Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 648–650

Synthesis of lactide from alkyl lactates catalyzed by lanthanide salts

Tatevik A. Egiazaryan, Valentin M. Makarov, Mikhail V. Moskalev, Danila A. Razborov and Igor L. Fedushkin

Experimental part

Equipment and materials. NMR ^{1}H spectra were registered using spectrometers “Bruker DPX 200” and “Bruker Avance III 400”. The degree of oligomerization of lactic acid esters (DP_n) was determined based on the ratio of integral intensities of signals in NMR ^{1}H spectra. Quantitative compositions of components of sublimated products and the lactide degree of purification were determined by NMR ^{1}H spectrometry methods and chromato-mass-spectrometry. Lactide content in the products mentioned above was determined by two methods of analysis and was compatible and differed by not more than 3-5 %. The chromato-mass-spectrometric analysis was made using device “Trace GC Ultra/ Polaris Q” (Thermo Electron Corporation, USA). Temperature of capillary column TR-35MC (60 m) varied from 60 to 300 °C at a rate of 10 °C/min. Temperature of the ion source was 230 °C, ionizing electron energy – 70 eV. Mass-spectra of positive ions were registered within the range of mass numbers 50-500. L-lactic acid aqueous solution (80 %, Galacide Food) was used in the research work. Amounts of $LnCl_3{\cdot}nH_2O$ were calculated on the quantity of lactic acid involved in the esterification process minus alkyl lactate removed during the alcohol distillation. The apparatus for the process is depicted in Figure S1.

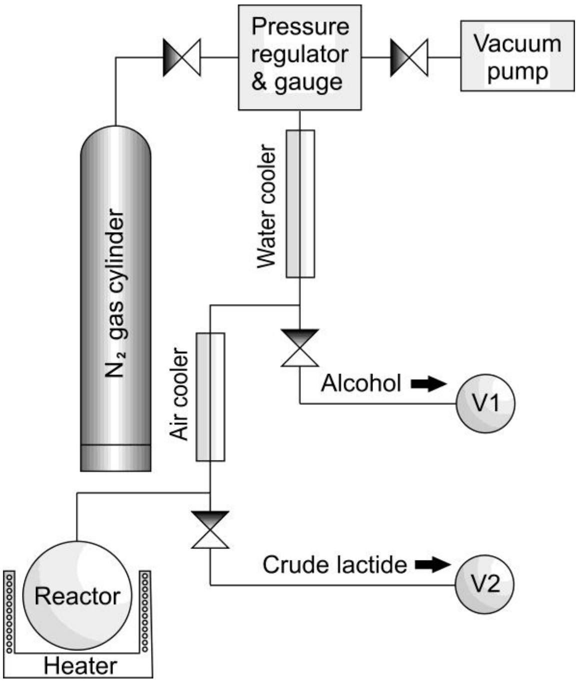

Figure S1. The apparatus for the process

Lactic Acid Esterification. Lactic acid aqueous solution was concentrated under reduced pressure using rotary vacuum evaporator "IKA RV 10 basic" as per the method described [S1]. Lactic acid obtained was placed into a round-bottomed flask with a backflow condenser, alcohol (aqueous solution of ethanol, isopropanol, n-butanol or isobutanol) and cationite "Purolite C100MBH" (5 % wt. of total quantity of lactic acid and alcohol) were added. The mixture was boiled under continuous agitation for 6 hours and then cooled to indoor temperature; the catalyst was separated by filtration; and fractions with a boiling point of 78-150 °C (for Et-*oligo*-LA), 82-155 °C (for iPr-*oligo*-LA), 95-185 °C (for n-butyl lactate) and 90-180 °C (for isobutyl lactate) were removed from the reaction mixture by distillation under atmospheric pressure.

Oligomerization of lactic acid esterification products and subsequent catalytic depolymerization of oligomers. Mixed esterification residual products containing equivalent of 320 mmol of lactile units (that correspond to 28.8 g of lactic acid) were placed into the reactor (thermostatically controlled flask) and then the catalyst was added ($CeCl_3{\cdot}7H_2O$: 1.191, 1.906, 2.383, 3.574 or 4.765 g for 1, 1.6, 2, 3 or 4 mol % accordingly; $NdCl_3{\cdot}6H_2O$: 1.834 g for 1.6 mol %; $SmCl_3{\cdot}6H_2O$: 1.866 g for 1.6 mol %) (the catalyst was not added in the controlled experiment) After that, the air backflow condenser was connected to the reactor; the condenser was equipped with receiver V1 intended for extracting the condensing solution; and a water backflow cooler was connected as well; then the system was filled with nitrogen in order to obtain a pressure of 780 Torr. When condensation in receiver V1 stopped, temperature in the reactor was increased by 10 °C. At the end of the process the maximum temperature was 190 °C. Mixed oligoesters produced in the process were analyzed by NMR ^{1}H spectrometry method for the purpose of determining the degree of oligomerization (DP_n) in $CDCl_3$ or DMSO-d_6. The oligomer yield was determined as the ratio of mass of the oligomer produced-to theoretical mass of the oligomer taking into consideration its average molecular mass calculated from the degree of oligomerization.

