

Racemization Behavior of L,L-Lactide during Heating

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Abstract

To control the depolymerization process of poly(L-lactic acid) into L,L-lactide for feedstock recycling, the racemization of L,L-lactide as a post-depolymerization reaction was investigated. In the absence of a catalyst, the conversion to *meso*-lactide increased with increase in the heating temperature and time at a higher rate than the conversion into oligomers. The resulting high composition of *meso*-lactide suggests that the direct racemization of L,L-lactide had occurred in addition to the known racemization mechanism that occurs on the oligomer chains. In the presence of MgO, the oligomerization rapidly proceeded to reach an equilibrium state between monomers and oligomers. The equilibrium among L,L-, *meso*-, and D,D-lactides was found to be a convergent composition ratio: L,L-:*meso*-:D,D-lactides = 1:1.22:0.99 (wt/wt/wt) after 120 min at 300 °C. This composition ratio also indicates that, in addition to the known racemization reaction on the oligomer chains, direct racemization among the lactides is also a frequent occurrence.

Keywords: poly(L-lactic acid) / L,L-lactide / chemical recycling / racemization / ester-semiacetal tautomerization

1. Introduction

Poly(L-lactic acid) [poly(L-lactide), PLLA], a well-known bioabsorbable and biodegradable material, is an attractive raw material, which is produced from renewable resources such as corn [1], potato, and garbage [2]. Because of the advantage of having a carbon neutral, the use of PLLA in industrial fields has been rapidly increasing in the form of molded parts for personal computers [3-5], mobile phones [6], and automobiles [7,8]. It is also anticipated to have many other future applications where environmental compatibility of materials is required, such as in mulching film and nursery boxes. However, PLLA has poor biodegradability in certain environments [9].

PLLA is generally prepared by the ring-opening polymerization of L,L-lactide as a cyclic monomer [10-12], and during its thermal degradation L,L-lactide is recovered [13,14]. This polymerization-depolymerization behavior is one of the particular properties of PLLA and the depolymerization has actually been used as one method of getting L,L-lactide from oligomers in an industrial production process [1]. Thus, this particular chemical property makes PLLA into a possible candidate for the feedstock recycling of plastics.

However, the thermal degradation of PLLA is more complex than the simple reaction that gives L,L-lactide. For example, Duda et al. [14] and Witzke et al. [15] have reported the ceiling temperature and thermodynamic parameters for the equilibrium polymerization of lactide. In spite of these studies, the reported parameters were distributed over a wide range of values. The activation energy, E_a , of degradation has also been reported to change irregularly in a range of 70-270 kJ·mol⁻¹ as degradation progresses [16-18], and many kinds of degradation products have been detected during the pyrolysis of PLLA [16,19], especially cyclic oligomers and their diastereoisomers. Another serious problem with the feedstock recycling of PLLA is racemization, which generates optical isomers: *meso*- and D,D-lactides that cause serious problems on the reproduction of PLLA, diminishing its crystallizability and

some other useful properties [16-18,20]. These examples illustrate that there are many mechanisms and factors that are influencing the depolymerization of PLLA. For feedstock recycling it is very important to control the mechanisms in the selective production of L,L-lactide from PLLA. If, through such control, feedstock recycling to L,L-lactide as the monomer could be achieved, then PLLA would certainly become more widely used as a reasonable choice for a sustainable future society [21].

Recently, the effects of including a trace amount of metal as a polymerization catalyst, such as Sn, were investigated with the aim of clarifying the diversity of degradation behavior exhibited by PLLA [22-24]. In addition, some catalysts effective in controlling the depolymerization of PLLA have been developed by Nishida et al. [25,26]. The catalysts used were MgO and Al(OH)₃, which reduced PLLA selectively into L,L-lactide. In spite of the development of these effective catalysts, racemization continues to be one of the serious problems associated with the feedstock recycling of PLLA. This is because the racemization may proceed not only during the depolymerization reaction, but also even in the cyclic monomer state after depolymerization. Thus far, Kopinke et al. have reported that the racemization proceeds *via* the ester-semiacetal tautomerization on the PLLA main chain (Scheme 1a) [16]. Fan et al. proposed another racemization mechanism: SN2 reaction at an asymmetrical methine carbon, which occurred as a back-biting reaction from an active chain end structure: R-COO⁻ Ca⁺ of PLLA (Scheme 1b) [21,27]. However, no report has investigated post-depolymerization reactions under heat of PLLA. In this report, we investigated the racemization of the stereoisomer L,L-lactide during heating. This subject had not previously been discussed, but has important implications for the design of a recovery process for L,L-lactide after the depolymerization of PLLA in feedstock recycling.

[Scheme 1]

2. Experimental

2.1 Materials

Monomer, L,L-lactide, obtained from Shimadzu Co. Ltd. was purified by recrystallizing three times from dry toluene and three times from dry ethyl acetate; it was then vacuum-dried, and stored in a N₂ atmosphere at 20 °C until use. After the above purification, *meso*-lactide as a main impurity was not detectable by gas chromatography (GC). A catalyst, magnesium oxide powder (MgO, 5 µm in average diameter × 50 µm in average length) was purchased from Wako Pure Chemical Industries, Ltd. (Wako) and used after heat-treatment at 300 °C for 2 h in a N₂ atmosphere. Other chemicals, such as chloroform and acetone, were obtained from Wako and used as received.

