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Synthesis of Micro ^{14}C-Labeled Polylactide for Environmental Assessment Analysis

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Polylactide (PLA), a biobased, biodegradable polyester derived from lactic acid, is recognized as an alternative to conventional plastics due to properties such as mechanical strength and compostability. Despite widespread use in applications from medical devices to packaging, PLA degradation in the environment, particularly its breakdown into microplastics, raises concerns. Conventional analytical methods are inadequate for quantifying PLA degradation in environments. To address this, radio tracking techniques using carbon-14 have emerged as a reliable method for PLA decomposition studies. The first step is producing labeled polymers from suitable monomers. Ring-opening polymerization (ROP) of lactide is widely used for synthesizing PLA, but this approach faces challenges due to the limited availability and high cost of ^{14}C-labeled precursors. We report the first use of a biocompatible zinc bisguanidine catalyst for the synthesis of ^{14}C-lactide from ^{14}C-lactic acid, enabling the production of ^{14}C-PLA. The process involves dehydration and oligomer formation, followed by catalytic depolymerization to yield ^{14}C-lactide, which is polymerized through ROP. Lactide production was optimized by comparing the toxic industrial catalyst tin(II) octanoate [Sn(Oct)$_2$] with our catalyst, the latter ultimately used for ^{14}C-lactide and ^{14}C-PLA production. The resulting micro-^{14}C-labeled PLA can be used to quantify degradation, assess environmental impact.

1. Introduction

Polylactide (PLA) is a thermoplastic aliphatic polyester. The hydrolyzable backbone of this eco-friendly polymer makes it susceptible to biodegradation.[1–4] In a circular economy, biodegradable plastics such as PLA offer promising alternatives to conventional materials like Polyethylene Terephthalate (PET), Polypropylene (PP), and Polystyrene (PS), due to their favorable attributes including ease of manufacturing, nontoxicity, biocompatibility, strong mechanical properties, thermal plasticity, and compostability.[1–6] The mechanical properties of PLA are comparable to those of traditional plastics, making it applicable in various fields, including medical devices, food packaging, films, and, more recently, in electronics, cosmetics, construction, and synthetic fiber production.[7–12] The growing use of PLA not only helps to conserve fossil resources but also lowers CO_2 emissions, thereby supporting environmental sustainability.[13]

Despite being promoted as a biodegradable and environmentally friendly alternative to conventional plastics, the environmental impact of PLA largely depends on how it is disposed of. PLA is specifically designed for industrial composting, requiring high temperatures, controlled humidity, and active microbial activity to degrade efficiently into nontoxic byproducts. Under such optimized conditions, typically found in industrial composting facilities, PLA can break down within weeks to months.[14,15] However, in natural environments such as landfills, soil, or aquatic systems where these conditions are absent, its degradation is slow or incomplete.[16,17] This leads to the accumulation of persistent PLA fragments and microplastics. Compounding this issue, large quantities of PLA are produced annually, yet only a small portion is recycled or incinerated due to the prevailing linear plastics economy. As a result, most PLA ends up in the environment, where it may degrade into low molecular weight polymers or microplastic particles (<5 mm), raising increasing concerns about their long-term environmental and health risks.[18–21]

Common analytical methods, including chromatography, gravimetry, visual detection, and mass spectrometry, are not capable to directly quantify the degradation of biodegradable plastics at realistic concentrations in complex environmental conditions over time, particularly when the degradation process is slow.[22–25]

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As a result, radio tracking techniques have become the most reliable method for quantifying and studying plastic decomposition in complex environmental matrices such as sewer water, activated sludge, freshwater, soil, compost, and sediment. This approach uses carbon-labeled monomers in polymer chains without altering the chemistry of polymers, allowing clear differentiation between CO_2 generated during degradation and other carbon sources, even at very low rates and despite high background effects. This enables accurate mass balance calculations in degradation studies. Additionally, it facilitates the analysis of polymers transport, leaching, plant uptake, and degradation products. Consequently, data interpretation becomes more precise and straightforward, even in the presence of various biological, chemical, and physical degradation factors.[26]

Optimization methods for the preparation of labeled polymers on a laboratory scale are a fundamental requirement for the precise study of polymer fate. There are four main types of radiolabeling: (a) specific labeling, where radioactive atoms occupy a known specific position in the molecule, (b) uniform labeling "U", where radioactive atoms are distributed in a statistically uniform pattern, and (c) general labeling "G", where they are randomly distributed. For polymer degradation studies, ^{14}C labeling is commonly used, either as specific or uniform labeling, depending on the experimental objectives.[27,28] Radiolabeled polymers can be prepared through various synthesis routes. Chemical synthesis typically starts with labeled precursors and follows chemical reactions. Alternatively, biochemical synthesis involves growing algae, plants, or bacteria with $^{14}CO_2$ or ^{14}C-precursors to incorporate the label into natural polymers.[29] In some cases, isotope exchange reactions are used.[30] Regardless of the approach, purification and characterization of the labeled compounds are necessary to ensure their integrity and suitability for experiments.[31]

