



# Racemization on Thermal Degradation of Poly(L-lactide) with Calcium Salt End Structure

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**Title:** Racemization on Thermal Degradation of Poly(L-lactide) with Calcium Salt End Structure

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Running Title: Racemization on Thermal Degradation of PLLA with Ca Salt End Structure

## **Abstract**

Poly(L-lactide) with calcium salt end structure (PLLA-Ca) is a promising material for PLLA recycling because of the ease of lactide recovery through the unzipping depolymerization process. However, the pyrolysis of PLLA-Ca also causes meso-lactide to form. In this article, the racemization in PLLA-Ca pyrolysis was analyzed in detail with Py-MS, Py-GC/MS, and a glass tube oven. The results suggested that at a temperature lower than 250°C, nucleophilic attack by a carboxylate anion end on an asymmetrical methyne carbon in a penultimate lactate unit occurred, resulting in the predominant formation of meso-lactide. On the other hand, also at temperatures over 320°C, by-reactions, such as enolization reactions, caused the meso-lactide to form, but not dominantly. In the temperature range of 250-320°C, L,L-lactide was produced exclusively, because unzipping depolymerization proceeded as the main reaction. This is a very significant result for PLLA recycling, because PLLA-Ca is an easily recyclable material, which depolymerizes based on the 1<sup>st</sup>-order weight loss process.

## **Keywords**

poly(L-lactide) / poly(L-lactic acid) / PLLA / thermal degradation / pyrolysis / racemization / calcium / end structure

## 1. Introduction

Poly(L-lactide) [poly(L-lactic acid), PLLA] is a well-known biodegradable polymer. It has received much interest for its medical, pharmaceutical, and environmental applications [1-3]. Nowadays, because of its many useful properties, such as mechanical strength, transparency, and compostability [4-6], PLLA and its related copolymers are attracting much attention as promising alternatives to the commodity resins [7]. The optically pure PLLA is a crystal polymer with a melting point at about 170°C. However, when the optical purity of polylactide is lowered, its crystallizability decreases, and most of its useful properties are lost [8,9]. Thus, to be practically usable, polylactide must have a high enough optical purity.

PLLA is generally prepared from L,L-lactide a cyclic dimer of L-lactic acid with a high optical purity. Thermal degradation of PLLA can result in L,L-lactide recovery, thus making PLLA into a possible candidate for feedstock recycling plastics. To control the degradation reaction of PLLA so as to reproduce the optically pure L,L-lactide, it is necessary to clarify its pyrolysis mechanism, and find out appropriate catalysts and pyrolysis conditions. Several groups [10-19] have studied the thermal degradation of PLLA using thermogravimetric analysis-differential thermal analysis (TG/DTA), pyrolysis-mass spectrometry (Py-MS), pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), and isothermal methods. The pyrolysis of PLLA has been reported as a rather complicated reaction, involving several mechanisms, such as intra- and inter-molecular transesterifications, *cis*-elimination, and other radical and nonradical reactions. Thus, clear kinetic parameters for the PLLA pyrolysis have not been reported so far. Some reasons for these complexity have been considered, for example, residual metals [14], molecular weight [14], chain end structure [10,18], and pyrolysis conditions [15].

To find an effective and non-toxic catalyst for the recycling of PLLA, we previously investigated the thermal degradation behavior of a metal free PLLA (PLLA-H) and a PLLA with

calcium salt end structure (PLLA-Ca). We found that the PLLA-H was pyrolyzed through a random scission reaction, whereas the PLLA-Ca degraded through an unzipping depolymerization as a main process, suggesting that the Ca ion is a promising catalyst for PLLA recycling [20].

However, the Ca ion-catalyzed depolymerization also caused considerable racemization considerable forming meso-lactide as a by-product. This is a serious problem for PLLA recycling. The racemization in the pyrolysis has scarcely been discussed in previously published works. Notable exceptions are Kopinke et al. [11,13], Khabbaz et al. [5], and Westphal et al. [21] who observed the diastereoisomers of cyclic oligomers during the thermal degradation of PLLA. To explain this phenomenon, Kopinke et al. proposed that an enolization mechanism occurred in a lactate unit during the pyrolysis. This speculation was based on results that more than two diastereoisomers were observed for each cyclic oligomer as pyrolyzates. However, even though the effects of temperature and catalysts are generally regarded to significantly effect pyrolysis behavior, no more discussion on this point took place. Thus, to employ the calcium ion as the catalyst for PLLA recycling, it is necessary to clarify and control the racemization during its pyrolysis.

In this article, racemization and its control in the pyrolysis of PLLA-Ca were investigated. Pyrolyzates of the PLLA-Ca were analyzed by Py-MS and Py-GC/MS with other measurements also being taken. Based on the results of these analyses, the pyrolysis mechanism of the PLLA-Ca was intensively discussed.

## **2. Experimental**

### *2.1. Materials*

Monomer, L,L-lactide, obtained from Shimadzu Co. Ltd. was purified by being recrystallized three times from dry toluene and one time from dry ethyl acetate. The vacuum dried L,L-lactide was stored in a N<sub>2</sub> atmosphere. After purification, meso-lactide was not detectable by gas

chromatography (GC). Polymerization catalyst, Sn(II) 2-ethylhexanoate, obtained from Wako Pure Chemical Industries, Ltd., was distilled under reduced pressure before use. Solvent, tetrahydrofuran (THF), was dried just before use by refluxing with sodium for 2 h and then distilled in N<sub>2</sub> atmosphere. Calcium hydride (CaH<sub>2</sub>) was purchased from Kanto Chemical Co., Inc. and used as received.

