

Thermal Catalytic Depolymerization of Poly(L-Lactic Acid) Oligomer into LL-Lactide: Effects of Al, Ti, Zn and Zr Compounds as Catalysts

Masaki NODA* and Hisashi OKUYAMA

Technology Research Laboratory, Shimadzu Corp., 1 Kuwabaracho, Nishinokyo, Nakagyo-ku, Kyoto 604, Japan.

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A series of Al, Ti, Zn and Zr compounds, *i.e.*, their metal alkoxides, organic acid and enolate salts, halid and oxide, were evaluated as intramolecular transesterification catalysts for the thermal depolymerization reaction of poly(L-lactic acid) oligomer resulting in LL-lactide, *meso*-lactide and *DD*-lactide by gas chromatography using a β -cyclodextrin chiral stationary phase capillary column. The activity of the intramolecular transesterification compared with that of stannous 2-ethylhexanoate was in the following order: Sn > Zn > Zr > Ti > Al.

Key words optically active lactide; thermal depolymerization catalyst; poly(L-lactic acid) oligomer

The use of L-lactic acid (L-LA) (**1**) to produce poly(L-lactic acid) (L-PLA) is well known in the medical industry as a biocompatible and biodegradable polymer for applications such as sutures, clamps, boneplates and biologically controlled devices. Recently, problems associated with the incineration of waste have led to the need for the development of truly biodegradable polymers to be utilized as substitutes for non-biodegradable petrochemical-based polymers in packaging, consumer goods, *etc.*¹⁾ The large-scale commercial production of L-PLA for use in non-medical product application should be maximized for yield and minimized for other overall cost factors to compete with low-cost polymers made from petrochemicals.

L-PLA has been conventionally produced by a ring-opening polymerization of LL-lactide (a cyclized dimer of L-LA) (**4a**), which is produced by the thermal depolymerization of a low molecular weight L-PLA oligomer (**2**).²⁾ Recently, the direct polymerization of L-LA has been realized with various Brønsted and Lewis acid catalysts through continuous azeotropic distillation.³⁾ Since L-LA has been produced by a multi-step purification process in the fermentation method, facile efficient purification of L-LA is crucial for producing L-PLA. Thus, the conventional L-PLA production *via* lactide, which can be produced from crude L-LA and is isolated as a purified intermediate, should be one of the efficient methods for producing L-PLA.

LL-Lactide production by thermal depolymerization of the L-PLA oligomer was reported in the presence of catalysts such as stannous 2-ethylhexanoate (Sn(oct)₂)^{4,5)} and Sb₂O₃.^{6,7)} These catalysts have been used in terms of activity and selectivity at the thermal depolymerization of the L-PLA oligomer. However, the reaction residue contains the metal compound used as the catalyst, as well as the unreacted oligomer, together with their decomposed materials. Treatment of the waste products of the residue is a problem in the commercial production of LL-lactide, depending on the toxicity of the catalysts. Studies on the catalysts of thermal depolymerization have not been extensively reported compared with the polymerization catalysts⁸⁾ of lactide to L-PLA. Practical catalysts for large scale lactide production must be investigated. This paper describes the evaluation of homogeneous catalysts such as metal alkoxides, organic acid and enolate salts of metals, and metal halide and oxide, which are less toxic metal compounds than tin compounds, compared with con-

ventionally used stannous 2-ethylhexanoate.⁹⁾

Results

The thermal depolymerization of L-PLA oligomer (**2**) with various catalysts was performed by distillation at 190–245 °C under 4–5 mmHg, in which intramolecular transesterification, *i.e.*, a “back-biting reaction” of the L-PLA oligomer, occurs to give LL-lactide (**4a**). The metals employed as alkoxides, organic acid and enolate salts were Al, Ti, Zn and Zr. These are Lewis acids with mild electrophilicity and are homogeneous catalysts. The distillate of crude LL-lactide (**4a**), accompanied by small amounts of the resulting *meso*-lactide (**4b**) and *DD*-lactide (**4c**) during depolymerization, was analyzed by gas chromatography (GC) using a β -cyclodextrin (CD) chiral stationary phase capillary column. The depolymerization conditions, yields of crude lactide and optically active lactide isomers (**4a**, **4b**, **4c**) are shown in Table 1.

