



Thermal Stability of Poly (L-lactide): Influence of End Protection by Acetyl Group

著者	Yujiang Fan, Nishida Haruo, Shirai Yoshihito, Endo Takeshi
journal or publication title	Polymer Degradation and Stability
volume	84
number	1
page range	143-149
year	2003-10-16
URL	http://hdl.handle.net/10228/00006741

doi: [info:doi/10.1016/j.polymdegradstab.2003.10.004](https://doi.org/10.1016/j.polymdegradstab.2003.10.004)

Thermal Stability of Poly (L-lactide): Influence of End Protection by Acetyl Group

Yujiang Fan^{a,b}, Haruo Nishida^{a*}, Yoshihito Shirai^b, and Takeshi Endo^{a,c}

^a *Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555,
Japan*

^b *Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 1-1
Hibikino, Kitakyushu, Fukuoka 808-0196, Japan*

^c *Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510,
Japan*

*Corresponding author: Haruo Nishida

Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka
820-8555, Japan

Tel / Fax: +81-948-22-5706.

E-mail address: hnishida@mol-eng.fuk.kindai.ac.jp (H. Nishida)

Abstract

Thermal stability of end-protected poly (L-lactide) (PLLA) was studied by dynamic thermal degradation and pyrolyzate analyses. The treatment of PLLA by acetic anhydride resulted in the acetylation of end hydroxyl groups, and at the same time a decrease in the residual Sn content in the polymer. The thermal degradation of the acetylated PLLA-Ac showed a shift to a 40-50°C higher degradation temperature range than that of untreated, high Sn content PLLA, but exhibited nearly the same degradation behavior as the untreated PLLA with a comparable Sn content. Purified metal-free PLLA-H showed good thermal stability, having the highest degradation temperature range. Interestingly, despite the end-protection, the acetylated metal-free PLLA-H/Ac decomposed at almost the same temperature as that of PLLA-H. From pyrolyzate and kinetic analyses, it was found that the contribution of the hydroxyl-end acetylation to the stability of PLLA was negligible, except for the stabilization effect due to the elimination of residual Sn during the acetylation process.

Keywords

poly (L-lactide) / poly (L-lactic acid) / PLLA / thermal degradation / thermal stability / pyrolysis / end-protection / acetylation / kinetics

1. Introduction

Recently, interest in poly (L-lactide) (PLLA) has moved beyond its traditional areas of biomedical and pharmaceutical applications to the area of commodity applications [1-3]. This is because PLLA can be derived from renewable resources, and has good properties, such as mechanical strength, transparency, and compostability. Much work has been put into developing the large-scale manufacture and processing of PLLA as well as into modifying its properties [4,5].

Similar to many other plastics, the main techniques for processing PLLA into varied products are injection molding, compression molding, extrusion, and other melt processing methods [6]. In all cases, after processing the final products are partially decomposed as compared to the original resin [7]. Aliphatic polyesters in particular are easy to hydrolyze and thermally degrade to monomers and oligomers, making the improvement of the thermal stability of PLLA an important subject as regards processing.

Many factors have been reported as affecting the thermal stability of PLLA, including moisture, molecular weight, residual monomers, and metal catalysts [8-14]. A mechanism reported as playing a significant role in PLLA pyrolysis is a back-biting reaction, which causes an unzipping depolymerization started from the hydroxyl ends of chains [9,11,13]. End-protection of the hydroxyl groups has been considered as a way of improving the thermal stability of PLLA and some reports have been published on end-protection by acetyl group (Scheme 1), resulting in an increase in the

degradation temperature of PLLA by tens of degrees [8,15]. However, the acetylation process not only causes end-protection, but it is also capable of eliminating the residual metals in PLLA by forming salts or complexes. The residual metals, such as Sn and Al, which come from the polymerization catalysts, are understood to greatly decrease the thermal stability of PLLA [11,14-19]. In previously published studies, however, few reports have discussed the relationship between the residual metal catalysts and end-protection. Jamshidi et al. demonstrated that the acetylation of the hydroxyl group inhibits the thermal degradation of the purified polymer to a significant extent [15]. Unfortunately, they purified the PLLA by repeated precipitation without determining the metal content. Thus, no report, in which the relationship is discussed quantitatively, has been published.

[Scheme 1 goes here]

In this paper, to evaluate the effect of the end-protection on the thermal degradation of PLLA, the relationship between the metal content and the acetylation was investigated. Degradation kinetics and the mechanisms of PLLA were also discussed.

2. Experimental

2.1. Materials

Monomer, L,L-lactide, was obtained from Shimadzu Co. Ltd. It was composed of L,L-lactide 99.4 % and meso-lactide 0.6 % according to a gas chromatography (GC). This monomer was

purified by recrystallization three times from dry toluene and one time from dry ethyl acetate. The vacuum dried L,L-lactide was stored in a N₂ atmosphere. After purification, *meso*-lactide was not detectable by GC. Tin(II) 2-ethylhexanoate {Sn(Oct)₂} was obtained from Wako Pure Chemical Industries, Ltd. and purified by distillation under reduced pressure before use. Solvents, chloroform and methanol were purchased from Kanto Chemical Co., Inc. and used without further purification. The ammonia solution (25%) and hydrochloric acid (1 M for atomic absorption spectrophotometry) were obtained from Wako Pure Chemical Industries, Ltd. and used as received.

