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Solvothermal Alcoholysis Routes for Recycling Polylactide Waste as Lactic Acid Esters

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ABSTRACT

In this work, we investigated the possible use of polylactide (PLA), a biodegradable polymer obtained from renewable bio-feedstock, to produce a range of industrially useful lactic acid esters. We describe a simple and convenient solvothermal alcoholysis method for large-scale recycling of PLA resins or residues from disposable packaging in the presence of the appropriate alcohol under catalyst-free or catalytic conditions. This process proceeds easily both without and with a catalyst. The results show that the best catalytic activity have magnesium and calcium alkoxides synthesized in situ from organometallic or metallic precursors and an alcohol. We determined the crystal structure of the chiral mononuclear post catalyst, $[Ca(Lac)_2(EL)_2]$ (**1**) (Lac = lactic acid anion, EL = ethyl lactate), obtained directly from the reactor. Particular emphasis is placed on the operating conditions and high activity of the catalyst used. Key factors that affect the catalytic activity and reaction mechanism are also highlighted.

KEYWORDS

polylactide, polymer recycling, alcoholysis reaction, solvothermal synthesis, green solvents, alkyl lactates, ethyl lactate

1. INTRODUCTION

In recent years there has been growing interest in the use of biomass as the feedstock for the production of chemical intermediates, because this is an attractive alternative to the use of traditional fossil-fuel-derived materials. A number of high-potential platform molecules have been created as precursors for value-added chemicals and building blocks. Much attention has focused on lactic acid and its alkyl esters, which are produced commercially from a range of agricultural residues and food by-products.[1] Alkyl lactates (ALs) are important ecofriendly chemicals, referred to as green solvents,[2] they are attractive alternatives to petrochemical solvents.[3] They are therefore a popular choice in many industrial scenarios, because they can be used safely without affecting the environment.[4,5] Because of their particular physicochemical properties, ALs have a number of industrial and commercial applications, e.g., as solvents or diluents for polymeric resins, dyes, oils, paints, inks, and pigments,[6] components of cleaning[7] or agriculturally useful compositions,[8] degreasers for paints, graffiti removal, and adhesives,[9] low-temperature lubricants,[10] emulsifiers or dispersants in pharmaceutical compositions,[11] and components of transdermal drug-delivery systems[12] or skin-care formulations[13]. Lactate esters have a number of advantages that make them excellent starting material for the synthesis of a range of chemicals.[14] Ethyl lactate (EL) is particularly useful and is one of the most promising green chemicals. EL is used in a multitude of mechanical and microelectronic applications and meets the high-purity requirements of the semiconductor industry.[15]

Currently, bulk production of lactate esters is based on esterification of lactic acid with the appropriate alcohol in the presence of acid catalysts.[16] The process is technologically complicated because the presence of water affects the reaction equilibrium and limits conversion, or self-esterification of lactic acid under prolonged heating.[17] The use of excess alcohol, catalysts, and separation processes are therefore essential for efficient AL synthesis.[18] The recent significant increase in industrial applications of bioplastics has also increased interest in the development of alternative processes based on chemical recycling of polylactides (PLAs). PLA recycling via thermal cracking to lactides,[19] conversion to functionalized macromolecules,[20] and hydrolytic degradation to lactic acid has been extensively studied.[21] The conversion of PLA waste by alcoholysis therefore has potential as an economically viable and environmentally sustainable method for producing ALs. The concept of lactic acid ester synthesis from PLA is well established and has been widely explored. Filiachione (1945) established that AL can be obtained by the acid-catalyzed reaction of PLA oligomers with aliphatic alcohols.[22] In an alternative method, developed by Du Pont, the reaction is performed at 150–190 °C, using 2–3 equiv of alcohol (ROH for R = Me, Et, nBu) per polymer unit, under the autogenic pressure of the reactants, with H_2SO_4 as the catalyst; 69–87% conversion of high-molecular-weight PLA to AL is achieved within 2 h.[23] Several studies have been devoted to the synthesis of AL using ionic liquids,[24] strong organic bases,[25] metal carboxylates,[26] halides,[27] and alkoxides[28] as catalysts, but these methods, which are performed in solution, and have low conversion rates or long reaction times, are unattractive as large-scale recycling techniques. Various routes for solvolytic recycling of PLA, such as conventional heating, microwave irradiation[29] and ultrasound treatment,[30] have also been proposed. However, our understanding of PLA alcoholysis needs to be improved; for example, there have been few direct investigations of PLA alcoholysis using metal-based

catalysts, and the information available in the literature mainly covers detailed analysis of the post-reaction composition, rather than the catalyst itself.

Recently, our group reported a method that enables the exclusive preparation of lactic acid esters by chemoselective alcoholysis of L-lactide mediated by magnesium alkoxides.[31] In this study, based on this concept, we developed a green and efficient technique for the transformation of PLA into a wide variety of industrially useful lactate esters. This method was designed specifically for chemical recycling of used, post-industrial, and post-consumer PLA.

2. RESULTS AND DISCUSSION

2.1 Catalyst-Free PLA Alcoholysis. We investigated the utility of our method by performing PLA alcoholysis of poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(D,L-lactide) (PDLLA). These materials had been used as commercial granules or were residues from disposable packaging. The detailed specifications of the PLA resins used in the alcoholysis reactions are presented in Table S1 in the Supporting Information. Typical reactions were performed using a steel pressure reactor of capacity 150 mL and then with a reactor of capacity 5 L equipped with a mechanical stirrer. We first conducted control experiments in the absence of a catalyst source. The PLLA and alcohol were placed in a reactor and heated at 200 °C for 1 h, using 4 equiv of EtOH per ester unit, *la* = −[OCH(CH_3)CO]−, in the polymer. The results show that PLLA alcoholysis occurs easily under solvothermal conditions, giving polymer degradation to a liquid consisting of lactic acid-based esters (Figure S1 in SI). Because little work has been done on PLA alcoholysis under solvothermal conditions in the absence of a catalyst, we examined this process first, because it opens up a new simple method for the synthesis of lactic acid esters. We therefore performed a series of catalyst-free PLA alcoholysis reactions. In the

standard procedure, the polymer and alcohol were placed in a reactor and heated at 180–260 °C for 1 h, using EtOH/*la* ratios ranging from 1 to 10 (see Table S2 in SI).

2.1.1. Detailed Analysis of PLA Alcoholysis Products and Reaction Conditions. ^{1}H NMR spectroscopic analysis of the obtained products showed three different methine peaks, at 5.05, 4.22, and 4.09 ppm, characteristic of PLLA oligomers end-capped with ethoxy groups (EL_n), ethyl lactyllactate (EL_2), and EL, as shown in Figure 1.

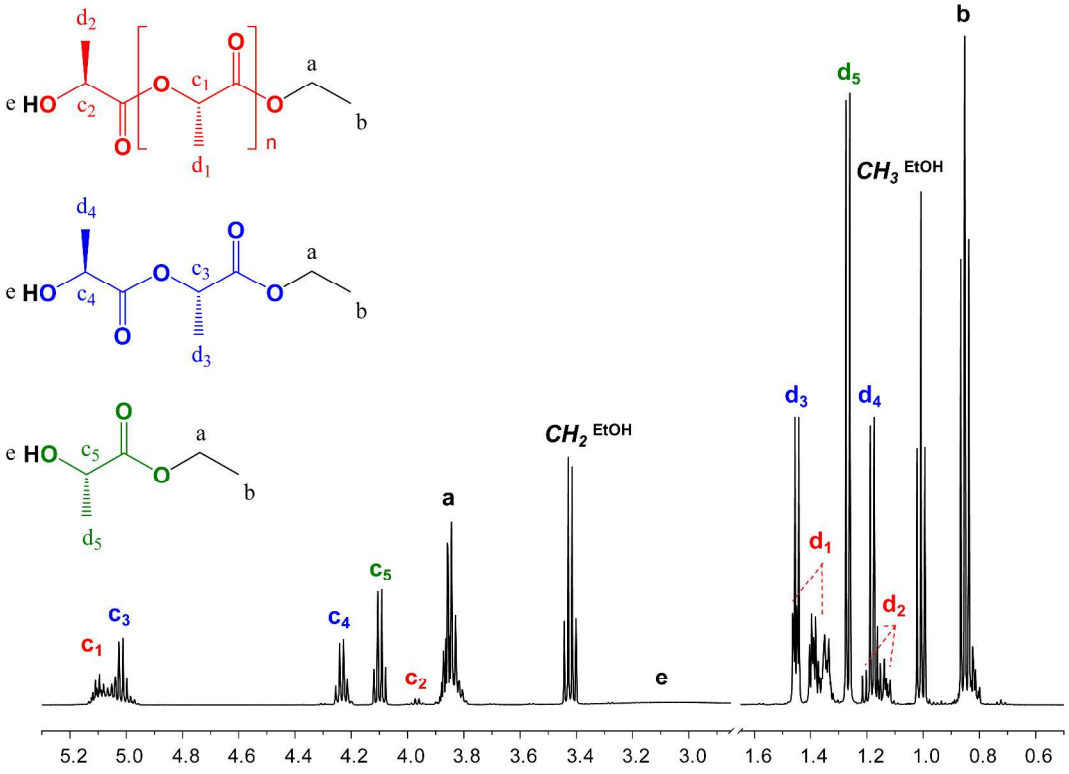


Figure 1. ^{1}H NMR spectrum in C_6D_6 of the PLLA degradation products by the alcoholysis reaction.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry studies of depolymerized samples confirmed the presence of lactyl oligomers separated by increments of 72 Da, with ethoxy end groups (Figure 2), suggesting that extensive transesterification of the initial PLLA sample had occurred. Gel-permeation chromatography analysis of the products of the reaction of PLLA with EtOH at 200 °C, using the stoichiometry *la*/EtOH = 1/1–10, showed that the weight-average molecular weight of the starting material decreased from an initial value of 137.9 kDa to 500–800 Da, corresponding to EL_n, with polydispersity indexes of 1.39–1.51.

