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Synthesis of Lactide from Lactic Acid and Its Esters in the Presence of Rare-Earth Compounds

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Abstract—A procedure is described for the synthesis of lactide by dehydration of L-lactic acid and subsequent depolymerization of its oligomer mixture in the presence of yttrium(III) and praseodymium(III) oxides, as well as of cerium(III) chloride heptahydrate. The catalytic activity of yttrium and praseodymium sesquioxides was determined at different temperatures at the oligomerization and deoligomerization stages. Ethyl lactate was prepared in the presence of Purolite C100 MB cation exchange resin and subjected to oligomerization followed by thermal decomposition of oligoester and oligolactic acid mixture in the presence of yttrium(III) and praseodymium(III) oxides and aqueous cerium(III) chloride.

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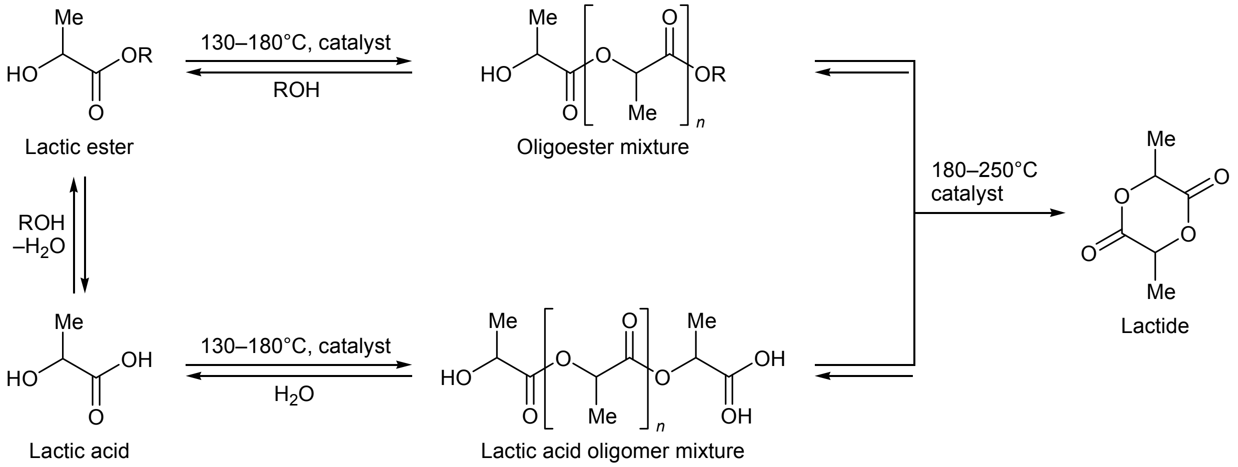
Polymeric materials obtained from renewable plant sources are valuable due to not only their capability for biodegradation in the environment but also biocompatibility, which opens prospects of using such polymers in medicine. An example of such materials is polylactic acid often called polylactide. As early as 1932, Carothers et al. [1] showed the possibility of synthesizing polylactide with a molecular weight of ~3 kDa from lactic acid (2-hydroxypropanoic acid). However, it is necessary to achieve high conversion of lactic acid to obtain polylactide with a molecular weight of several tens kilodaltons [2]. The resulting polymer is characterized by a high polydispersity index, and materials based thereon have unsatisfactory physicochemical characteristics. At present, preference is given to the catalytic synthesis of polylactic acid by ring-opening polymerization of its dimer, lactide (3,6-dimethyl-1,4-dioxane-2,5-dione) [3–8]. Magnesium derivatives of 1,2-bis(2,6-diisopropylphenyl)iminoacenaphthene (dpp-bian) [9, 10] were shown to efficiently catalyze polymerization of lactide with formation of polylactic acid with a high molecular weight (57–78 kDa) and low polydispersity index (1.38–1.46).

