

Effect of Exogenous Carboxyl and Hydroxyl Groups on Pyrolysis Reaction of High Molecular Weight Poly(L-Lactide) under the Catalysis of Tin

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Electronic Supplementary Information

Abstract The effect of exogenous hydroxyl, carboxyl groups and/or Sn^{2+} on pyrolysis reactions of poly(L-lactide) (PLLA) was investigated by thermogravimetric analysis (TGA). The activation energy (E_a) of pyrolysis reactions was estimated by the Kissinger-Akahira-Sunose method. The kinetic models were also explored by the Malek method, and the random degradation behavior was determined by comparing the plots of $\ln\{-\ln[1 - (1 - w)^{0.5}]\}$ versus $1/T$ for experimental data from TGA with model reactions. The pyrolysis reaction rate of PLLA was affected slightly by exogenous hydroxyl and carboxyl groups at lower levels of Sn with $65\text{--}70\text{ mg}\cdot\text{kg}^{-1}$ but increased appreciably in the presence of extraneous Sn^{2+} , $-\text{COOH}/\text{Sn}^{2+}$, or $-\text{OH}/\text{Sn}^{2+}$. The E_a values for the pyrolysis reactions of the PLLAs that provided lactide were different under the catalysis of Sn^{2+} in different chemical environments because Sn^{2+} can form the new Sn-carboxylate and Sn-alkoxide with exogenous carboxyl and hydroxyl groups, which were different in steric hindrance for the formation of activated complex between Sn^{2+} and PLLA. Under the catalysis of Sn^{2+} , a lactide molecule can be directly eliminated selectively at a random position of PLLA molecular chains, and the molecular chain of PLLA cannot change two PLLA fragments at the elimination site of lactide. However, it was regenerated into a new PLLA molecule with the molecular weight reduced by $144\text{ g}\cdot\text{mol}^{-1}$.

Keywords Poly(L-lactide); Pyrolysis mechanism; Carboxyl group; Hydroxyl group; Tin

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INTRODUCTION

Poly(lactic acid) (polylactide, PLA), as a well-known biodegradable polymer, has wide applications in the fields of medical, pharmaceutical and environmentally-friendly polymeric materials. High molecular weight PLA is usually prepared by the ring-opening polymerization of L-, D-, and meso-lactides. The ring-opening polymerization is a reversible reaction, so the content of lactide monomer is temperature-dependent.^[1] Therefore, the thermal depolymerization of PLA can also regenerate lactides. The actual thermal degradation of PLA involves a complex reaction process in relation to the pyrolysis conditions and can be enhanced in the presence of active groups, active chain end-groups, residual monomers, residual catalysts, inorganic/organic fillers, plasticizers, H_2O and other impurities. Furthermore, in addition to lactide as the main product, the thermal degradation of PLA can generate linear

and cyclic oligomers, diastereoisomers of the oligomers, CO , CO_2 , methylketene and acetaldehyde.^[2–5] The thermal depolymerization or stability of PLA is an extensive concern because of its direct relevance to production, processing, application, thermal recycling and complete life cycle.^[6–8]

Several techniques have been used to improve the thermal stability of PLA.^[9] For example, residual monomers are strictly removed after polymerization;^[10] active $-\text{OH}$ end-groups are capped with anhydrides or isocyanates;^[11,12] some stabilizers such as phosphites (*i.e.*, tris(nonylphenyl) phosphite (TNPP) and triphenyl phosphite (TPP)), epoxides (*i.e.*, JONCRYL®ADR-4370-S, BASF), and carbodiimide are used;^[9,13–15] PLA resin is dried strictly to remove moisture since PLA, as a type of aliphatic polyester, is sensitive to moisture.^[16]

The thermal degradation of PLA has been investigated by many technologies, such as thermogravimetric analysis (TGA), gel permeation chromatography (GPC),^[6,8,17] TGA/Fourier transform infrared spectroscopy (TGA-FTIR),^[18,19] and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS).^[7,19,20] The pyrolysis process of PLA has been proved as random main chain scission and unzipping depolymerization reac-