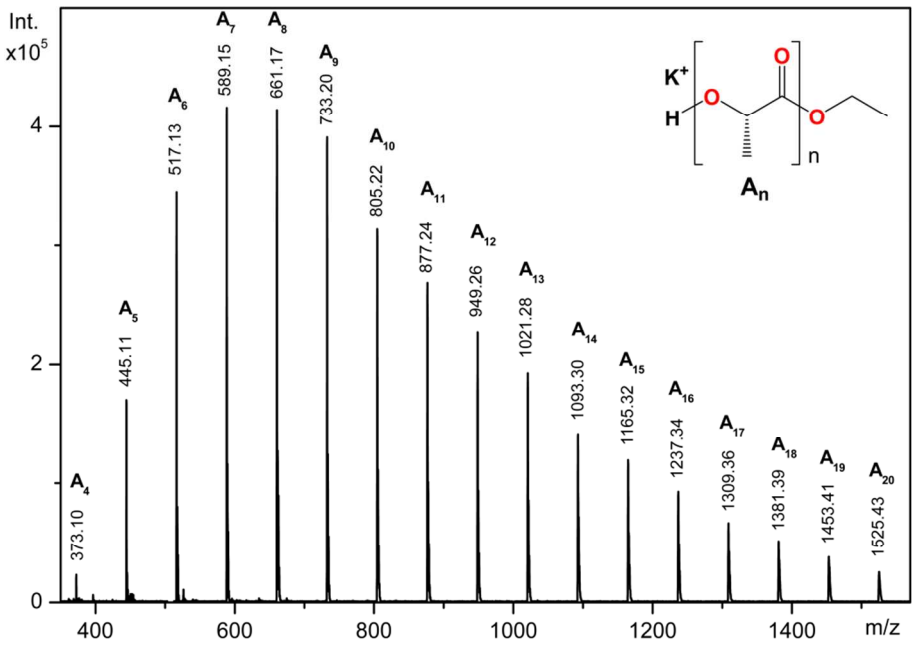


Figure 2. MALDI spectrum of the potassium cationized lactyl oligomers with a incorporated -OEt end group formed in the PLLA alcoholysis reaction.

These results show that as the reaction progressed, the amount of PLA decreased, with simultaneous increases in the amounts of EL_n oligomers and the final products, i.e., EL and EL_2.

The experimental data, summarized in Table S2, suggest that excess alcohol, and a high temperature are necessary for the efficient synthesis of EL. Graphical analysis of the obtained results (Figure 3) shows that for a given reaction stoichiometry, the amount of EL gradually increased with increasing temperature; for example, when the reaction was performed with the stoichiometry *la*/EtOH = 1/1 at 260 °C for 1 h, the maximum PLLA conversion to EL was 50%; increasing the amount of EtOH in the reaction system 2-, 4-, and 10-fold increased the conversions to 77%, 96%, and 99%, respectively.

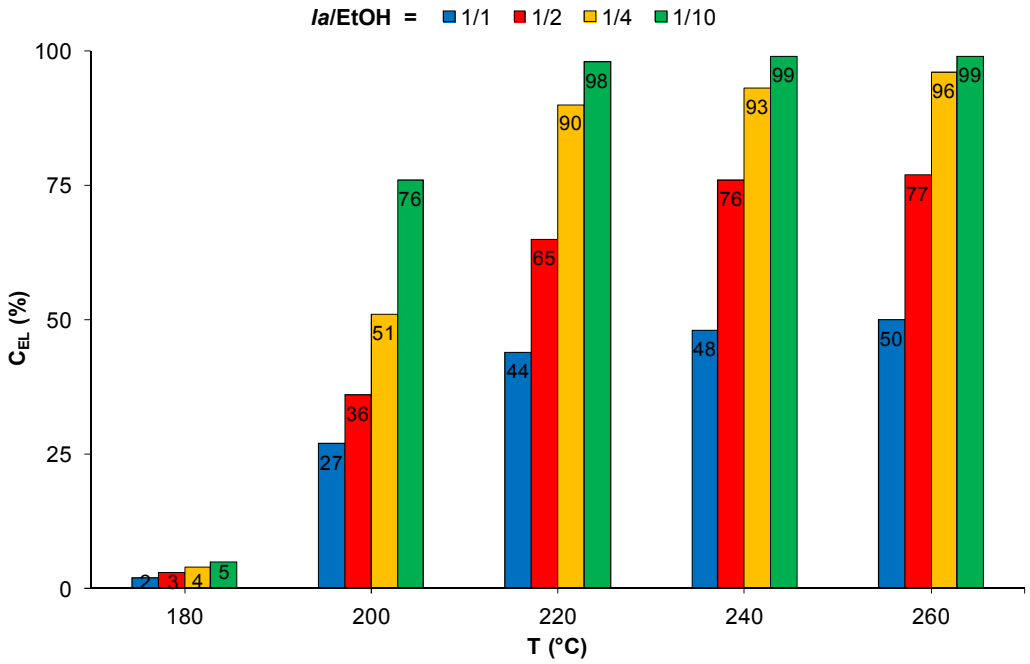


Figure 3. Effect of temperature and alcohol amount on ethanolysis of PLLA.

The amount of alcohol influences the reaction kinetics, and therefore it is important to reach a compromise that avoids the need to remove a large excess of alcohol during the following purification steps. For economic reasons and to achieve a high yield of EL, we recommend performing the reaction with a stoichiometry of *la*/EtOH = 1/4 at 220–260 °C. It is worth noting that the upper limit of the reaction temperature can be higher than 260 °C, but should not exceed

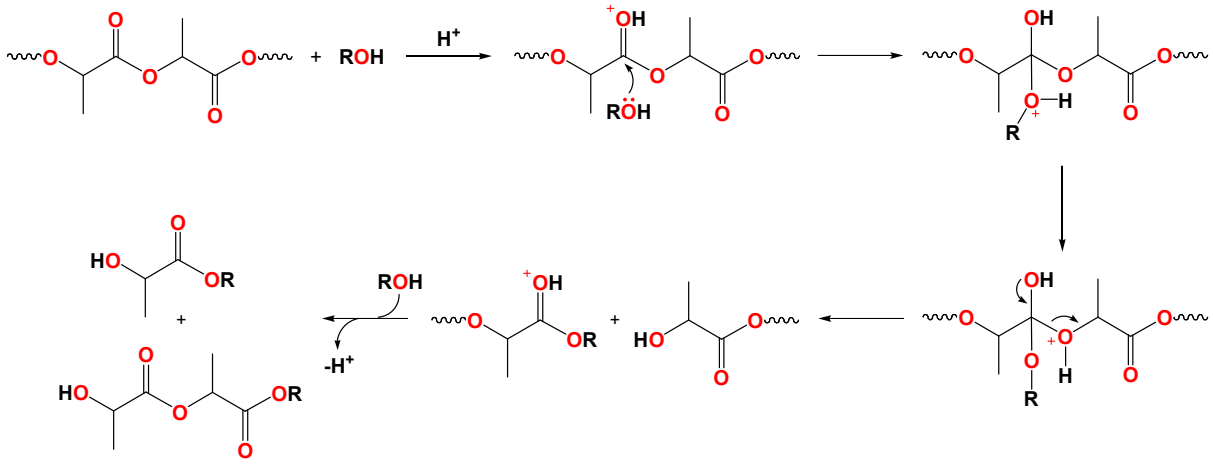
the decomposition temperature of the polymer used. Thermogravimetric analysis/differential thermal analysis showed that weight loss and degradation of the PLLA resin began at around 330 ºC (for details see Table S1, and Figure S2 in SI). Time-dependent alcoholysis reactions with a reactant stoichiometry *la*/EtOH = 1/4 at 220 °C showed that the slowest reaction step is the transformation of EL_2 to EL; for example, when the reaction was performed for 15 min, the PLLA conversions to EL/EL_2 were 69%/24%, whereas for a reaction time of 40 min, the conversion were 90%/10%, but the conversions did not change on further increasing the reaction time to 60 min. Leibfarth reported slow transesterification of EL_2, taking over 12 min to produce >90% EL, using triazabicyclodecene (TBD) as a catalyst.[25b] We used various PLA resins as starting materials and observed that the reaction rate strongly depended on the molecular weight, microstructure and material properties of the used polymer; for example, for reactions performed using PDLA with the stoichiometry *la*/EtOH = 1/4 at 220 °C conversion to EL was 58%, whereas for PLLA and PDLLA, the conversions were 90% and 96%, respectively. (Tables S2 – S3 in SI).

We optimized EL_2 formation, and obtained significant quantities, by varying the reactant stoichiometry and the reaction temperature. These experiments show that to achieve significant amounts of EL_2 it is necessary to perform the reaction using less than 2 equiv of alcohol per *la* unit at 200 °C (Table S2 in SI). It is worth noting that this method enables the synthesis of EL_2 with *ca*. 40% yield of product that is in industrial demand and that is currently difficult to produce in commercial quantities.

2.1.3. Summary. We have developed a method for the catalyst-free production of lactic acid esters by breaking down the ester linkages between the constituent units of PLA, followed by protonation of the carbonyl group and nucleophilic attack on the ion pair by the alcohol, as

shown in Scheme 1. The carbonyl group is protonated by the carboxylic acid end group of the polymer chain. However, it is not possible to exclude the formation of lactic acid resulting from moisture from the polymer or alcohol.

Scheme 1. Mechanism of carboxylic acid-catalyzed PLA alcoholysis reaction.



Also, commercial PLAs are synthesized by ring-opening polymerization of lactides initiated by $Sn(Oct)_2$,[32] and therefore the final products are contaminated with Sn residues from the catalyst.[33] Inductively coupled plasma optical emission spectroscopy showed that the amount of Sn in the used PLAs ranged from 3.5 to 16.5 mg of Sn per 1 kg of polymer (Table S1). We therefore cannot exclude the participation of catalyst residues in the investigated reactions.

2.2. PLA Alcoholysis in Presence of Catalyst. An important economic aspect of the present process is to achieve rapid depolymerization under mild reaction conditions, including a low pressure, temperature, and alcohol content. Once we had found a suitable system for the alcoholysis of PLA to the corresponding AL, we investigated the use of catalysts to achieve high product yields under gentler reaction conditions, which has financial benefits. We decided to explore the use of metal alkoxides synthesized in situ from organometallic or metallic precursors

in direct reactions with alcohols under solvothermal conditions as catalysts. The use of magnesium and calcium alkoxides is preferred because they are highly reactive, do not damage human health or the environment, and can be synthesized in one-pot reactions from safe and easily stored compounds. First, we performed PLLA alcoholysis, using $Mg(OEt)_2$ prepared in situ from $MgBu_2$ and EtOH as the catalyst, with stoichiometries of *la*/EtOH/Mg = 1/1–10/0.01 in the temperature range 80–200 °C for 1 h (Tables S4-5 in SI). The results (Figure 4) show that 78–96% conversion of the polyester to EL can be achieved at 140 °C using 2–10 equiv of alcohol per *la* unit.