Removal of water from a 80% solution of lactic acid leads to its oligomerization which is accompanied by formation of a small amount of lactide. The known methods for the synthesis of lactide generally include preparation of a mixture of lactic acid oligomers [11–13] or a mixture of oligoesters (from lactic acid esters) [14, 15] and subsequent catalytic or thermal depolymerization with formation of lactide (Scheme 1).

A high yield of lactide was achieved with the use of tin [11, 13–15], antimony [12], and lead compounds [15]. However, the presence of even small amounts of these heavy metals in polymeric materials excludes their further use in medicine or food industry. Therefore, search for low-toxic catalysts ensuring synthesis of lactide in high yield from lactic acid or its esters is an important problem. Herein we report the effect of yttrium(III) and praseodymium(III) oxides and cerium(III) chloride on the yield of lactide from lactic acid, ethyl lactate, and oligomers of the latter. We believe that our results may be useful for the design of catalytic systems for the synthesis of lactide of food and medicinal purity.

Initially, we examined the possibility of using yttrium(III) and praseodymium(III) oxides and ceri-

Scheme 1.



um(III) chloride to catalyze oligomerization of lactic acid with subsequent depolymerization of the resulting oligomers to lactide. In the first stage, a solution of lactic acid was subjected to dehydration in the presence of the above catalysts at different temperatures (T_{olig}; Table 1). The efficiency of the process was estimated by the degree of oligomerization (DP_n) of lactic acid on the basis of the ^{1}H NMR data. The degree of oligomerization was calculated as the ratio of the overall intensity of CH signals of lactic acid and oligomers to the overall intensity of CH signals of lactic acid and C**H**OH signals of oligomers [16]. The results were compared with those obtained in blank experiments carried out without a catalyst. As follows from the data in Table 1, the DP_n value increases as the oligomerization temperature rises. However, catalytic effect was observed only in the presence of praseodymium(III) oxide and cerium(III) chloride at 180°C; the degree of oligomerization reached a value of 4.7 or 4.2, respectively (run nos. 9, 10). Both these catalysts are soluble in aqueous lactic acid solution. Praseodymium(III) oxide is likely to be converted to the corresponding lactate which catalyzes oligomerization of lactic acid. Cerium(III) chloride gives rise to solvates with variable compositions, which are less active than praseodymium lactate. Yttrium(III) oxide is insoluble in aqueous lactic acid (run nos. 4–6), and it does not catalyze oligomerization of lactic acid.

Oligomer samples obtained as described above were subjected to thermal depolymerization at 180 and 200°C (T_{dep}) without purification from rare earth compounds (Table 1). Thermal degradation of oligomers was carried out under reduced pressure (0.05 mm) in a setup consisting of a reactor, air-cooled reflux condenser, and receiver cooled with liquid nitrogen. Two fractions were collected: fraction *1* was a mixture of lactic acid and lactide which crystallized in the reflux condenser, and fraction *2* is the residue remained in the reactor (oligomeric and polymeric compounds). The weight fractions ω_1 and ω_2 were calculated relative to the initial weight of the oligomer. The yield of lactide (fraction *1*) was determined by ^{1}H NMR.

The data in Table 1 show that in each series of experiments performed at T_{dep} 180°C the yield of lactide increases in parallel with the DP_n value for the initial oligomer. An exception was the blank run where thermal degradation of oligomer (DP_n 1.4) afforded 20% of lactide (run no. 1). Presumably, in this case the rate of dehydration of lactic acid to lactide and removal of the latter from the reaction zone together with lactic acid and water vapor exceeds the rate of polymerization. This follows from the low yield of fraction *2* (10%) and the absence of polymer fraction.