2.2. Preparation of poly (L-lactide) samples

PLLA was synthesized by the ring-opening polymerization of L,L-lactide catalyzed by Sn(Oct)₂. Purified L,L-lactide 5g (34.69 mmol) was added into a reaction tube in a glove box under N₂ atmosphere. Then, Sn(Oct)₂/toluene solution 868 μL {0.02 mol L⁻¹, 17.3 μmol of Sn(Oct)₂} was added by using a micro syringe. The reaction tube was connected to a vacuum line and the toluene was allowed to evaporate for 48 h *in vacuo*. After sealing in a flame, the tube was immersed into an oil bath at 110 °C for 48 h. The obtained raw PLLA was dissolved in chloroform (3 % w/w) and then precipitated with 6-fold of methanol to prepare the sample PLLA (*M_n* 181,000; PDI 1.69).

The PLLA 1.0 g was dissolved in 30 mL of dry chloroform and acetic anhydride 2.0 g (0.02 mol) was added to the solution. The solution was heated at 60 °C for 4 h while being stirred in an N₂

atmosphere. After the reaction, PLLA was reprecipitated twice with 10-fold of methanol, washed thoroughly with methanol, and finally dried *in vacuo* at 40 °C for 48 h to prepare the acetyl end-capped PLLA-Ac.

The PLLA was purified in a three stages process; firstly dissolving the PLLA 5.0 g in chloroform 150 mL and extracting the residual Sn catalyst from the PLLA/chloroform solution three times with 500 mL of 1M HCl aqueous solution, then washing with distilled water until the aqueous phase became totally neutral, and finally precipitating the polymer with methanol to prepare the purified PLLA-H.

The PLLA-H 1.0 g was also acetylated by the same procedure as that used for the preparation of PLLA-Ac to prepare the purified and end-protected PLLA-H/Ac.

The four kinds of PLLA samples are listed in Table 1. For preparing sample films, each chloroform solution of the corresponding sample was cast in a glass Petri dish. After the evaporation of the solvent, the formed film was washed by methanol and then vacuum dried.

[Table 1 goes here]

2.3. Measurements

The molecular weight of PLLA samples was measured by gel permeation chromatography (GPC) at 40 °C using a TOSOH HLC-8220 GPC system equipped with a TOSOH TSKgel Super

HM-H column 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.

The residual Sn 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 HCl, and then measured by AA.

Thermogravimetric analysis was conducted on a SEIKO EXSTAR 6200 TG/DTA 6200 system under a constant nitrogen flow (100 mL min^{-1}) using about 5 mg of the PLLA film sample. The pyrolysis data were collected by an EXSTAR 6000 platform, and recorded into an analytical computer system.

Pyrolysis-gas chromatography / mass spectrometry (Py-GC/MS) was conducted on a Frontier Lab PY-2020D double-shot pyrolyzer connected to a Shimadzu GCMS-QP5050 chromatograph / mass spectrometer, which was equipped with an Ultra Alloy⁺-5 capillary column. High purity helium at 100 mL min^{-1} was used as a carrier gas. A PLLA sample was put in the pyrolyzer and heated from 40 to 400 °C at a heating rate of 10 °C min^{-1} . The volatile pyrolysis products were conducted into the GC through the selective sampler. The temperature of the column oven was first set at 40 °C. After the pyrolysis process had finished, the column was heated according to the following program: 40 °C for 1 min; 40-120 °C at 5 °C min^{-1} , 120-320 °C at 20 °C min^{-1} ; 320 °C for 13 min. Mass spectrum measurements were recorded 2 times s^{-1} during this period.

3. Results and Discussion

3.1. Purification and End-protection of Poly (*L*-lactide)

To clarify the relationship between the protection of the hydroxyl end and the residual Sn content on the thermal stabilization of PLLA, four samples were prepared. Original PLLA was synthesized through the ring-opening polymerization catalyzed by tin 2-ethylhexanoate {Sn(Oct)₂}. After the polymerization, raw product was precipitated with methanol, obtaining a 98.7 % yield of PLLA. Then, PLLA was treated with acetic anhydride to protect the hydroxyl ends of polymer chains, preparing the end-protected PLLA-Ac. Metal free polymer, PLLA-H, was prepared by extracting the metals in the polymer/chloroform solution using a 1M HCl aqueous solution [11,14]. Further, the end-protected metal free polymer, PLLA-H/Ac, was prepared by treating the PLLA-H with acetic anhydride in the same manner as for the PLLA-Ac preparation. The molecular weight and Sn content of these samples are listed in Table 1.

It has been reported that a trace amount of residual water is the actual initiator in the Sn(Oct)₂ catalyzed polymerization of L,L-lactide, leading to a carboxylic acid chain end [21]. Another end structure is generally assumed to be Sn alkoxide in an as-polymerized state, which would finally change into a hydroxyl chain-end during the precipitation process with methanol [22]. However, it is known that the Sn compound cannot be eliminated effectively through a precipitation process with

methanol [14,23]. Calculated Sn content in the feed for polymerization was 410 ppm according to the mol ratio of $[\text{Sn}(\text{Oct})_2]/[\text{L,L-lactide}] = 1/2000$. Measured Sn content in the precipitated PLLA was 437 ppm by the AA analysis, which, in terms of the polymer yield, is in accordance with the calculated value.