Thermal depolymerization with 1 mol% of aluminum alkoxides and enolate salt (Al(iso-PrO)₃, Al(etic)₃, (AlO(iso-PrO))₃) gave about 40% yield of crude lactide at 190–230 °C for 2 h, and further depolymerization gave 72–75% yields at 230–245 °C for an additional 1 h. Depolymerization

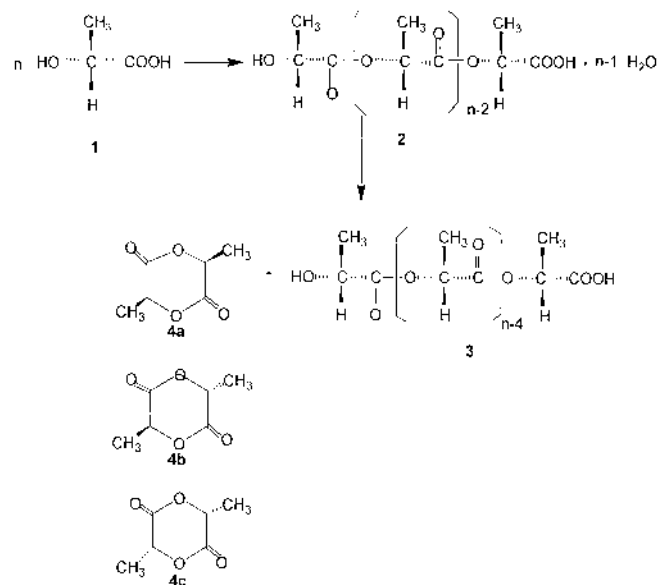


Chart 1

* To whom correspondence should be addressed.

Table 1. LL-Lactide (**4a**), *Meso*-Lactide (**4b**) and *DD*-Lactide (**4c**) Formation in Thermal Depolymerization of L-PLA Oligomer