Depolymerization of oligomers with close DP_n values (1.4 and 1.5) in the presence of yttrium(III) and praseodymium(III) oxides, respectively (run nos. 4, 7), gave a lower yield of lactide (7% in the presence of Y_2O_3 and 13% in the presence of Pr_2O_3). Here, the contribution of polymerization of lactic acid oligomers increases; this is reflected in increased yield of fraction *2* (25 and 33% for Y_2O_3 and Pr_2O_3, respectively) which contains a small amount of polylactide (≤4 wt % relative to the initial oligomers) with an average molecular weight M_w of ~2 kDa (run nos. 2, 5, 8). Yttrium(III) oxide showed no catalytic activity at T_{dep} = 180°C, as followed from comparison of the yields of lactide in run nos. 2 and 5, as well as from the weights of fractions *1* and *2*. The yield of lactide in the presence of Pr_2O_3 was higher by 8%, and of fraction *2*, lower by

Table 1. Oligomerization of lactic acid and thermal decomposition of lactic acid oligomers in the presence of rare earth catalysts

Run no.[a]	Catalyst[b]	T_{olig}, °C	DP_n	T_{dep}, °C	ω_1, %	ω_2, %	Yield of lactide, %
1	–	130	1.4		34	10	20
2	–	150	2.0	180	30	59	14
3	–	180	3.2		29	64	19
4	Y_2O_3	130	1.4		13	25	7
5	Y_2O_3	150	1.9	180	30	61	15
6	Y_2O_3	180	3.2		30	64	19
7	Pr_2O_3	130	1.5		44	33	13
8	Pr_2O_3	150	2.1	180	31	46	22
9	Pr_2O_3	180	4.7		28	68	27
10	$CeCl_3\cdot 7H_2O$	180	4.2	180	31	58	25
11	–	180	3.2	200	60	33	24
12	Pr_2O_3	130	1.5		70	21	8
13	Pr_2O_3	150	2.1	200	73	17	19
14	Pr_2O_3	180	4.7		80	16	52
15	$CeCl_3\cdot 7H_2O$	180	4.2	200	47	15	46

[a] In run nos. 11–15 oligomers obtained in the first stage in run nos. 3 and 7–10, respectively, were subjected to depolymerization.
[b] Amount of the catalyst: 0.8 mol % of Y_2O_3 or Pr_2O_3 or 1.6 mol % of $CeCl_3\cdot 7H_2O$ (relative to lactic acid).

13% than in blank experiment. Presumably, Pr_2O_3 exhibits higher depolymerizing activity. Fractions *2* of all three samples contained polylactide (M_w ~3 kDa).

The results of depolymerization of oligomer samples with $DP_n = 3.2$ at $T_{\text{dep}} = 180°\text{C}$ (run nos. 3, 6) showed that yttrium(III) oxide does not affect the thermal degradation; in both cases, the yield of lactide increases on the average by 5% in comparison to depolymerization of oligomers with DP_n ~2 (run nos. 2, 5). The thermal decomposition of the oligomer with $DP_n = 4.7$ (obtained in the presence of Pr_2O_3; run no. 9) was also characterized by increase of the yield of lactide by 5% compared to the oligomer obtained at $T_{\text{olig}} = 150°\text{C}$ using the same catalyst (run no. 8). The yield of lactide in the presence of cerium(III) chloride (25%, run no. 10) was comparable with that obtained with praseodymium(III) oxide.

The amount of undepolymerized product (still residue in the reactor) after thermal degradation of oligomers with $DP_n \geq 2$ was fairly large. In order to improve the yield of lactide, the depolymerization temperature was raised to 200°C. Experiments were carried out with oligomers obtained in the presence of Pr_2O_3 and $CeCl_3$ and with a sample with $DP_n = 3.2$, which was synthesized without a catalyst (run nos. 11–15). It was found that increase of the temperature of depolymerization of Pr_2O_3-containing samples with $DP_n = 1.5$ and 2.1 led to reduced yields compared to experiments at $T_{\text{dep}} = 180°\text{C}$ (run nos. 7, 8 and 12, 13, respectively), despite lower amount of fraction *2*. Presumably, removal of lactic acid from the reactor predominates over its dehydration due to high rate of removal of low molecular weight components from the reactor at 200°C. However, the yield of lactide in the depolymerization of oligomers with $DP_n = 4.7$ and 4.2 at $T_{\text{dep}} = 200°\text{C}$ was higher than at $T_{\text{dep}} = 180°\text{C}$ by 25 and 22% for Pr_2O_3 and $CeCl_3$, respectively (run nos. 9, 14, 10, 15). Thermal decomposition of the oligomer with $DP_n = 3.2$ containing no rare earth compounds showed an insignificant increase of the yield (by 5%; run nos. 3, 11). In this case, the residue in the reactor contained polylactide with $M_w \approx 13$ kDa, whereas the average molecular weights of the polymeric residues in run nos. 14 and 15 were only 2.4 and 2.8 kDa, respectively. These data indicate catalytic character of the depolymerization of oligomers synthesized in the presence of praseodymium(III) oxide and cerium(III) chloride.