The treatment of PLLA with acetic anhydride slightly affected the molecular weight of the resulting PLLA-Ac (Table 1). Even after the treatment, because of the remaining high molecular weight, the protected end structure of PLLA-Ac could not be directly confirmed by any means. Thus, to determine the existence of the protected end-structure through a model reaction, an oligo(L-lactic acid) was synthesized using a similar procedure as for polymerization under the following conditions: $[\text{Sn}(\text{Oct})_2]/[\text{H}_2\text{O}]/[\text{L,L-lactide}] = 1/200/2000$ at 120 °C for 48 h. The oligo(L-lactide) (OLLA) with $M_n = 2680$, which was calculated from the integration values of the peaks in $^1\text{H-NMR}$ spectrum, was obtained with a 32% yield. Then, OLLA was treated in the same way with acetic anhydride to prepare an end-protected oligo(L-lactide), OLLA-Ac. The end structure of the obtained OLLA-Ac was confirmed by $^1\text{H-NMR}$. In the $^1\text{H-NMR}$ spectrum (Figure 1a) of the original OLLA, a weak quartet and doublet at 4.28 and 1.49 ppm were observed. These were in addition to the main quartet and doublet at 5.16 and 1.59 ppm for the $-\underline{\text{C}}\text{H}(\text{CH}_3)\text{-OCO-}$ and $-\text{CH}(\underline{\text{C}}\text{H}_3)\text{-OCO-}$ in the main chain. From $^1\text{H-}^1\text{H}$ COSY spectrum, the weak peaks were assigned to $-\underline{\text{C}}\text{H}(\text{CH}_3)\text{-OH}$ and $-\text{CH}(\underline{\text{C}}\text{H}_3)\text{-OH}$ in chain end units. After the acetylation (Figure 1b), the weak peaks at 4.28 and 1.49

ppm disappeared and a new singlet at 2.14 ppm for acetyl group appeared [8]. The molecular weight of OLLA-Ac was $M_n = 2590$, which was calculated from the integration values of the peaks at 5.16 and 2.14 ppm in the $^1\text{H-NMR}$ spectrum. This means that the acetylation proceeded quantitatively under the conditions. From these results of the oligomer modification, it can be reasonably inferred that the same treatment of PLLA with acetic anhydride resulted in the acetylation of the hydroxyl ends of the polymer chains to produce the end-protected PLLA-Ac. A crucial aspect is that this treatment effectively decreases the Sn content in the polymer, in fact, the Sn content of PLLA-Ac decreased to 74 ppm from 437 ppm in the precipitated PLLA.

The residual Sn compounds in the PLLA were eliminated by a three times repeated liquid-liquid extraction using 1M HCl aqueous solution to prepare the purified PLLA-H [11,14]. From AA analysis, PLLA-H was found to contain 13.7 ppm of Sn, a level only just detectable under these experimental conditions. Thus, PLLA-H is regarded as being metal-free PLLA. Molecular weight and polydispersity (PDI) of PLLA-H did not show any significant deviation from those of the precipitated PLLA.

The metal-free PLLA-H was also treated with acetic anhydride to prepare the metal-free and end-protected PLLA-H/Ac with nearly equal molecular weights and Sn contents at the lower limits of detection (Table 1).

The results in Table 1 allow us to evaluate the relationship between the end-protection and the

residual Sn content on the thermal degradation of PLLA without any consideration needing to be given to the influence of the molecular weight of the samples.

[Figure 1. ^1H NMR spectra of OLLA and OLLA-Ac]

3.2. *Dynamic thermal degradation*

Thermogravimetric analysis (TG) is a commonly employed approach for evaluating the thermal properties of polymer materials. To analyze the thermal degradation behavior of PLLA before and after the acetylation, the dynamic thermal degradation of film samples was conducted with TG/DTA by measuring the weight loss as a function of linear increase in temperature in a nitrogen flow. Figure 2 shows the weight loss profiles for the PLLA samples, namely, PLLA, PLLA-Ac, PLLA-H, and PLLA-H/Ac, respectively, at heating rate (ϕ) $5\text{ }^\circ\text{C min}^{-1}$.

[Figure 2. TG curves (5 K min^{-1})]

In Figure 2, the profile of the precipitated PLLA with the highest Sn content, 437 ppm, showed the lowest pyrolysis temperature. Its degradation started at $260\text{ }^\circ\text{C}$ and finished at about $315\text{ }^\circ\text{C}$. An obvious increase in degradation temperature was shown in the profile of the acetylated PLLA-Ac. The weight loss of PLLA-Ac started at $300\text{ }^\circ\text{C}$ and proceeded smoothly to complete degradation at about $360\text{ }^\circ\text{C}$, showing a degradation temperature range for PLLA-Ac reaching a $40\text{-}50\text{ }^\circ\text{C}$ higher upper limit than that for PLLA. McNeill et al. and Jamshidi et al. also reported a similar increase in

degradation temperature after the end-acetylation of PLLA [8,15]. A similar stabilization has been reported for the pyrolysis of poly(propylene carbonate)s, which were treated not only with acetic anhydride but also with benzoyl chloride, ethyl silicate, and phosphorous oxychloride. Unfortunately, there was no determination of end-capping structures, nor any information on metal content [24].

