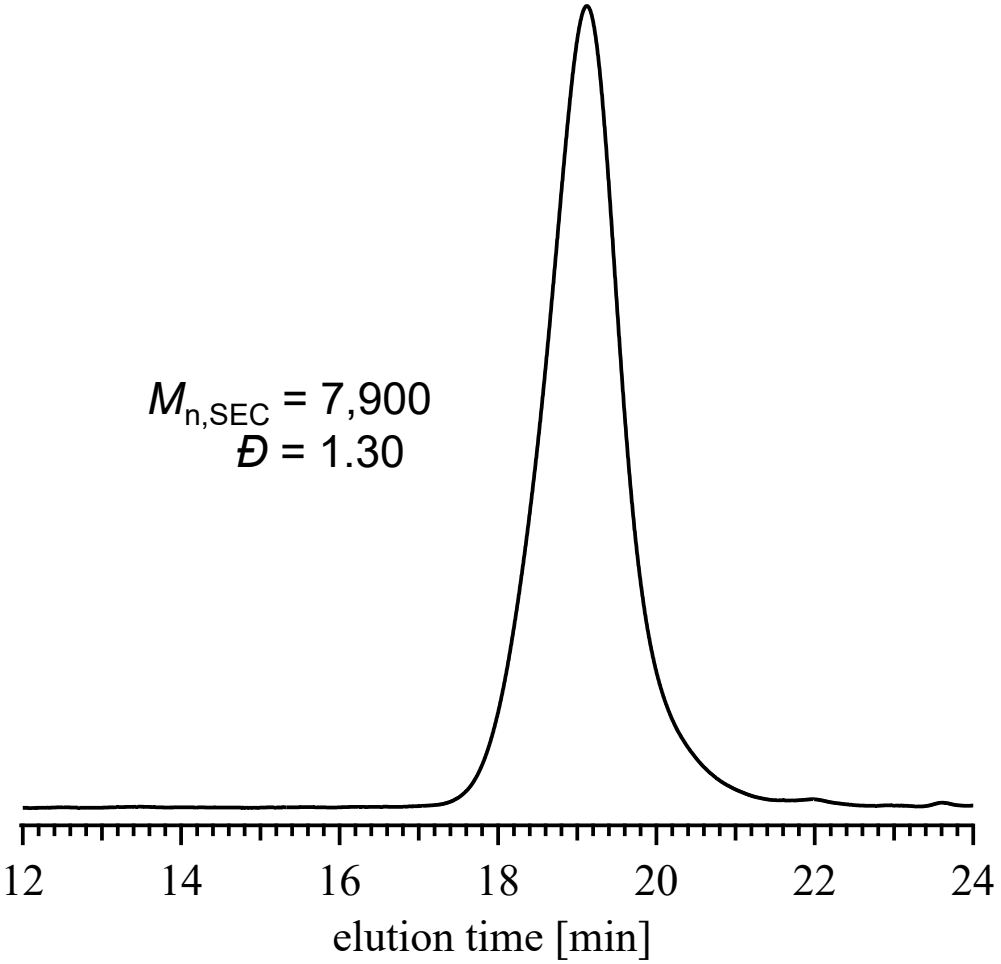


Fig. S15 SEC trace of the PLLA-*stat*-PCL using SA and SNa as a mixed catalyst (SA:SNa=1:4) obtained from run 7 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1})