We failed to obtain lactide in a high yield by condensation of lactic acid, followed by thermal decomposition of oligomers. Therefore, we tried to synthesize it by oligomerization of alkyl lactates and subsequent depolymerization of oligoesters. This method was successful with the use of tin and lead catalysts

[14, 15], and the best yields of both oligoesters and lactide were achieved with ethyl lactate as initial compound [14].

It is known that the equilibrium in esterification reactions is shifted toward ester formation in acid medium; the use of sulfuric acid to catalyze the synthesis of ethyl lactate was reported [17]. However, isolation of the ester from the reaction mixture by distillation without preliminary neutralization of the acid was accompanied by tarring. The known method for the synthesis of esters using molecular iodine as catalyst [18] involves laborious procedures for isolation of the product and separation of the catalyst.

Efficient methods have been reported for the synthesis of ethyl lactate in the presence of cation exchangers [19–22], including those containing phosphotungstic and phosphomolybdic heteropolyacids [23]. Preyssler acid [24], zeolite membranes [25], and combinations of some acid catalysts with pervaporation zeolite membranes [26] were also used to catalyze the synthesis of ethyl lactate. Among the above methods, the most convenient is esterification catalyzed by Amberlyst-15 cation exchanger, which afforded satisfactory yield of ethyl lactate. Taking into account similar proton capacities of Amberlyst-15 and Purolite C100 MBH (52–57 and 51–55%, respectively), we used more accessible Purolite C100 MBH as catalyst in an amount of 5 wt % relative to the overall amount of ~100% lactic acid and ~80% aqueous ethanol at a molar ratio of 1 : 4. The conversion of lactic acid to esterification products (ethyl lactate and di- and trilactic acid esters) was 70% in 6 h. Apart from unreacted lactic acid, the reaction mixture contained its oligomers. The esterification products were analyzed by ^{1}H NMR spectroscopy, including ^{1}H–^{1}H COSY experiments. The results insignificantly differed from those obtained with the use of semipermeable zeolite membrane [25], which confirmed the efficiency of our method.

