Supporting informations

Poly(L-lactide) epimerization and chain scission in the presence of organic bases

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MALDI ToF analyses

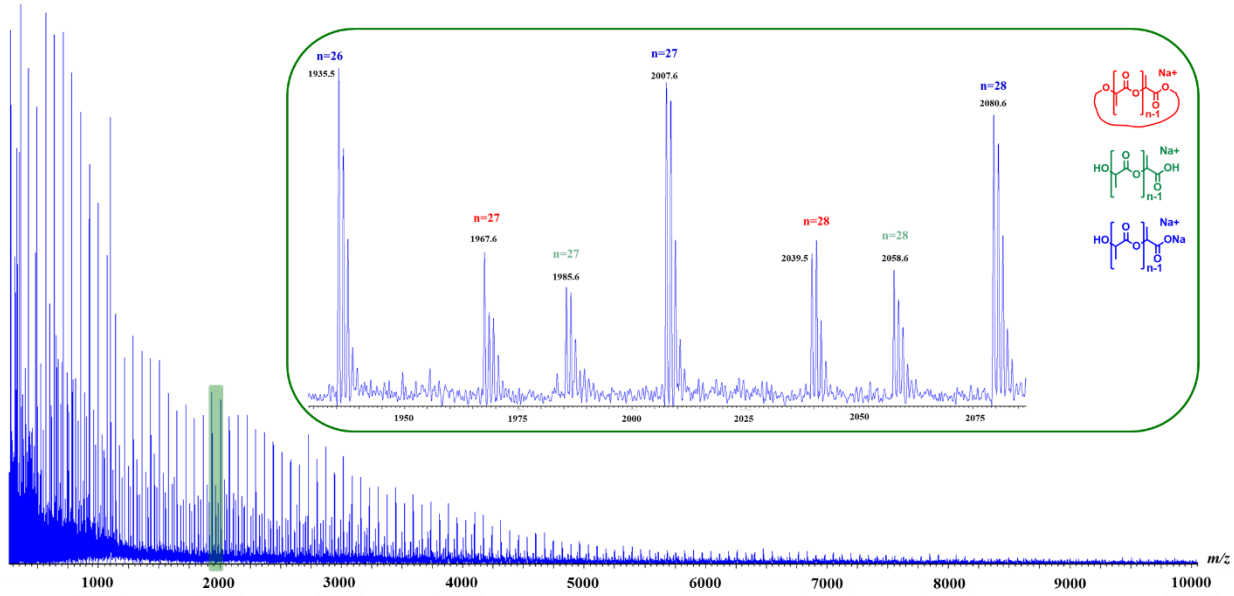

Figure S1. MALDI ToF analysis of entry 4 (DBU as catalyst)