In this case, it must be noted that the Sn content also decreased from 437 to 74ppm during the acetylation of the hydroxyl end-groups. We previously reported on the effect of Sn content on the pyrolysis of PLLA, namely that unprotected PLLA samples containing Sn in a range of 20-607 ppm each showed an individual degradation behavior depending on their particular Sn content [20]. For example, PLLA containing 60 ppm of Sn showed about a 50-60 °C higher degradation temperature range (300-365 °C) than that of PLLA containing 485 ppm of Sn (250-310 °C). Thus, the increase in thermal degradation temperature after the acetylation must also result in part from a decrease in Sn content.

To clarify the contribution of acetyl end-protection on the thermal degradation, the influence of residual Sn must be minimized. Thus, in Figure 2, both weight loss profiles of metal free PLLA-H and acetylated metal free PLLA-H/Ac were also plotted. The PLLA-H degraded at the highest temperature, which was about 10 °C greater than that of PLLA-Ac. The profile of PLLA-H/Ac also appeared at nearly the same degradation temperature range to that of PLLA-H. Thus, the acetylation of the hydroxyl end was not found to have an effect when examined by TG analysis.

These results suggest that the effect of acetylation of the hydroxyl ends is in practice due to the removal of Sn compounds in PLLA during the acetylation process, resulting in an increase in pyrolysis temperature, and a consequent, increase in the thermal stability of PLLA.

3.3 Pyrolyzates

Next, the effects of the end-protection were examined by analysis of pyrolyzates from the PLLA samples. Figure 3 shows Py-GC/MS chromatograms of PLLA, PLLA-Ac, PLLA-H, and PLLA-H/Ac evolved in a temperature range of 40-400 °C at a heating rate of 10 °C min⁻¹. All the samples showed two peaks at about 12.5 and 13.8 min in retention time. These peaks have been confirmed to be *meso*- and L,L/D,D-lactides, respectively, by comparing them with the standard substances [25,26]. A series of peaks periodically appearing in groups at 23-35 min represent cyclic oligomers from trimer to nonamer, which are made up of each group of diastereoisomers [11,20,26-28].

[Figure 3. Py-GC/MS chromatograms]

Pyrolysis of PLLA containing 437 ppm of Sn resulted in the formation of dominant L,L-lactide (>96 %) with a very small amount of *meso*-lactide (2.3 %) and cyclic oligomers (0.4 %). This selective L,L-lactide formation agrees with the pyrolysis of PLLA in the previous report, which contained 607 ppm of Sn [20]. In contrast, the chromatogram of pyrolyzates from PLLA-H was

composed of a lot of ingredients, including L,L/D,D-lactide (53.6 %), *meso*-lactide (15.7 %), and cyclic oligomers (30.7 %).

The chromatogram of pyrolyzates from end protected PLLA-Ac comprised of L,L/D,D-lactide (77.3 %) as a main product, *meso*-lactide (20.9 %), and a small amount of cyclic oligomers (1.9 %). The high content of *meso*-lactide implies nucleophilic attacks by carboxyl groups on asymmetric carbons and/or the occurrence of ester-semiacetal tautomerization at temperatures greater than 320 °C [11,25]. The presence of a small amount of oligomers suggests that the residual Sn (74 ppm) is making some contribution to the pyrolysis mechanism of PLLA-Ac [20]. In the case of metal free PLLA-H/Ac, the chromatogram of pyrolyzates showed nearly the same profile as that of PLLA-H, including L,L/D,D-lactide (45.3 %), *meso*-lactide (18.2 %), and cyclic oligomers (36.5 %).

These results indicate that the influence of the end-protection on the pyrolyzates composition is small as compared with that of Sn content.

3.4. Apparent activation energy of thermal degradation

To analyze the influence of end-protection on the thermal degradation kinetics, the thermal degradation of PLLA samples was conducted at various heating rates of 1, 3, 5, 7, and 9 K min⁻¹ in TG. Apparent activation energy, E_a , of the thermal degradation was then estimated from the weight loss data according to a previously published method [29-32]. Figure 4 shows changes in E_a value

during the pyrolysis of PLLA, PLLA-Ac, PLLA-H, and PLLA-H/Ac with changes in the fractional weight, w .

[Figure 4. Changes in E_a value]

The E_a value of PLLA (Sn content: 437 ppm) was relatively constant at 128-130 kJ mol⁻¹ during the whole pyrolysis. This result is comparable with that of unprotected PLLA containing 396 ppm of Sn as reported previously [20]. This small change in E_a value suggests that a simple reaction route covers the whole degradation process. In the case of PLLA-Ac (Sn content: 74 ppm), the E_a value increased continuously from 140 to 160 kJ mol⁻¹ with increase in weight loss. Similar continuous increases in E_a value were found on the pyrolysis of unprotected PLLA containing 60 ppm of Sn, during which the E_a value increased linearly from 124 to 163 kJ mol⁻¹ with decrease in w [20]. Obviously, the E_a change for PLLA-Ac is similar to that of the unprotected PLLA with 60 ppm of Sn content.