Entry	Catalyst	Cat./L-PLA oligomer ^{a)} wt % (mol% ^{b)})	Distillation ^{c)} time (min)	Yields (%)	GC analysis of distillate lactide ^{d)}				ee ^{e)} (%)
					LL	DD	<i>meso</i>	by-products	
1	Al(<i>iso</i> -PrO) ₃	2.7 (1)	180 ^{l)}	75.4	78.89	2.14	16.50	1.47	95.40
2	Al(<i>etac</i> ^{f)}) ₃	5.36 (1)	180 ^{l)}	72.5	79.21	2.18	16.41	2.05	95.14
3	Al(<i>etac</i> ^{f)}) ₃	1.13 (0.2)	160 ^{l)}	59.0	87.46	1.10	10.48	0.96	97.52
4	(AlO(<i>iso</i> -PrO)) ₃	4.01 (1)	180 ^{l)}	71.6	78.59	2.98	17.65	0.78	94.52
5	Ti(<i>iso</i> -PrO) ₄	0.77 (0.2)	80	41.9	90.91	0.36	7.18	0.64	99.22
6	Ti(<i>iso</i> -PrO) ₄	3.74 (1)	100	42.7	87.41	0.67	9.16	2.72	98.48
7	Ti(<i>iso</i> -PrO) ₂ (<i>acac</i> ^{j)}) ₂	0.99 (0.2)	80	42.8	91.20	0.33	6.67	1.87	99.28
8	Ti(<i>acac</i> ^{j)}) ₄	1.20 (0.2)	80	43.4	89.62	0.48	8.70	1.20	98.94
9	Ti(OH) ₂ (LA) ₂	0.71 (0.2)	80	46.5	92.83	0.34	5.61	1.23	99.28
10	Zn(<i>hexa</i> ^{g)}) ₂	0.81 (0.2)	140 ^{l)}	76.3	94.70	0.24	2.94	2.13	99.50
11	Zn(<i>hexa</i> ^{g)}) ₂	3.92 (1)	80	86.0	93.58	0.20	3.55	2.68	99.58
12	Zn(<i>stea</i> ^{h)}) ₂	1.70 (0.2)	160 ^{l)}	92.0	93.70	0.16	4.04	2.10	99.66
13	Zn(<i>stea</i> ^{h)}) ₂	7.95 (1)	120	84.9	94.88	0.10	3.60	1.43	99.78
14	Zn(<i>naph</i> ⁱ⁾) ₂	2.19 (0.2)	100 ^{l)}	90.0	93.83	0.20	4.00	1.97	99.16
15	Zn(<i>naph</i> ⁱ⁾) ₂	10.06 (1)	80	87.3	97.38	0	2.14	0.48	100
16	ZnCl ₂	1.83 (1)	80	89.3	95.72	0	2.44	1.13	100
17	Zr(<i>n</i> -PrO) ₄	0.89 (0.2)	120 ^{l)}	77.4	94.41	0.18	4.51	0.90	99.62
18	Zr(<i>n</i> -PrO) ₄	4.92 (1)	100	78.0	89.36	0.74	8.76	1.14	98.36
19	ZrO(<i>stea</i> ^{h)}) ₂	1.82 (0.2)	160 ^{l)}	70.4	96.98	0.14	2.53	0.36	99.72
20	ZrO(<i>stea</i> ^{h)}) ₂	8.42 (1)	120	82.8	92.14	0.60	6.55	0.71	98.70
21	Zr(<i>acac</i> ^{j)}) ₄	1.32 (0.2)	120 ^{l)}	66.4	93.11	0.21	5.42	1.26	99.54
22	Zr(<i>acac</i> ^{j)}) ₄	6.24 (1)	100	84.9	90.83	0.78	8.39	0	98.30
23	Zr(<i>n</i> -BuO) ₃ (<i>acac</i> ^{j)})	11.05 (1)	80	74.0	88.78	0.88	9.21	1.13	98.04
24	Zr(<i>n</i> -BuO) ₃ (<i>acac</i> ^{j)})(<i>etac</i> ^{f)}) ₂	9.97 (1)	100	83.2	90.25	0.76	7.63	1.36	98.32
25	ZrO(AcO) ₂	7.68 (1)	100	72.9	91.58	0.55	7.20	0.66	98.80
26	ZrO(OH) ₂	1.89 (1)	120	50.6	96.47	0	1.66	1.87	100
27	ZrO ₂	1.65 (1)	180	63.8	96.75	0	2.01	1.24	100
28	Sn(<i>oct</i> ^{k)}) ₂	1.09 (0.2)	60	89.3	97.88	0	1.67	0.46	100

a) Mw=1170, L-PLA oligomer consists of 16 units of LA. b) Mole numbers of PLA oligomer were calculated as LA unit constituents. c) At 190–230 °C under 4–5 mm Hg. d) β-CD-stationary phase chiral column (CHROMPACK, CP-cyclodextrin-β-236M-19) was used. e) ee (%) is calculated from **4a** and **4c** values. f) *etac*: ethyl acetoacetate. g) *hexa*: hexanoate. h) *stea*: stearate. i) *naph*: naphthenate, j) *acac*: acetylacetonate. k) *oct*: octoate (2-ethylhexanoate). l) Distillation at 190–245 °C.