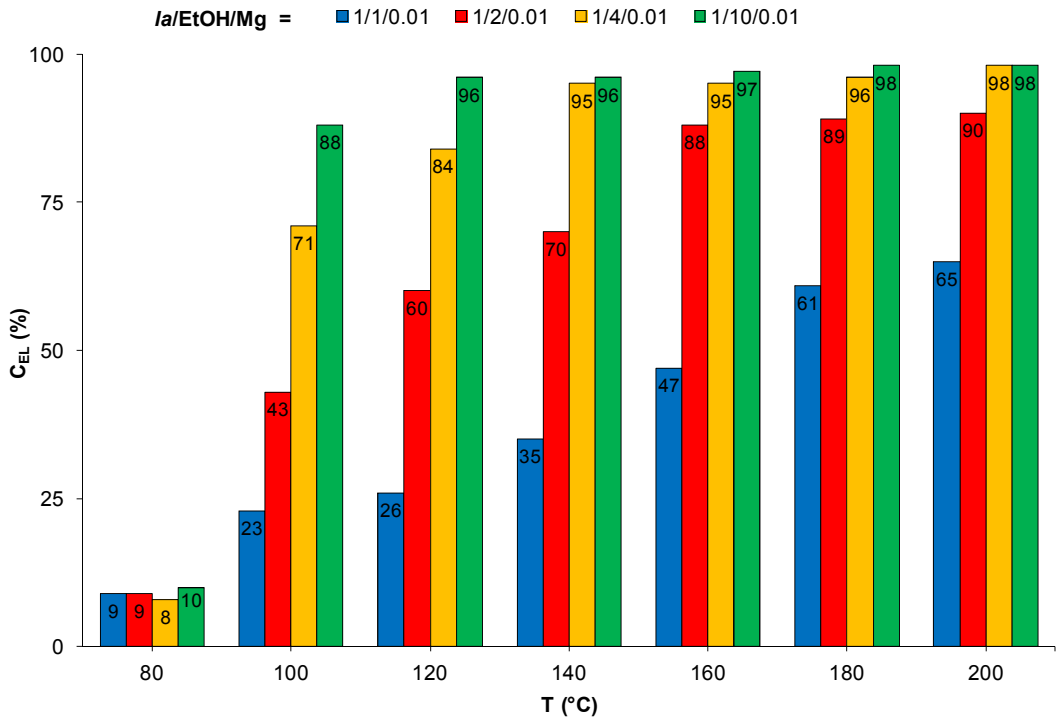


Figure 4. Effect of temperature and alcohol amount on ethanolysis of PLLA using $MgBu_2$ as precatalyst.

However, to prevent excessive use of alcohol, we suggest conducting the PLLA alcoholysis at temperatures above 160 °C with stoichiometries of *la*/EtOH/Mg = 1/2/0.01, or above 140 °C

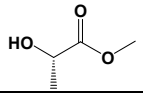
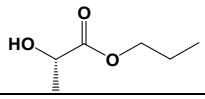
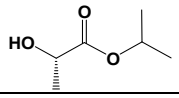
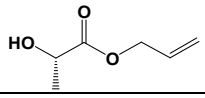
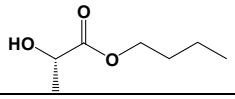
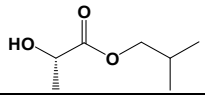
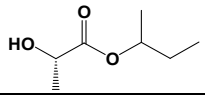
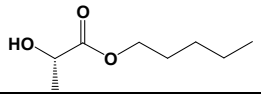
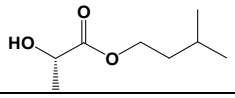
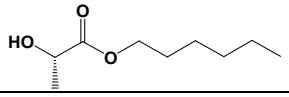
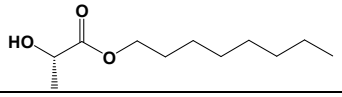
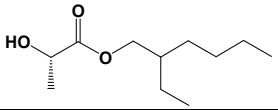
with *la*/EtOH/Mg = 1/4/0.01. A comparison of these results with those for catalyst-free reactions shows that the use of a magnesium alkoxide enables 90% conversion to be achieved in reactions performed at temperatures lower than 80–100 °C and under pressures several times lower. The results in Table S6 show that the amount of catalyst also significantly affects the yield of the final product. Magnesium ethoxide works efficiently when the amount used is 0.75–1 mol% per *la* unit for a stoichiometry of *la*/EtOH = 1/2, and from 0.5–1 mol% per *la* unit for a stoichiometry of *la*/EtOH = 1/4.

2.2.1. Alcoholysis of EL_2. Results of our study show that the main difficulty in this process is not only achieving polymer degradation but also getting the high conversion of EL_2 to EL. Therefore, to better understand the test process, we additionally conducted transesterification reactions of EL_2 with EtOH at stoichiometry EL_2/EtOH/Mg = 1/1-10/0.01 at 25 and 60 °C and monitored these reactions in the function of time by ^{1}H NMR spectroscopy. The results presented in Figures S5-6 (SI) show significant increase in conversion of EL_2 to EL with increasing reaction temperature and amount of the EtOH added. This effect is particularly visible at stoichiometry of the reactants EL_2/EtOH/Mg: 1/1/0.01 and 1/10/0.01. Used of 10-fold excess of alcohol or increasing the reaction temperature to 60 °C caused four-fold increase in conversion. For example, at 25 °C with EtOH/EL_2 ratio of 1 after 2h the conversion was 3% and for ratio 10 equals 11%. While the reaction was carried out at 60 °C, also after 2 h for the same molar ratios the conversion reached the value of 13% and 51%, respectively. The performed kinetic analysis indicating that alcoholysis proceeds with a second-order dependence on EL_2 concentration (Figures S7-8 in SI). These observations are more typical for the ROP of LA initiated by magnesium alkoxide,[34] than for existing data for chemical recycling of polymers.

2.2.2. Kinetic Studies of PLA Alcoholysis. The kinetic studies for safety reason have been carried out in toluene at 90 °C for reactants concentration: [*la*] = 0.5 M; [EtOH] = 0.5, 1, 2, 5 M; [Mg] = 2.5, 5, 7.5, 10, 12.5 mM. The influence of catalyst and alcohol amount on the PLLA ethanolysis process have been presented on the plots of C_{EL} *vs*. time (Figures S9-10 in SI). The plots of $1/[la]_t - 1/[la]_0$ *vs*. time for a wide range of [Mg] or [EtOH] are linear, indicating the second order dependence on *la* concentration (Figures S11-12 in SI). Thus, the rate expression can be written as $-d[la]/dt = k_{obs}[la]^2$, where $k_{obs} = k_p[Mg]^n[EtOH]^m = k_1[Mg]^n = k_2[EtOH]^m$. From the plots of $\ln(k_{obs})$ *vs*. ln[Mg] the order of [Mg] is 4.15 (Figure S13 in SI). While from the plot of $\ln(k_{obs})$ *vs*. ln[EtOH] the order of [EtOH] is 2.19 (Figure S14 in SI). The PLLA alcoholysis process demonstrates the following rate law: $d[la]/dt = k_p[la]^2[Mg]^{4.15}[EtOH]^{2.19}$. These studies show that the use of $MgBu_2$ in combination with EtOH leads to formation of a tetranuclear catalyst adduct, whereupon two PLLA unit can attach to it to be converted to EL.

2.2.3. PLA Alcoholysis Using C1–C8 Alcohols. We broadened our research by investigating a wide range of aliphatic C1–C8 alcohols in PLLA transesterification, using *la*/ROH/Mg = 1/2/0.01 at 200 °C as the standard conditions. The results, which are listed in Table 1, show that methanol, *n*-propanol, *n*-butanol, *sec*-butanol, isobutanol, *n*-pentanol, isopentanol, *n*-hexanol, and allyl alcohol provided fast and efficient depolymerization. The alcohol reactivity in PLLA degradation decreases with increasing number of carbon atoms in the main chain; for example, to achieve a PLLA conversion of about 70% using *n*-butanol it was necessary to conduct the reaction for 1.5 h, whereas for *n*-pentanol and *n*-octanol, the time increased to 2 and 6 h, respectively. The slowest reaction was observed when isopropanol was used.

Table 1. Synthesis of a wide range of AL by alcoholysis of PLLA using metallic Mg or $MgBu_2$ as precatalyst.[a]

No.	Ester	t (h)	C_{AL} (%)[b]	C_{AL2} (%)[b]	Y_{AL} (%)[c]
1[d]		1.5	88	11	81
2[d]		1.5	87	12	80
3[d]		10	57	33	50
4		1.5	73	19	64
5[d]		1.5	66	24	59
6		2	89	7	82
7		2	85	12	79
8		2	66	19	60
9		2	65	26	60
10		3	91	7	85
11[e]		6	68	26	59
12[e]		6	88	11	82

[a] Alcoholysis conditions: *la*/ROH/Mg = 1/2/0.01, 30g of PLLA (IngeoTM 2003D). Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants, at temperature 200 °C. [b] Obtained from ^{1}H NMR analysis according equation C_{AL} = [AL]/[PLLA]$_0$ and C_{AL2} = 2[AL$_2$]/[PLLA]$_0$. [c] Reaction yields calculated based on the amount of isolated AL. [d] Reaction performed using metallic Mg as precatalyst. [e] Reaction performed using 15g of PLLA.

In order to determine the influence of alcohols structure and steric effect for PLLA alcoholysis process, we have conducted detailed studies using different butanol isomers, including n-butanol, isobutanol, sec-butanol, and tert-butanol. PLLA butanolysis reactions were carried out with the stoichiometry *la*/ROH/Mg = 1/2/0.01 at 160 and 200 °C for 1 h. The results showed that the reactivity of butanols decreases in the order isobutanol > n-butanol > sec-butanol > tert-butanol (Table S7 in SI). The lower reactivity sec- and tert-butanol may be explained by the influence of steric effect, while the higher reactivity of isobutanol than n-butanol, can be elucidated by alcohols' main chain length, formally C3 *vs*. C4. A similar effect was also observed in reactions of 2-ethylhexanol and n-octanol, wherein the first one was much more active. These observations may be also explained by the fact that primary alcohols with shorter main chains can better penetrate the surface of polymer and simultaneously due to their lower boiling points exert a higher pressure in the reactor, what result in a higher conversion of PLLA. Moreover, PLLA alcoholysis tests carried out using cyclopentanol and cyclohexanol confirmed that the presence of a sterically hindered aliphatic groups in the alcohols caused lower PLLA conversion, which in both cases at 200 °C were approximately 30% (Table S7 in SI). In order to better understand the effect of ROH substituents on the reactivity in PLLA alcoholysis, we choose electron rich and poor alcohols as reagents. According to the results shown in Table S8 in SI reactivity of used alcohols has decreased in the following order: $(CH_3)_2NCH_2CH_2OH$ > $CH_3OCH_2CH_2OH$ > $PhCH_2CH_2OH$ > CF_3CH_2OH > $PhCH_2OH$ > Cl_3CH_2OH. These studies confirmed that the reaction of PLLA with primary ethanol derivatives is accelerated by electron-donating substituents that promote nucleophilic attack of the ROH on the carbon atom of the ester group. Summarizing the above results, we have concluded that PLLA conversion depends not only on structural and electronic effects of the alcohol but can be also influenced by various factors such

as the ramification of ROH, solubility of the resulting polymer in alcohol, or catalyst aggregation. These explain, among other things weak reactivity of $PhCH_2OH$.