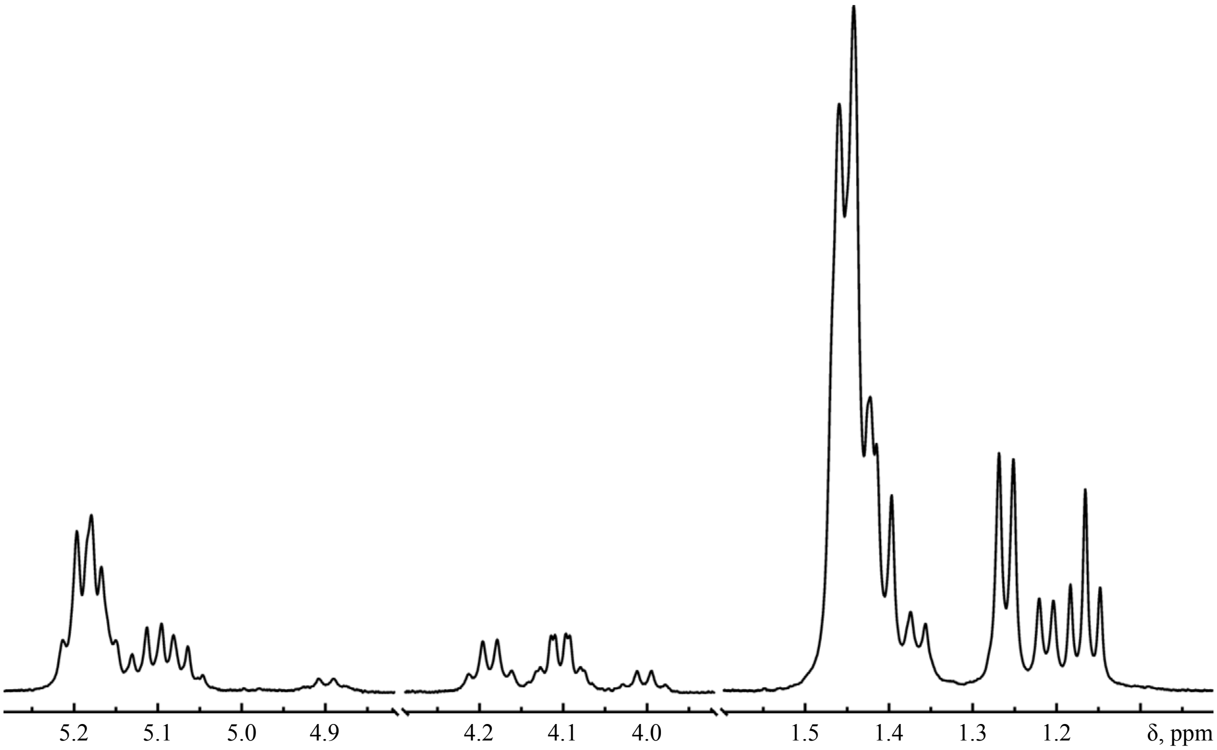
The products can readily be separated from the catalyst, but we failed to isolate pure ethyl lactate in high yield from the product mixture. The largest amount of ethyl lactate (92%) was present in the fraction collected at 150–160°C on distillation of the reaction mixture, while its overall yield did not exceed 31%. Distillation at a temperature higher than 160°C led to oligomerization of components of the still residue, and the overall yield of ethyl lactate decreased. As shown by ^{1}H NMR, the fraction collected in the temperature range from 78 to 150°C contained a small amount of ethyl lactate (14% of the theoretical yield).

The still residue boiling above 150°C contained ethyl lactate in a mixture with oligoesters and unreacted lactic acid and its oligomers. This residue was subjected to oligomerization in the presence of yttrium and praseodymium oxides and cerium chloride; the results are given in Table 2. The amount of the catalyst for oligomerization of the still residue was calculated for the initial lactic acid (less lactic acid removed as ethyl lactate in fractions boiling below 150°C). The oligomerization was carried out at 160°C under nitrogen (780 mm) in the setup used previously for dehydration of lactic acid. After removal of alcohol–water mixture, the pressure was reduced to 10 mm, and the mixture was kept for 2 h at 160°C. The catalytic effect was estimated by comparing the degree of oligomerization of components of the still residue obtained in the esterification of lactic acid with that in the blank experiment (Table 2). The degree of oligomerization was determined by ^{1}H NMR. While interpreting the ^{1}H NMR spectra, it was taken into account that the region δ 4.22–3.98 ppm comprises both CH proton signals and signals of methylene protons of the ethoxy groups. Therefore, the intensity of the CH signals was calculated by subtracting the intensity of OCH_2 signals corresponding to methyl proton signals in the region δ 1.19–1.13 ppm from the overall signal intensity in the region δ 4.22–3.98 ppm (see figure).

As follows from the data in Table 2, yttrium(III) oxide does not affect the degree of oligomerization to an appreciable extent (run nos. 1, 2). However, the yield of oligomer in the presence of Y_2O_3 was higher by 12% than in blank experiment, indicating higher conversion of ethyl lactate and di- and trilactic acid esters, $DP_n = 6.3$.