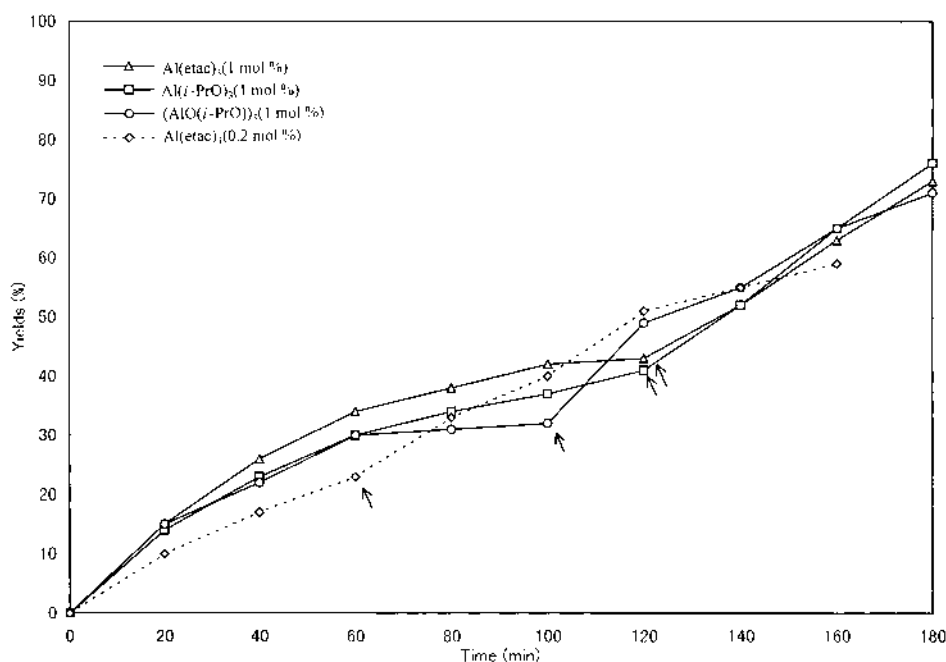


Fig. 1. Lactide Formation by the Thermal Depolymerization of L-PLA Oligomer in the Presence of Organoaluminum Compounds

From the point indicated with an arrow, the reaction was heated at 230–245 °C.

with 0.2 mol% of Al(*etac*)₃ provided a low yield of lactide (59%, at 190–245 °C for 2.7 h) (Fig. 1). The lactide distilled under the depolymerization with 1 mol% of these aluminum compounds contain rather higher yields of **4b** and **4c** (16.4–

17.7% and 2.1–3.0%, respectively). However, 0.2 mol% of Al(*etac*)₃ provided lower yields of **4b** and **4c** (10.5 and 1.1%, respectively) than those of the lactide obtained by the depolymerization with 1 mol% of the catalysts (Table 1, en-

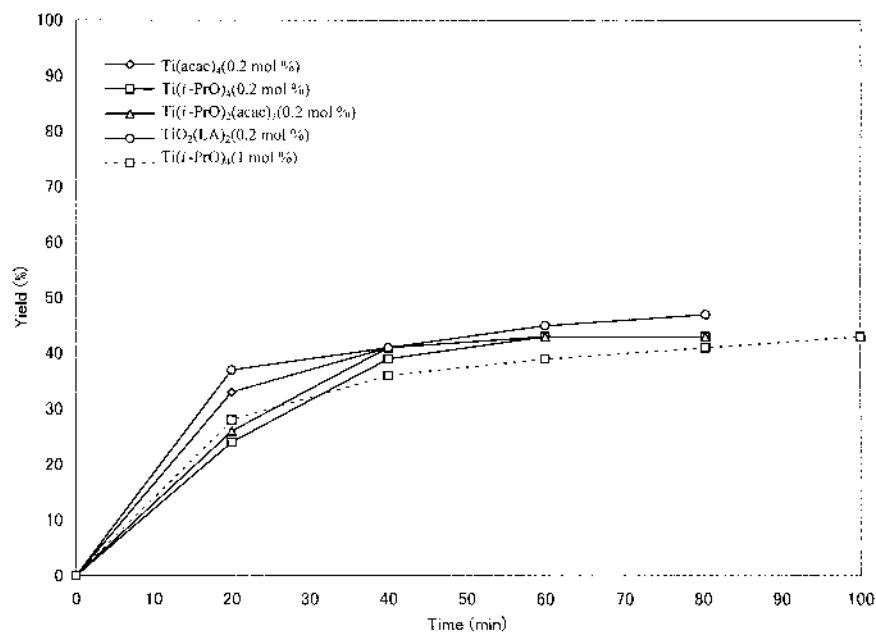


Fig. 2. Lactide Formation by the Thermal Depolymerization of L-PLA Oligomer in the Presence of Organotitanium Compounds