In the case of PLLA-H, the E_a value started from about 149 kJ mol⁻¹ and rose up to 176 kJ mol⁻¹ as degradation progressed. These results agreed closely with the previously reported E_a value changes from 141 to 177 kJ mol⁻¹ for purified unprotected PLLA [32]. The E_a value of the end-protected PLLA-H/Ac showed almost the same change as that of PLLA-H, starting at 141 kJ mol⁻¹ and gradually converging at 176 kJ mol⁻¹ with decrease in w .

Thus, the influence of end-protection of PLLA on the E_a value of pyrolysis must be very small

compared to that of Sn content.

3.5 Kinetics and mechanism of thermal degradation

Kinetic parameters of pyrolysis of the PLLA samples were analyzed from the thermogravimetric data. In this study, the well-known integral method and an improved random degradation analytical method were employed to analyze the pyrolysis data [30,31,33,34]. According to our previous studies [20,25,32], it is considered that the thermal degradation of metal free PLLA-H proceeds mainly through the random scission, evolving many kinds of pyrolyzates. And, PLLA with a high Sn content degrades in accordance with a zero-order weight loss process by Sn-catalyzed lactide elimination, producing principally L,L-lactide.

In Figure 5, the improved random degradation analysis plots of $\log[-\log\{1-(1-w)^{1/2}\}]$ vs $1/T$ for PLLA-H/Ac (9 K min^{-1}) and model reactions are illustrated with kinetic parameters, $E_a=176 \text{ kJ mol}^{-1}$, $A=3.5 \times 10^{11} \text{ s}^{-1}$, as compared to the corresponding weight loss curve. To analysis the main degradation route of the random pyrolysis pathway of this metal sample, the plot of 9 Kmin^{-1} was selected in order to minimize the influence of the by-reactions at the initial stage. Obviously, the experimental data plot overlapped on the n th-order reaction plots at the first stage, and shifted on a random degradation plot with $L=4$ in the following stage, where L means the least number of repeating units of oligomer not volatilized [30]. This simulation of PLLA-H/Ac pyrolysis is nearly

the same as that for the PLLA-H pyrolysis without any influence of acetylation.

[Figure 5. PLLA-H/Ac Random degradation method]

Integral method plots of experimental $A\theta$ vs w of PLLA-Ac (5 K min^{-1}) and model reactions with kinetic parameters, $E_a=150 \text{ kJ mol}^{-1}$ and $A=1.7\times 10^{10} \text{ s}^{-1}$, are illustrated in Figure 6. The simulation indicates that the pyrolysis of PLLA-Ac proceeds through at least two processes, i.e., an initial slow degradation process followed by a rapid weight loss process. This is because a random degradation process dominates in the beginning, whereas a zero-order weight loss process dominates in the latter stages. The main mechanism in these mixed processes gradually changes as the degradation progresses. A similar gradually shifting process was found on the pyrolysis of unprotected PLLA sample with Sn content of 60 ppm [20]

[Figure 6. PLLA-Ac Integral method]

It is assumed that a random degradation process occurs in both PLLA-H/Ac and PLLA-Ac pyrolysis. It has been reported that some random degradation processes, such as *cis*-elimination and nucleophilic attacks of hydroxyl and carboxyl ends on electron-poor carbons, occur in the PLLA pyrolysis, generating new chain ends, hydroxyl, carboxyl, and acryl groups [11,25,32]. Though the protection of hydroxyl groups may slow down the degradation process in the beginning, the random scissions caused by carboxyl ends would diminish any influences of the end-protection. The degradation temperature, E_a value, and kinetics of end-protected PLLA-Ac and PLLA-H/Ac imply

that their degradation behaviors are almost the same as those of unprotected PLLAs with corresponding Sn contents.

Thus, unless the degradation process is restricted to one reaction, which was started from hydroxyl ends, the end-protection of hydroxyl ends will be a negligible factor in the total degradation process, compared to other significant factors, such as the Sn content.

4. Conclusion

The treatment of PLLA by acetic anhydride resulted in the acetylation of end hydroxyl groups, and at the same time led the Sn content in the polymer to significantly decrease. The thermal degradation of the acetylated PLLA showed a shift to a higher degradation temperature range than that of untreated PLLA with high Sn content, but showed nearly the same degradation behavior as the untreated PLLA with a comparable Sn content. An extensively purified PLLA, which was free of residual Sn, showed the highest degradation temperature range, even when compared to the end-protected metal-free PLLA. Moreover, pyrolyzate and kinetic analyses of the pyrolysis of end-protected PLLAs indicated that the thermal stabilization of PLLA by the acetic anhydride treatment was mainly due to a decrease in Sn content occurring during the acetylation process.

Acknowledgement

This study was financially supported by Special Coordination Funds of the Ministry of Education, Culture, Sports, Science and Technology, the Japanese Government.