2.2 Characterization methods

¹H NMR spectra were recorded on a JEOL INOVA300 NMR spectrometer operating at 300 MHz for proton investigation in a chloroform-*d* solution with tetramethylsilane as an internal standard. The optical purity of L,L-lactide was examined by gas chromatography (GC) on a Shimadzu GC2014 gas chromatograph with a Varian cyclodextrine-2-236M-19 capillary column (50 m × 0.25 mm i.d.; film thickness, 0.25 µm) at 150 °C, using helium as a carrier gas. The column and injector were set isothermally at 150 and 220 °C, respectively. The sample (5 mg) was dissolved in acetone (2 mL) and a 1 µL aliquot of the solution was injected. The peaks for *meso*-, D,D-, and L,L- lactides were identified by comparison with peaks of pure substances.

Molecular weight was measured by gel permeation chromatography (GPC) on a TOSOH HLC-8220 GPC system at 40 °C using TOSOH TSKgel Super HM-H column (linearity range: 1×10³ - 8×10⁶; molecular weight exclusion limit: 4×10⁸) and a chloroform eluent (0.6

mL·min⁻¹). Low polydispersity polystyrene standards with M_n from 5.0×10^2 to 1.11×10^6 were used for calibration.

2.3 Heat treatment

Heat treatment of L,L-lactide (50 mg) was carried out in a NMR sample tube (5 mm) with or without MgO (5 wt%) as a catalyst. To make MgO powder disperse homogeneously in L,L-lactide melt, a powder mixture of L,L-lactide and MgO was vigorously stirred with a magnetic mixer for 15 min at room temperature, and then put in the tube. The sample tube was sealed and heated in a silicon bath thermostated at prescribed temperatures in a range of 180-300 °C. After a prescribed time ranging from 1-120 min, the sample tube was quenched at 4 °C in a water-bath, and then opened by cutting the glass. Chloroform-*d* (0.5 mL) was then added to dissolve the lactide for ¹H NMR measurement. Changes in the chemical structure of L,L-lactide after the heat treatment were evaluated by ¹H NMR and GC analyses. Number and weight average molecular weights (M_n and M_w) of the formed oligomers were measured by GPC.

Each heat treatment experiment was repeated 3 or 4 times. Similar results with the same tendency were obtained in all the repetitions. Experimental error bars were found by calculating the standard deviation.

2.4 Molecular orbital calculations

All computations were done on a Dell Optiplex GX60, equipped with 2.00GHz Celeron CPU board with use of Hulinks Spartan '04. Geometries were optimized with by the Hartree-Fock/3-21G* method and the reaction coordinate system was derived from the energy profile obtained by using the semi-empirical molecular orbital method PM3 Hamiltonian.

3. Results and discussion

3.1 Heat treatment of L,L-lactide in bulk

To determine the intra-molecular racemization of lactide during heating, L,L-lactide was heated in bulk without any catalyst. The heat treatment of L,L-lactide was carried out in a temperature range of 180-300 °C. The products obtained were composed of L,L-lactide, *meso*-lactide, D,D-lactide, and oligomers. In a ¹H NMR spectrum of the products, three isolated doublets were detected at 1.65-1.68, 1.70-1.75, and 1.45-1.64 ppm, which were assigned to methyl groups of L,L/D,D-lactides, *meso*-lactide, and oligomers, respectively. However, it was impossible to distinguish between the methyl groups of L,L-lactide and D,D-lactide by ¹H NMR analysis. The composition ratio of L,L-, D,D-, and *meso*-lactides as volatilizable components was estimated quantitatively by GC analysis using an optically active capillary column. In the GC profile, the *meso*-, L,L-, and D,D-lactides were detected as completely isolated signals at 6.30, 8.20, and 8.65 min, respectively.

The weight ratio of L,L-/D,D-lactides:*meso*-lactide:oligomers was evaluated by ¹H NMR analysis after heat-treatment for 1-120 min at prescribed temperatures in a range of 180-300 °C. Changes in the composition ratio of L,L-/D,D-lactides, *meso*-lactide, and oligomers are illustrated in Figure 1. At temperatures less than 200 °C, the conversion into *meso*-lactide and oligomers was scarcely found. After the heating for 120 min at 200 °C, a trace amount (4.5 wt%) of *meso*-lactide was detected. At temperatures over 230 °C, the conversion into *meso*-lactide gradually increased with heating temperature and time, reaching a maximum conversion value of 38.7 wt% after 120 min at 300 °C. Oligomers were formed at temperatures higher than 230 °C. The weight ratio of oligomers was less than that of *meso*-lactide, and never exceeded 10 wt% at temperatures under 270 °C. Even at 300 °C, the production of oligomers only reached a maximum value of approximately 20 wt%. Molecular weight of the oligomers formed at 250 °C was measured by GPC, resulting in a range of 360

to 600 in M_n and 1300 to 3300 in M_w .

The results in Figure 1 suggest that the *meso*-lactide was formed by an intra-molecular reaction of L,L-lactide, rather than *via* the oligomerization of L,L-lactide and ester-semiacetal tautomerization on the oligomer chain. This indicates that the racemization occurred as a transformation of the cyclic structure of lactide.

[Figure 1]

In Figure 2, results of GC analysis of changes in the composition ratio of L,L- and D,D-lactides are shown. The composition ratio of L,L-lactide decreased with increasing temperatures. The production of D,D-lactide was scarcely detected up to 60 min even at 300 °C. Over 60 min, the composition ratio of D,D-lactide rapidly increased at 300 °C up to 26.1 % after 120 min. However, at lower temperatures the production was very slow and even at 270 °C only increased up to 5.2 wt% after 120 min. The measured composition ratio of L,L-lactide in Figure 2(1) must be a resultant of an aggregate of factors that includes not only of the conversion to *meso*-lactide, D,D-lactide, and oligomers, but also of reverse reactions from *meso*-lactide and oligomers as expressed in Scheme 2.