2.2.4. Synthesizes EL of various optical activity. In asymmetric synthesis, EL can be used as the starting material for the preparation of a wide range of optically active compounds.[35] We therefore used our method to synthesize lactic acid esters with various optical activities. These were determined by the PLA microstructure; for example, we used isotactic PLLA or PDLA to prepare the corresponding L-EL or D-EL esters. D,L-EL (racemic mixture) were prepared from atactic PDLLA as the substrate. The Mg-based catalysts did not cause significant epimerization of the resulting lactate ester during the recycling process. This was verified using circular dichroism (Figure 5) and optical purity determination by polarimetry. The optical rotation measurements were used to determinate the enantiomeric excess, which were equal to 92% for L-EL and 93% for D-EL.

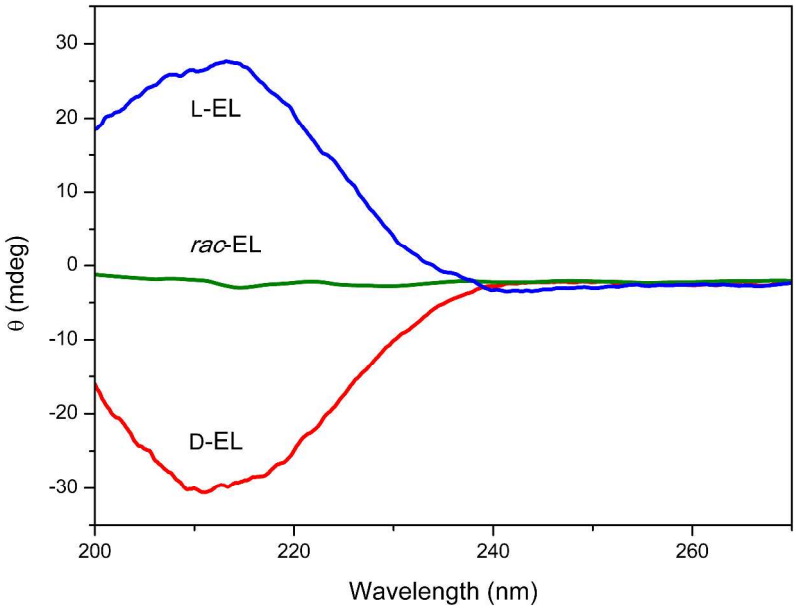


Figure 5. CD spectra of L-EL, D-EL and D,L-EL obtained using PLA resins with different chain microstructure.

2.2.5. Upscaling of PLA Alcoholysis. After optimization of the PLLA alcoholysis parameters, we increased the reaction scale 100- and 150-fold, using a 5 L reactor and Mg chips as the precatalyst (Table 2). The developed technique was successfully used to achieve 89% conversion of PLA and isolated EL yields of 86% (2.05 L) starting from 1.5 kg of polyester. The scale of the reaction did not affect the composition of the reaction products and the performance of the process.

Table 2. Large scale synthesis of EL by alcoholysis of PLLA using metallic Mg as precatalyst.[a]

No.	T (°C)	t (h)	C_{EL} (%)[d]	C_{EL2} (%)[d]	Y_{EL} (%)[e]	P_{max} (bar)[f]
1[b]	160	1	82	16	79	10
2[b]	200	1	88	11	85	14
3[b]	200	2	88	9	-	14
4[c]	200	1	89	10	86	18

[a] Alcoholysis conditions: *la*/EtOH/Mg = 1/2/0.01. [b - c] Reaction performed using 1 (b) or 1.5 kg (c) of PLLA (IngeoTM 2003D) in pressure reactor with a capacity of 5 L under N_2 atmosphere and autogenous pressure of reactants. [d] Obtained from ^{1}H NMR analysis according equation C_{EL} = [EL]/[PLLA]$_0$ and C_{EL2} = 2[EL$_2$]/[PLLA]$_0$. [e] Reaction yields calculated based on the amount of isolated EL. [f] The maximum pressure in the reactor observed throughout the course of the reaction.

2.2.6. Screening Activities of Various Catalysts in PLLA Alcoholysis. We examined the catalytic activities of various catalysts in PLLA alcoholysis, by performing reactions using selective metal halides, hydroxides, carboxylates, alkoxides, metallic chips, and organometallic compounds. Table 3 shows results of the compounds having the highest catalytic activity in the examined process. We found that metal alkoxides generated in situ from organometallic or metallic precursors have one of the highest catalytic activities in the ethanolysis of PLLA. When metallic Mg and Ca were used as precatalysts, the PLLA conversions and product yields were

comparable to those achieved industrially using $Sn(Oct)_2$.[36] Good catalytic activities were also observed for $SnCl_2$, $ZnCl_2$, and TBD.

2.2.7. Catalyst characterization. In these studies, for most of the alcoholysis reactions, the catalyst residues were isolated as insoluble precipitates, which made it impossible to perform spectroscopic studies in solution. It was difficult to obtain crystals of the used catalyst suitable for X-ray diffraction (XRD) from the post-reaction mixture, because amorphous solid materials rapidly formed. However, after multiple repeated syntheses, and using a slow crystallization technique, we managed to obtain, for the first time, crystals appropriate for XRD studies directly from the reactor, using metallic Ca as the catalyst precursor. The crystal structure of the mononuclear complex $[Ca(LAc)_2(EL)_2]$ (**1**, 42%) was determined. In the molecular structure of chiral compound **1**, the Ca^{2+} ion is coordinated with two lactic acid anions LAc^- and two neutral EL ligands, forming an eight-coordinated polyhedron with surrounding O_8 donors, as shown in Figure 6 (see also 1.cif file). The LAc^- ligands around the central atom display enantiomeric disorder, and two equivalent positions for the methine group are observed. Racemization of the lactate unit was previously observed during thermal degradation of Ca-end-capped PLLA.[37] We dissolved $CaCl_2$ in an EL/EtOH mixture (1:4) to check whether EtOH molecules can also coordinate with the Ca^{2+} center in the presence of EL. A previously unknown crystalline ionic compound $[Ca(EL)_4]Cl_2$ (**2**, 80%) was formed. The solid-state structure of **2** is similar to that of **1**, and contains a Ca1 ion eight-coordinated with O_8 donor atoms from four EL ligands. The absence of an alcohol molecule in the metal coordination sphere suggests that the used compounds function as typical transesterification catalysts.[38]

Table 3. Screening the catalytic activity of different catalysts in PLLA ethanolysis reaction.[a]

No.	Catalyst/Precatalyst	C_{EL} (%)[b]	C_{EL2} (%)[b]	P_{max} (bar)[c]
1	Li	82	15	9
2	Na	79	16	7
3	K	83	12	7
4	Mg	89	11	13
5	Ca	91	7	14
6	Sr	85	10	10
7	Ba	81	13	9
8	Na(OEt)	80	14	13
9	K(OEt)	83	12	13
10	$Ca(OMe)_2$	78	19	20
11	$Sn(OEt)_4$	81	18	23
12	$Sn(Oct)_2$	87	12	10
13	LiMe	83	15	12
14	$ZnEt_2$	85	14	13
15	$SnEt_2Cl_2$	87	11	15
16	$AlEt_3$	64	29	21
17	NaOH	77	17	15
18	KOH	77	16	13
19	$SnCl_2$	86	12	12
20	$ZnCl_2$	85	15	16
21	TBD	81	13	11

[a] Alcoholysis conditions: *la*/EtOH/M = 1/2/0.01, 10 g of PLLA (IngeoTM 2003D). Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants, at temperature 200 °C through 1h. [b] Obtained from ^{1}H NMR analysis according equation C_{EL} = [EL]/[PLLA]$_0$ and C_{EL2} = 2[EL$_2$]/[PLLA]$_0$. [c] The maximum pressure in the reactor observed throughout the course of the reaction.

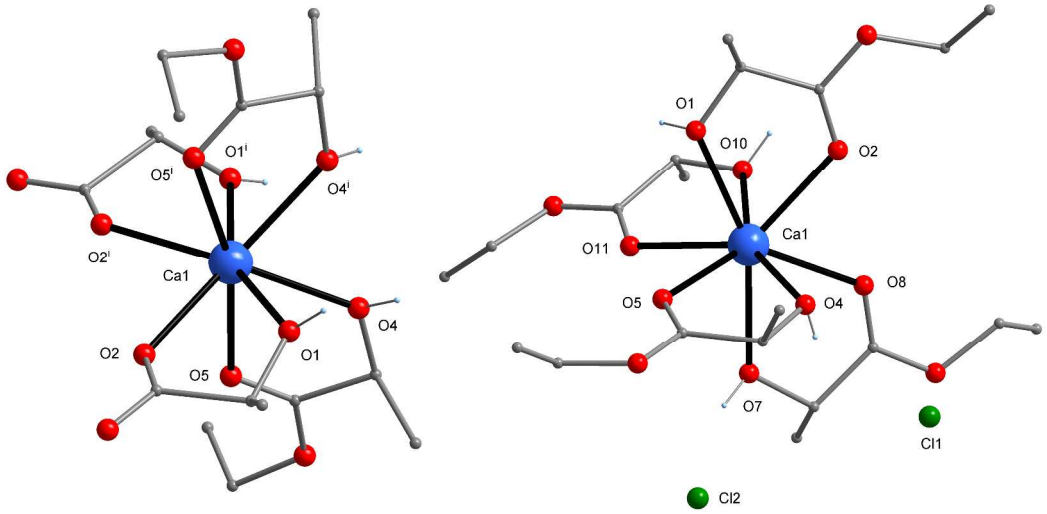
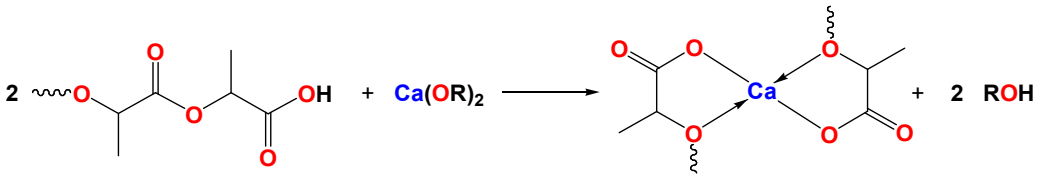