PLA can be synthesized through three distinct methods: direct condensation polymerization, azeotropic dehydrative condensation polymerization, and ring-opening polymerization (ROP) using lactide, the cyclic dimer of LA (**Figure 1**).[32,33] Among these methods, direct condensation and ROP are the most widely used production techniques. Polycondensation does not produce PLA with high quality and optical purity, and the lack of control over the molecular weight results in low polydispersity.[34] Consequently, industrial PLA is typically manufactured via a catalytic ROP process, which is carefully controlled to yield monodisperse PLA with a higher molecular weight.[35,36] Molecular weight is a critical characteristic of PLA, influencing its subsequent applications. It impacts physical and mechanical properties such as strength, heat resistance, viscosity, decomposition rate, and microstructure. Generally, a higher molecular weight correlates with increased strength and heat resistance of the polymer.[37] In the ROP process, in order to produce the monomer lactide via a two-step synthesis, lactic acid (LA) is required. LA, which are water-soluble organic acids, can be produced either through chemical synthesis from petrochemicals or through the fermentation of feedstocks like starch, glucose, corn starch, sugarcane, or cassava roots making PLA bio-based. Lactic acid exists in two stereoisomers, l-lactide, d-lactide, which affect the physical properties of PLA, enabling it to be either amorphous or semicrystalline depending on the ratio of these enantiomers.[13,38,39]

The lack of access to ^{14}C-labeled lactide for PLA polymerization through ROP prompted us to adopt a two-step synthesis route starting from LA. First, we focused on dehydration and oligomer production from ^{14}C-LA monomers, followed by catalytic depolymerization to generate ^{14}C-lactide. This is the most commonly used and well-established industrial approach, extensively documented in patent literature for lactide production.[40] Additional patents discuss the gas-phase synthesis of lactide using packed solid catalyst beds.[41] Then, this step was followed by polymerization using ROP to produce ^{14}C-PLA.

Producing lactide is both energy and time-intensive, requiring catalysts and careful optimization of temperature and pressure. Achieving a high reaction yield is particularly challenging, especially when valuable radiolabeled monomers are involved. Maintaining optical purity and preventing racemization, along with minimizing the formation of side products, are crucial factors that determine the efficiency of the reaction. Depending on the purity of the LA and the catalysts used, byproducts such as oligomers, water, meso-lactide, and other impurities alongside lactide are produced.

Lactide exists in three stereoisomeric forms: l-lactide, d-lactide, and meso-lactide. Meso-lactide, an optically inactive molecule, is produced as a byproduct during the catalytic lactide reaction. This byproduct has a lower melting point compared to the other stereoisomers (Figure 1) and can negatively impact the

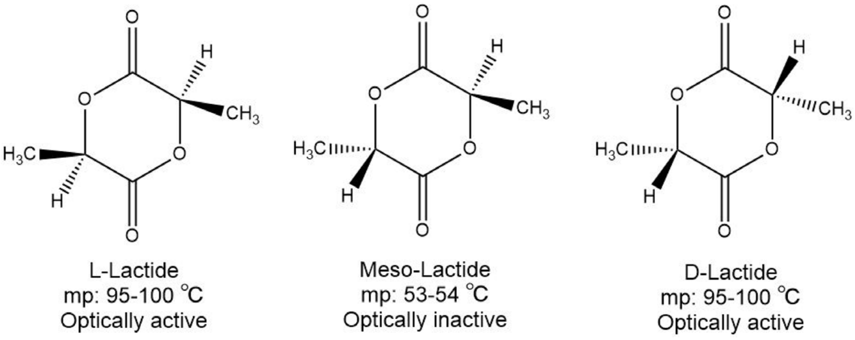


Figure 1. Lactide stereoisomers.

quality of the final polymer. It is essential to optimize the reaction conditions to minimize the production of meso-lactide and to remove it through purification processes.[42] Achieving high-purity lactide is particularly important in specialized applications, such as radiolabeling studies, where the presence of impurities can interfere with experimental accuracy. On the other hand, radiolabeling polymers is complex, expensive, and constrained by synthesis methods, purification challenges, and the limited availability of labeled precursors from commercial suppliers. This highlights the need for novel synthesis approaches to expand research capabilities, particularly for the downscaling of complex synthesis procedures. Additionally, working with ^{14}C requires a specialized license, which restricts collaboration opportunities for research groups and limits the broader application of this method.

2. Experimental Section

2.1. Materials and Instruments

L-Lactic acid solution in $H_2O \geq 85\%$ was purchased from Sigma–Aldrich Chemie GmbH, Thailand. Four units of L-Lactic acid ^{14}C (U) sodium salt in the ethanol:water (7:3) mixture solvents with 50–150 mCi mmol^{-1} (1.85–5.55 GBq mmol^{-1}) activity, concentration (0.1 mCi mL^{-1}), quantity (250 μCi (9.25 MBq)) were ordered from Campro Scientific Company and Biotrend Company in Germany. l-Lactide was donated by Total Corbion PLA company. Dichloromethane, ethanol, and dried toluene were provided by Merck, Germany, in analytical grade. Tin(II) 2-ethylhexanoate 92.5–100% was bought from Sigma–Aldrich Chemie GmbH, Japan. Tetrahydrofuran THF (HPLC grade, Fisher Scientific). The catalyst $[Zn(DMEG_2ch)_2](OTf)_2 \cdot THF$ was synthesized according to the literature.[43] Liquid nitrogen and N_2 capsule provided inside the laboratory. LSC cocktails: Oxysolve C-400 (Zinsser analytic) and Ultima gold XR (PerkinElmer).

Overhead stirrer (KFA GmbH), Chiller Circulators (Julabo F25), Magnetic Stirrer Hot Plate (IKA RCT basic), balance weight scale (Mettler Toledo, Sartorius), Ball Mill (Retsch). Vacumme pump (LeMybold Vakuum GmbH), Heat gun (Metabo HF 20–600), Freeze dryer (ScanVac CoolSafe), Liquid Scintillation Counter (LSC) (PerkinElmer Tri-Carb 3110 TR, Software: QuantaSmart 4.02). Oxidizer (Hidex 600 OX).