[Figure 2]

[Scheme 2]

To express easily the effect of heating, averaged composition ratios of the components after the heating at various temperatures for 60-120 min are illustrated in Figure 3. At 200 °C, a trace amount of *meso*-lactide was detected and with increase in temperature the composition ratio of *meso*-form constantly increased maintaining a higher level than that of the oligomers.

Although D,D-lactide was found as a minor component in a range of 230~270 °C, at 300 °C it rapidly increased and started approaching an expected equilibrium among the lactides. Based on the results in Figures 1 and 2, the composition ratio of lactides was calculated as being L,L-:*meso*-:D,D-lactides = 1:1.47:0.95 (wt/wt/wt) after 120 min at 300 °C. If the equilibrium among the lactides is achieved *via* an equilibrium polymerization and racemization on the polymer chains and not on the lactide rings, the statistically predicted composition ratio in an equilibrium state should be L,L-:*meso*-:D,D-lactides = 1:2:1 (wt/wt/wt), because the racemization must occur randomly on the chains. The found composition ratio: 1:1.47:0.95 (wt/wt/wt) supports the presence of an equilibrium based on the reciprocal conversions among L,L-lactide, *meso*-lactide, and D,D-lactide, that is, the direct racemization as shown in Scheme 2.

The composition ratio of oligomers was approximately 20 wt% at the maximum value as shown in Figure 1. Previously, the ceiling temperature has been reported in a range of 275-786 °C [10,14,15]. If the found composition ratios of oligomers: less than 10 wt% at temperatures lower than 270 °C and 20 wt% at 300 °C, are results produced without a state of equilibrium having been reached, then it should be assumed that the racemization occurred on the cyclic structure of lactides to change them into other stereoisomers in addition to the known process *via* the oligomerization and racemization occurring on oligomer chains. In order to determine the equilibrium between monomers and oligomers under the same conditions, accelerated reactions were investigated in the presence of MgO (5wt%) as a reaction catalyst for oligomerization and depolymerization [25].

[Figure 3]

3.2 Heat treatment of L,L-lactide in the presence of MgO

It is well known that magnesium compounds function as catalysts for both polymerization [28] and depolymerization [25]. The heat treatment of L,L-lactide in the presence of MgO (5 wt%) was carried out in bulk, in which MgO was homogeneously dispersed without marked aggregation. Results of NMR and GC analyses after heat treatment are illustrated in Figures 4-6.

From ^1H NMR analysis (Figure 4), it was found that the oligomerization rapidly proceeded until equilibrium was attained between the cyclic monomers and oligomers after 10-60 min under heat. As a result of the production of a large amount of oligomers, L,L-/D,D- and *meso*-lactides became minor components except for the case at 300 °C. The equilibrium composition ratio of oligomers over the total components was located at 90-60 wt% at 180-270 °C and approximately 20-30 wt% at 300 °C. The equilibrium composition ratio of oligomers at 300 °C is close to the value of approximately 20 wt% found without the catalyst (Figure 1(3)). These results indicate that, although in the presence of MgO the equilibrium between monomers and oligomers is smoothly achieved, when MgO is absent the process gradually proceeds as shown in Figure 1. Thus, the observed high conversion values into *meso*-lactide in Figure 1, under which conditions the equilibrium between the monomers and oligomers is incomplete, must be caused by the contribution of the direct racemization of L,L-lactide.

[Figure 4]

From GC analysis of volatile components (Figure 5), it was found that at temperatures lower than 200 °C the composition ratio of D,D-lactide gradually increased with heating time, whilst at temperatures over 230 °C the equilibrium among L,L-, *meso*-, and D,D-lactides was achieved smoothly in a short time, resulting in a convergence to approximately 20-25 wt %.

The composition ratio of L,L-lactide also approached a range of 25-35 wt% at temperatures over 230 °C. In spite of the rapid conversion within 10 min at temperatures over 230 °C, the composition rate of L,L-lactide gradually decreased during the 10-120 min taken to reach the convergent values (Figure 5(1)). This suggests a retardation of the conversion rate caused by the reverse reaction to L,L-lactide from oligomers that had accumulated a large amount of L-lactate unit in their chains during the beginning period up to 10 min.

[Figure 5]

In Figure 6, averaged composition ratios of the components after heating for 60-120 min are illustrated in the same way as for Figure 3. In the presence of MgO, the oligomerization proceeded rapidly even at low temperatures. The equilibrium concentration of lactides increased with increase in temperature, whereas the oligomer's concentration decreased with increase in temperature. These results clearly indicate typical behavior for the equilibrium polymerization. The equilibrium among L,L-, *meso*-, and D,D-lactides was also achieved at higher temperatures than 270 °C, as shown in Figure 6, finally resulting in a composition ratio: L,L-:*meso*-:D,D-lactides = 1:1.22:0.99 (wt/wt/wt) after 120 min at 300 °C. This composition ratio means that the transformation frequently occurs among the lactides in the presence of MgO as shown in Scheme 2.

[Figure 6]

From the above results, it was determined that the direct racemization among the lactides was proceeding in addition to the known racemization reaction that occurs on polymer chains. Possible overall equilibrium reactions are illustrated in Scheme 2. The

amount of each lactide will be influenced not only by the equilibrium achieved among the lactides and oligomers, but also by the ester-semiacetal tautomerization on the oligomer chains.