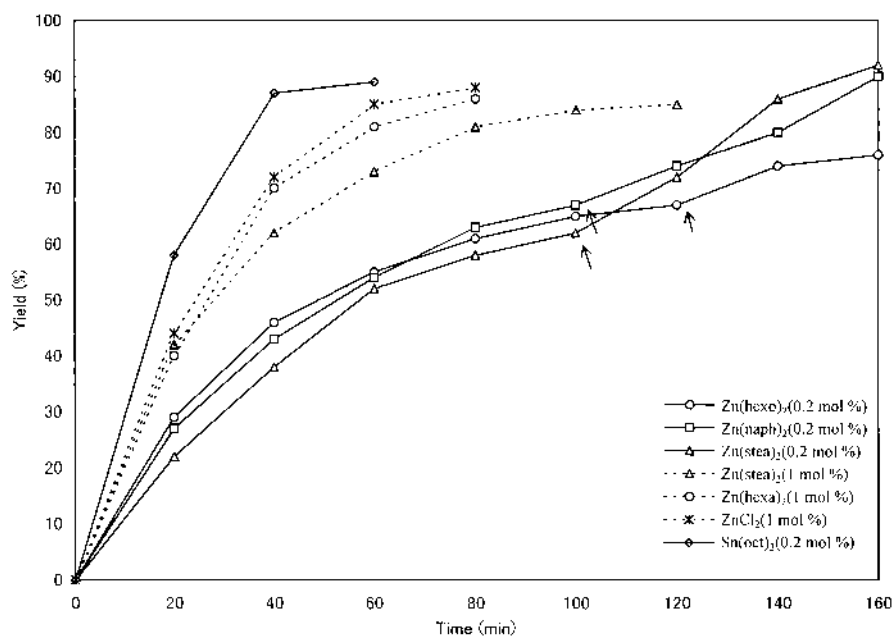


Fig. 3. Lactide Formation by the Thermal Depolymerization of L-PLA Oligomer in the Presence of Organozinc Compounds and Stannous 2-Ethylhexanoate From the point indicated with an arrow, the reaction was heated at 230–245 °C.

tries 1–4).

The results of titanium alkoxides, enolate and acid salts ($\text{Ti}(\text{iso-PrO})_4$, $\text{Ti}(\text{iso-PrO})_2(\text{acac})_2$, $\text{Ti}(\text{acac})_4$, $\text{Ti}(\text{OH})_2(\text{LA})_2$) are shown in Fig. 2 and Table 1, entries 5–9. The depolymerization with 0.2 mol% of the catalysts provided 42–47% of crude lactide at 190–230 °C for 1.3 h. There were no differences in the yields of the lactide depending on the catalyst concentrations (0.2 and 1 mol%), or the alkyl groups of alkoxide, carboxylic acid and enolate of the titanium compounds. These catalysts have the activity of the back-biting reaction of the L-PLA oligomer with low concentrations of the catalysts (0.2 mol%), as well as strong activity of polymerization of the oligomer resulting in a higher molecular weight of L-PLA. The yields of **4b** and **4c** were 5.6–9.2 and

0.3–0.7%, respectively.

Organic acid salts of zinc (hexanoate, stearate and naphthenate) and zinc chloride were evaluated (Fig. 3, Table 1, entries 10–16). Depolymerization with the acid salts of zinc (0.2 mol%) gave 67–72% yields of lactide at 190–230 °C for 2 h, and further reaction gave a 76–92% yield at 230–245 °C. The depolymerization with $\text{Zn}(\text{hexa})_2$ and ZnCl_2 (1 mol%) provided an 85–87% yield of lactide at 190–230 °C for 1.3 h, and the reaction with $\text{Zn}(\text{stea})_2$ (1 mol%) gave 85% yield at 190–230 °C for 2 h, respectively. The results of ZnCl_2 provided almost the same yield of lactide as that of $\text{Zn}(\text{hexa})_2$. The crude lactide obtained from the depolymerization with zinc compounds (1 mol%) contained **4b** (2.1–3.6%) and **4c** (0–0.2%), respectively. However, the depoly-