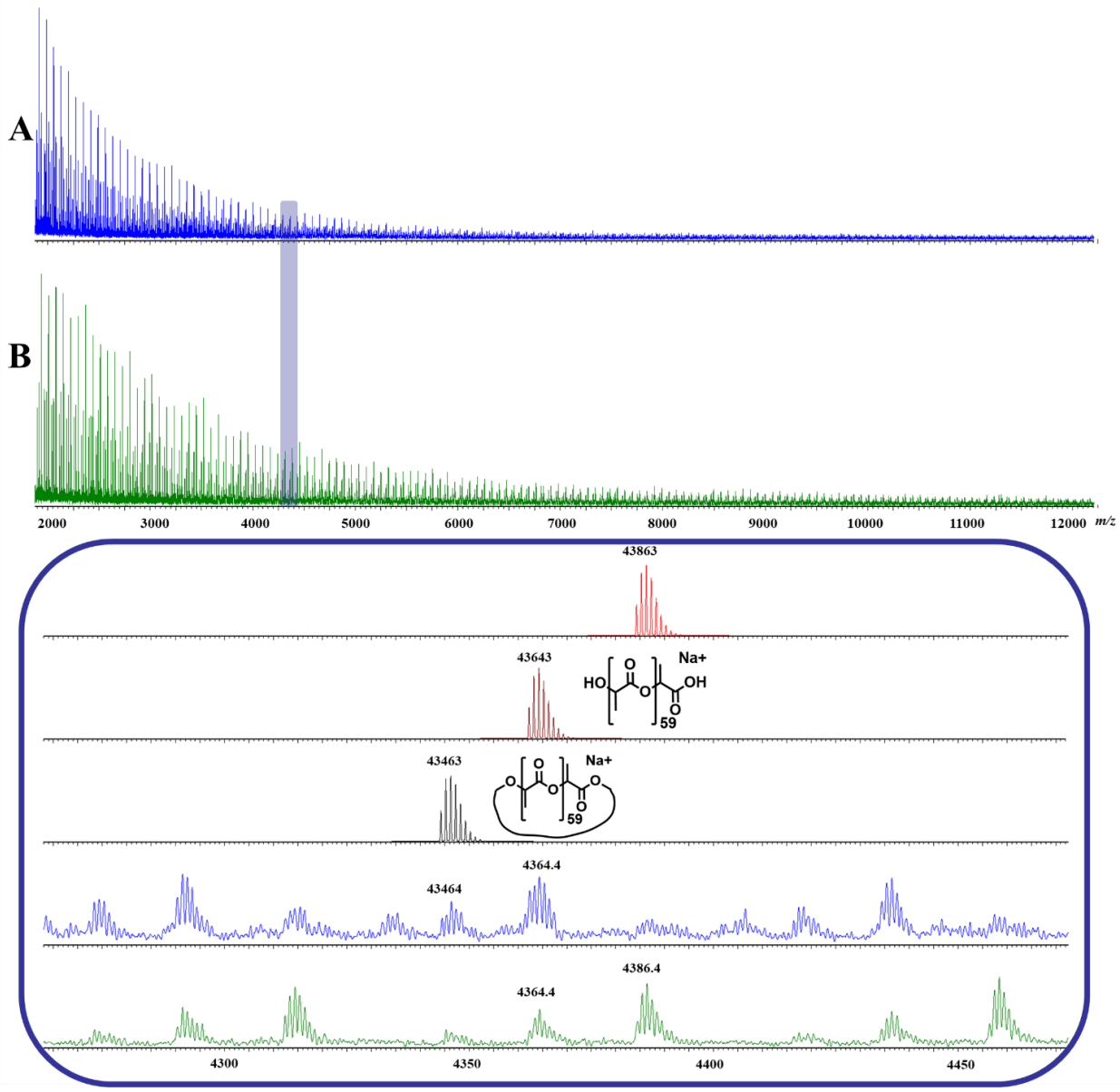

Figure S2. MALDI ToF analyses of the PLLA precursor (A, blue) and a PLA after epimerization (entry 11, B, green) with *t*-BuP_4 as the catalyst

PLA acetylation and resulting experiments

Hydroxyl-ended PLLA is acetylated in the presence of triethylamine and acetyl chloride to obtain acetate end-capped PLLA. The reaction is quantitative as shown by ^{1}H NMR (Figure S3). Indeed, the C*H*-OH chain end signal (at 4.4 ppm) of the precursor is not detected on the acetylated PLA spectrum and new signal appears at 2.2 ppm represented C*H*$_3$-CO-O of the new chain end group. The evolution of the microstructure of the hydroxyl-ended PLLA and the acetate-ended PLLA after 24h of stirring in toluene at 105°C with 0.65 mol% of *t*-BuP$_4$ is presented in Table S1. The resulting number-average molecular weight is of the same order of magnitude, suggesting that the cleavage is not due to depolymerization and cyclization initiated by the PLA hydroxyl end-group.