3.3 Molecular orbital calculation of ester-semiacetal tautomerization on lactides

The direct racemization through the ester-semiacetal tautomerization on the lactides was investigated by well-known molecular orbital calculation methods. To estimate activation energy, E_a , values of the reactions, structures of transition states were calculated by the Hartree-Fock/3-21G* method and the reaction coordinate system was derived from the energy profile obtained by using a PM3 Hamiltonian. In Figure 7, the reaction coordinate system is illustrated. High activation energy values: 477 and 327 kJ·mol⁻¹ were obtained for the ester-semiacetal tautomerization from L,L-/D,D-lactides and *meso*-lactide, to the corresponding tautomers, respectively. Apparent E_a value of the transformation of L,L-lactide was also calculated based on the found conversion values shown in Figures 1 and 2 (see Appendix for the calculation of the rate constant for the transformation), resulting in a range of 50-60 kJ·mol⁻¹ (Figure 8). The high E_a values estimated by the PM3 method are due to a simulation in space without any interaction. Actually, the ester-semiacetal tautomerization must proceed under some catalytic effects, such as the electrostatic effect produced by surrounding lactides in bulk. Looking at it from a different angle, these high E_a values also suggest the structural stabilization of vaporized lactides after the depolymerization of PLLA.

The gap between the E_a values of the transformation from L,L-/D,D-lactides and *meso*-lactide: 150 kJ·mol⁻¹ suggests a shift in the equilibrium among lactides from *meso*-lactide to L,L- and D,D-lactides. The found composition ratios: L,L-:*meso*-:D,D-lactides = 1:1.47:0.95 and 1:1.22:0.99 (wt/wt/wt) under the absence and presence of MgO, respectively, must have been influenced by the shift of the equilibrium to L,L- and D,D-lactides predicted by

the calculation.

[Figure 7]

[Figure 8]

4. Conclusions

The structural changes of L,L-lactide during heating were monitored with ^1H NMR and GC. In the absence of a catalyst, although scarcely any change of L,L-lactide was detected under 200 °C, the conversion to *meso*-lactide increased with increases in heating temperature and time at a higher rate than for conversion into oligomers. Taking into consideration the fact that the oligomer concentration had not yet reached an equilibrium value, the higher *meso*-lactide concentration suggests the occurrence of direct racemization of L,L-lactide to *meso*-lactide, and, further, that the racemization was not limited to a route *via* oligomerization and the known racemization reaction on the oligomer chains. In the presence of MgO as a reaction catalyst, the oligomerization rapidly proceeded to reach an equilibrium state between monomers and oligomers. The equilibrium among L,L-, *meso*-, and D,D-lactides was also achieved at higher temperatures over 270 °C. The convergent composition ratio was L,L-:*meso*-:D,D-lactides = 1:1.22:0.99 (wt/wt/wt) after 120 min at 300 °C. This composition ratio means that the direct racemization among the lactides frequently occurs in addition to the known racemization process *via* the oligomerization and the ester-semiacetal tautomerization on the formed oligomer chains.

The results obtained in this work will be used as an effective way of controlling the feedstock recycling of PLLA to L,L-lactide.

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Appendix

Rate constant refer to the transformation of L,L-lactide:

Reactions among lactides and oligomers are shown in Figure 9. In this figure, rate constants: k_1 , k_1' , k_2 , and k_2' , refer to equilibrium reactions between lactides, that is, the racemization on lactide rings. Other rate constants: k_3 , k_3' , k_4 , k_4' , k_5 , and k_5' , refer to equilibrium polymerizations between lactides and oligomers.

[Figure 9]

In this study, the apparent rate constant of the transformation of L,L-lactide to meso-lactide, k_1 , was calculated according to the equations below.

Changes in the concentration of components: C_{LL} , C_{meso} , C_{DD} , and C_{oligo} , are expressed below.

$$\begin{aligned} -\frac{dC_{LL}}{dt} &= k_1 C_{LL} - k_1' C_{meso} + k_3 C_{LL} - k_3' C_{oligo} \\ \frac{dC_{meso}}{dt} &= k_1 C_{LL} - k_1' C_{meso} - k_2 C_{meso} + k_2' C_{DD} - k_4 C_{meso} + k_4' C_{oligo} \\ \frac{dC_{DD}}{dt} &= k_2 C_{meso} - k_2' C_{DD} - k_5 C_{DD} + k_5' C_{oligo} \\ \frac{dC_{oligo}}{dt} &= k_3 C_{LL} - k_3' C_{oligo} + k_4 C_{meso} - k_4' C_{oligo} + k_5 C_{DD} - k_5' C_{oligo} \end{aligned}$$

In an equilibrium state among lactides, the composition ratio of lactides is constant.

Thus,

$$\begin{aligned}
C_{LL} : C_{meso} : C_{DD} &= 1 : P : 1 \text{ (mole ratio)} \\
C_{meso} &= PC_{LL}, \quad C_{DD} = C_{LL} \\
k_1 C_{LL} &= k_1' C_{meso} = k_1' PC_{LL} \\
k_1' &= \frac{1}{P} k_1
\end{aligned}$$

where parameter P may depend on the temperature.

Term: $(k_3 C_{LL} - k_3' C_{oligo})$ means an apparent polymerization rate of L,L-lactide. Thus,

$$\begin{aligned}
-\frac{dC_{LL}}{dt} &= k_1 C_{LL} - \frac{1}{P} k_1 C_{meso} + k_p C_{LL} \\
&= k_1 \left(C_{LL} - \frac{C_{meso}}{P} \right) + k_p C_{LL}
\end{aligned}$$

where the initial values of C_{LL} and C_{meso} are 1 and 0, respectively.