## 2.2. Methods and measurement

Molecular weight of PLLA-H and PLLA-Ca was measured by gel permeation chromatography (GPC) on a TOSOH HLC-8220 GPC system at 40°C using TOSOH TSKgel Super HM-H column and a chloroform eluent (0.6 mL min<sup>-1</sup>). Low polydispersity polystyrene standards with *M<sub>n</sub>* from 5.0×10<sup>2</sup> to 1.11×10<sup>6</sup> were used for calibration. The residual metal content in the PLLA samples was measured with a Shimadzu AA-6500F atomic absorption flame emission spectrophotometer (AA). The samples were degraded by a 25% ammonia solution, dissolved in 1M-hydrochloric acid, and then measured by AA. Gas chromatography (GC) measurements were recorded on a Shimadzu GC-9A gas chromatograph with a Varian cyclodextrine-2-236M-19 capillary column (0.25mm×50m) using helium as the carrier gas. The column and injector were set isothermally at 150 and 220°C, respectively. The sample (3mg) was dissolved in acetone (1mL), and a 1μL aliquot of the solution was injected. The peaks for meso-, L,L-, and D,D-lactide in the GC chromatogram were identified by comparison with the peaks for pure substances [20]. <sup>1</sup>H-NMR spectra were recorded on a Varian INOVA400 NMR spectrometer operating at 400 MHz for proton investigation in a chloroform-*d* solution using tetramethylsilane as the internal standard. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer from KBr pellets. Thermogravimetric analysis was conducted on a SEIKO EXSTAR 6200 TG/DTA 6200 system in an aluminium pan under a constant nitrogen flow (100 mL min<sup>-1</sup>) using about 5 mg of the PLLA film

sample.

### 2.3. Preparation of calcium ion end capped poly(L-lactide)

The calcium ion end capped poly(L-lactide) (PLLA-Ca) was prepared as described in the previous report [20]. PLLA was synthesized by the ring-opening polymerization of L,L-lactide, catalyzed by Sn(II) 2-ethylhexanoate, Sn(Oct)<sub>2</sub>. The obtained raw PLLA was purified in a three stage process; firstly extracting the catalyst and residues from the PLLA/chloroform solution with a 1M HCl aqueous solution, then washing with distilled water until the aqueous phase became totally neutral, and finally precipitating the polymer in methanol. The purified PLLA-H ( $M_n=118,600$ ;  $M_w/M_n=2.0$ ; Sn content, 13ppm by AA) was vacuum dried and dissolved in THF (2g in 200 mL). The polymer solution was treated by stirring with CaH<sub>2</sub> (0.2g, 4.76mmol) at room temperature for 1 h. After filtrating off the unreacted CaH<sub>2</sub>, the PLLA was precipitated in methanol, and dried *in vacuo* to obtain the Ca ion end capped sample (PLLA-Ca,  $M_n=115,400$ ;  $M_w/M_n=2.0$ ; Ca content, 210ppm by AA).

The molecular weight of the PLLA-Ca was recalculated as  $M_n=92,600$ , and  $M_w/M_n=1.76$  using the universal calibration curve from the Mark-Houwink-Sakurada constants for PLLA [22-24]. Using the recalculated  $M_n$  and Ca content, it can be estimated that the molar ratio of the Ca ion to the polymer chain is 0.49. If we consider Ca<sup>2+</sup>, almost all the carboxylic groups of PLLA are in the salt form. Thus, the end structure of the PLLA-Ca sample would consist mostly of a carboxylic acid Ca salt form and a hydroxyl group.

### 2.4. Pyrolysis of PLLA-Ca in glass tube oven

About 200 mg of the PLLA-Ca sample was put into a Shibata GTO-350D glass tube oven. The sample was heated gradually to 250°C in a N<sub>2</sub> atmosphere and then kept at this temperature for 60,

120, and 240min. The volatile pyrolyzates were collected in a chilled trap and analyzed by GC.

### 2.5. Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) analysis

Py-GC/MS spectra were measured on a Frontier Lab PY-2020D double-shot pyrolyzer with a Frontier Lab SS-1010E selective sampler and a Shimadzu GCMS-QP5050 gas chromatograph/mass spectrometer. High purity helium was used as a carrier gas at a flow rate of  $50\text{mL min}^{-1}$ .

For the evolved gas analysis (EGA), the GC injection port and mass spectrometer were connected with a short deactivated metal capillary tube ( $0.15\text{mm}\times 2.5\text{m}$ ), which was held isothermally at  $280^\circ\text{C}$  in a column oven. At first, the PLLA-Ca sample was put into the pyrolyzer at  $60^\circ\text{C}$ . Then the temperature of the pyrolyzer was increased continuously to  $400^\circ\text{C}$  at a heating rate  $10^\circ\text{C min}^{-1}$ . The evolved gases were directly conducted to the mass spectrometer through the short deactivated metal capillary tube, and the total ion current was recorded simultaneously.