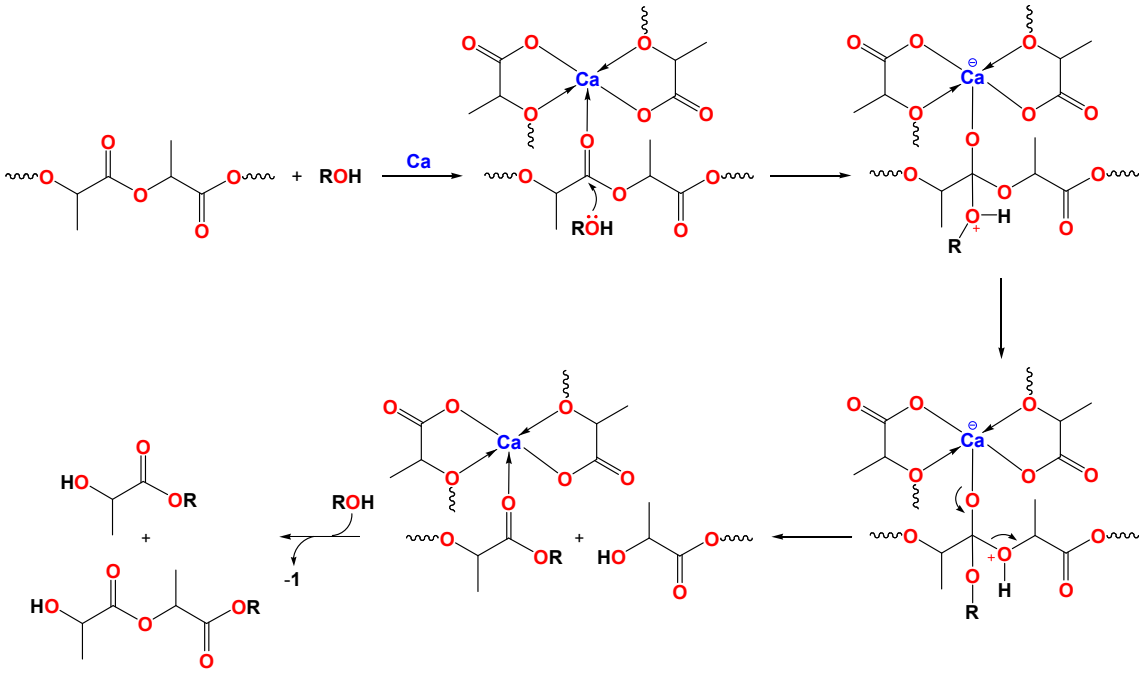
Figure 6. The molecular structures of $[Ca(LAc)_2(EL)_2]$ (**1**, left) and $[Ca(EL)_4]Cl_2$ (**2**, right); hydrogen atoms and disorders of ligands are omitted for clarity [symmetry code: (i) $-x+1$, y, $-z+1$].

The solid-state structures of **1–2** give insights into the possible metal-binding environments of PLA, and provide molecular models that help us to understand the formation of reaction intermediates. The structural data confirm that during PLA alcoholysis calcium lactate species are formed, which act as discrete catalysts in the investigated reactions. It was established that the first step involves the formation of a calcium–lactic acid complex via the reaction of $Ca(OR)_2$ with the −COOH end group in the polymer, as shown in Scheme 2. On the basis of these results, we propose that PLA alcoholysis proceeds as shown in Scheme 3 During alcoholysis, the O=C group of the PLA molecule coordinates with the metal center, and this increases the positive charge on the carbonyl carbon. This facilitates attack by the oxygen atom in ROH on the carbon atom of the ester group, resulting in breakage of the C−O bond and lactyl oligomer formation. The oligomers react further with ROH to generate the main products, AL and AL_2. However, we do not rule out the participation of moisture from the polymer or alcohol in the formation of $–(COO)_2Ca$ species.

Scheme 2. Proposed scenarios formation of metal lactate species as the results of reaction of $Ca(OR)_2$ with the −COOH end group in polymer.



Scheme 3. The proposed course of PLA alcoholysis reaction catalyzed by calcium lactate species synthesized *in situ* from metallic Ca.



When we conducted the process of PLLA alcoholysis in the presence of compounds **1** and **2**, at stoichiometry of the reactants *la*/EtOH/Ca = 1/2/0.01 at 200 °C for 1 h, the results were similar to catalyst free process. It follows from this that both compounds are not active in PLLA alcoholysis. Lack of reactivity of both compounds is due to their high coordination number around the calcium atoms which is 8. It is especially visible on the example of compound **1** where the coordination of two additionally chelating EL ligands to $\{Ca(lac)_2\}$ unit, maked it

catalytically inactive. We confirmed this experimentally by using commercial $[Ca(lac)_2]\cdot 5H_2O$ as a catalyst. In this case the conversion of PLLA to EL was 58%.

CONCLUSION

In this work, we developed a simple and environmentally friendly method for large-scale chemical recycling of PLA by alcoholysis under solvothermal conditions to lactic acid esters. This method can be used in either the absence or presence of a catalyst. The use of a metal catalyst enables the reaction to be conducted at lower temperatures, i.e., 80–100 °C, and pressures, with conversions comparable to those achieved under catalyst-free conditions. The crystal structure of **1** strongly suggests that metal–lactic acid complexes act as discreet catalysts in PLA alcoholysis when metal alkoxides are used as precatalysts. We believe that the current results represent an important advance in understanding the course of polyester alcoholysis mediated by metal complexes and explain the flexibility in the formation of active forms of the catalyst. Our study will be helpful in the design of new efficient catalysts for the transformation of green polymers and other polyesters to many useful chemicals. This could have direct impacts on their use and result in financial benefits.

EXPERIMENTAL SECTION

All reactions were performed under N_2 atmosphere using a steel pressure reactors with a capacity of 150 mL (Paar) or of 5 L (Amar) equipped with a mechanical stirrer. All reagents were purchased from commercial sources. PLA resins: PLLA (IngeoTM 2003D, NatureWorks LLC; or Naturesse® PLA cup, Naturesse), PDLA (PURASORB® PD24, Purac), PDLLA (BIOCOP®, BioMatPol); metallic Mg (Chempur), $MgBu_2$ solution 1.0 M in heptanes, toluene (99.7%, VWR), CD_2Cl_2 and C_6D_6 (Sigma-Aldrich). Mentioned below alcohols were purchased in the anhydrous form (water impurities < 0.005%) from Sigma-Aldrich and were used without any

purification: n-propanol (99.7 %), isopropanol (99.5 %), n-butanol (99.8 %), isobutanol (99.5 %), sec-butanol (99.5%), n-pentanol (≥99%), isopentanol (≥99%), n-hexanol (≥99 %), n-octanol (≥99%) and benzyl alcohol (99.8%). While the 2-phenylethanol (>99%, Merck), 2,2,2-trifluoroethanol (99.8%, ROTH) and 2,2,2-trichloroethanol (99%, Sigma-Aldrich) were dried by storage in an inert atmosphere through 3-4 days with molecular sieves (3Å, Sigma-Aldrich), which were before thermal activated under vacuum, in 280 °C for 24 hours. In turn, methanol (99.8%, Chempur), ethanol (99.8%, Chempur), tert-butanol (≥99%, ROTH), 2-ethylhexanol (≥99%, Sigma-Aldrich,), N,N-dimethyl-2-aminoethanol (99.5%, Sigma-Aldrich,), 2-methoxyethanol (≥99.5%, Sigma-Aldrich), cyclopentanol (99%, POCH) and cyclohexanol (99%, POCH) were dried by reflux and distillation over metallic magnesium, usually through from 5 to 12h. 2,2,2-tribromoethanol (98%, POCH) was three times purified by crystallization from hexane. Allyl alcohol and phenol (≥99%, Sigma-Aldrich) because of their high toxicity and very high irritation effect were used without any purification. Reagents were purified by standard methods: toluene was distilled over Na, CD_2Cl_2 was distilled over P_2O_5. Nuclear magnetic resonance (NMR) spectra were recorded at room temperature using a Bruker Avance 500 MHz spectrometer. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. Fourier-transform infrared (FT-IR) spectra were recorded as Nujol mulls using a Bruker 66/s FT-IR spectrometer. Elemental analysis was determined on a Perking-Elmer 2400 CHN Elemental Analyzer. Thermogravimetric analysis-differential thermal analysis (TGA-DTA) was performed under N_2 atmosphere using a SETSYS 16/18 system (SETARAM); a heating rate of 10 °C min^{-1} was used. Thermal decompositions of PLA were performed at 500 °C using a NT 1313 Furnace equipped with a KXP3+ thermostat (NEOTHERM). The concentrations of the metal ions in polymer resins after thermal

decompositions were determined by inductively coupled plasma atomic emission spectrometry (ICP-OES) using an ARL 3410 sequential spectrometer (Fisons Instruments). Size exclusion chromatography (SEC) traces were recorded using an Agilent 1100 Series isocratic pump, a degasser, an autosampler thermostatic box for columns, and a set of TSK Gel columns (2 × PLGel 5 microns MIXED-C) at 30 °C. A Wyatt Optilab rEX interferometric refractometer and a MALLS DAWN EOS Laser Photometer (Wyatt Technology Corp., USA) were applied as detectors. Methylene chloride was used as the eluent, at a flow rate of 0.8 mL min−1. Mn and Mw/Mn were calculated from the experimental traces using a Wyatt ASTRA v 4.90.07 program. The value of molecular weight and PDIs index for high molecular weight polymers were determinated by SEC-MALLS technique. While the molecular weight of PLA oligomers were determined relative to polystyrene standards and the obtained M_w values were multiplied by correction factor of 0.58.[39] Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectra were registered using a Voyager Elite mass spectrometer (PerSeptive Biosystems, USA) equipped with a N_2 laser (337 nm, 4-ns pulse width) and a time-delayed extraction ion source. Mass spectra were obtained in the linear mode. The sample solution in CH_2Cl_2 (5 mg/mL) were mixed with a CH_2Cl_2 solution of the matrix (dithranol 10 mg/mL). For the enhancement of ion formation KTFA was added to the matrix. The circular dichroism spectra were recorded on a JASCO J-715 spectrometer at 25°C in a 0.1cm path length quartz cuvette in EtOH at sample concentration of 0.01 M. Optical rotation were measured on a Jasco DIP-1000 polarimeter at 25°C using a Na lamp (589 nm) in a 50 mm cell length quartz cuvette in EtOH at sample concentration of 3%. Because of the large discrepancies in the literature values of specific rotation of L-EL, the reference value $[\alpha]_D^{25}$-10.5 $_{(3.00,\ EtOH)}$ was calculated based on optical rotation measurements of commercial products with *ee* of 98 and 99% (Sigma-Aldrich,

VWR). X-ray diffraction (XRD) data were collected at 80 K for 1, and 100 K for 2, using Xcalibur Ruby or Xcalibur PX diffractometer.[40] The experimental details and crystal data are given in Table S9 (SI). The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL package.[41] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were positioned geometrically and added to the structure factor calculations, but were not refined. The molecular graphics were created using Diamond, version 3.1e.[42] Crystallographic data for the structural analyses reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC), numbers CCDC 1465242-1465243. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; Homepage: http://www.ccdc.cam.ac.uk).