In Figures 1 and 2, it was found that C_{oligo} was less than 10%, except for the values at 300 °C for 90 and 120 min. Therefore, the constant rate, k_1 , was tentatively calculated based on the equation below.

$$-\frac{dC_{LL}}{dt} \cong k_1 \left(C_{LL} - \frac{C_{meso}}{P} \right)$$

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Scheme and Figure Captions

Scheme 1. Racemization mechanisms. (a) Ester-semiacetal tautomerization, (b) S_N2 reaction on asymmetrical methine carbon.

Scheme 2. Plausible equilibrium reactions among lactides and oligomers.

Figure 1. 1H NMR analysis of the changes in the composition ratios of (1) L,L/D,D-lactides, (2) *meso*-lactide, and (3) oligomers during the heat treatments in bulk.

Figure 2. GC analysis of the changes in the composition ratios of (1) L,L-lactide and (2) D,D-lactide during the heat treatments in bulk.

Figure 3. Averaged composition ratios of the components after the heating of L,L-lactide for 60-120 min in bulk. (1) L,L-lactide; (2) *meso*-lactide; (3) D,D-lactide; and (4) oligomers.

Figure 4. NMR analysis of the changes of L,L-lactide into (a) oligomers and (b) *meso*-lactide during the heat treatments in the presence of MgO 5 wt%.

Figure 5. GC analysis of the changes of (a) L,L-lactide into (b) D,D-lactide during the heat treatments in the presence of MgO 5 wt%.

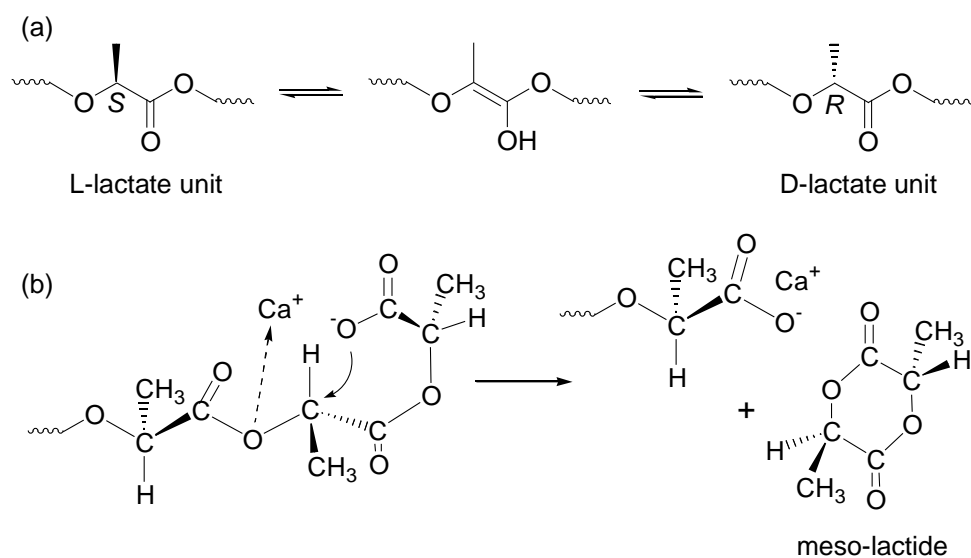
Figure 6. Averaged composition ratios of the components after the heating of L,L-lactide for 60-120 min in the presence of MgO (5 wt%). (1) L,L-lactide; (2) *meso*-lactide; (3) D,D-lactide; and (4) oligomers.

Figure 7. Reaction coordinates of ester-semiacetal tautomerization on lactides. Activation energy was calculated by the semi-empirical molecular orbital method PM3.

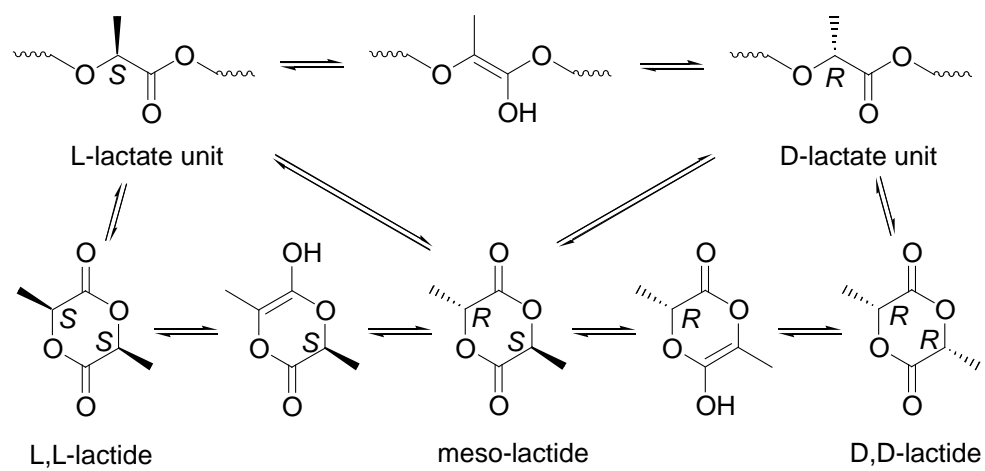
Figure 8. Relationships between apparent $\ln k$ and $1/T$ on the transformation of L,L-lactide without MgO in bulk.

Figure 9. Reactions among lactides and oligomers.

Schemes and Figures



Scheme 1. Racemization mechanisms. (a) Ester-semiacetal tautomerization, (b) S_N2 reaction on asymmetrical methine carbon.



Scheme 2. Plausible equilibrium reactions among lactides and oligomers.