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tions. The random degradation reaction involves hydrolysis, oxidative degradation, *cis*-elimination, and intra-/inter-molecular transesterification.^[21] The unzipping depolymerization reaction mainly involves a selective elimination reaction for lactide under the catalysis, such as Sn^{2+} .^[3,22,23] The degradation behavior is different between pure and Sn-containing PLLAs,^[3] and is affected by other compounds of metals, such as Sn, Zn, Al and Fe.^[24] The TGA curves of poly(L-lactide) (PLLA)-Sn samples with an increase in Sn content shift to a lower degradation temperature range, and a decrease in activation energy is observed.^[23] The pyrolysis reaction of PLA results in molecular weight reduction by random scissions of molecular chains^[25,26] and in weight-loss by release of volatile products.

In the present work, we investigated the effect of exogenous hydroxyl, carboxyl groups, and/or Sn^{2+} on the pyrolysis reaction of PLLA. Exogenous hydroxyl, carboxyl groups, and/or Sn^{2+} were introduced into high-molecular-weight PLLA matrix by solution blending. These PLLAs were depolymerized by TGA to obtain the kinetic parameters and mechanism of the pyrolysis reaction, that is, the high-molecular-weight PLLA provided lactide in the presence of $-\text{COOH}$, $-\text{OH}$, and/or Sn^{2+} .

EXPERIMENTAL

Instruments and Materials

TGA was conducted on a TA instrument TGA-Q50. A Ni standard reference was used for the temperature correction of TGA. The nitrogen flow rate was $40.0 \text{ mL}\cdot\text{min}^{-1}$ through the balance and $60.0 \text{ mL}\cdot\text{min}^{-1}$ over the sample. The mass of the loaded sample was 4–6 mg in a platinum pan. Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (XSERIES 2, Thermo Fisher Scientific, US) was used to quantify the Sn content in the samples. The sample was decomposed with HNO_3 (65 wt%) in a sealed microwave digestion vessel at 120°C for 6 h and then used to determine the Sn content. The high-molecular-weight PLLA (Revode 190, Optical purity 99.5%) was obtained from Zhejiang Hisun Biomaterials Co., Ltd., Taizhou, Zhejiang, China. The number-average, weight-average molecular weights (M_n , M_w), and molecular weight polydispersity index (PDI) of the polymer are $M_n=84.1 \text{ kg}\cdot\text{mol}^{-1}$, $M_w=155.9 \text{ kg}\cdot\text{mol}^{-1}$, and $\text{PDI}=1.85$, respectively. Stannous octanoate ($\text{Sn}(\text{Oct})_2$, 95%) and stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) (STA, 98%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Poly(ethylene glycol) (PEG-600) (CP) with di-hydroxyl end-groups was produced from Xilong Scientific Co., Ltd. (Guangdong, China). Dichloromethane (AR) was made in China and used directly without further purification.

Procedures

The PLLA films, including the raw PLLA, PLLA($-\text{COOH}$), PLLA($-\text{OH}$), PLLA(Sn^{2+}), PLLA($-\text{COOH}$, Sn^{2+}) and PLLA($-\text{OH}$, Sn^{2+}) films, were prepared by the solution blending of high-molecular-weight PLLA with a small amount of PEG-600, STA, and/or $\text{Sn}(\text{Oct})_2$ using dichloromethane as solvent. The solvent in the samples was carefully evaporated, and then the obtained PLLA films were dried at 100°C for 4 h under vacuum, and then