General alcoholysis procedure. A typical reaction procedure was exemplified by the synthesis of EL. Typically 10 g of PLA resin were placed in steel pressure reactor with a capacity of 150 mL and dried under vacuum through 15 - 30 min. Next under N_2 atmosphere from 8.1 to 81.1 mL anhydrous ethanol were introduced in the amount from 1 to 10 equivalents of EtOH per ester unit in polymer (*la*). Optionally, in a next step we can introduce $MgBu_2$ as precatalyst in an amount of 1 mol% per *la* unit. Then reaction were performed under autogenous pressure of reactants, through 1h, at varying temperature range depends on the type of studied reaction. For catalyst free reaction at temperature range from 200 to 260 °C, and from 80 to 200 °C when $MgBu_2$ was used. Conversion of PLA into lactate esters were determined from ^1H NMR spectra in C_6D_6 by integrating methine peaks at 5.05, 4.22 and 4.09 ppm characteristic for PLA and/or their oligomers end-capped with ethoxy group (EL_n), ethyl lactyllactate (EL_2) and

ethyl lactate (EL). The samples for NMR studies were taken from the reactor at 60 – 80 °C when the postreaction mixtures were homogeneous.

Kinetic studies of EL_2 alcoholysis. $MgBu_2$ (0.1 mL, 0.1 mmol) was added to the 1.9 g of EL_2 (10 mmol) and from 0.58 to 5.8 mL of EtOH at stoichiometry of reactants EL_2/EtOH/Mg = 1/1, 2, 4, 10/0.01 at 25 and 60 °C. The reactions were monitored in time by ^{1}H NMR spectroscopy. Aliquots (0.1 mL) were periodically withdrawn from the reaction mixture, cooled in liquid N_2, and stopped by removing EtOH in vacuo. The residues were dissolved in C_6D_6 and analyzed by ^{1}H NMR spectroscopy at room temperature.

Kinetic studies of PLLA alcoholysis. A typical PLLA alcoholysis procedure was exemplified using $MgBu_2$ as precatalyst. To a solution of PLLA (1.44g, 20 mmol): a) in 37.6 mL of toluene, 2.34 mL of EtOH, and from 0.1 to 0.5 mL of $MgBu_2$ ($[la]_0$ = 0.5 M; $[Mg]_0$ = 2.5, 5, 7.5, 10, 12.5 mM); or b) in from 38.84 to 28.4 mL of toluene, from 1.16 to 11.6 mL of EtOH, and 0.2 ml of $MgBu_2$ were added ($[la]_0$ = 0.5 M, [EtOH] = 0.5, 1, 2, 5 M). For all performed reactions, starting total volume of toluene and EtOH were equal to 40 ml. The reactions were carry out in round bottom flask with a volume of 150 mL under reflux at 90 °C. Aliquots (0.2 mL) were periodically withdrawn from the reaction mixture, cooled in liquid N_2, and stopped by removing EtOH in vacuo. The residues were dissolved in C_6D_6 and analyzed by ^{1}H NMR spectroscopy at room temperature.

General AL purification procedure. After PLA alcoholysis, the individual components of the reaction mixture were separated by distillation under reduced pressure using a rotary evaporator. First, the alcohol was distilled off, then the corresponding AL and finally the AL_2. Then, isolated AL was purified by double distilling and characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S15-42 in SI).

methyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.02 (1H, qd, J = 6.9, 5.3 Hz, HO*CH*), 3.20 (3H, s, O*CH*$_3$), 2.77 (1H, d, J = 5.3 Hz, *OH*), 1.21 (3H, d, J = 6.9 Hz, *CH*$_3$). ^{13}C NMR (125 MHz; C_6D_6): δ 176.1 (1C, *C*=O), 66.8 (1C, HO*CH*), 51.8 (1C, O*CH*$_3$), 20.4 (1C, *CH*$_3$). IR (cm^{-1}, Nujol mull): 3448 (vs), 2987 (s), 2957 (s), 2910 (m), 2853 (m), 2588 (w), 2340 (w), 2065 (w), 1958 (w), 1889 (w), 1742 (vs), 1455 (s), 1438 (s), 1408 (w), 1373 (m), 1271 (s), 1223 (vs), 1133 (vs), 1083 (w), 1048 (m), 980 (m), 918 (w), 843 (w), 758 (w), 649 (w), 535 (w), 494 (w).

ethyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.05 (1H, qd, J = 6.9, 5.3 Hz, HO*CH*), 3.83 (2H, m, O*CH*$_2$CH$_3$), 2.78 (1H, d, J = 5.3 Hz, *OH*), 1.24 (3H, d, J = 6.9 Hz, *CH*$_3$), 0.82 (3H, t, J = 7.1 Hz, OCH$_2$*CH*$_3$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.7 (1C, *C*=O), 66.8 (1C, HO*CH*), 61.2 (1C, O*CH*$_2$CH$_3$), 20.5 (1C, *CH*$_3$), 14.0 (1C, OCH$_2$*CH*$_3$). IR (cm^{-1}, Nujol mull): 3458 (vs), 2985 (s), 2940 (m), 2909 (m), 2879 (w), 2816 (w), 2782 (w), 2676 (w), 2360 (w), 2339 (w), 2247 (w), 2074 (w), 1979 (w), 1877 (w), 1737 (vs), 1451 (s), 1393 (s), 1372 (s), 1268 (vs), 1215 (vs), 1133 (vs), 1097 (s), 1047 (s), 1020 (s), 932 (s), 860 (s), 796 (w), 757 (m), 649 (m), 582 (w), 534 (w), 503 (w), 451 (w), 437 (w), 421 (w), 402 (w), 388 (w), 374 (w).

ethyl L-lactyllactate. ^{1}H NMR (500 MHz; C_6D_6): δ 5.01 (1H, q, J = 7.1 Hz, O*CH*), 4.18 (1H, q, J = 6.9 Hz, HO*CH*), 3.84 (2H, qd, J = 7.1, 2.2 Hz, OC*H2*CH3), 2.63 (1H, s, O*H*), 1.41 (3H, d, J = 6.9 Hz, HOCH*CH*$_3$), 1.16 (3H, d, J = 7.1 Hz, OCH*CH*$_3$), 0.83 (3H, t, J = 7.1 Hz, OCH$_2$*CH*$_3$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.3 (1C, (*C*=O)OC$_2$H$_5$), 170.1 (1C, HOCH(*C*=O)), 69.5 (1C, O*CH*), 66.9 (1C, HO*CH*), 61.3 (1C, O*CH*$_2$CH$_3$), 20.7 (1C, HOCH*CH*$_3$), 16.6 (1C, OCH*CH*$_3$), 13.9 (1C, OCH$_2$*CH*$_3$). IR (cm^{-1}, Nujol mull): 3484 (s), 2987 (s), 2942 (m), 2910 (m), 2881 (m), 2612 (w), 2406 (w), 2339 (w), 2248 (w), 2081 (w), 1992 w), 1746 (vs), 1452 (s), 1394 (m), 1379 (s), 1372 (s), 1349 (m), 1305 (m), 1273 (s), 1201 (vs), 1133 (vs), 1097 (vs), 1050 (s), 1020 (m), 943 (w), 918 (w), 863 (m), 761 (w), 749 (w), 685 (w), 576 (w), 545 (w).

n-propyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.08 (1H, m, HO*CH*), 3.81 (2H, m, O*CH*$_2$CH$_2$CH$_3$), 2.85 (1H, d, J = 4.9 Hz, *OH*), 1.28 (2H, m, OCH$_2$*CH*$_2$CH$_3$), 1.26 (3H, d, J = 6.9 Hz, *CH*$_3$), 0.62 (3H, t, J = 7.4 Hz, OCH$_2$CH$_2$*CH*$_3$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.9 (1C, *C*=O), 66.8 (1C, HO*CH*), 66.7 (1C, O*CH*$_2$CH$_2$CH$_3$), 22.0 (1C, OCH$_2$*CH*$_2$CH$_3$), 20.5 (1C, C*H*$_3$), 10.1 (1C, OCH$_2$CH$_2$*CH*$_3$). IR (cm^{-1}, Nujol mull): 3463 (vs), 2972 (vs), 2940 (s), 2898 (m), 2882 (m), 2684 (w), 2444 (w), 2349 (w), 2339 (w), 1968 (w), 1736 (vs), 1462 (s), 1391 (m), 1381 (m), 1372 (m), 1350 (w), 1311 (m), 1268 (s), 1213 (s), 1132 (vs), 1083 (m), 1045 (m), 977 (w), 951 (m), 930 (w), 911 (w), 892 (w), 855 (w), 837 (w), 756 (m), 648 (w), 540 (w), 457 (w).

isopropyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.90 (1H, hept, J = 6.3 Hz, O*CH*(CH$_3$)$_2$), 4.09 (1H, q, J = 6.9 Hz, HO*CH*), 3.05 (1H, d, s, *OH*), 1.27 (3H, d, J = 6.9 Hz, *CH*$_3$), 0.93 (6H, dd, J = 6.3, 1.0 Hz, OCH(*CH*$_3$)$_2$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.4 (1C, *C*=O), 68.9 (1C, O*CH*(CH$_3$)$_2$), 66.9 (1C, HO*CH*), 21.5, 21.4 (2C, OCH(*CH*$_3$)$_2$), 20.5 (1C, C*H*$_3$). IR (cm^{-1}, Nujol mull): 3472 (vs), 2983 (vs), 2940 (vs), 2880 (m), 2738 (w), 2081 (w), 1733 (vs), 1647 (w), 1469 (s), 1457 (s), 1387 (s), 1376 (vs), 1271 (vs), 1219 (vs), 1183 (s), 1134 (vs), 1108 (vs), 1043 (s), 983 (w), 942 (s), 911 (m), 862 (m), 822 (m), 759 (m), 636 (w), 508 (w), 464 (w), 426 (w).