For the Py-GC/MS analysis of the volatile products, an Ultra Alloy<sup>+</sup>-5 capillary column ( $30\text{m}\times 0.25\text{mm i.d.}$ ; film thickness,  $0.25\text{mm}$ ) was used. A PLLA sample was put in the pyrolyzer and heated from  $60^\circ\text{C}$  to a predetermined end temperature at a heating rate of  $10^\circ\text{C min}^{-1}$ . The volatile pyrolyzates were introduced into the GC through the selective sampler. The temperature of column oven was first set at  $40^\circ\text{C}$ . After the pyrolysis process had finished, the column was heated according to the following program: holding at  $40^\circ\text{C}$  for 1 min; heating at  $5^\circ\text{C min}^{-1}$  from  $40$ - $120^\circ\text{C}$ ; at  $20^\circ\text{C min}^{-1}$  from  $120$ - $320^\circ\text{C}$ ; and finally holding at  $320^\circ\text{C}$  for 13 min. Mass spectrum measurements were recorded  $2\text{ times s}^{-1}$  during this period.

For isothermal pyrolysis, the pyrolyzer was preheated to  $250^\circ\text{C}$ , and then the PLLA-Ca sample was dropped into it. The pyrolyzates volatilized in the predetermined time were conducted into the GC through the selective sampler. The temperature of column oven was first set at  $40^\circ\text{C}$ . After the pyrolysis process had finished, the pyrolyzates were analyzed according to the forgoing



heating program.

### 3. Results and Discussion

#### 3.1. Evolved Gas Analysis on Dynamic Pyrolysis

In our previous report [20], it was suggested that the initial period of pyrolysis of PLLA-Ca started through a random degradation, and then changed into the unzipping depolymerization as the main route, as expressed in the 1<sup>st</sup>-order weight loss process. During the pyrolysis process, some amount of meso-lactide also evolved in addition to L,L-lactide as a main product. To clarify the relationship between the pyrolysis process and the racemization of the evolved lactide, the PLLA-Ca pyrolysis was analyzed by pyrolysis-mass spectrometry (Py-MS) and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS).

The dynamic pyrolysis behavior of PLLA-Ca was examined by evolved gas analysis with Py-MS. Figure 1 illustrates a total ion chromatogram (TIC) of the evolved gas from PLLA-Ca in the temperature range of 60-400°C at a heating rate 10°C min<sup>-1</sup>. The gas evolution was detected as a broad peak in the temperature range of 200-370°C. This result accorded well with the DTA curve on a TG/DTA measurement (the data is not shown here). After a slow increase in gas evolution in the range of 200-300°C, a rapid increase in the evolution was found at temperatures greater than 320°C. Thus, in each temperature range the degradation of PLLA-Ca might proceed through a different reaction route. This result is in accordance with the results of the kinetics study in previous report [20].

**Figure 1** goes here

Typical mass spectra (MS) of the evolved gas in the former and later ranges, namely, 210-310°C and 320-370°C, are illustrated in Figure 2. These show a similar signal pattern, main fragments of  $m/z=15$ , 28, 45, and 56, which are similar to those of lactides and other cyclic

oligomers. Thus, despite the different degradation routes having been expected, the evolved gases were apparently the same that based on the MS analysis.

**Figure 2** goes here

To analyze the pyrolysis products of PLLA-Ca in detail, Py-GC/MS analysis was performed. In Figure 3, Py-GC/MS chromatograms of the pyrolysis products in temperature ranges from 60°C to different end temperatures are shown. As discussed in our previous report [20], the peaks at 13.1 and 13.9 min in these chromatograms represent meso-lactide and D,D-/L,L-lactides, respectively. The groups of peaks appearing periodically after 20 min were assigned to higher cyclic oligomers than lactide [5,13]. The plural peaks for each cyclic oligomer indicate that the racemization reaction, producing the diastereoisomers, occurred during the thermal degradation, since the original PLLA is composed of almost 100% of L-lactate unit. Interestingly, the chromatograms of pyrolyzates that evolved in the different temperature ranges were not same as each other, and differed from the results of MS analysis. The pyrolyzates that evolved in the temperature range of 60-200°C dominantly contained meso-lactide, but not D,D-/L,L-lactide. This means that, as discussed in a later section, the reaction in this temperature range caused one L-form of two neighboring L-lactate units to change to a D-form, resulting in the formation of meso-lactide. On the other hand, the meso-lactide content decreased relative to an increase in the end temperature up to 320°C. In the range 60-360°C, the meso-lactide content in pyrolyzates, as well as oligomers content, increased again.

**Figure 3** goes here

The amount of meso-lactide formed in each temperature range was calculated from the meso-lactide content based on the Py-GC/MS analysis and total evolved gas amount integrated with the Py-MS (TIC), as illustrated in Figure 4. The results clearly indicate that racemization took place in the two temperature ranges of lower than 250°C and higher than 320°C. Interestingly, at

temperatures lower than 250°C meso-lactide was dominantly formed (especially, > 75% at lower than 220°C), but at temperatures higher than 320°C it was one of the components (meso-lactide < 50%). Surprisingly, a “window”, that is, a meso-lactide free range, was found from 250-320°C with almost no meso-lactide formed within this temperature range. These results support the discussion about the foregoing Py-MS (TIC) results, that is, at each temperature range the degradation of PLLA-Ca appears to proceed through a different reaction route.