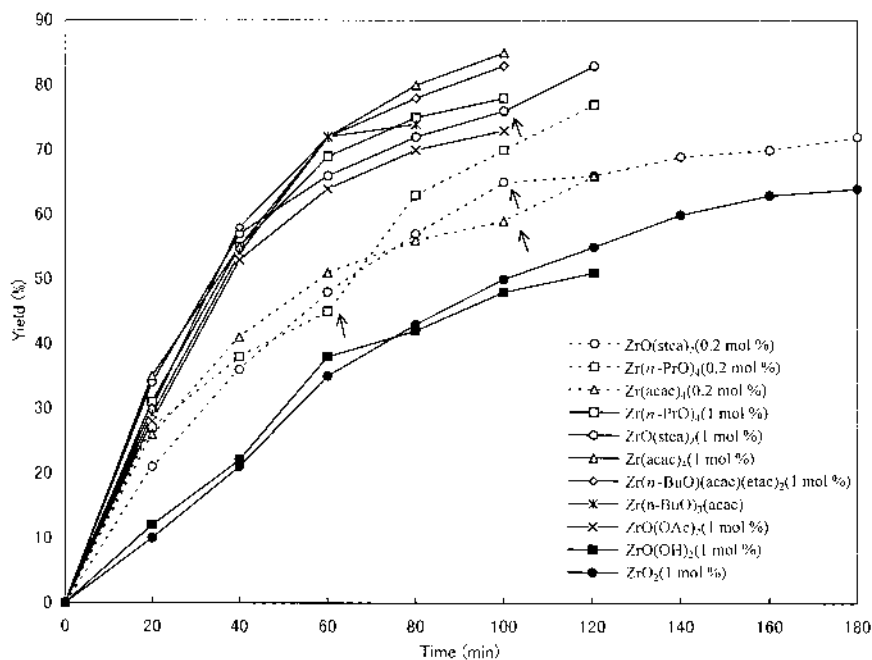


Fig. 4. Lactide Formation by the Thermal Depolymerization of L-PLA Oligomer in the Presence of Zirconium Compounds
From the point indicated with an arrow, the reaction was heated at 230–245 °C.

merization with low concentrations of the zinc compounds (0.2 mol%) afforded rather higher yields of **4b** and **4c** (2.9–4.0%, and 0.2%, respectively). Zirconium alkoxides, enolates ($Zr(n\text{-PrO})_4$, $Zr(\text{acac})_4$, $Zr(n\text{-BuO})_3(\text{acac})$, $Zr(n\text{-BuO})(\text{acac})(\text{etac})_2$), zirconyl stearate ($Zr\text{O}(\text{stea})_2$), zirconyl acetate ($Zr\text{O}(\text{AcO})_2$), zirconyl hydroxide ($Zr\text{O}(\text{OH})_2$) and zirconium oxide ($Zr\text{O}_2$) were evaluated (Fig. 4, Table 1, entries 17–27). Depolymerization with 0.2% mole of zirconium compounds ($Zr(n\text{-PrO})_4$, $Zr(\text{acac})_4$, $Zr\text{O}(\text{stea})_2$) provided a 66–77% yield of lactide at 190–245 °C for 2 h. The reaction with 1 mol% of the zirconium catalysts, except zirconyl hydroxide and zirconium oxide, under the same depolymerization conditions gave a 78–85% yield of lactide. Depolymerization with zirconyl hydroxide (1 mol%) and zirconium oxide (1 mol%) provided 51–55% yields of lactide for 2 h, which are lower yields than those from the other zirconium compounds. The yields of **4b** and **4c** in the case of the 1 mol% of the catalysts were 6.6–9.2% and 0.6–0.9%, respectively, and in the case of 0.2 mol% of the catalysts, 2.5–5.4% and 0.1–0.2%, respectively.

Depolymerization with stannous 2-ethylhexanoate (0.2 mol%) most efficiently provided 89% yield of lactide at 190–230 °C for 1 h (Fig. 3). The yields of **4b** and **4c** were 1.7% and 0%, respectively (Table 1, entry 28).