The highest degree of oligomerization was observed for the oligomer obtained in the presence of praseodymium(III) oxide (run no. 3). The yield was close to that in the absence of a catalyst. Presumably, lactide formed at the oligomerization stage is removed to the receiver under reduced pressure. The DP_n value obtained with cerium(III) chloride as catalyst occupies an intermediate position (run no. 4). In this case, the maximum yield of oligomer was reached, indicating more complete and selective conversion of ethyl lactate to nonvolatile compounds without formation of an appreciable amount of lactide.

The resulting oligomers were subjected to depolymerization at 200°C (5 mm) without purification from



^{1}H NMR spectrum (400 MHz, 296 K, DMSO-d_6) of oligomers obtained in the presence of yttrium(III) oxide from the still residue in the esterification of lactic acid catalyzed by Purolite C100 MBH.

rare earth compounds in the same setup as that used for thermal decomposition of lactic acid oligomers. Likewise, two fractions were obtained: fraction *1* contained volatile ethyl lactate, oligoeesters, and lactide, and fraction *2* was the still residue. Their weight fractions ω_1 and ω_2 were calculated on the initial oligomer. The yield of lactide in fraction *1* was determined by ^{1}H NMR. All rare earth compounds showed catalytic activity at the oligomer depolymerization stage, as seen from the high yields of fraction *1* and lactide in comparison to blank experiment. However, despite comparable yields of lactide-containing fraction *1*, the selectivity for lactide increased in the series $Y_2O_3 < Pr_2O_3 < CeCl_3$. Presumably, the lower yield of lactide in the presence of Y_2O_3 and Pr_2O_3 is related to side formation of polylactide which cannot undergo depolymerization under the given conditions; this follows from fairly large amounts of the still residue. In the depolymerization of oligomer with lower DP_n value in the presence of Y_2O_3, fast removal of volatile oligoesters from the reaction zone also leads to reduction of the yield of lactide.

The maximum yield of lactide was achieved in the presence of $CeCl_3$ (run no. 4), and this catalyst displayed high selectivity in depolymerization of both oligoesters (97%) and lactic acid oligomers (98%) at 200°C (run no. 15). The catalytic activity of cerium(III) chloride in the synthesis of lactide from lactic acid oligomers is comparable with the activity of some tin and lead compounds [14, 15].

Table 2. Oligomerization of the still residue obtained after esterification of lactic acid and thermal decomposition of oligoester mixture in the presence of rare earth catalysts

Run no.	Catalyst[a]	DP_n	Yield of oligomer, %	ω_1, %	ω_2, %	Yield of lactide, %
1	–	6.5	68	36	62	27
2	Y_2O_3	6.3	80	83	14	55
3	Pr_2O_3	8.0	70	83	12	64
4	$CeCl_3 \cdot 7H_2O$	7.3	83	87	2	84

[a] Amount of the catalyst: 0.8 mol % of Y_2O_3 or Pr_2O_3 or 1.6 mol % of $CeCl_3 \cdot 7H_2O$.

Thus, praseodymium(III) oxide and cerium(III) chloride heptahydrate can be used to catalyze the synthesis of lactide from lactic acid and mixtures of ethyl lactate with lactic acid oligoesters. To improve the yield of lactide it is necessary to optimize the conditions for the transformation of lactic acid to lactide, in particular optimal catalyst concentration, pressure, temperature, reactant contact time, etc., should be found.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker DPX 200 and Bruker Avance III 400 spectrometers. The degree of oligomerization of lactic acid and/or its esters (DP_n) was determined from signal intensity ratios in the ^{1}H NMR spectra. The molecular weight of polylactide was determined by gel permeation chromatography at 20°C with a Knauer Smartline chromatograph [Phenogel Phenomenex column, 300×7.5 mm, grain size 5 μm; refractometric and UV detectors (λ 254 nm)]; standard polystyrene samples with medium and high molecular weights (2 to 2570 kDa) were used for calibration. The experimental molecular weights were corrected with account taken of Mark–Houwink coefficient (0.58) [27, 28]. Commercially available aqueous solution of L-lactic acid (79%, Galacide Food) was used.