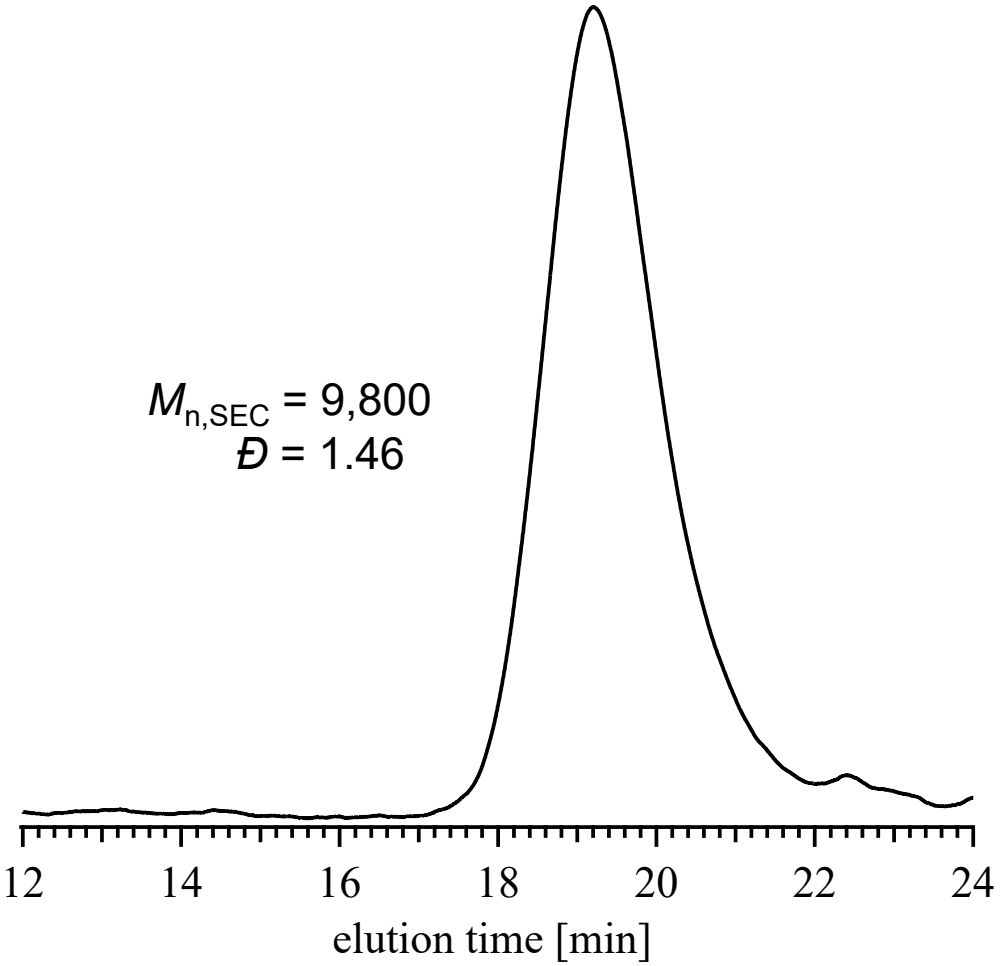


Fig. S16 SEC trace of the PLLA-*stat*-PCL using SA and SNa as a mixed catalyst (SA:SNa=3:2) obtained from run 8 in **Table 3** (eluent, THF; flow rate, 1.0 mL min^{-1})

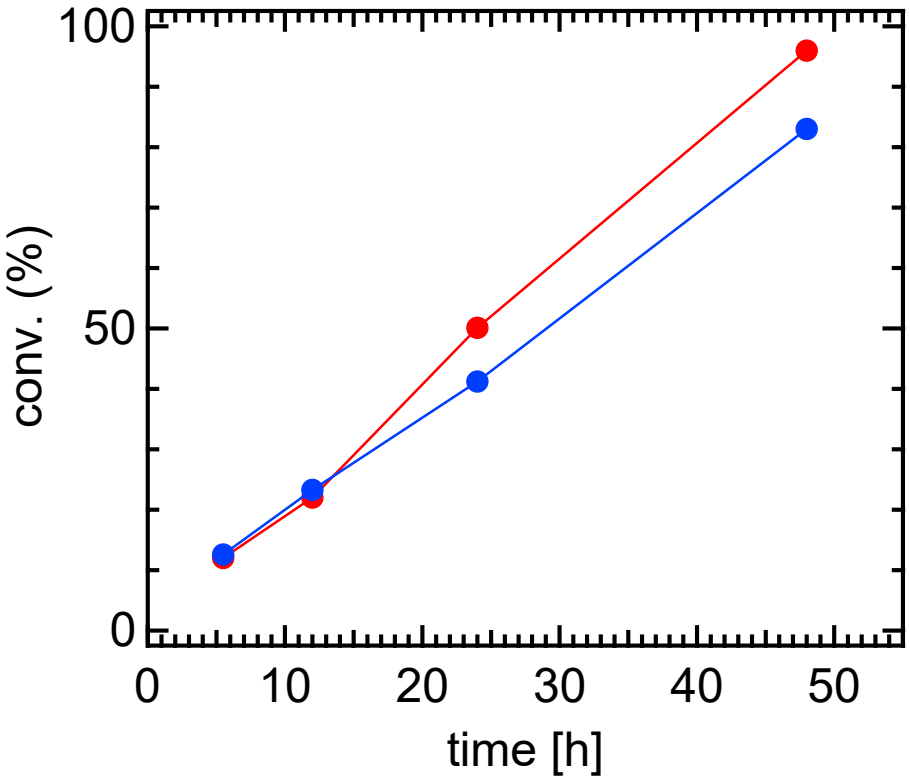


Fig. S17 Plot of monomer conversion vs. time (run 9 in **Table 3**).