**Figure 4** goes here

A Py-GC/MS chromatogram of the pyrolyzates that evolved in the range of 250-320°C is shown in Figure 5. A small amount of meso-lactide (2.1%), with almost no higher oligomeric diastereoisomers, was detected as pyrolyzates, indicating that racemization hardly occurred in this temperature range.

**Figure 5** goes here

### *3.2. Isothermal pyrolysis of PLLA-Ca*

The isothermal pyrolysis of PLLA-Ca at 250°C was performed in the pyrolyzer. The sample was instantaneously heated up to 250°C by dropping the PLLA sample directly into the pyrolyzer under helium flow. Figure 6 illustrates the change in the Py-GC/MS chromatogram of the evolved gases from the sample pyrolyzed at 250°C. The chromatograms showed a trace amount of methyl lactate and meso-lactide at 12.8 and 13.1 min besides D,D/L,L-lactides at 13.9 min as the main product. Though a small amount of meso-lactide was still formed, the instantaneous heating process in the pyrolyzer caused the temperature to quickly pass through the range in which exclusive racemization of lactide occurs. This isothermal process caused the new production of a small amount of methyl lactate, which suggests the presence of an end structure derived from –Ca-OMe. The isothermal pyrolysis at 250°C also resulted in a decrease of meso-lactide content with holding time,

from 5% in 30 s to 2.4% in 600 s.

**Figure 6** goes here

A similar phenomenon was observed on the isothermal pyrolysis in a glass tube oven. The PLLA-Ca sample was pyrolyzed by heating from room temperature to 250°C and holding for 60, 120, and 240 min at this temperature. Pyrolyzates from this process were analyzed by GC, <sup>1</sup>H-NMR, and FT-IR. Almost no other product was detected besides lactides. The results were listed in Table 1. It was found that the production of meso-lactide and D,D-lactide decreased with holding time, similarly to the results of the isothermal pyrolysis in pyrolyzer (Figure 6). The cumulative total amount of meso-lactide was kept at 3.8-3.9 mg during the holding time, indicating that, after being heated up to 250°C, meso-lactide was scarcely produced during the holding period. The formation of D,D-lactide was negligible compared to the meso-lactide formation as shown in Table 1.

**Table 1** goes here

### 3.3. Mechanism of PLLA-Ca pyrolysis

As discussed previously [20], the main reaction of the PLLA-Ca pyrolysis proceeds through unzipping depolymerization. The unzipping depolymerization was presumed to be caused by the attack of the alkoxide end on the ester carbonyl carbon, which is the most electrophilic point in a repeating unit of PLLA. This nucleophilic attack does not influence the configuration of the neighboring asymmetrical methyne carbon, thus it would not cause racemization. Racemization during PLLA-Ca pyrolysis cannot be explained by the unzipping depolymerization process. Kopinke et al. suggested a mechanism based on the enolization in a lactate unit, that is, ester-semiacetal tautomerization, to explain the racemization during the pyrolysis (Scheme 1) [13]. The appearance of plural diastereoisomers for each cyclic oligomer in the higher temperature range could be properly described by this mechanism. That is, the diastereoisomer production by enolization could be

facilitated by increasing the temperature. However, intense racemization occurred in a rather low temperature range. Obviously, a different racemization mechanism is occurring in this lower temperature range.

**Scheme 1** goes here

The meso-lactide formation means that the racemization should follow the SN2 reaction mechanism on the asymmetrical methyne carbon (Scheme 2). This means that, the asymmetrical carbon atom in the penultimate unit is attacked by the carboxylate anion in an end unit, followed by scission of the bond between methyne carbon and ester oxygen. This results in the inversion of the configuration and the meso-lactide formation. Though the cleavage of the alcoholic C-O bond in a secondary ester is considered to hardly occur under normal conditions, Ca ion as a counter cation may accelerate the SN2 reaction leading into the meso-lactide formation. In a previous report [20], we discussed the random transfer process in the initial period as shown in Scheme 3. The presumed reaction in Scheme 2 is considered to be a typical one for the reaction (a) in Scheme 3 in the lower temperature range.

**Scheme 2** goes here

**Scheme 3** goes here

With an increase in temperature, the degradation mechanism of PLLA-Ca changes into unzipping depolymerization, which proceeds through a backbiting attack by an alkoxide end on a carbonyl carbon. Accordingly, there should be a process that transfers Ca ion from the carboxylate end to the alkoxide end of the chain. This transfer reaction has not been clarified yet, but it might include a nucleophilic attack by a carboxylate anion on a carbonyl carbon in any position on the polymer, as shown in Scheme 3 (b). **From an MM2 calculation of model reactions, it was suggested that the reaction (a) in Scheme 3 easily proceeds more than the reaction (b). Thus, the SN2 reaction is considered to proceed at lower temperature, but the reaction (b) occurs at higher temperature to**

make the dominant backbiting depolymerization start.

The reaction (a) in Scheme 3 produces an inversed asymmetrical carbon inside a polymer chain, which could lead to a small amount of meso-lactide formation even during the unzipping depolymerization at 250-320°C, as shown in Figures 4-6.