2.2. Characterization of Synthesized Lactide and Polymer

2.2.1. NMR Spectroscopy

NMR spectra were recorded on a Bruker Avance III HD 400 (software: TopSpin version 2.1) or a Bruker Avance NEO 400 (software: TopSpin version 4.0.2 or TopSpin 4.5.0) nuclear resonance spectrometer at 25 °C. Resonances were referenced to the residual solvent resonance, relative to TMS (^{1}H-NMR: $CDCl_3$: $\delta = 7.26$ ppm). Data in the ^{1}H NMR spectra are stated as follows: chemical shift (δ in ppm), (multiplicity, coupling constant (J in Hz), integration). To describe the multiplicity of the signals, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof. For the Bruker Avance III HD 400, the software Topspin (Version 3.5 pl 7) from Bruker and for the Bruker Avance NEO 400 the software TopSpin (Version 4.2.0, 4.4.1) from Bruker were used for data acquisition. For visualization and examination of the NMR spectra, the software MestReNova (Version 14.2.3–29,241) from Mestrelab Research was used(SI, Figure S1–S9, Supporting Information).

2.2.2. Size Exclusion Chromatography (SEC)

The average molar masses and the mass distributions of the used PLA samples were determined by SEC on a Viscotek GPCmax VE-2001 applying a flow rate of 1 mL min^{-1} at 25 °C with THF as the mobile phase. The device was equipped with an HPLC pump, two Malvern Viscotek T columns (porous styrene divinylbenzene copolymer) with maximum pore sizes of 500 and 5000 Å, a refractive index detector (VE-3580), and a viscometer (Viscotek 270 Dual detector). The software Omnisec—5.12 was used for data acquisition. The results were evaluated using conventional calibration (polystyrene) with a Mark–Houwink correction factor of 0.58 for PLA (Figure S10, Supporting Information).[44,45]

2.2.3. Infrared Spectroscopy (FT-IR)

FT-IR spectra were recorded with a Shimadzu IRTracer 100 using a CsI beam splitter in combination with an ATR unit (Quest model from Specac utilizing a robust monolithic crystalline diamond) in a 2 cm^{-1} resolution. For data acquisition, the software LabSolution IR (Version 2.15) from Shimadzu was used. The obtained IR data are stated as reciprocal wave numbers of the absorption (cm^{-1}). The vibration bands of the spectra are characterized based on the Würzburger Model as follows: vw = very weak, w = weak, m = medium, s = strong, and vs = very strong (Figure S11, Supporting Information).

2.2.4. Differential Scanning Calorimetry (DSC)

DSC curves of selected polymer samples were recorded on a Netzsch DSC 204 F1 Phenix equipped with an intra-cooler. The samples were weighed into 50 µL aluminum pans and sealed with punctuated aluminum lids. For all measurements, four cycles were performed, starting at -60 °C and subsequent heating to 200 °C. A heating rate of 10 K min^{-1} and a nitrogen flow of 40 mL min^{-1} were applied. The analysis of data was performed with the software NETZSCH Proteus—Thermal Analysis (Figure S12, Supporting Information).

2.2.5. Thermogravimetric Analysis (TGA)

The TGA of the PLA polymer sample was performed using a Linseis STA PT1600 (Software Linseis TA Software\STA2) with the HDSC Type S measuring unit (Pt10%/Pt-Rh) and the L75/240 RT-1600 furnace. The measurement was performed using a synthetic air flow of 80 mL min^{-1} in a temperature range from 25 °C–600 °C with a heating rate of 5 °C min^{-1} (Figure S13, Supporting Information).

2.2.6. Field Emission Scanning Electron Microscopy (FE-SEM)

Field emission scanning electron microscopy (FE-SEM, FEI Quanta FEG 250 (Thermo Fisher Scientific)) was employed to analyze the morphology and size distribution of micro-PLA particles (20–500 μm). The xT Microscope Server Software was utilized to operate the instrument and enable high-resolution imaging. (Figure S14–S15, Supporting Information)

2.2.7. Safe Use of Radioisotopes

Handling of ^{14}C-labeled materials requires adherence to standard radiochemical safety protocols, despite the low-energy beta emission of the carbon isotope and minimal external radiation hazard. The primary concern with ^{14}C is internal exposure through ingestion, inhalation, or dermal absorption. Therefore, all procedures involving ^{14}C should be conducted in designated radioactive work areas, clearly labeled and equipped for radiological use. Personal protective equipment, including lab coats, gloves, and eye protection, is mandatory. Operations must be performed within a chemical fume hood to prevent the release of radioactive vapors. Accurate labeling of containers, samples, and radioactive waste, along with storage in secondary containment, is essential for safe laboratory practice.[46,47]

2.2.8. Process Optimization for Lactide Production and Polymerization

The lactide production is initiated by the dehydration of the lactic acid (LA) monomers, which generates prepolymer chains consisting of oligomers and low molecular weight PLA. This reaction starts with 90 mL of L-LA (aqueous solution 85 wt%) in a 100 mL three-neck flask with an overhead stirrer attached to a collecting bottle via a glass bridge, which is maintained in an ice bath and connected to a Liebig condenser (**Figure 2**). The mixture is heated at 150–160 °C for 7 h to remove water and produce oligomers under a nitrogen flow. This flow facilitates the removal of water. ≈20 mL of a mixture of water and LA is collected in the collecting bottle, and oligomers are produced in the reaction bottle. In the case of ^{14}C-labeling, the oligomers are then cooled down, and 2.5 mL of ^{14}C-labeled LA monomers (9.25 MBq) are added to the oligomers and allowed to react for 1 h at 160 °C in a sealed bottle. After that, the N_2 flow is attached to this bottle, and it is allowed to stir for another hour. This step enables the labeled monomers to attach to the oligomer chains without significant radiolabeled monomer loss during the process.