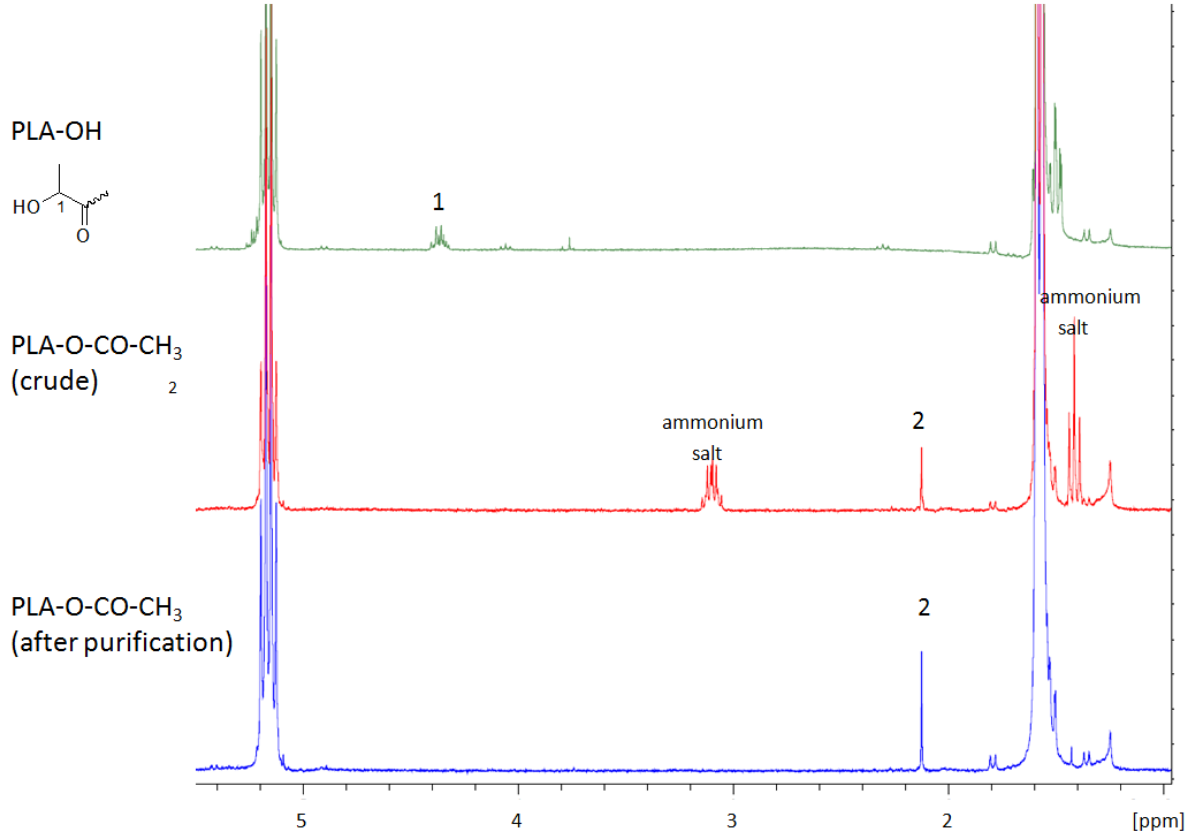

Figure S3 ^{1}H NMR spectra of PLLA-OH, and acetate end capped PLLA before and after purification in $CDCl_3$, 300 MHz.

Table S1.

Reaction of OH end-capped PLLA and acetate end-capped PLLA with a phosphazene [a]

		Entry	Yield (%)	$[a]_D^{20}$ (°) [b]	Epimerization D(%) [c]	M_n corrected (g/mol) [d]	Đ
OH end-capped PLA	Starting polymer	-	/	-153.3	0	61 000	1.6
	After reaction	15	96	-134.6	6.1	10 100	1.8
acetate end-capped PLA	Starting polymer	-	/	-151.8	0.5	63 000	1.7
	After reaction	22	86	-118.6	11.3	12 400	1.9

[a] *t*-BuP_4 (0.65 mol%), in anhydrous toluene at 105°C, 24h

[b] Specific optical rotation determined by polarimetry (chloroform, 20 °C, λ = 598 nm, standard deviation ± 2.5 °)

[c] Determined with equation 2 (standard deviation ± 0.6%)

[d] M_n corrected = $M_{n\ SEC}$ x 0.58, SEC (THF, standard PS, 40 °C)