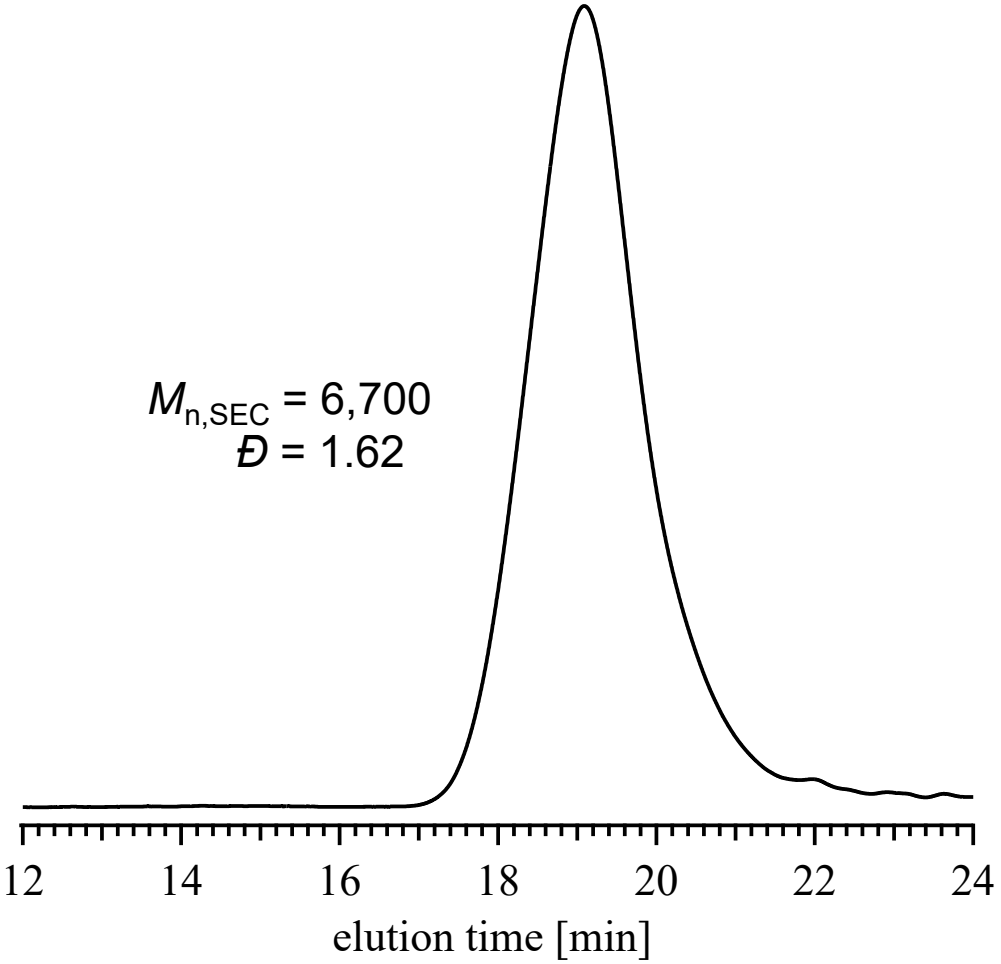


Fig. S18 SEC trace of the PLLA-*stat*-PCL using SA and SNa as a mixed catalyst (SA:SNa=3:2) obtained from run 9 in **Table 3**. The polymerization was conducted at 160 °C (eluent, THF; flow rate, 1.0 mL min^{-1})