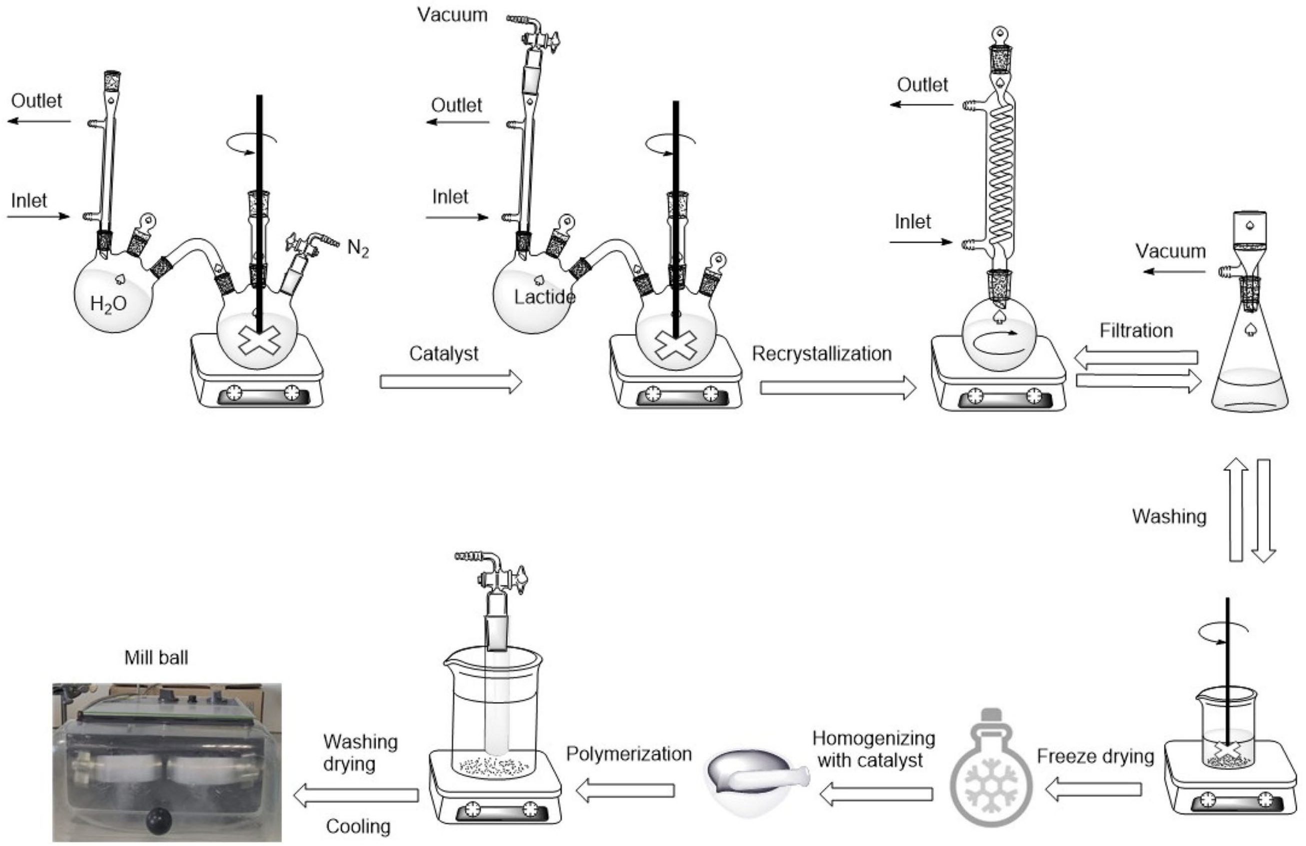
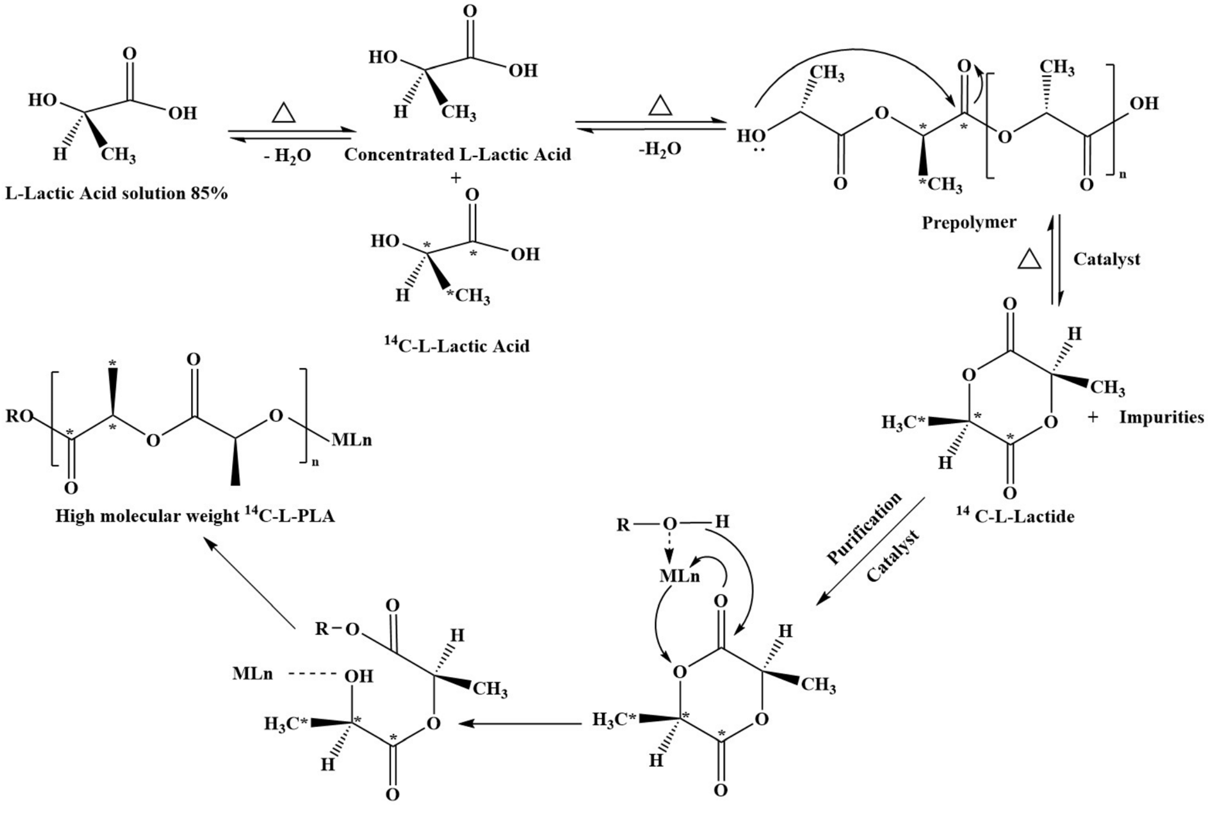