Discussion

The focus of this research has been to evaluate metal compounds for developing practical catalysts for the large-scale commercial production of lactide. It is well known that thermal depolymerization of the L-PLA oligomer gave **4a** via intramolecular transesterification, *i.e.*, a back-biting reaction. It is also well known that metal alkoxides such as aluminium isopropoxide,¹⁰ titanium¹¹) or zirconium propoxides are good transesterification catalysts under conditions used for the technical production of polyesters. Metal alkoxide compounds with free *d* or *p* orbitals react as coordination (or

complexation) initiators. Due to these factors, our investigation centered on Al, Ti, Zn and Zr compounds as intramolecular transesterification catalysts.

The main trend of the results of aluminum alkoxides and enolate salt was that the depolymerization of the L-PLA oligomer needed a higher temperature and a longer time to produce lactide, which contains rather higher yields of **4b** and **4c**. These results indicate that the aluminum compounds are the least reactive catalysts in intramolecular transesterification.¹²)

Evaluation of the titanium compounds revealed that the lactide was produced at a low concentration of the catalysts (0.2 mol%), but these catalysts also caused an acceleration of polymerization of the L-PLA oligomer. The results indicate that these titanium compounds are good transesterification catalysts, so that the yields of lactide were low. In the patent literature,⁷) depolymerization with titanium alkoxides gave more good yields of lactide distilled under 1–2 mmHg. When using the titanium compounds, the lactide yields could be increased under strictly low-pressure distillation.

On the other hand, the zinc and the zirconium compounds, except zirconium hydroxide and zirconium oxide, are relatively reactive catalysts in the intramolecular transesterification and produce lactide in good yield. A higher concentration (1 mol%), the zinc compounds provided slightly higher yields of lactide than the zirconium compounds. Concerning the constituents of optically active lactides, the yields of **4b** and **4c** derived from the zinc compounds (1 mol%) were smaller (2.1–3.6% and 0–0.2%, respectively) than those from zirconium compounds (6.6–9.2% and 0.6–0.9%, respectively). These results indicate that the zinc compounds afford better desired results than zirconium compounds. In spite of the increased heat and time needed for the complete depolymerization with a low concentration (0.2 mol%) of the zirconium catalysts, the constituents of **4b** and **4c** of the dis-

tillate were lower (2.5–5.4% and 0.1–0.2%, respectively) than those obtained from the reaction with 1 mol% of the catalysts. The same results were observed, except for the zinc compounds, when using a lower concentration (0.2%) of the metal catalysts. There are no big differences in lactide yields depending on the alkyl groups of metal alkoxides, carboxylic acid salts of metal, and metal ligands in these homogeneous catalysts. However, the zirconium oxide and zirconium hydroxide of heterogeneous catalysts afforded low yields of lactide.

The results obtained from the zinc compounds are compared with conventionally used stannous 2-ethylhexanoate. The low concentration (0.2 mol%) of stannous 2-ethylhexanoate provided a slightly greater activity of lactide formation than those from 1 mol% of zinc hexanoate and zinc chloride. The formation of **4b** and **4c** provided from stannous 2-ethylhexanoate was lower (1.7% and 0%) than those of zinc compounds (2.9% and 0.24%). These results indicate that the activity of stannous 2-ethylhexanoate in the intramolecular transesterification of the thermal depolymerization of the L-PLA oligomer is more than five times greater than that provided by the zinc compounds.

In conclusion, Al, Ti, Zn, and Zr compounds were evaluated compared with conventionally used stannous 2-ethylhexanoate as intramolecular transesterification catalysts in the thermal depolymerization of L-PLA oligomer. The first step of their reaction is the complexation of L-PLA oligomer at the carbonyl oxygen with coordination initiators of these metal catalysts. The next step is ring cyclization followed by cleavage of the acyl-oxygen bond of the L-PLA oligomer. Optical and chemical yields of the lactide are dependent on the coordination activity of the catalysts. The intramolecular transesterification activity of the metal compounds is in the following order: Sn > Zn > Zr > Ti > Al. The aluminum and titanium compounds did not yield the desired results. In spite of the low lactide producing activity of the zinc compounds and zirconium compounds compared with that of stannous 2-ethylhexanoate, some of these cheap catalysts could be used as economical catalysts to produce non-toxic waste products of the reaction residue.