The instantaneous heating in the isothermal process caused the production of a small amount of methyl lactate. In Scheme 4 (b), an expected mechanism of the methyl lactate production is illustrated. The  $-Ca-OMe$  group would be prepared in the precipitation of the reactant with  $CaH_2$  in methanol. Generally, the methoxide group easily reacts with a carboxyl group to be converted into methanol and vaporized at lower temperature in a heating process {Scheme 4 (a)}. However, in the case of the instantaneous heating process, the methoxide group could react with carbonyl carbon to be converted into a methyl ester end structure. After the depolymerization from another end of a polymer chain, residual methyl ester end groups would react with proton donors to produce the methyl lactate. This speculation was also supported by the MM2 calculation of model reactions.

**Scheme 4** goes here

Therefore, in summary, at temperatures lower than 250°C the predominant reaction is the random nucleophilic attack by a carboxylate anion end on an electrophilic carbon in a polymer chain, accompanied by Walden's inversion at an asymmetrical center and meso-lactide formation. With an increase in temperature, almost all the carboxylate anion ends are changed into the alkoxide anion ends, and unzipping depolymerization as main reaction proceeds, resulting in the predominant formation of L,L-lactide. When the temperature rises to a range above 320°C, other by-reactions such as the enolization reaction might occur, causing meso-lactide formation to be exhibited again.

#### 4. Conclusion

To control PLLA pyrolysis, the racemization in PLLA-Ca pyrolysis was analyzed in detail

with Py-MS, Py-GC/MS, and glass tube oven. It was suggested that at each different temperature range the pyrolysis of PLLA-Ca proceeds through a different reaction route. At a temperature lower than 250°C, the reaction by a nucleophilic attack by a carboxylate anion end on an electrophilic carbon in polymer chain occurred accompanying the Walden's inversion at an asymmetrical center, resulting in predominant meso-lactide formation. On the other hand, at temperatures over 320°C, by-reactions, such as the enolization reaction, cause meso-lactide to form, but not dominantly. Surprisingly, in the temperature range of 250-320°C, L,L-lactide formation was predominant. Because, in this temperature range, almost all carboxylate anion-ends were changed into the alkoxide anion ends, and the unzipping depolymerization as main reaction proceeded predominantly. This is a very significant result for the PLLA recycling, because PLLA-Ca is an easily recyclable material, which depolymerizes based on the 1<sup>st</sup>-order weight loss process.

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Table 1

Results of PLLA-Ca pyrolysis in glass tube oven

Holding time at 250°C (min)	60	120	240
Amount of PLLA-Ca Sample (mg)	205	212	213
Yield (%)	15.4	29.5	56.1
L,L-lactide (%)	84.7	93.0	96.3
D,D-lactide (%)	3.4	0.8	0.4
meso-lactide (%)	12.0	6.2	3.3
Amount of meso-lactide (mg)	3.8	3.9	3.9

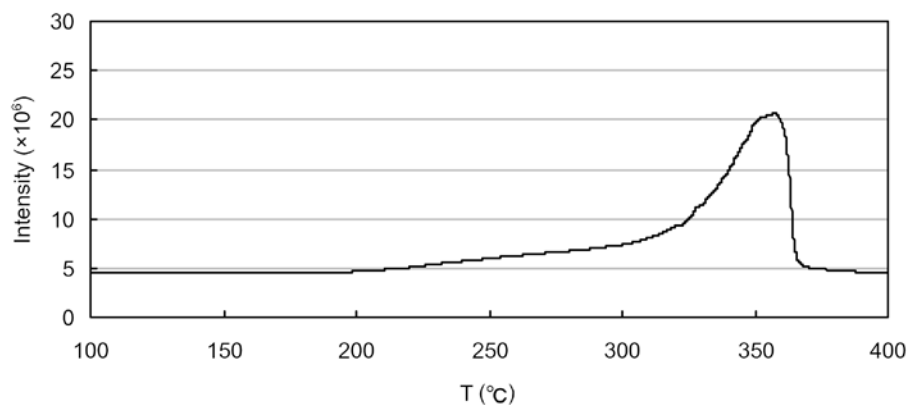


Figure 1. Total ion chromatogram (TIC) of evolved gas on PLLA-Ca pyrolysis in the temperature range of 60-400°C at a heating rate of 10°C min<sup>-1</sup>.

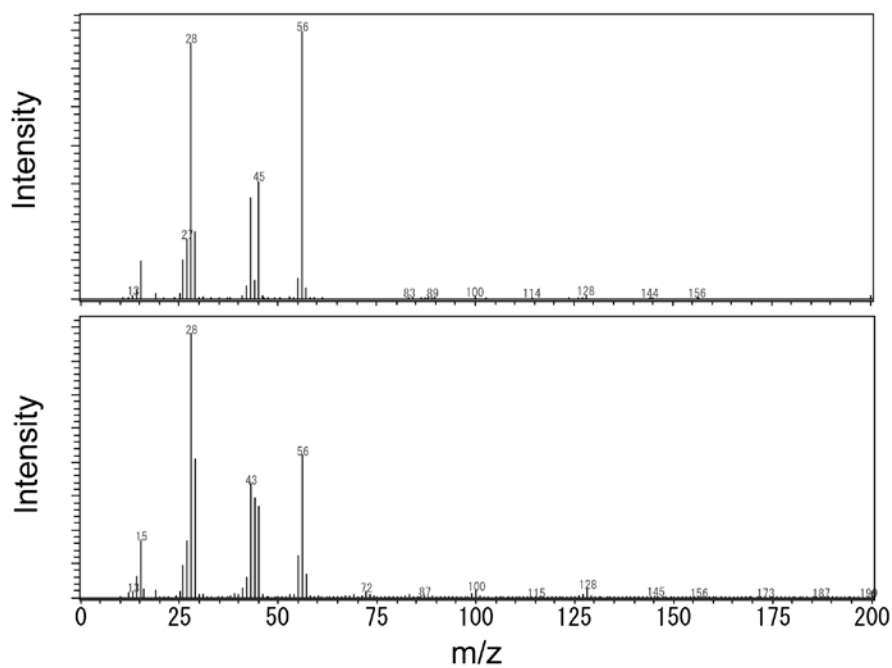


Figure 2. Py-MS spectra of gases evolved in the temperature ranges of 210-310°C (upper) and 320-370°C (lower).