Figure 2. Schematic procedure for micro-^{14}C-PLA production.

In the following process, the oligomers are cooled down, and a catalyst (Sn or Zn, ≈0.1 wt% of oligomer) is added to the prepolymers and mixed at 160 °C for 1 h. The mixture is then heated in an inert atmosphere for another hour to allow sufficient time for catalyst activation. By gradually increasing the temperature to 190 °C and reducing the pressure to below 10 mbar, crude l-lactide is collected in a three-neck round-bottom flask. The reaction typically required an average of 54 h to complete (**Scheme 1**). The l-lactide obtained from this reaction typically contains LA, water, meso-LA, dimers, trimers, and other low molecular weight linear LA oligomers. It should be purified by recrystallization and washing processes. For recrystallization, dried toluene is added to the crude lactide in a 1:2 ratio and heated at 150 °C for 1 h under reflux conditions. The mixture of lactide in dried toluene is then cooled in the refrigerator and washed with cold, dried toluene, followed by filtration using a Büchner funnel. This recrystallization should be performed at least twice. Although a second recrystallization may improve purity, it inevitably results in a loss of 20–30% of the lactide.[40,48]

After vacuum drying, the lactide is dissolved and washed with cold water twice in a 1:2 ratio, then filtered using a Büchner funnel and dried in a freeze dryer. To ensure that all impurities have been removed, ^{1}H-NMR analysis is required. If impurities are still present, this process must be repeated. These purification steps are a critical part of the reaction, as impurities such as unreacted LA remaining in the lactide can inhibit polymerization, and residual meso-lactide can make the polymer amorphous. The unreacted LA, meso-lactide, and short-chain oligomers recovered from recrystallization and washing processes can be reused. This means that toluene and water should be removed using a rotary evaporator, after which the entire process can be restarted. The radioactivity of the final ^{14}C-lactide was measured by dissolving 10 mg of the dried and purified ^{14}C-lactide in 1 mL of dichloromethane and mixing it with the LSC cocktail. The resulting average radioactivity was ≈10.4 kBq.

The purified ^{14}C-lactide is now ready for the ROP reaction using a zinc bisguanidine complex (known from literature) in monomer-to-initiator ([M]/[I]) ratios of 500:1.[43] 1 g ^{14}C-lactide (100 mg of labeled lactide (≈10.4 kBq) mixed with 900 mg of nonlabelled commercial lactide) and 14.6 mg of the catalyst were homogenized and heated at 150 °C for 3 min. The reaction was stopped by removing the reaction vessel from the oil bath and taking it under cold running water. After the reaction was completed, a sample was taken for ^{1}H NMR spectroscopy to determine the conversion (Figure S3, Supporting Information). The polymer was dissolved in an appropriate amount of DCM, then precipitated in ethanol at room temperature and purified under vacuum (Figure S4, Supporting Information). Combustion of 100 mg of ^{14}C-PLA using an oxidizer followed by LSC analysis revealed an average radioactivity of 10.3 kBq.



Scheme 1. ^{14}C-PLA production from ^{14}C-LA mechanisms. Catalysts: metal catalysts such as zinc (Zn) and tin (Sn). *Carbon-14.

3. Result and Discussion

3.1. Mechanism of Reaction in Lactide Production

This reaction begins with the dehydration of an aqueous L-LA solution 85%, which is converted into concentrated L-LA through heating and water removal. During this process, two L-LA molecules undergo esterification, where the hydroxyl (–OH) group of one molecule reacts with the carboxyl (–COOH) group of another, forming an ester bond and releasing water. As heating continues, oligomers (short PLA chains) form through repeated polycondensation reactions, progressively removing water. To drive the reaction forward and prevent hydrolysis, an inert gas flow is applied.[49]

Lactide is generated through the depolymerization of oligomeric PLA via both back-biting and end-biting reactions.[50,51] The back-biting process is typically facilitated by nonrecoverable metal salts, such as tin, or heterogeneous catalysts in a single-step approach.[42] This reaction involves the intramolecular interaction between the carboxyl end group and the ester bond in the polymer backbone, leading to the formation of cyclic compounds. Specifically, the hydroxyl end group, which carries a partial positive charge due to its interaction with the catalyst, attacks the carbonyl carbon of PLA, initiating lactide formation (Scheme 1).[50] In contrast, end-biting refers to a ring-closure reaction occurring at the polymer chain's terminus. Both reactions are equilibrium processes influenced by factors such as temperature and ring size. The key distinction between them lies in their products. While back-biting generates both cyclic and linear compounds, end-biting produces a cyclic compound along with water.[52]