allyl L-lactate. ^{1}H NMR (500 MHz, C_6D_6): δ 5.59 (1H, ddt, J = 17.2, 10.5, 5.7 Hz, OCH$_2$*CH*=CH$_2$), 5.01 (1H, ddd, J = 10.4, 2.6, 1.3 Hz, OCH$_2$CH=*CH*$_2$), 4.92 (1H, ddd, J = 10.4, 2.6, 1.3 Hz, OCH$_2$CH=*CH*$_2$), 4.33 (2H, qdt, J = 13.2, 5.7, 1.4 Hz, O*CH*$_2$CH=CH$_2$), 4.10 (1H, m, HO*CH*), 3.03 (1H, d, J = 5.2 Hz, *OH*), 1.26 (3H, d, J = 6.9 Hz, *CH*$_3$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.4 (1C, *C*=O), 132.1 (1C, OCH$_2$*CH*=CH$_2$), 118.2 (1C, OCH$_2$CH=*CH*$_2$), 66.9 (1C, HO*CH*), 65.7 (1C, O*CH*$_2$), 20.4 (1C, C*H*$_3$). IR (cm^{-1}, Nujol mull): 3457 (vs), 3088 (m), 2986 (s), 2941 (m), 2886 (m), 2586 (w), 2453 (w), 2339 (w), 2112 (w), 1968 (w), 1740 (vs), 1649 (m),

1456 (s), 1425 (m), 1414 (m), 1374 (m), 1273 (s), 1209 (vs), 1131 (vs), 1088 (m), 1045 (s), 980 (s), 931 (s), 858 (w), 837 (w), 757 (m), 656 (w), 556 (w).

n-butyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.08 (1H, q, J = 6.9 Hz, HO*CH*), 3.88 (2H, qt, J = 10.8, 6.6 Hz, O*CH*$_2$(CH$_2$)$_2$CH$_3$), 2.83 (1H, s, *OH*), 1.30 – 1.23 (m, 2H, OCH$_2$*CH*$_2$CH$_2$CH$_3$), 1.26 (3H, d, J = 6.9 Hz, *CH*$_3$), 1.07 (2H, dq, J = 14.8, 7.4 Hz, O(CH$_2$)$_2$*CH*$_2$CH$_3$), 0.70 (3H, t, J = 7.4 Hz, O(CH$_2$)$_3$*CH*$_3$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.9 (1C, *C*=O), 66.8 (1C, HO*CH*), 65.1 (1C, O*CH*$_2$(CH$_2$)$_2$CH$_3$), 30.7 (1C, OCH$_2$*CH*$_2$CH$_2$CH$_3$), 20.5 (1C, *CH*$_3$), 19.1 (1C, O(CH$_2$)$_2$*CH*$_2$CH$_3$), 13.6 (1C, O(CH$_2$)$_3$*CH*$_3$). IR (cm^{-1}, Nujol mull): 3465 (vs), 2962 (vs), 2937 (vs), 2876 (s), 2740 (w), 2669 (w), 2447 (w), 2396 (w), 2349 (w), 2306 (w), 2172 (w), 1737 (vs), 1650 (w), 1643 (w), 1632 (w), 1573 (w), 1563 (w), 1461 (m), 1435 (w), 1391 (m), 1383 (m), 1371 (m), 1270 (vs), 1212 (vs), 1132 (vs), 1084 (m), 1060 (m), 1044 (s), 1019 (m), 997 (m), 965 (m), 944 (m), 843 (m), 809 (w), 757 (m), 739 (m), 651 (w), 532 (w), 511 (w), 484 (w), 469 (w), 453 (w), 437 (w), 421 (w), 388 (w).

isobutyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.09 (1H, qd, J = 6.9, 4.8 Hz HO*CH*), 3.76 (1H, dd, J = 10.6, 6.7 Hz, O*CH*$_2$CH(CH$_3$)$_2$), 3.66 (1H, dd, J = 10.6, 6.7 Hz, O*CH*$_2$CH(CH$_3$)$_2$), 2.88 (1H, d, J = 4.8 Hz, *OH*), 1.62 (1H, dp, J = 13.4, 6.7 Hz, OCH$_2$*CH*(CH$_3$)$_2$), 1.27 (3H, d, J = 6.9 Hz, *CH*$_3$), 0.65 (6H, dd, J = 6.7, 1.6 Hz, OCH$_2$CH(*CH*$_3$)$_2$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.8 (1C, *C*=*O*), 71.2 (1C, O*CH*$_2$CH(CH$_3$)$_2$), 66.8 (1C, HO*CH*), 27.8 (1C, OCH$_2$*CH*(CH$_3$)$_2$), 20.6 (1C, *CH*$_3$), 18.8 (1C, OCH$_2$CH(*CH*$_3$)$_2$), 18.7 (1C, OCH$_2$CH(*CH*$_3$)$_2$). IR (cm^{-1}, Nujol mull): 3464 (vs), 2965 (vs), 2897 (s), 2877 (s), 2728 (w), 1736 (vs), 1471 (s), 1395 (m), 1379 (n), 1371 (n), 1343 (w), 1268 (s), 1213 (vs), 1131 (vs), 1083 (m), 1046 (s), 988 (s), 968 (m), 947 (m), 935 (m), 874 (w), 835 (w), 820 (w), 799 (w), 757 (w), 650 (w), 540 (w), 432 (w).

sec-butyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.80 (1H, m, O*CH*(CH_3)CH_2CH_3), 4.09 (1H, m, HO*CH*), {2.90, 2.88 (1H, d, J = 5.3 Hz, *OH*)}, {1.32, 1.19 (m, 2H, OCH(CH_3)*CH_2*CH_3)}, {1.27, 1.26 (3H, d, J = 6.9 Hz, *CH_3*)}, {0.94, 0.93 (3H, d, J = 6.3 Hz, OCH(*CH_3*)CH_2CH_3), {0.65, 0.63 (3H, m, OCH(CH_3)CH_2*CH_3*)}. ^{13}C NMR (125 MHz; C_6D_6): δ {175.7, 175.6 (1C, *C*=O)}, 73.5 (1C, O*CH*(CH_3)CH_2CH_3), {66.9, 66.8 (1C, HO*CH*)}, {28.9, 28.7 (1C, OCH(CH_3)*CH_2*CH_3)}, {20.7, 20.6 (1C, C*H_3*)}, {19.3, 19.2 (1C, OCH(*CH_3*)CH_2CH_3)}, {9.5 (1C, OCH(CH_3)CH_2*CH_3*)}. IR (cm^{-1}, Nujol mull): 3471 (vs), 2977 (vs), 2939 (s), 2882 (s), 2741 (w), 2338 (w), 2079 (w), 1980 (w), 1732 (vs), 1458 (s), 1380 (s), 1268 (vs), 1219 (vs), 1179 (m), 1128 (vs), 1114 (vs), 1094 (s), 1043 (s), 1027 (m), 995 (m), 968 (m), 937 (m), 886 (m), 865 (s), 829 (w), 782 (w), 758 (w), 652 (w), 575 (w), 542 (w), 493 (w), 435 (w).

n-pentyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.11 (1H, qd, J = 6.9, 5.4 Hz, HO*CH*), 3.90 (2H, m, O*CH_2*(CH_2)$_3CH_3$), 2.97 (1H, d, J = 5.4 Hz, *OH*), 1.32 (2H, m, OCH_2*CH_2*(CH_2)$_2CH_3$), 1.28 (3H, d, J = 6.9 Hz, *CH_3*), 1.07 (4H, m, O(CH_2)$_2$*(CH_2)$_2$*CH_3), 0.77 (3H, t, J = 7.1 Hz, O(CH_2)$_4$*CH_3*). ^{13}C NMR (125 MHz; C_6D_6): δ 175.9 (1C, *C*=O), 66.9 (1C, HO*CH*), 65.4 (1C, O*CH_2*(CH_2)$_3CH_3$), 28.4 (1C, OCH_2*CH_2*(CH_2)$_2CH_3$), 28.1 (1C, O(CH_2)$_2$*CH_2*CH_2CH_3), 22.4 (1C, O(CH_2)$_3$*CH_2*CH_3), 20.6 (1C, *CH_3*), 14.0 (1C, O(CH_2)$_4$*CH_3*). IR (cm^{-1}, Nujol mull): 3465 (s), 2959 (vs), 2935 (vs), 2874 (s), 2863 (s), 2735 (w), 1736 (vs), 1467 (s), 1459 (s), 1380 (m), 1372 (m), 1265 (s), 1210 (vs), 1132 (vs), 1080 (m), 1046 (s), 969 (m), 930 (w), 868 (w), 757 (w), 730 (w), 648 (w), 517 (w), 467 (w).

isopentyl L-lactate. ^{1}H NMR (500 MHz; C_6D_6): δ 4.11 (1H, m, HO*CH*), 3.95 (2H, qt, J = 10.9, 6.8, O*CH_2*CH_2CH(CH_3)$_2$), 2.95 (1H, d, J = 3.5 Hz, *OH*), 1.40 (1H, m, O(CH_2)$_2$*CH*(CH_3)$_2$), 1.28 (3H, d, J = 6.9 Hz, *CH_3*), 1.23 (2H, ddd, J = 14.0, 6.9, 1.3 Hz, OCH_2*CH_2*CH(CH_3)$_2$), 0.70 (6H, dd, J = 6.7, 1.7 Hz, O(CH_2)$_2$CH(*CH_3*)$_2$). ^{13}C NMR (125 MHz; C_6D_6): δ 175.9 (1C, C=O),

66.9 (1C, HO*CH*), 64.0 (1C, O*CH*$_2$CH$_2$CH(CH$_3$)$_2$), 37.4 (1C, O(CH$_2$)$_2$*CH*(CH$_3$)$_2$), 25.1 (1C, OCH$_2$*CH*$_2$CH(CH$_3$)$_2$), 20.5 (1C, *CH*$_3$), {22.4, 22.3 (2C, OCH$_2$CH$_2$CH(*CH*$_3$)$_2$)}. IR (cm^{-1}, Nujol mull): 3464 (vs), 2960 (vs), 2936 (vs), 2873 (vs), 2723 (w), 2654 (w), 1736 (vs), 1466 (s), 1432 (w), 1387 (m), 1369 (s), 1344 (w), 1334 (w), 1268 (s), 1212 (vs), 1171 (m), 1131 (vs), 1083 (m), 1046 (s), 1006 (w), 967 (m), 959 (m), 950 (m), 923 (w), 867 (w), 851 (w), 827 (w), 755 (w), 647 (w), 522 (w), 462 (w).