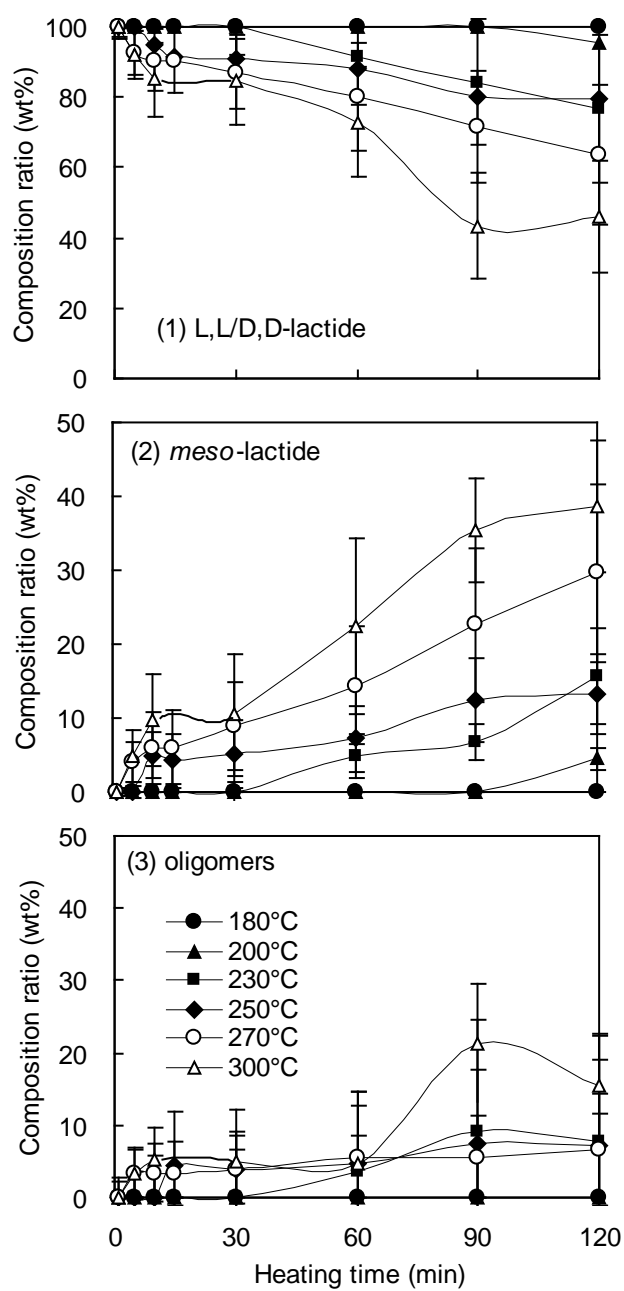


Figure 1. ^1H NMR analysis of the changes in the composition ratios of (1) L,L/D,D-lactides, (2) *meso*-lactide, and (3) oligomers during the heat treatments in bulk.

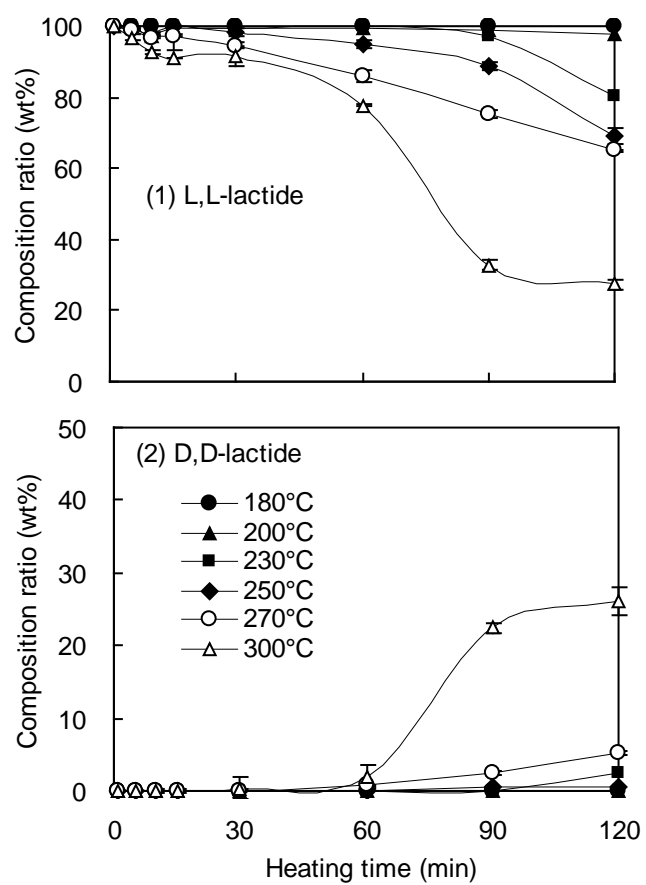


Figure 2. GC analysis of the changes in the composition ratios of (1) L,L-lactide and (2) D,D-lactide during the heat treatments in bulk.

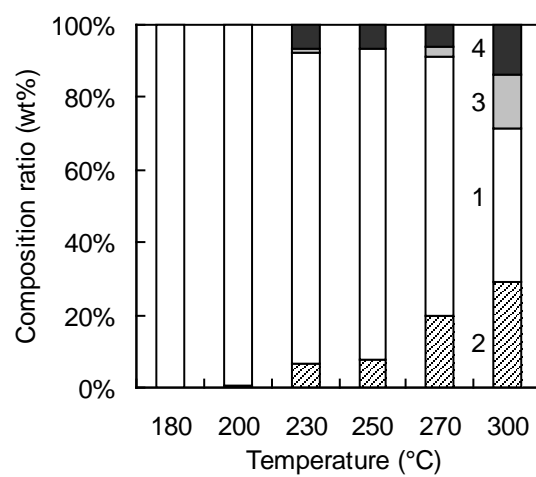


Figure 3. Averaged composition ratios of the components after the heating of L,L-lactide for 60-120 min in bulk. (1) L,L-lactide; (2) *meso*-lactide; (3) D,D-lactide; and (4) oligomers.