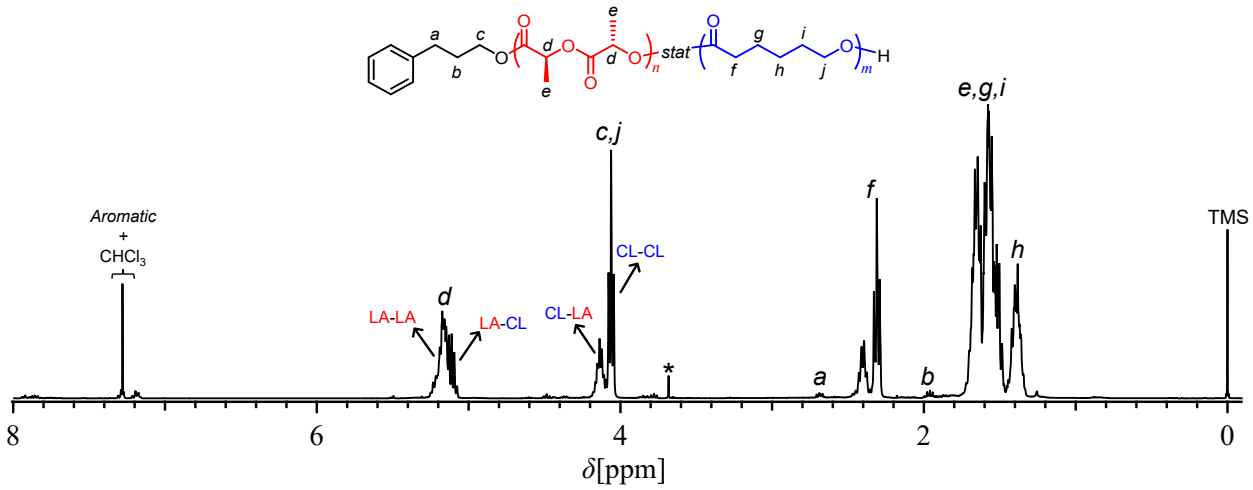


Fig. S19 ^{1}H NMR spectrum of the PLLA-*stat*-PCL using SA and SNa as a mixed catalyst (3:2) obtained from run 8 in **Table 3** (solvent, $CDCl_3$; 400 MHz).

The average sequence lengths of L-LA units and ε-CL units ($L_{L\text{-}LA}$ and $L_{\varepsilon\text{-}CL}$) were calculated using the following equation. Here, [XXX] represents the peak intensity of each triad observed in the ^{13}C NMR spectrum of the PLLA-*stat*-PCL, corresponding to the content of each sequence in the copolymer chain.

$$L_{L-LA} = \frac{[LL\underline{L}LL] + [LL\underline{L}LC] + [CL\underline{L}LL] + [CL\underline{L}C]}{[CL\underline{L}C] + \frac{1}{2}([CL\underline{L}LL] + [LL\underline{L}LC])}$$

$$= \frac{[LL\underline{L}LL] + [LL\underline{L}LC] + [CL\underline{L}LL] + [CL\underline{L}C]}{[CL\underline{L}C] + [C\underline{L}LLL] + [LLL\underline{L}C]} \quad (\because [CL\underline{L}LL] = [C\underline{L}LLL], [LL\underline{L}LC] = [LLL\underline{L}C])$$

$$= \frac{103.75 + 176.75}{103.75} = 2.7$$

$$L_{\varepsilon-CL} = \frac{[C\underline{C}C] + [C\underline{C}LL] + [LL\underline{C}C] + [LL\underline{C}LL]}{[LL\underline{C}LL] + \frac{1}{2}([C\underline{C}LL] + [LL\underline{C}C])}$$

$$= \frac{[C\underline{C}C] + [C\underline{C}LL] + [LL\underline{C}C] + [LL\underline{C}LL]}{[LL\underline{C}LL] + [C\underline{C}LL]} \quad (\because [LL\underline{C}C] = [C\underline{C}LL])$$