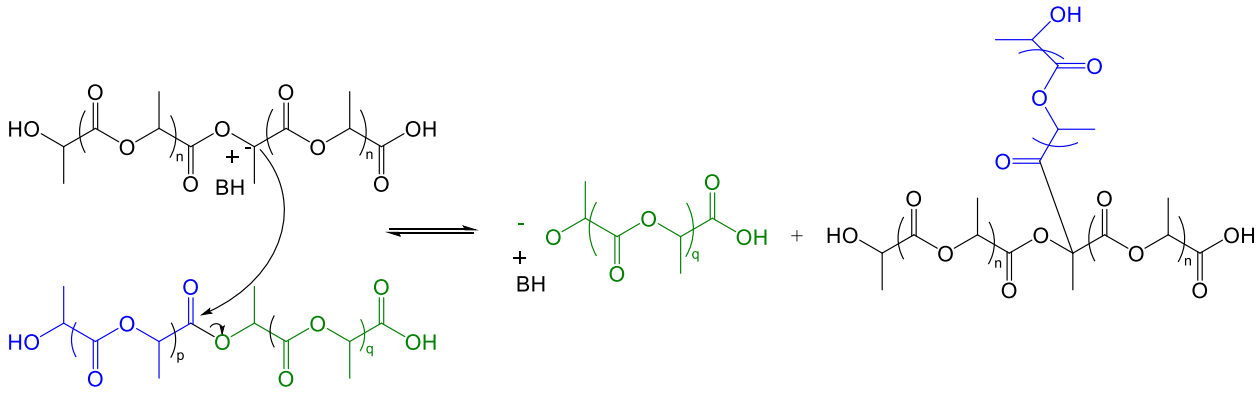

Figure S4. Hypothetical anionic / enolate mechanism

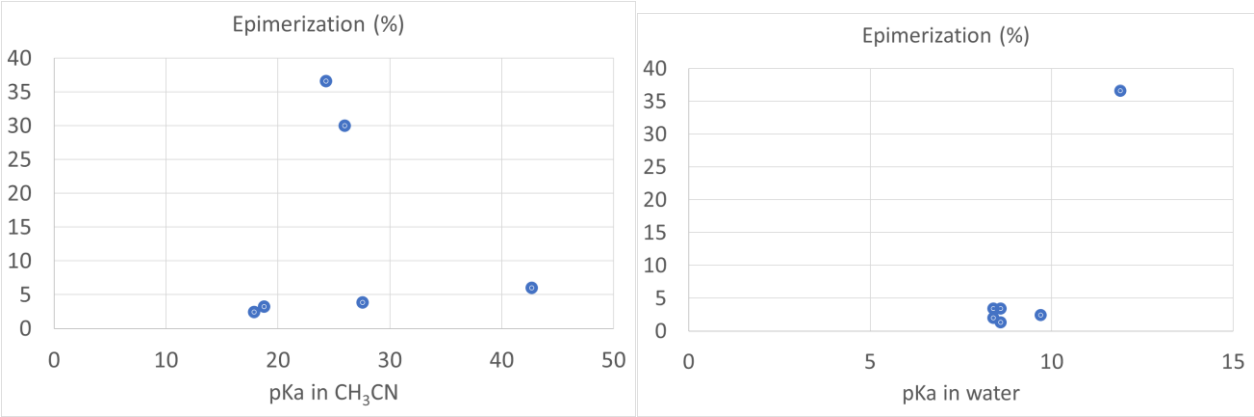

Figure S5. Influence of the pKa on the epimerization rate

Influence of the water content

We did experiments with non-purified toluene, *i.e* a solvent containing more water, using TBD, DBU and DMAP as selected catalyst. The results are given below in Table S2.

Table S2. Epimerization of poly(L-lactide) in the presence of an organic base as catalyst. Influence of solvent purification [a.]

Entry	Catalyst	solvent	$[a]_D^{20}$ (°) [b]	Epimerization D(%) [c]	$M_{n\ corrected}$ (g/mol) [d]	$Đ_M$ [d]
	Starting PLLA	-	-162.3	0	35 400	1.7
1	No catalyst	-	-159.4	0.9	33 500	1.8
3	DMAP	Purified	-154.5	2.4	19 200	1.8
SI1	DMAP	Non purified	-150	3.8	17 400	1.8
4	DBU	Purified	-43.5	36.6	5 800	1.5
SI2	DBU	Non purified	-107	17.1	5 200	1.4
5	TBD	Purified	-64.9	30	6 000	1.6
SI3	TBD	Non purified	-100	19.3	5 800	1.6

[a] 1 mol% of catalyst, 0.5 g PLLA (Mn = 35 400 g/mol), 48h, T = 105 °C, anhydrous toluene (3 mL, 2.3 mol/L)
[b] Specific optical rotation determined by polarimetry (chloroform, 20 °C, λ= 598 nm, standard deviation ± 2.5 °)
[c] Determined with equation 2 (standard deviation ± 0.6%)
[d] M_n corrected = M_n SEC x 0.58, $Đ_M$ is the dispersity, SEC (THF, standard PS, 40 °C)

For all three catalysts, the resulting molecular weight is slightly lower, which can be explained by some slight hydrolysis reactions. Regarding the epimerization, there are significant differences for DBU and TBD, with a lower extent of epimerization using the non-purified solvent. This can be explained by a competitive interaction of the base with water *vs.* the -C*H* proton of PLA. For DMAP, the epimerization is already weak with the purified solvent, and there is no significant evolution with the as-received one. For lower amounts of water, we did a few experiments using PLA after azeotropic distillation, with TBD as the catalyst, and the results were similar to those obtained using our standard drying procedure.