Following lactide formation, the ROP of lactide can proceed through five different mechanisms: cationic, anionic, organocatalytic, the activated monomer mechanism, and the coordination-insertion mechanism.[2] The latter is employed by metal catalysts such as zinc (Zn) and tin (Sn) (Scheme 1).[40] A detailed explanation of this mechanism is provided by Schäfer et al.[53]

3.2. Controlling Factors in Lactide Production

Temperature, pressure, and catalyst amount are important factors in lactide production. Shorter prepolymers exhibit low viscosity, which enhances heat transfer during the depolymerization process and speeds up the removal of lactide from the prepolymer mass.[54] As the reaction progresses and oligomer concentration increases, the required temperature rises. It is important to gradually increase the temperature while avoiding temperatures above 240 °C, which can result in higher molecular weight, increased racemization, and more meso-lactide formation.[42] When the initial molecular weight of LA oligomers reaches 1800 g mol^{-1}, the yield of meso-lactide significantly increases.[55] Unfortunately, molecular weight continues to rise throughout the reaction, ultimately forming a black, high-viscosity product at the bottom of the reaction vessel. This product, with a boiling point over 200 °C, is hard, brittle, and poorly soluble in solvents at room temperature, leading to a lower lactide yield.[37]

A lower vacuum pressure drives the reaction forward, but when the pressure falls below 10 mbar, meso-lactide production increases.[55] Therefore, the pressure used must be higher than this value.

The type and quantity of catalysts are crucial factors to consider. An increase in catalyst concentration leads to a higher percentage of meso-lactide being produced.[37] Various catalysts are used in lactide production and ROP reactions, including tin (Sn),[54,56] zeolites,[33] metal-organic frameworks,[57] Zn-based catalysts,[58] and bases sometimes added as cocatalysts.[57] While a higher catalyst amount can increase the reaction rate, it also results in a greater yield of meso-lactide. It is advisable to limit catalyst concentration to less than 0.1 wt% by weight of the oligomers.[55]

3.3. Purification

The crude lactide is not immediately suitable for polymerization due to the presence of various impurities. Purification is essential, as the properties of the polymer, such as molecular weight, melting point, crystallinity, and mechanical strength, improve with the degree of lactide purification.[59] Meso-lactide, an unavoidable byproduct in lactide synthesis, must be removed during purification to enhance stoichiometric purity.[37] A higher meso-lactide content in the monomer decreases the resistance of polymers to high temperatures during transportation, storage, and use. Such amorphous PLA is only suitable as an easy-to-process material for packaging production.[60]

Recrystallization from solvents is the laboratory method that achieves the highest purity product, especially when repeated multiple times. Common organic solvents are used for recrystallization to remove meso-lactide, and oligomers include ethyl acetate, anhydrous toluene, ethanol, isopropanol, and butyl acetate.[37,40] The solubility of lactide and oligomers in these solvents increases with temperature.[61–63] Considerable loss of lactide with each attempt is a significant drawback. Recrystallization alone is insufficient because unreacted LA in crude lactide is not soluble in many organic solvents, like toluene, ethanol, and isopropyl alcohol. If LA remains as an impurity, it can hinder polymerization of lactide when combined with catalysts. The most effective method for removing LA involves a repeated washing process with cold water (Figure S2, Supporting Information). To avoid low overall yields and minimize waste, the meso-lactide and LA recovered from the recrystallization and washing processes should be recycled back into the production of lactide.[42] Purification of lactide produced with $Sn(Oct)_2$ requires additional washing steps to remove LA, which leads to greater loss. Therefore, we decided not to use this catalyst for our experiments with valuable ^{14}C-labeled monomers.

It is worth mentioning that, the clean reaction vessels and working under N_2 atmosphere is necessary to obtain high molecular weights polymer. The molecular weight of the synthesized PLA indicates how pure the lactide is.[37]

3.4. Comparison between Zinc Bisguanidine Complex and $Sn(Oct)_2$ Catalysts

The optimization process for lactide production was done for two different catalysts. Lactide production for Zn catalyst starts faster but takes longer to complete compared to the Sn catalyst. $Sn(Oct)_2$ based on the literature data has stereoselective properties that would allow minimizing the formation of *D*-form and meso-lactide.[37] Due to the easier handling of the zinc-based catalyst in the lactide synthesis at laboratory scale, the ^{14}C-lactide production was performed with $[Zn(DMEG_2ch)_2](OTf)_2 \cdot THF$. It is much easier to perform purification for the lactide produced from this reaction and needs few steps for recrystallization and washing. Another benefit of the zinc-based catalyst is its biocompatibility, which makes it an interesting candidate for the entire life cycle of PLA.[43,64,65]

Table 1 presents the SEC analysis of PLA synthesized using the Zn catalyst, following dissolution of 5–7 mg of PLA in 1 mL of THF and subsequent filtration. We were unable to obtain PLA conversion results using the $Sn(Oct)_2$ catalyst due to the presence of lactic acid impurities, which interfered with lactide polymerization.

In addition to the SEC analysis of the resulting PLA, further analytical methods were used to characterize the polymer in more detail. The FT-IR spectrum shows characteristic —CH— stretching, bending, and deformation vibrations, along with a distinct —C=O carbonyl stretch vibration at 1748 cm^{-1} (Figure S11, Supporting Information).[66] Furthermore, the DSC thermogram shows a glass transition temperature (T_g) of 52 °C and a melting point (T_m) of 137 °C. The polymer has a decomposition range starting at 200 °C, which can be explained by the chain length and dispersity of the obtained PLA.