References

- [1] Ikada Y, Tsuji H. Biodegradable polyesters for medical and ecological applications. *Macromol Rapid Commun* 2000;21(3):117-32.
- [2] Amass W, Amass A, Tighe B. A review of biodegradable polymers: Uses, current developments in the synthesis and characterization of biodegradable polyesters, blends of biodegradable polymers and recent advances in biodegradation studies. *Polym Int* 1998;47(2):89-144.
- [3] Anderson JM, Shive MS. Biodegradation and biocompatibility of PLA and PLGA microspheres. *Advan Drug Delivery Rev.* 1997;28 (1):5-24.
- [4] Ajioka M, Enomoto K, Suzuki K, Yamaguchi A. The basic properties of poly (lactic acid) produced by the direct condensation polymerization of lactic acid. *J Environ Polym Degrad* 1995;3(4):225-34.
- [5] Lunt J. Large-scale production, properties and commercial applications of polylactic acid polymers. *Polym Degrad Stab* 1998;59:145-52.
- [6] Eling B, Gogolewski S, Pennings AJ. Biodegradable materials of poly(L-lactic acid): 1. Melt-spun and solution-spun fibres. *Polymer* 1982;23:1587-93.
- [7] Migliaresi C, Cohn D, De Lollis A, Fambri L. Dynamic mechanical and calorimetric analysis of compression-molded PLLA of different molecular weights: Effect of thermal treatments. *J Appl Polym Sci* 1991;43:83-95.
- [8] McNeill IC, Leiper HA. Degradation studies of some polyesters and polycarbonates-1. *Poly lactide: General features of the degradation under programmed heating conditions.* *Polym Degrad Stab* 1985;11:267-85.

- [9] McNeill IC, Leiper HA. Degradation studies of some polyesters and polycarbonates-2. Polylactide: Degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. *Polym Degrad Stab* 1985;11:309-26.
- [10] Kopinke, FD, Mackenzie K. Mechanism aspects of the thermal degradation of poly(lactic acid) and poly (2-hydroxybutyric acid). *J Anal Appl Pyrolysis* 1997;40-41:43-53.
- [11] Kopinke FD, Remmler M, Mackenzie K, Moder M, Wachsen O. Thermal decomposition of biodegradable polyesters-II. Poly (lactic acid). *Polym Degrad Stab* 1996;53:329-42.
- [12] Aoyagi Y, Yamashita K, Doi Y. Thermal degradation of poly[(R)-3-hydroxybutyrate], poly [μ-caprolactone], and poly[(S)-lactide]. *Polym Degrad Stab* 2002;76:53-9.
- [13] Babanalbandi A, Hill DJT, Hunter DS, Kettle L. Thermal stability of poly(lactic acid) before and after ³-radiolysis. *Polym Int* 1999;48:980-4.
- [14] Cam D, Marucci M. Influence of residual monomers and metals on poly (L-lactide) thermal stability. *Polymer* 1997;38:1879-84.
- [15] Jamshidi K, Hyon SH, Ikada Y. Thermal characterization of polylactides. *Polymer* 1988;29:2229-34.
- [16] Södergård A, Näsman JH. Stabilization of poly(L-lactide) in the melt. *Polym Degrad Stab* 1994;46:25-30.
- [17] Wachsen O, Platkowski K, Reichert KH. Thermal degradation of poly-L-lactide – studies on kinetics, modeling and melt stabilization. *Polym Degrad Stab* 1997;57:87-94.
- [18] Degée P, Dubois P, Jérôme R. Bulk polymerization of lactides initiated by aluminium isopropoxide, 3 Thermal stability and viscoelastic properties. *Macromol Chem Phys* 1997;198:1985-95.
- [19] Noda M, Okuyama H. Thermal catalytic depolymerization of poly(L-lactic acid) oligomer into L,L-lactide: Effects of Al, Ti, Zn, and Zr compounds as catalysts. *Chem Pharm Bull* 1999;47:467-71.
- [20] Nishida H, Mori T, Hoshihara S, Fan Y, Shirai Y, Endo T. Effect of tin on poly (L-lactic acid) pyrolysis. *Polym Degrad Stab* 2003;81:515-23.

- [21] Nijenhuis AJ, Grijpma DW, Pennings AJ. Lewis acid catalyzed polymerization of L-lactide. Kinetics and mechanism of the bulk polymerization. *Macromolecules* 1992;25:6419-24.
- [22] Kricheldorf HR, Saunders IK, Boettcher C. Polylactones: 31. Sn(II)octoate-initiated polymerization of L-lactide: a mechanistic study. *Polymer* 1995;36:1253-9.
- [23] Schwach G, Coudane J, Vert M. Zn lactate as initiator of DL-lactide ring opening polymerization and comparison with Sn octoate. *Polym Bull* 1996;37:771-6.
- [24] Peng S, An Y, Chen C, Fei B, Zhuang Y, Dong L. Thermal degradation kinetics of uncapped and end-capped poly (propylene carbonate). *Polym Degrad Stab* 2003;80:141-7.
- [25] Fan Y, Nishida H, Shirai Y, Endo T. Racemization on thermal degradation of poly(L-lactide) with calcium salt end structure. *Polym Degrad Stab* 2003;80:503-11.
- [26] Fan Y, Nishida H, Shirai Y, Endo T. Control of racemization for feedstock recycling of PLLA. *Green Chem* 2003; in press.
- [27] Khabbaz F, Karlsson S, Albertsson AC. Py-GC/MS an effective technique to characterizing of degradation mechanism of poly (L-lactide) in the different environment. *J Appl Polym Sci* 2000;78:2369-78.
- [28] Westphal C, Perrot C, Karlsson S. Py-GC/MS as a means to predict degree of degradation by giving microstructural changes modeled on LDPE and PLA. *Polym Degrad Stab* 2001;73:281-7.
- [29] Doyle CD. Kinetics analysis of thermogravimetric data. *J Appl Polym Sci* 1961;5:285-92.
- [30] Ozawa T. A new method of analyzing thermogravimetric data. *Bull Chem Soc Japan* 1965;38:1881-6.
- [31] Nishida H, Yamashita M, Endo T. Analysis of initial process in pyrolysis of poly (*p*-dioxanone). *Polym Degrad Stab* 2002;78:129-35.
- [32] Fan Y, Nishida H, Hoshihara S, Shirai Y, Tokiwa Y, Endo T. Pyrolysis Kinetics of Poly(L-lactide) with Carboxyl and Calcium Salt End Structures. *Polym Degrad Stab* 2003;79:547-62.
- [33] Flynn JH, Wall LA. General treatment of the thermogravimetry of polymers. *J Res Nat Bur*