$$= \frac{53.86 + 100}{53.86} = 2.9$$

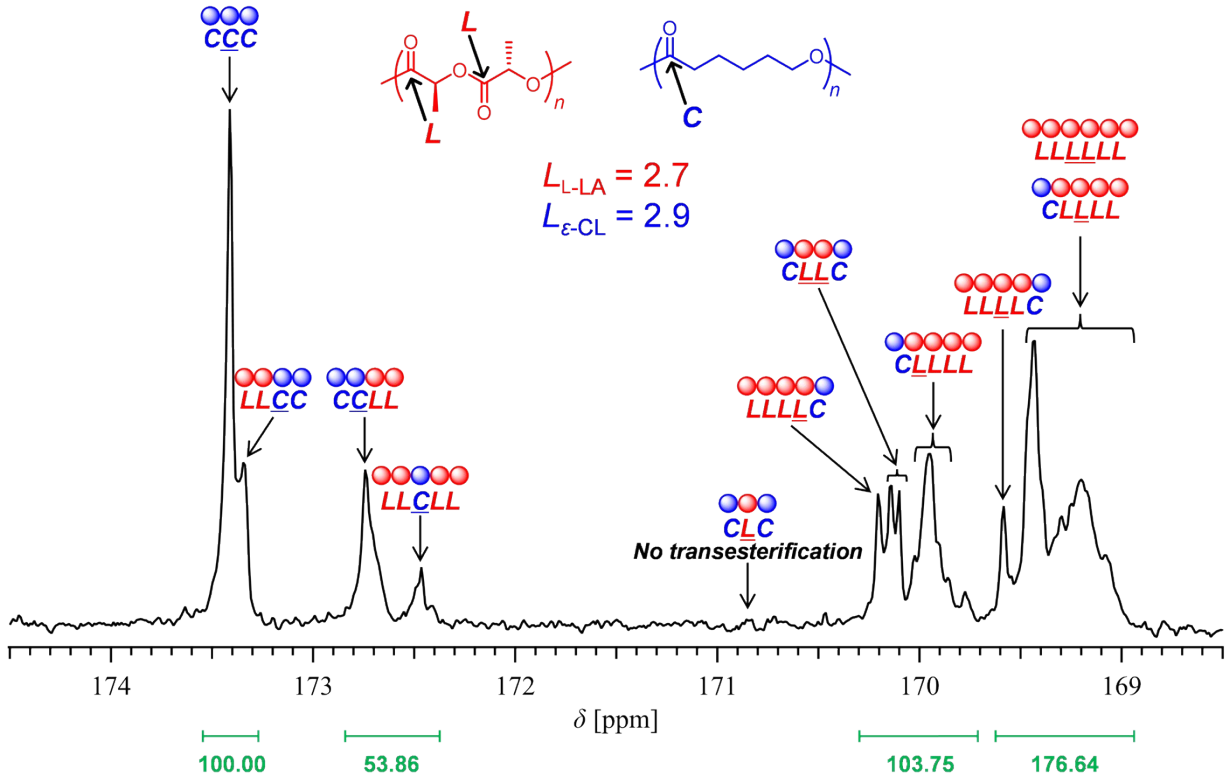


Fig. S20 Determination of the average sequence length by quantitative ^{13}C NMR (PLLA-*stat*-PCL using SA and SNa as a mixed catalyst (3:2) obtained from run 8 in **Table 3**).

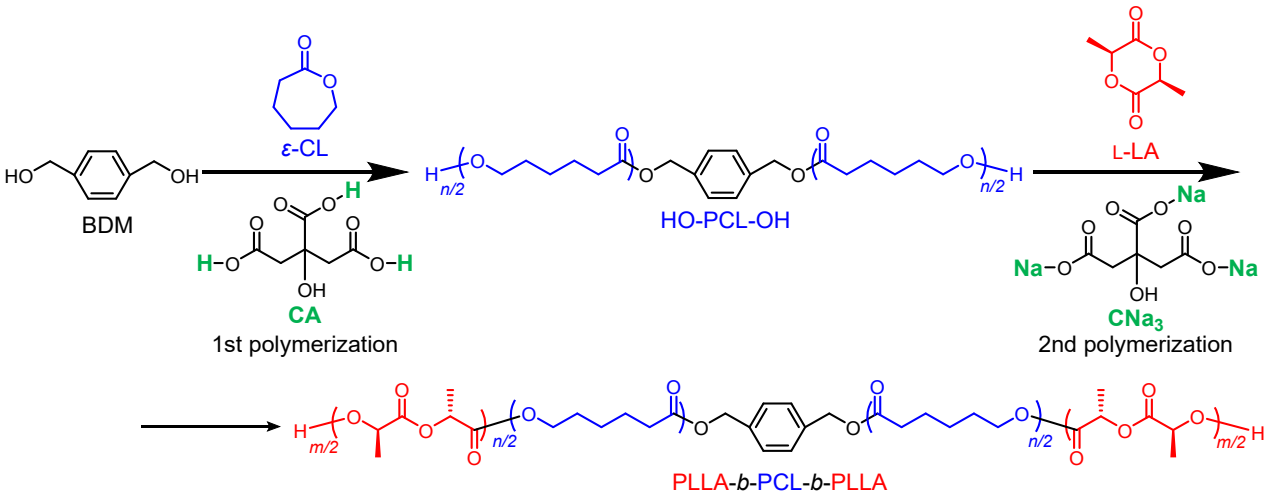


Table S4 One-pot synthesis of PLLA-*b*-PCL-*b*-PLLA [a]