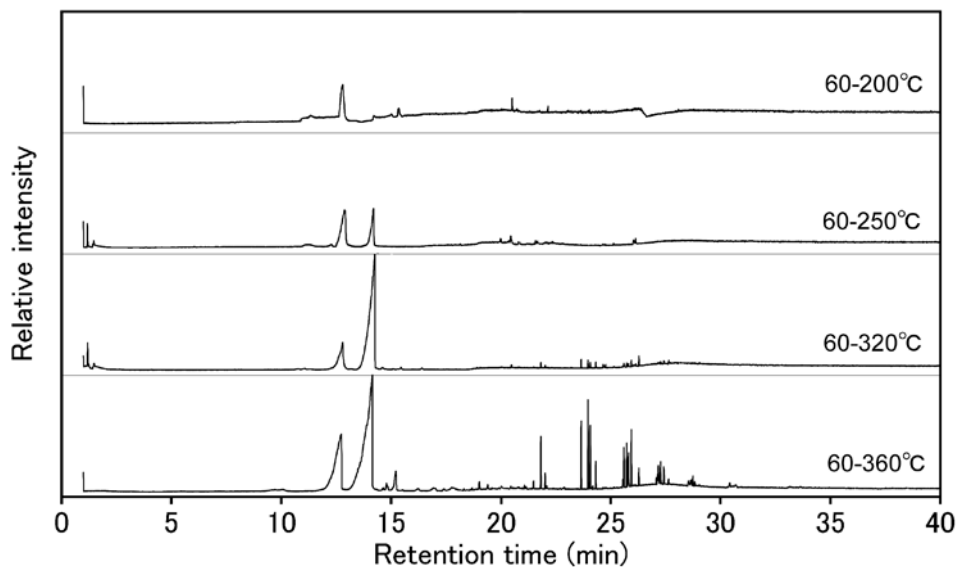


Figure 3. Py-GC/MS (TIC) chromatograms of PLLA-Ca pyrolysis products in heating processes from 60°C to the different end temperatures of: 200, 250, 320, and 360°C

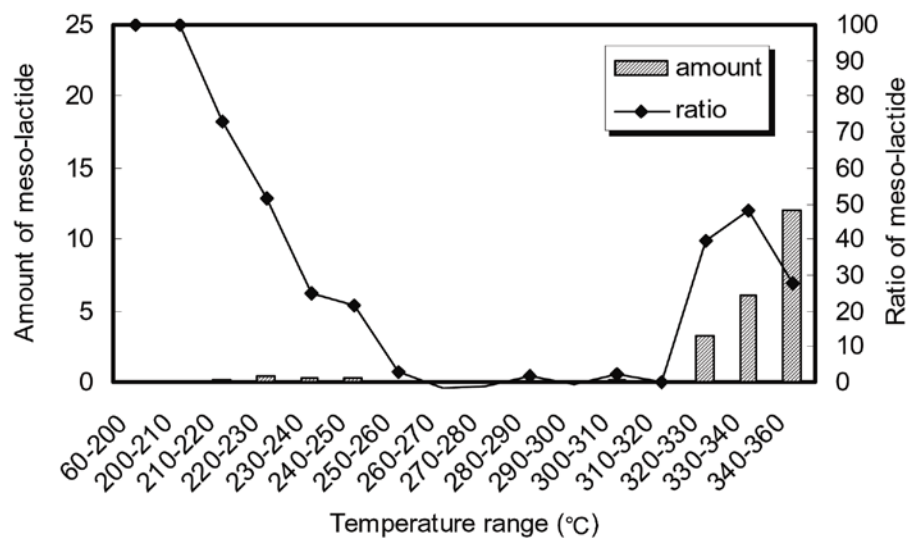


Figure 4. Racemization on PLLA-Ca pyrolysis in different temperature ranges. Bar graph: amount of meso-lactide formed (integration value of TIC peak); line: relative content ratio (%) of meso-lactide in total lactides.