Stand 1966;70A:487-523.

- [34] Nishida H, Yamashita M, Hattori N, Endo T, Tokiwa Y. Thermal decomposition of poly(1,4-dioxan-2-one). *Polym Degrad Stab* 2000;70:485-96.

Table 1. PLLA samples prepared with various approaches

Sample	Description	M_n	M_w	Sn(ppm)
PLLA	Precipitated	181,000	305,000	437
PLLA-Ac	Acetylated	165,000	282,000	74
PLLA-H	HCl aq. extracted	186,000	303,000	13.7
PLLA-H/Ac	HCl aq. extracted and acetylated	174,000	295,000	15.1

Figure legends

Scheme 1. Protection of hydroxyl group end of PLLA by acetic anhydride.

Figure 1. ^1H NMR spectra of precipitated oligo(L-lactic acid) (OLLA) and acetylated OLLA-Ac.

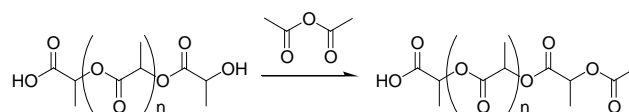
Figure 2. TG curves of PLLA, PLLA-Ac, PLLA-H, and PLLA-H/Ac (5 K min^{-1})

Figure 3. Py-GC/MS (TIC) chromatograms of PLLA, PLLA-Ac, PLLA-H, and PLLA-H/Ac pyrolyzates degraded in the pyrolyzor from 40 to 400°C. GC measurement was conducted through heating the column from 40 to 320 °C.

Figure 4. Apparent E_a values of PLLA, PLLA-Ac, PLLA-H, and PLLA-H/Ac at various residual weight fractions.

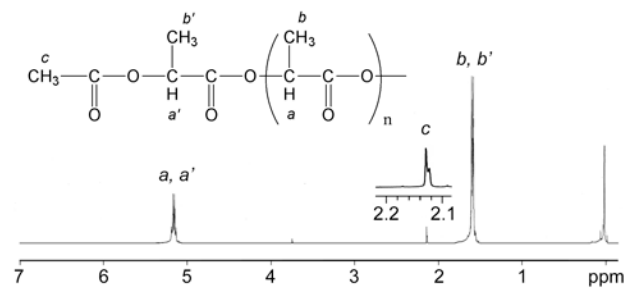
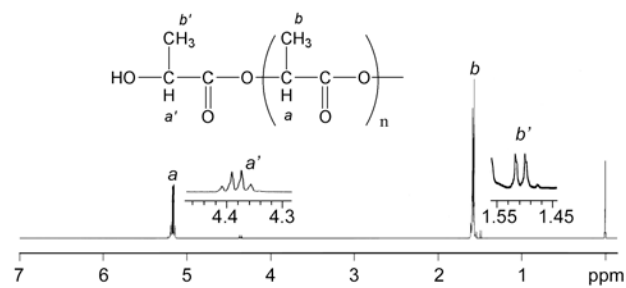
Figure 5. Plots of $\log[-\log\{1-(1-w)^{1/2}\}]$ vs. $1/T$ for thermogravimetric data of PLLA-H/Ac at a heating rate of 9 K min^{-1} ($E_a=176\text{ kJ mol}^{-1}$, $A=3.5\times 10^{11}\text{ s}^{-1}$), and for model reactions. Model reactions: zero ($n=0$), half ($n=0.5$), 1st ($n=1$), and 2nd-order ($n=2$), and random degradations (Random $L=2-4$).

Figure 6. Integral method plots of experimental $(A E_a / \phi R) p(y)$ ($=A \theta$) vs. w of PLLA-Ac at a heating rate 5 K min^{-1} ($E_a=150\text{ kJ mol}^{-1}$ and $A=1.7\times 10^{10}\text{ s}^{-1}$), and $-\int dw / g(w)$ vs. w for model reactions. Model reactions: zero ($n=0$), 1st ($n=1$), and 2nd-order ($n=2$), and random degradations (Random $L=2-4$).