Table 1. SEC analysis of PLA for the Zn catalyst.

$[Zn(DMEG_2ch)_2](OTf)_2$ THF
Conversion (Lactide to PLA):70%
[a]M_w: 41,700 g mol^{-1}
[b]M_n: 27,300 g mol^{-1}
[c]Đ: 1.5

[a][M_w]: Weight-average molecular weight; [b][M_n]: Number-average molecular weight; [c][Đ]: Dispersity, distribution of molecular weight $Đ = \frac{M_w}{M_n}$.

The yield percentages for two different catalysts and the radiolabeling results for four batches are summarized in **Table 2**. It should be noted that these results are comparable to those reported in other studies.[37,52,58] In our study, a nontoxic and environmentally friendly catalyst was employed, demonstrating high efficiency in both the synthesis of lactide and the subsequent ROP processes. The catalyst functions effectively in small quantities and under solvent-free conditions, contributing to a more sustainable process and reducing the risk of radioactive contamination.

Lactide synthesis at the laboratory scale typically presents challenges due to difficulties in maintaining constant temperature and ensuring efficient heat transfer; however, these were successfully addressed through careful setup design. By optimizing reaction conditions, we significantly minimized the formation of undesired meso-lactide, thereby improving the quality of the resulting polymer. Furthermore, the implementation of recovery steps for recycling unreacted monomers and residual materials can lead to a notable increase in the overall lactide product yield.

3.5. Drying and Storage Conditions

Studies have demonstrated that extended exposure to oxygen and moisture can result in lactide undergoing racemization, hydrolysis, or both.[67] In this process, water is not consumed, so the chemical composition of lactide remains unchanged, although its stereochemical structure is altered. The conversion of d/l-lactide to meso-lactide is a reversible and endothermic reaction when catalyzed by water, and the hydrolysis rate of meso-lactide to LA is faster than that of d- or l-lactide.[63] In the absence of water or other catalysts at low temperatures, pure lactide remains stable and is resistant to racemization.[68] It is advisable to avoid drying at higher temperatures, as they can increase the risk of thermal degradation and racemization.

Vacuum drying involves reducing the pressure to lower the boiling point of water in lactide, which increases the evaporation rate and aids in drying lactide. This method is quick and efficient but requires a powerful pump and consumes a significant amount of energy. Spray drying, on the other hand, entails atomizing the lactide into fine droplets and exposing them to hot air in

Table 2. Lactide production yield percentages for two types of catalysts and four experimental batches (Both nonlabeled and labeled reactions begin with 90 mL of L-LA; the labeled reaction additionally includes 2.5 mL of ^{14}C-labeled L-LA (9.25 MBq)).

Feed	Catalyst	Crude lactide yield [%][a]	Practical lactide yield [%][b]	Radiochemical yield [%][c]
LA	$Sn(Oct)_2$	85	–	–
LA	$[Zn(DMEG_2ch)_2](OTf)_2$ THF	87	–	–
^{14}C-LA	$[Zn(DMEG_2ch)_2](OTf)_2$ THF	84	18	15
^{14}C-LA	$[Zn(DMEG_2ch)_2](OTf)_2$ THF	70	15	10
^{14}C-LA	$[Zn(DMEG_2ch)_2](OTf)_2$ THF	97	16	12
^{14}C-LA	$[Zn(DMEG_2ch)_2](OTf)_2$ THF	87	15	16

[a]Crude lactide yield (%):(crude lactide(g)/oligomer(g))*100. [b]Practical lactide yield (%):(dry and purified lactide(g)/oligomer(g))*100.[58,85,86] [c]RCY (%) :(Activity of feed (MBq)/Activity of lactide (MBq)) × 100.

a drying chamber. As the droplets lose moisture, they form dry particles that are collected either at the bottom of the chamber or in a cyclone separator. While spray drying is scalable and adaptable, it can potentially impact the optical purity of lactide.[69] Desiccant drying involves placing lactide in a container with a desiccant, a substance that absorbs moisture from the air. Although desiccant drying is straightforward and cost-effective, it may not be sufficient for achieving very low moisture levels.[69]

Freeze drying involves freezing the lactide and then sublimating the ice crystals under vacuum. While this method helps preserve the structure and quality of lactide, it is time-consuming and costly. In our experiment, the water-washed lactide after freezing in liquid N_2 was placed in a freeze dryer set to an ice condenser temperature of -50 °C and a pressure of 0.043 hPa overnight.[69] Since lactide is hygroscopic, its storage conditions are critical to maintaining its purity. It is essential to store lactide in a dry environment, such as in a desiccator or a sealed container with a desiccant, to ensure its long-term stability and quality. Consequently, in this study, all synthesized lactide was stored in a vacuum-sealed container in a -20 °C freezer to minimize side reactions.[48]

3.6. Converting Bulk PLA to Micro-PLA

Microplastic particles are generally defined as plastic fragments smaller than 5 mm.[70] In investigating the degradation of microplastics in natural environments like soils, it is crucial to choose particles closely resemble those found in the environment to ensure accurate results.[71] Microplastics can be categorized not only by size but also by their origin, dividing them into primary and secondary microplastics. Primary microplastics that are produced through technical processes and intentionally introduced into the product for a specific function are then released into ecosystems in that form. While secondary microplastics which account for more than 99% of microplastics emitted into the environment are formed through the degradation and fragmentation of larger plastic particles within the environment.[72]

For assessing the environmental impact of ^{14}C-PLA in soils, secondary micro-PLA is needed. These microplastics are produced through various degradation processes, such as abrasion or other mechanical forces, often combined with UV light, water, or heat. Unlike primary microplastics, which typically have a defined shape and size (usually round), secondary microplastics are more irregularly shaped, featuring cuts and rough edges. These irregularities give secondary microplastics a much larger specific surface area than primary particles, making them more prone to sorption processes and other environmental interactions.[71]