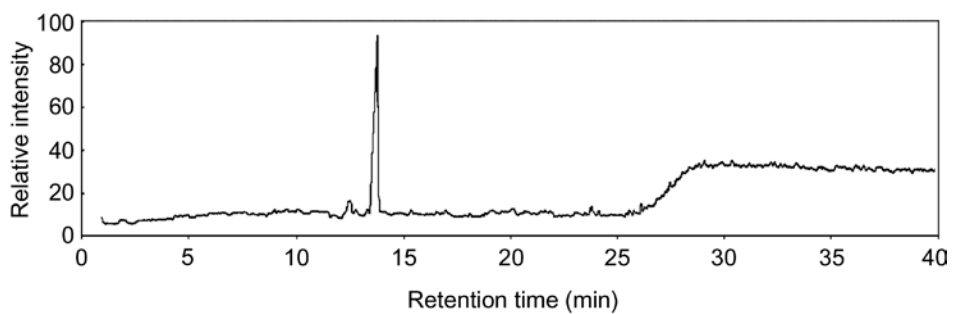


Figure 5. Py-GC/MS (TIC) chromatogram of PLLA-Ca pyrolyzates produced at 250-320°C in a degradation process from 60 to 320°C at heating rate of 10°C min<sup>-1</sup>.

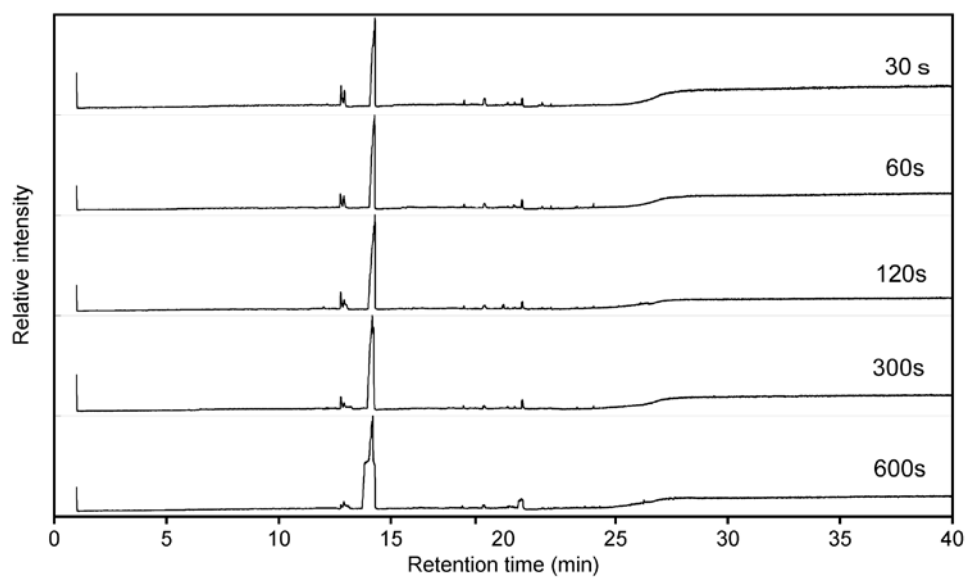
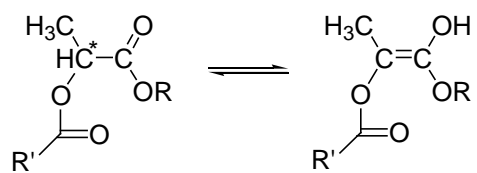
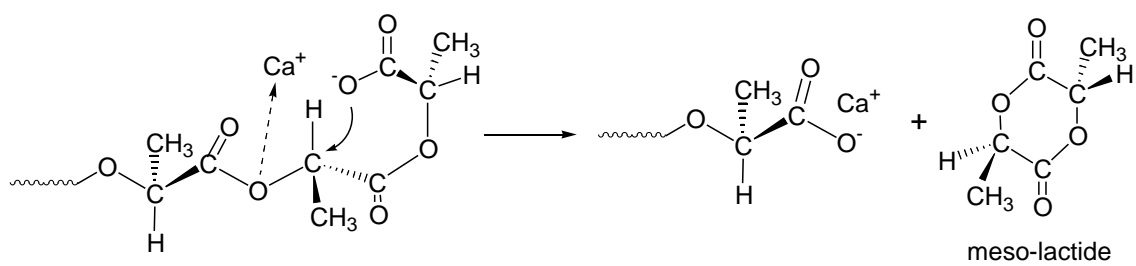