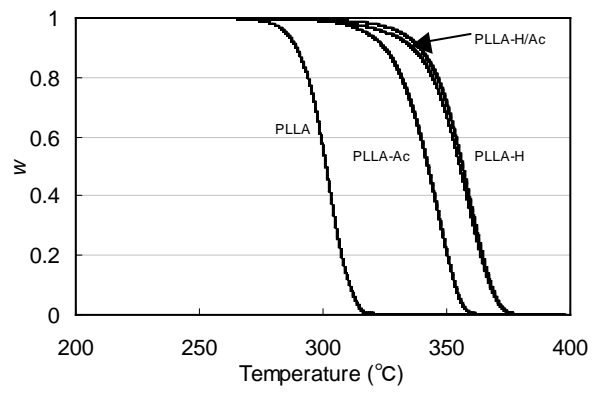
Fan & Nishida

Scheme 1.

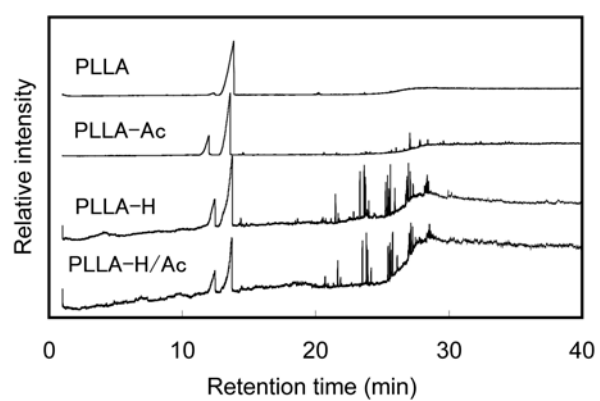


Fan & Nishida

Figure 1

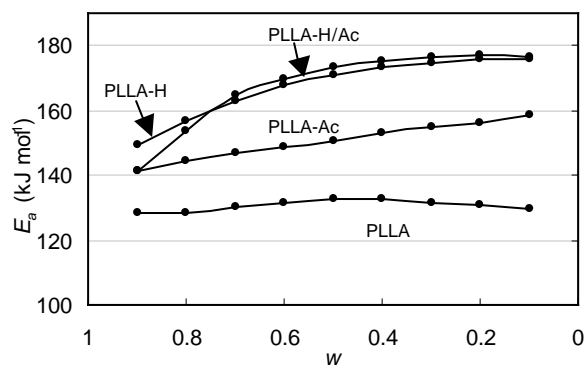


Fan & Nishida
Figure 2

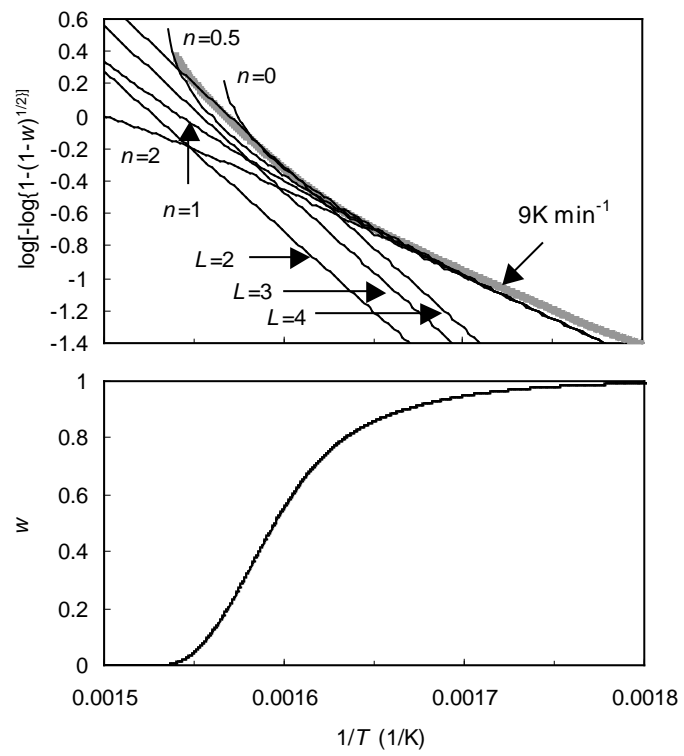


Fan & Nishida

Figure 3.

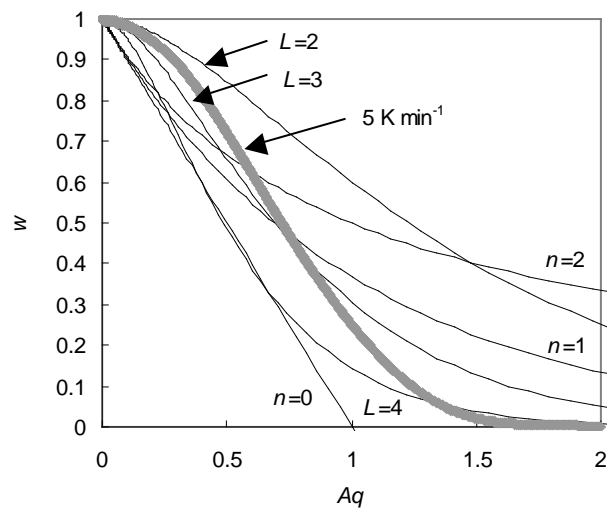


Fan & Nishida
Figure 4



Fan & Nishida

Figure 5.



Fan & Nishida

Figure 6.