Mixture of lactic acid with the catalyst obtained in the process was catalytically depolymerized. For this purpose, the pressure in the system was reduced to 5 Torr and the stream was rerouted into receiver V2. At this stage a temperature of 200 °C was maintained for 1 h. Time duration was increased to 2 hours if temperature of the deplolymerization process was increased gradually from 180 to 230 °C at a rate of 25 $°C \cdot hour^{-1}$ and pressure was reduced from 50 to 5 Torr at a rate of 22.5 Torr h^{-1}. In this case 2 or 3 mol % $CeCl_3 \cdot 7H_2O$ was used for Et-*oligo*-LA and 2 mol % $CeCl_3 \cdot 7H_2O$ for iPr-*oligo*-LA. Sublimated products collected into the receiver were analyzed by NMR ^{1}H spectrometry method. The lactide yield was calculated from the ratio of lactide mass to oligoester mass taken for depolymerization. Lactide content in the sublimated product was determined using NMR ^{1}H spectrometry method based on the ratio of integral intensities of signals of lactide and toluene used as the reference standard (Figure S2).

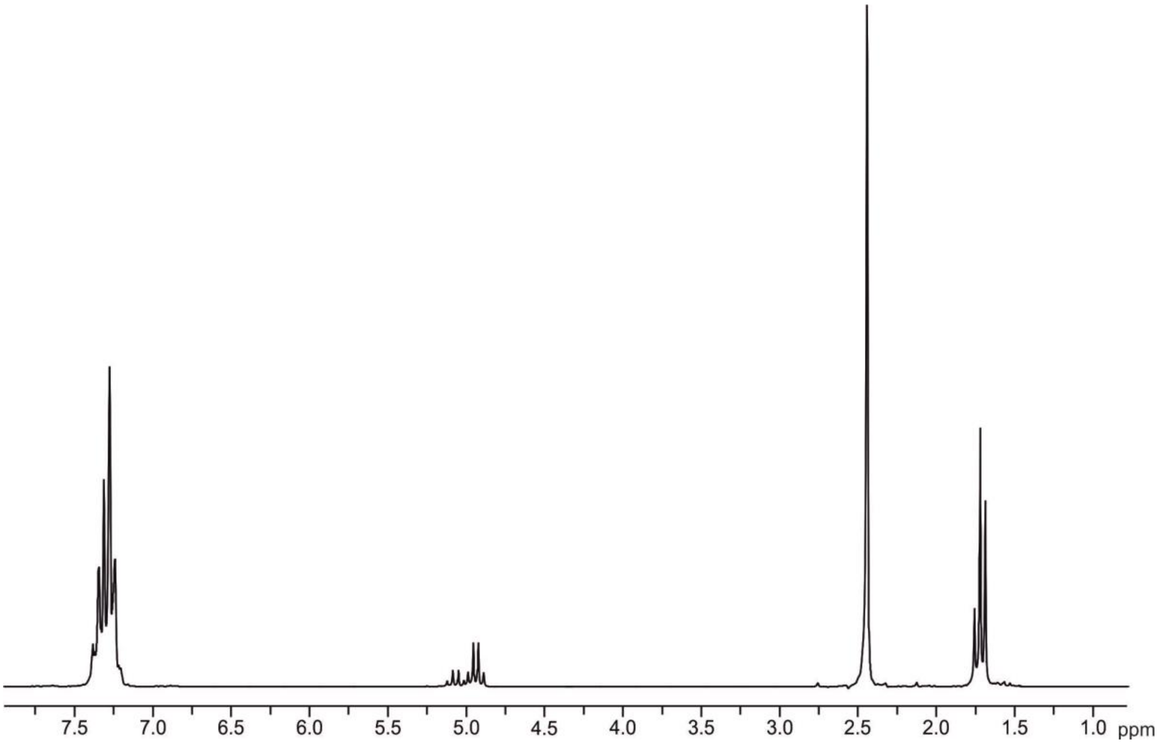

Figure S2. ^{1}H NMR spectrum (200 MHz, 296 K, $CDCl_3$) of sublimated products obtained with of 2 mol % of $CeCl_3 \cdot 7H_2O$ the iPr-*oligo*-LA

Table S1. Catalytic conversion of ethyl and isopropyl oligoesters into lactide with the use of various amounts of cerium chloride heptahydrate (III)

Exp. no	Oligoester	$CeCl_3 \cdot 7H_2O$, mol %	DP_n	Lactide yield, %	Selectivity, %		
					L-lactide[a]	D-lactide[a]	meso-lactide
1	Et-*oligo*-LA	1	3.3	34	94.9	0.1	5
2		2	4.4	52	90.8	0.2	9
3		3	4.5	59	87.6	0.4	12
4		4	3,1	29	79.9	1.1	19
5	iPr-*oligo*-LA	1	3.8	46	87.6	0.4	12
6		2	3.7	58	83.2	0.8	16
7		3	3.4	48	81.0	1.0	18

Note: [a]L- and D-lactide selectivity was calculated by a known method [S2].

Table S2. Catalytic conversion of ethyl and isopropyl oligoesters into lactide with step-down pressure at the depolymerization stage

Exp. no	Oligoether	Amount of catalyst, mol. %	DP$_n$	Lactide yield, %	Selectivity, %		
					L-lactide[a]	D-lactide[a]	meso-lactide
1	Et-*oligo*-LA	2	4.4	87	66.6	3.4	30
2		3	4.5	89	61.3	4.7	34
3		-	1.7	21	97.0	0.0	3
4	iPr-*oligo*-LA	2	3.7	94	67.9	3.1	29
5		-	1.4	14	96.0	0.0	4

Note: [a] L- and D-lactide selectivity was calculated by a known method [S2].

References

[S1] E. A. Poryvaeva, T. A. Egiazaryan, V. M. Makarov, M. V. Moskalev, D. A. Razborov and I. L. Fedushkin, *Russ. J. Org. Chem.*, 2017, **53**, 344 (*Zh. Org. Khim.*, 2017, **53**, 346).

[S2] L. Feng, X. Chen, X. Bian, S. Xiang, B. Sun and Z. Chen, *Chemom. Intell. Lab. Syst.*, 2012, **110**, 32.