n-hexyl L-lactate. ^{1}H NMR (500 MHz; C$_6$D$_6$): δ 4.09 (1H, q, J = 6.8 Hz, HO*CH*), 3.90 (2H, qt, J = 10.7, 6.7 Hz, O*CH*$_2$(CH$_2$)$_4$CH$_3$), 2.79 (1H, s, *OH*), 1.32 (m, 2H, OCH$_2$*CH*$_2$(CH$_2$)$_3$CH$_3$), 1.27 (3H, d, J = 6.9 Hz, *CH*$_3$), 1.16 (2H, m, O(CH$_2$)$_2$*CH*$_2$(CH$_2$)$_2$CH$_3$), 1.06 (4H, m, O(CH$_2$)$_3$(*CH*$_2$)$_2$CH$_3$), 0.82 (3H, t, J = 7.3 Hz, O(CH$_2$)$_5$*CH*$_3$). ^{13}C NMR (125 MHz; C$_6$D$_6$): δ 175.9 (1C, *C*=O), 66.8 (1C, HO*CH*), 65.5 (1C, O*CH*$_2$(CH$_2$)$_4$CH$_3$), 31.5 (1C, OCH$_2$*CH*$_2$(CH$_2$)$_3$CH$_3$), 28.7 (1C, O(CH$_2$)$_2$*CH*$_2$(CH$_2$)$_2$CH$_3$), 25.6 (1C, O(CH$_2$)$_3$*CH*$_2$CH$_2$CH$_3$), 22.8 (1C, O(CH$_2$)$_4$*CH*$_2$CH$_3$), 20.6 (1C, *CH*$_3$), 14.1 (1C, O(CH$_2$)$_5$*CH*$_3$). IR (cm^{-1}, Nujol mull): 3465 (vs), 2958 (vs), 2933 (vs), 2873 (vs), 2861 (vs), 2733 (w), 2673 (w), 2338 (w), 1736 (vs), 1467 (s), 1459 (s), 1379 (m), 1268 (s), 1216 (vs), 1132 (vs), 1081 (m), 1045 (m), 1007 (w), 982 (w), 937 (w), 908 (w), 864 (w), 845 (w), 815 (w), 758 (w), 727 (w), 648 (w), 541 (w), 479 (w).

n-octyl L-lactate. ^{1}H NMR (500 MHz; C$_6$D$_6$): δ 4.11 (1H, q, J = 6.9 Hz, HO*CH*), 3.93 (2H, qt, J = 10.7, 6.7 Hz, O*CH*$_2$(CH$_2$)$_6$CH$_3$), 2.91(1H, s, *OH*), 1.35 (2H, m, OCH$_2$*CH*$_2$(CH$_2$)$_5$CH$_3$), 1.29 (3H, d, J = 6.9 Hz, *CH*$_3$), 1.25 (2H, m, O(CH$_2$)$_2$*CH*$_2$(CH$_2$)$_4$CH$_3$), 1.17 (4H, m, O(CH$_2$)$_3$(*CH*$_2$)$_2$(CH$_2$)$_2$CH$_3$), 1.10 (4H, m, O(CH$_2$)$_5$(*CH*$_2$)$_2$CH$_3$), 0.89 (3H, t, J = 7.2 Hz, O(CH$_2$)$_7$*CH*$_3$). ^{13}C NMR (125 MHz; C$_6$D$_6$): δ 175.9 (1C, *C*=O), 66.9 (1C, HO*CH*), 65.5 (1C, O*CH*$_2$(CH$_2$)$_6$CH$_3$), 32.1 (1C, OCH$_2$*CH*$_2$(CH$_2$)$_5$CH$_3$), 29.5 (1C, O(CH$_2$)$_2$*CH*$_2$(CH$_2$)$_4$CH$_3$), 29.4 (1C, O(CH$_2$)$_3$*CH*$_2$(CH$_2$)$_3$CH$_3$), 28.8 (1C, O(CH$_2$)$_4$*CH*$_2$(CH$_2$)$_2$CH$_3$), 26.0 (1C,

$O(CH_2)_5CH_2CH_2CH_3$), 23.0 (1C, $O(CH_2)_6CH_2CH_3$), 20.6 (1C, CH_3), 14.3 (1C, $O(CH_2)_7CH_3$). IR (cm^{-1}, Nujol mull): 3464 (vs), 2957 (vs), 2928 (vs), 2872 (vs), 2857 (vs), 2686 (w), 2349 (w), 1736 (vs), 1467 (s), 1459 (s), 1378 (m), 1265 (s), 1212 (vs), 1132 (vs), 1082 (m), 1044 (s), 955 (m), 885 (w), 864 (w), 756 (w), 724 (w), 671 (w), 647 (w), 541 (w).

2-etylhexyl L-lactate. ^1H NMR (500 MHz; C_6D_6): δ 4.13 (1H, q, J = 6.9 Hz, HO*CH*), 3.95 (2H, dtd, J = 21.1, 10.8, 5.8 Hz, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$), 3.00 (1H, s, *OH*), 1.36 (1H, m, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$), 1.29 (3H, d, J = 6.9 Hz, CH_3), {1.17, 1.11 (m, 8H, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$)}, 0.85 (3H, td, J = 7.1, 0.7 Hz, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$), 0.75 (3H, td, J = 7.4, 0.9 Hz, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$). ^{13}C NMR (125 MHz; C_6D_6): δ 176.0 (1C, *C*=O), {67.7, 67.6 (1C, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$)}, 66.9 (1C, HO*CH*), {39.1, 39.0 (1C, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$)}, {30.6, 30.5 (1C, $OCH_2CH(CH_2CH_3)CH_2(CH_2)_2CH_3$)}, {29.1, 29.0 (1C, $OCH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$)}, {24.0, 23.9 (1C, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$)}, {23.3, 23.2 (1C, $OCH_2CH(CH_2CH_3)(CH_2)_2CH_2CH_3$)}, 20.6 (1C, CH_3), {14.2, 14.1 (1C, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$)}, {11.0, 10.9 (1C, $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$)}. IR ($cm^{-1}$, Nujol mull): 3472 (s), 2961 (vs), 2932 (vs), 2875 (vs), 2862 (vs), 2734 (w), 2675 (w), 2349 (w), 2305 (w), 2164 (w), 1735 (vs), 1654 (w), 1647 (w), 1636 (w), 1617 (w), 1577 (w), 1560 (w), 1540 (w), 1521 (w), 1507 (w), 1462 (s), 1381 (m), 1266 (s), 1214 (vs), 1131 (vs), 1083 (m), 1045 (s), 997 (w), 979 (w), 962 (w), 868 (w), 844 (w), 825 (w), 771 (w), 756 (w), 728 (w), 671 (w), 648 (w), 534 (w), 522 (w), 484 (w).

Synthesis of $[Ca(LAc)_2(EL)_2]$ (1). 10 g of PLLA (IngeoTM 2003D) were placed in steel pressure reactor with a capacity of 150 mL and dried under vacuum through 15 - 30 min. Next under N_2 atmosphere 16.2 mL of anhydrous ethanol and 0.056g of metallic calcium were

introduced. Then reaction were performed under autogenous pressure of reactants, through 1h, at 200 °C. Single crystals for XRD analysis were obtained from the concentrated mother liquor at 25 °C. The crystals were filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield 0.27 g (42%). Anal. Calcd for $C_{16}H_{30}O_{12}Ca$: C, 42.28; H, 6.65. Found: C, 42.30; H, 6.68. ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 5.20 (2H, m, HO^{LAc}), 5.11 (2H, m, HOCH^{LAc}), 4.33 (2H, m, HOCH^{EL}), 4.17 (4H, m, OCH_2CH$_3$), 2.61 (2H, dd, J = 5.8, 2.7 Hz, HO^{EL}), {1.57, 1.50 (6H, J = 7.1, Hz, CH_3^{LAc})}, 1.45 (6H, d, J = 6.9 Hz, CH_3^{EL}), 1.26 (6H, t, J = 7.1, OCH$_2CH_3$). ^{13}C NMR (125 MHz, CD_2Cl_2, ppm):δ {170.5, 170.4 (2C, C=O^{LAc})}, 170.1 (2C, C=O^{EL}), {69.8, 69.5 (2C, HOCH^{LAc})}, 67.1 (2C, HOCH^{EL}), 61.9 (2C, OCH_2CH$_3$), 20.7 (2C, CH_3^{EL}), 17.0 (2C, CH_3^{LAc}), 14.3 (2C, OCH$_2CH_3$). IR (cm^{-1}, Nujol mull): 3301 (s), 2954 (vs), 2924 (vs), 2854 (vs), 2731 (w), 2349 (w), 2301 (w), 1750 (vs), 1590 (vs), 1462 (vs), 1434 (s), 1378 (s), 1314 (m), 1262 (s), 1216 (s), 1199 (s), 1129 (vs), 1096 (s), 1048 (s), 1023 (m), 932 (w), 860 (w), 803 (w), 774 (w), 721 (w), 673 (w), 664 (w), 552 (w).

Synthesis of [Ca(EL)$_4$]Cl$_2$ (2). To a solution of 1.2 g of $CaCl_2$ in 20 mL of EtOH was added 5 mL of EL. Next the mixture was stirred at 60 °C, through 1h. Single crystals for XRD analysis were obtained from the concentrated mother liquor at 25 °C. The crystals were filtered off, washed with hexane (10 × 5 mL), and dried under vacuum. Yield 5.05 g (80%). Anal. Calcd for $C_{20}H_{40}O_{12}Cl_2Ca$: C, 41.17; H, 6.91; Cl, 12.15. Found: C, 41.19; H, 6.92; Cl, 12.13. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 5.39 (4H, s, *OH*), 4.46 (4H, qd, J = 6.9, 3.6 Hz, HO*CH*), 4.26 (8H, q, J = 7.1 Hz, OCH_2CH$_3$), 1.48 (12H, d, J = 6.9 Hz, CH_3), 1.29 (12H, t, J = 7.1 Hz, OCH$_2CH_3$). ^{13}C NMR (125 MHz, CD_2Cl_2, ppm): δ 178.5 (4C, C=O), 68.1 (4C, HO*CH*), 63.0 (4C, OCH_2CH$_3$), 20.6 (4C, CH_3), 14.2 (4C, OCH$_2CH_3$). IR (cm^{-1}, Nujol mull): 3107 (vs), 2704 (w), 1872 (w), 1812 (w), 1705 (vs), 1668 (w), 1463 (s), 1416 (s), 1374 (s), 1330 (s), 1313 (s), 1283 (m), 1234

(s), 1163 (w), 1120 (s), 1096 (w), 1047 (w), 1014 (m), 939 (m), 875 (w), 864 (m), 806 (w), 758 (w), 694 (w), 643 (w), 497 (w), 445 (w), 399 (w).

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:.

SEC-MALLS and TGA/DTA analysis of used PLA resins, tables containing experimental data of performed reactions, kinetic experimental data, NMR spectra of synthesized esters (PDF), crystallographic data (CIF).

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Notes

The authors declare no competing financial interest.

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