A key challenge in environmental assessment analysis is the lack of sources and suitable methods for creating microplastics that accurately replicate those found in nature.[71] There are two primary methods for producing plastic microparticles: bottom-up and top-down. Bottom-up methods involve creating particles from molecular building blocks, such as monomers and polymers, while top-down methods include breaking down larger objects into smaller particles. The formation of microplastic particles in the environment generally follows top-down processes. In contrast, bottom-up production techniques for microparticles include polymerization or precipitation from a solution, which are common procedures in nanoparticle production.[73–75] In these techniques, polymers are dissolved in solvents and then reprecipitated by either lowering the temperature or introducing a different solvent.[76–78]

Both methods were explored for producing micro-PLA. The top-down approach can be achieved through techniques such as grinding, ultrasonic treatment, and melting.[71] The first technique, milling, involves reducing larger plastic pieces into smaller particles. Grinding and milling plastics have been used since at least the 1970s, but this method presents challenges.[79] Unlike polymerization, which rarely produces particles larger than 50 µm, milling often struggles to achieve such small sizes. Milling thermoplastics is particularly challenging because, above their glass transition temperatures (T_g), these materials deform elastically rather than breaking.[79] To overcome this, the plastics must be made brittle by cooling before milling. The process typically involves cutting the material into smaller chunks, then milling it into particles, often using liquid nitrogen for cooling, using mechanical ball mills or cryogenic milling devices.

In the bottom-up experiment, PLA was dissolved in dichloromethane, and this solution was added dropwise to a water and ethanol mixture (2:1). Then, this solution was centrifuged to separate the microplastics from the liquid. Chemical stress reduced molecular weight (M_w) more significantly than thermal or mechanical stress, so most of the polymer remained dispersed in the liquid.[76] Consequently, the top-down technique was chosen for our experiment. Bulk ^{14}C-PLA (T_g: around 60 °C) after drying overnight in a freeze dryer is cut into small pieces, transferred to cylinders with metal balls, cooled down in liquid nitrogen for 10 min, and grind for 5 min at 200 rpm. To achieve better results, it is recommended to repeat this process two or three times.

The shape and size of microplastics are largely influenced by the type of polymer and the methods used in their production. Common techniques for determining particle size distribution include laser scattering measurements,[80,81] optical analysis,

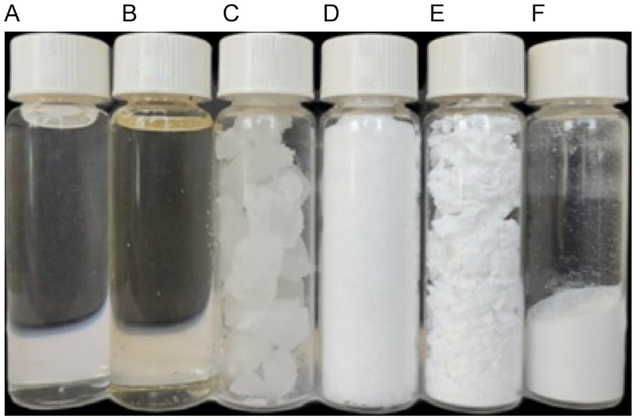


Figure 3. A: L-Lactic acid, B: Oligomers, C: Crude lactide, D: Purified lactide, E: Bulk PLA, F: Micro-PLA (20–500 µm).

and sieving.[82,83] For size determination following grinding with a ball mill, the sieving technique was selected, resulting in particles with a size distribution ranging from 20–500 µm, which are ready for use in degradation studies. In **Figure 3**, different materials from LA to micro-PLA are shown.

4. Conclusion

Understanding the environmental behavior of bioplastics as alternatives to fossil-based plastics, along with their interactions with ecosystems and the factors influencing their degradation, is crucial. This requires extensive studies using precise measurement tools and specialized techniques. Unlike other analytical methods that primarily track qualitative changes, the Carbon-14 radiolabeling technique enables the quantification of the degradation process. The prerequiste for such studies requires optimizing the synthesis conditions of labeled polymers on a laboratory scale.

In this study, we present a zinc triflate bisguanidine catalyst for the synthesis of lactide from lactic acid and compare it with the industrial $Sn(Oct)_2$ catalyst. The activity is almost identical, whereas the zinc catalyst enables a more effective purification of lactide. We therefore introduce for the first time a zinc triflate bisguanidine catalyst utilized for the synthesis of ^{14}C-lactide and ^{14}C-PLA. Future research could focus on the quantitative degradation of this microbioplastic, using ^{14}C radiolabeling to monitor $^{14}CO_2$ release over time. Additionally, further studies could investigate its fate and environmental impact in soil ecosystems.

A dataset associated with this paper is available in the RADAR metadata repository.[84]

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Sara Adeleh: writing—original draft (equal). **Tabea Becker**: writing—original draft (equal). **Sonja Herres-Pawlis**: project administration (lead); supervision (lead); writing—review & editing (lead). **Roland Bol**: project administration (lead); supervision (lead); writing—review & editing (lead). **Birte Drewes**: formal analysis (supporting); writing—review & editing (supporting). **Thomas Pütz**: project administration (lead); supervision (lead); writing—review & editing (lead). **Sara Adeleh** and **Tabea Becker** have been treated as co-first authors.

Data Availability Statement

The data that support the findings of this study are openly available in Radar at https://www.radar-service.eu/radar/en/dataset/ck37qkdet7mrfu3w?token=mAyyWJMeURkiyuDawUql#, reference number 1234.

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