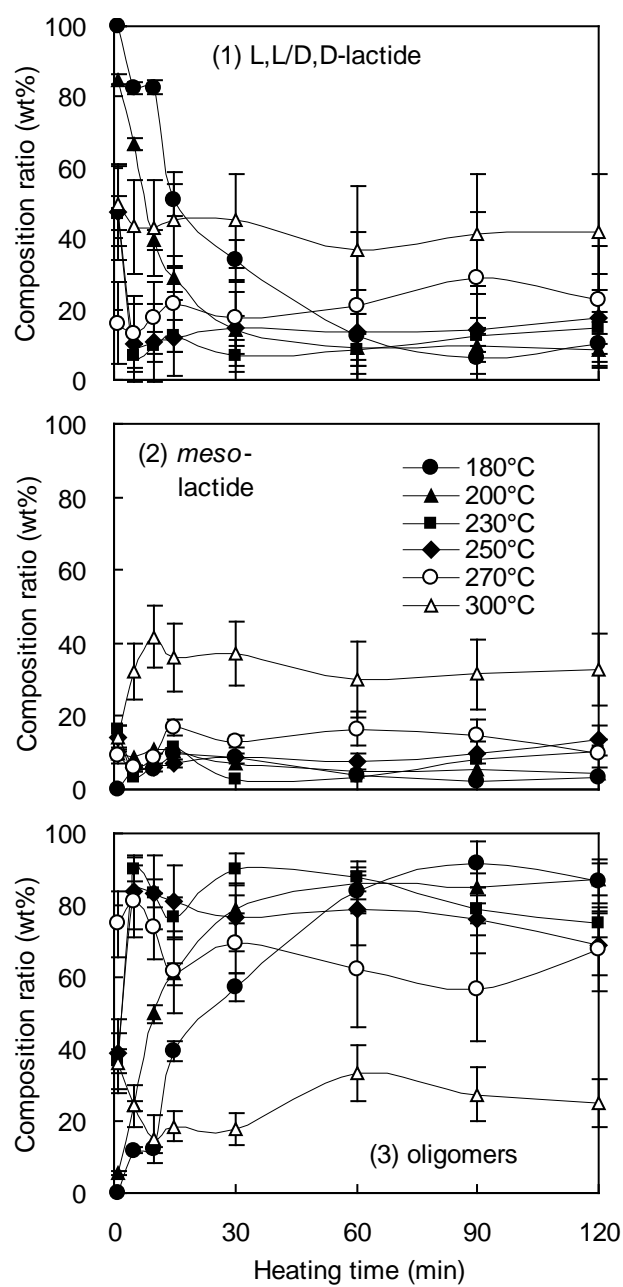


Figure 4. NMR analysis of the changes of L,L-lactide into (a) oligomers and (b) *meso*-lactide during the heat treatments in the presence of MgO 5 wt%.

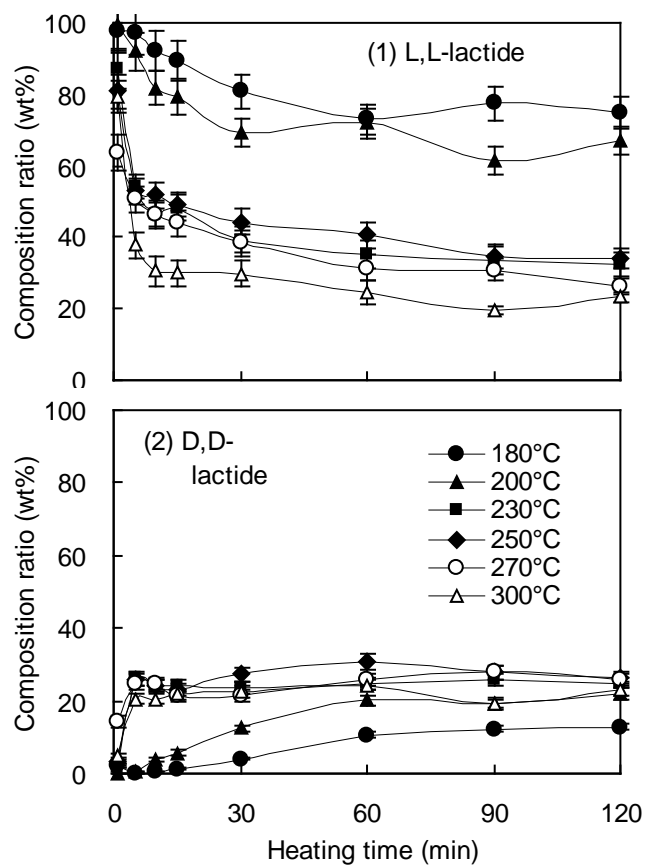


Figure 5. GC analysis of the changes of (a) L,L-lactide into (b) D,D-lactide during the heat treatments in the presence of MgO 5 wt%.