Sample	Monomer	Cat.	$[M]_0/[BDM]_0/[Cat.]$	$conv._{CL}$ (%) [b]	$conv._{LA}$ (%) [b]	$M_{n,th.}$ (g mol^{-1}) [c]	$M_{n,NMR}$ (g mol^{-1}) [b]	$M_{n,SEC}$ (g mol^{-1}) [d]	$Đ$ [d]
1st	ε-CL	CA	50/1/1	**84.5**	-	5,260	-	**9,100**	1.09
2nd	ε-CL + L-LA	CA + CNa_3	(50 + 50)/1/(1 + 5)	**89.8**	74.3	10,600	7,810	**14,000**	1.18

[a] Polymerization conditions: atmosphere, Ar; initiator, BDM; temperature, 100 ºC (1st polymerization), 130 ºC (2nd polymerization); solvent, toluene. [b] Determined by ^{1}H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Calculated from $[LA]_0/[BDM]_0 \times conv._{LA} \times$ (M.W. of LA) + $[CL]_0/[BDM]_0 \times conv._{CL} \times$ (M.W. of CL). [d] Determined by SEC in THF using polystyrene standard.

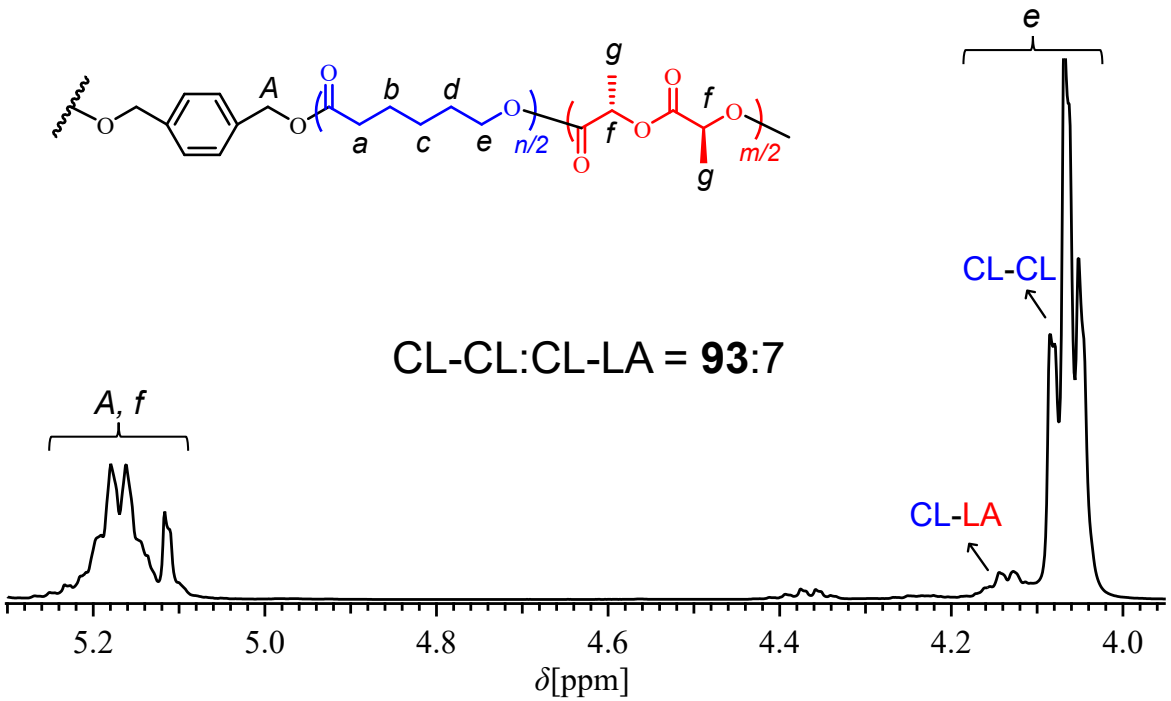


Fig. S21 ^{1}H NMR spectra of the PLLA-*b*-PCL-*b*-PLLA (solvent, $CDCl_3$; 400 MHz). (expanded spectrum ranging from 3.8 ppm to 5.3 ppm.)