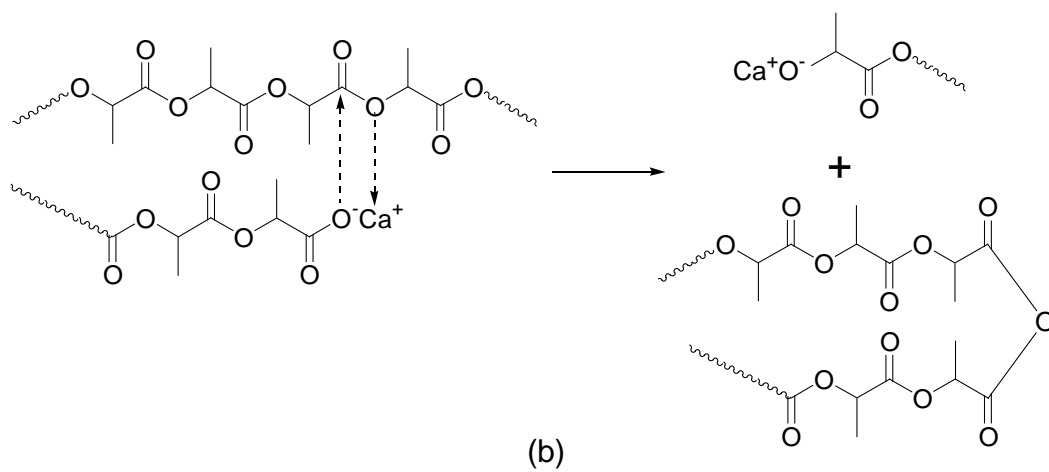
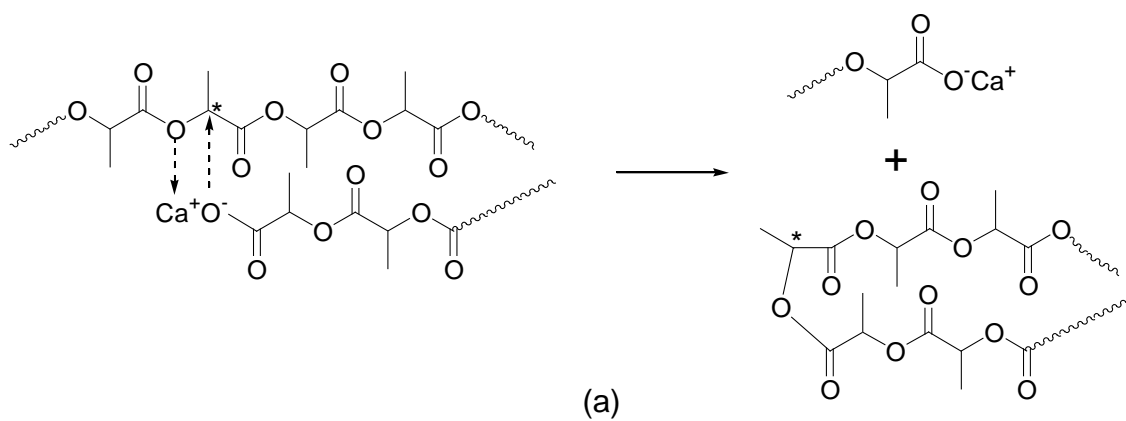
Figure 6. Py-GC/MS (TIC) chromatograms of PLLA-Ca pyrolyzates in the isothermal degradation process in glass tube oven at 250°C. Holding times of: 30, 60, 120, 300, and 600s.



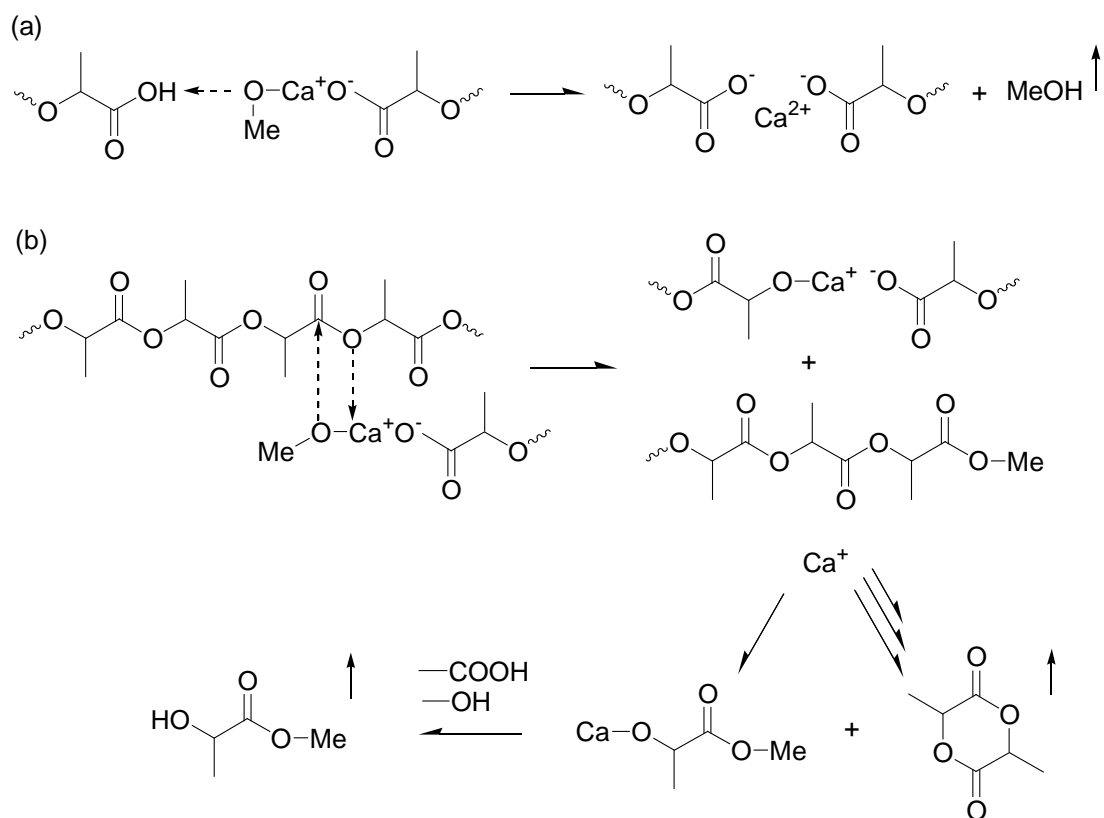
Scheme 1. Enolization in lactate unit.



Scheme 2. Meso-lactide formation by the SN2 reaction on asymmetrical methyne carbon.



Scheme 3. Possible random transfer reactions in the initial period of PLLA-Ca pyrolysis.



Scheme 4