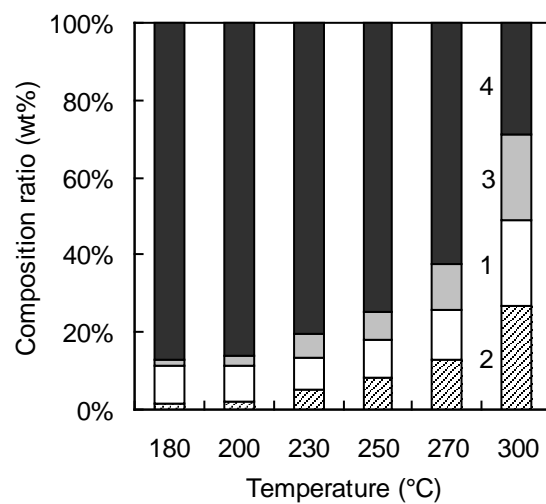


Figure 6. Averaged composition ratios of the components after the heating of L,L-lactide for 60-120 min in the presence of MgO (5 wt%). (1) L,L-lactide; (2) *meso*-lactide; (3) D,D-lactide; and (4) oligomers.

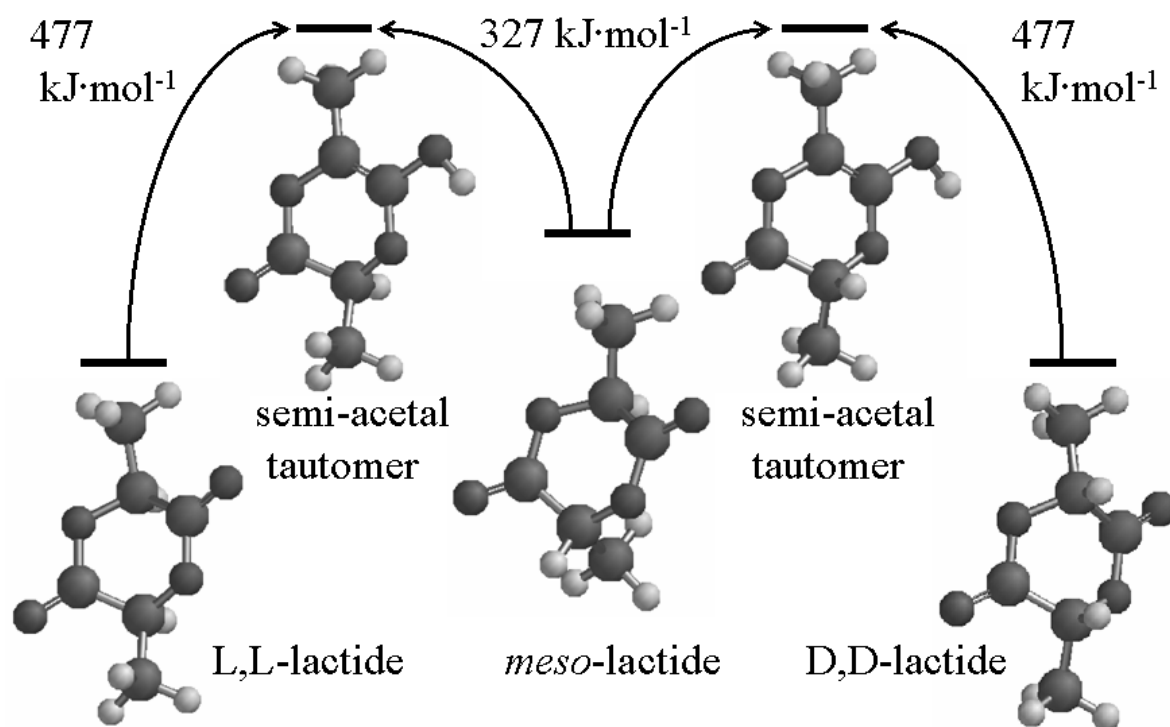


Figure 7. Reaction coordinates of ester-semiacetal tautomerization on lactides. Activation energy was calculated by the semi-empirical molecular orbital method PM3.

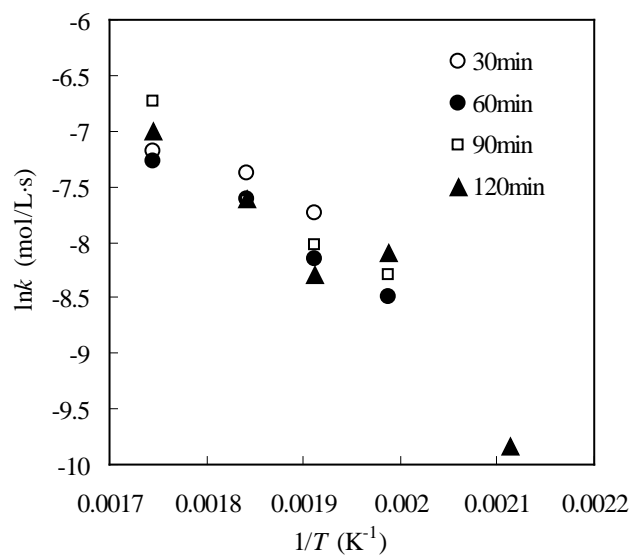


Figure 8. Relationships between apparent $\ln k$ and $1/T$ on the transformation of L,L-lactide without MgO in bulk.

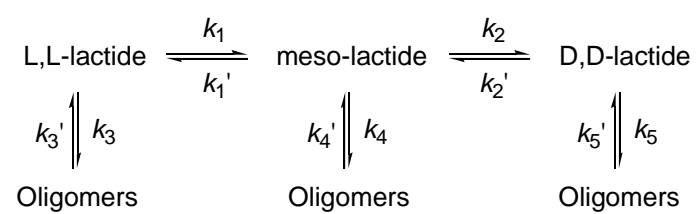


Figure 9. Reactions among lactides and oligomers.