Experimental

Materials L-Lactic acid (90 wt %, L-lactic acid content: 98–99%) was purchased from Purac Biochem Co. (Holland). L-PLA oligomer (Mw = 1170) was produced by 90 wt % L-lactic acid by heating for 3 h at 135–160 °C under reduced pressure (50–30 mmHg). The weight-average molecular weight (Mw) of the L-PLA oligomer was determined by gel permeation chromatography (GPC) on a Shimpack (GPC-801C×2, GPC-802.5×2: 300×8 mm) at a flow rate of 1 ml/min in CHCl₃ at 40 °C.

Al(iso-PrO)₃; aluminum tri-isopropoxide (AIPD), Al(etc)₃; aluminum tris(ethylacetoacetate) (ALCH-TR), and (AlO-(iso-PrO))₃; cyclic aluminum oxide isopropoxide (Algomer) were supplied by Kawaken Fine Chemicals (Tokyo, Japan). Zn(hexa)₂; zinc hexanoate, Zn(stea)₂; zinc stearate and Zn(naph)₂; zinc naphthenate were supplied by Toei Chemical Industry Co., Ltd. (Osaka, Japan). Ti(iso-PrO)₄; titanium isopropoxide (TA-10), Ti(iso-PrO)₂(acac)₂; titanium di-isopropoxide bis(acetylacetonate) (TC-100), Ti(acac)₄; titanium tetrakis(acetylacetonate) (TC-401), Ti(OH)₂(LA)₂; titanium dihydroxide bis(lactate) (TC-310), Zr(*n*-PrO)₄; zirconium tetrakis(*n*-propoxide) (ZA-40), Zr(acac)₄; zirconium tetrakis(acetylacetonate) (ZC-150), Zr(*n*-BuO)₃(acac); zirconium tri-*n*-butoxide acetylacetonate (ZC-540), and Zr(*n*-BuO)(acac)(etc)₂; zirconium *n*-butoxide bis(ethylacetoacetate)acetylacetonate (ZC-570) were supplied by Matsumoto Trading Co., Ltd. (Tokyo, Japan). ZrO(stea)₂; zirconyl stearate (noricon 113 M), ZrO(AcO)₂; zirconyl acetate, and ZnO₂; zirconium oxide were supplied by Shinnippon Kinzokukogyo Co., Ltd. (Osaka, Japan). Sn(oct)₂; (stannous 2-

ethylhexanoate) (neostatin U-28) was supplied by Nitou Kasei Co., Ltd. (Osaka, Japan).

General Procedure of Thermal Depolymerization of L-PLA Oligomer Into a 300 ml three-necked flask equipped with a mechanical stirrer, a thermometer and a Vigreux distillation column (15×250 mm) were placed the L-PLA oligomer (50 g, 2.73 mol of lactic acid unit, calculated from the oligomer (Mw: 1170) consisting of 16 units of LA) and a catalyst (0.2–1 mol% of lactic acid unit). The mixture was heated and distilled at 190–230 °C with stirring under reduced pressure (4–5 mmHg). When more heat was needed for the depolymerization, the reaction mixture was heated at 230–245 °C, then distilled. The condenser was heated by circulating hot water (about 80 °C) to prevent crystallization of the distillate from sticking. The distillate was collected at a temperature above 110 °C and analyzed by GC with a capillary column. Yields of optically active lactide isomers are listed in Table I.

GC conditions GC was performed on a Shimadzu GC 9AM using a β -cyclodextrin (CD) chiral stationary phase capillary column (CHROMPACK, CP-cyclodextrin- β -236M-19, 0.52 mm i.d.×50 m, df=0.25 μ m) purchased from Hewlett-Packard Co. Analytical conditions: carrier He gas (2.5 kg/cm²), make-up He gas (50 ml/min), air (0.8 kg/cm²), column temp. (150 °C), inject temp. (250 °C), FID detector.

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