Oligomerization of lactic acid. Oligomerization of lactic acid in the presence of yttrium(III) and praseodymium(III) oxides and cerium(III) chloride, as well as in the absence of a catalyst, was carried out under continuous stirring under nitrogen (780 mm) in a flask maintained at a required temperature. The flask was connected with an air-cooled reflux condenser equipped with a bottom plate for removal of condensate. The reactions were carried out at 130, 150, and 180°C for each catalyst. In each run, 0.569 g (2.52 mmol) of yttrium(III) oxide, 0.831 g (2.52 mmol) of praseodymium(III) oxide, or 1.885 g (5.06 mmol) of cerium(III) chloride heptahydrate was added to 36 g of a 79% aqueous solution of lactic acid. The mixture was heated for 4 h at a constant temperature. The condensate was removed from the plate receiver, and the still residue (lactic acid oligomers) was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR. The degree of oligomerization (DP_n) was determined from the ratio of the overall intensity of the CH proton signals of lactic acid and oligomers to the overall intensity of the CH proton signals of lactic acid and C**H**OH signals of oligomers according to [16].

Esterification of lactic acid. Concentration of 250 g of a 79% aqueous solution of lactic acid for 1 h at 90°C under reduced pressure on an IKA RV 10 basic rotary evaporator afforded 100% lactic acid after removal of 52.5 g of water. A mixture of 50 g (0.56 mol) of 100% lactic acid, 129 g of 80% aqueous ethanol, and 7.5 g of Purolite C100 MBH (5 wt % of the overall amount of lactic acid and ethanol) was refluxed for 6 h with continuous stirring. The mixture was cooled to room temperature, the catalyst was filtered off, and the mixture was distilled under atmospheric pressure to collect a fraction boiling in the range from 78 to 150°C.

Oligomerization of components of the still residue obtained after esterification of lactic acid. The reactions were carried out in a setup analogous to that used for oligomerization of lactic acid. A flask was charged with 0.578 g (2.56 mmol) of Yt_2O_3, 0.844 g (2.56 mmol) of Pr_2O_3, or 1.907 g (5.12 mmol) of $CeCl_3 \cdot 7H_2O$, 33.1 g of the still residue was added, and the mixture was heated at 160°C under nitrogen (780 mm) until condensate no longer accumulated in the receiver. The system was then evacuated to a residual pressure of 10 mm and kept for 2 h at 160°C to remove volatile compounds. The composition of the condensate collected at 780 and 10 mm was determined by ^{1}H NMR. Oligomer mixture in the still residue was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR to determine the degree of oligomerization (DP_n). The yield of oligomers was determined as the ratio of the oligomer weight to the theoretical weight with account taken of its average molecular weight calculated from the degree of oligomerization.

Depolymerization and isolation of lactide. The mixture of lactic acid oligomers or oligoeesters and catalyst obtained after oligomerization was subjected to thermal decomposition. For this purpose, oligomer mixture, 3 g, was placed in a flask connected to an air-cooled reflux condenser (receiver) and a trap cooled with liquid nitrogen. The flask was heated for 4 h at 180 or 200°C at a residual pressure of 5 or 0.05 mm. The sublimate collected in the receiver was analyzed by ^{1}H NMR. The yield was calculated as the weight ratio of lactide and initial oligomer. The concentration of lactide in the sublimate was determined by ^{1}H NMR from the signal intensity ratio of lactide and naphthalene used as standard. The unsublimed residue (polylactide) was dissolved in tetrahydrofuran (3 mL), precipitated with methanol (100 mL) or diethyl ether (100 mL), and dried under reduced pressure. The molecular weight distribution of polylactide was determined by gel-permeation chromatography.

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