used for TGA. As for the raw PLLA, the contents of original hydroxyl and carboxyl groups are less than $10 \text{ mmol}\cdot\text{kg}^{-1}$. The contents of exogenous carboxyl groups are $100 \text{ mmol}\cdot\text{kg}^{-1}$ for PLLA($-\text{COOH}$) and PLLA($-\text{COOH}$, Sn^{2+}). The contents of exogenous hydroxyl groups are $100 \text{ mmol}\cdot\text{kg}^{-1}$ for PLLA($-\text{OH}$) and PLLA($-\text{OH}$, Sn^{2+}), and the Sn contents are 65, 70, 68, 349, 368 and $380 \text{ mg}\cdot\text{kg}^{-1}$ for raw PLLA, PLLA($-\text{COOH}$), PLLA($-\text{OH}$), PLLA(Sn^{2+}), PLLA($-\text{COOH}$, Sn^{2+}) and PLLA($-\text{OH}$, Sn^{2+}), respectively. The PLLA films were thermally depolymerized by TGA. The samples were equilibrated at 120°C isothermally for 3 min, and then heated to 450°C at different rates, including 5, 7, 10, 15, 20 and $30^\circ\text{C}\cdot\text{min}^{-1}$.

These samples, including $\text{Sn}(\text{Oct})_2$, STA, PEG-600, $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7, W/W), and $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7, W/W), were also used for TGA at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature to 450°C . $\text{Sn}(\text{Oct})_2$, STA, and PEG-600 were directly tested, but the $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7, W/W) and the $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7, W/W) blends were initially heated at 100°C in an oven to form a homogeneous mixture, and then the hot mixture was rapidly placed into a platinum pan for TGA.

Methods

Kinetic parameters

The kinetic parameters, including activation energy (E_a) and pre-exponential factor ($\lg A$), of the pyrolysis reactions of PLLAs were calculated by the Kissinger-Akahira-Sunose (KAS) method,^[22,27,28] as shown in Eq. (1). The relationship between $\ln\left(\frac{\beta}{T^2}\right)$ and $1/T$ is a straight line at a certain conversion (α) for a set of TG curves at different heating rates (β), and the values of E_a and A are obtained from the slope $\left(-\frac{E_a}{R}\right)$ and the intercept $\left(\ln\left(\frac{AR}{E_a}\right)\right)$ of this straight line regardless of the mechanism function of the pyrolysis reaction.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT} \quad (1)$$

where β is the heating rate ($\text{K}\cdot\text{min}^{-1}$), A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature (K).

Mechanism model

The Malek method^[22,29–34] was used to explore the most probable mechanism model of pyrolysis reactions, as shown in Eqs. (2) and (3). The most probable kinetic model functions $f(\alpha)$ and $G(\alpha)$ can be inferred by comparing the shapes of $y_{\text{Exp}}(\alpha)$ and $y_{\text{Std}}(\alpha)$.

$$y_{\text{Std}}(\alpha) = \frac{f(\alpha) \cdot G(\alpha)}{f(0.5) \cdot G(0.5)} \quad (2)$$

$$y_{\text{Exp}}(\alpha) = \left(\frac{T}{T_{0.5}}\right)^2 \frac{da/dT}{(da/dT)_{0.5}} \quad (3)$$

where $y_{\text{Std}}(\alpha)$ and $y_{\text{Exp}}(\alpha)$ are the standard model function and the experimental curve; α is the fractional conversion; T and da/dT are the absolute temperature (K) and the temperature differential; $f(\alpha)$ and $G(\alpha)$ are the differential and integral forms for the most probable mechanism functions; $T_{0.5}$, $(da/dT)_{0.5}$, $f(0.5)$, and $G(0.5)$ are the values of the absolute temperature,

the temperature differential, the differential, and integral forms of the most probable mechanism functions at $\alpha=0.5$ as the reference point.

Random scission kinetic analysis

Random scission behavior was determined by the plots of $\ln\{-\ln[1 - (1 - w)^{0.5}]\}$ versus $1/T$ for model reactions and experimental data from TGA for polymers in the initial stage of the pyrolysis reactions ($w=0.99-0.85$) according to the reference.^[22] In the equation, w and T are the residual weight fraction and the absolute temperature (K), respectively.

RESULTS AND DISCUSSION

Reactions of $\text{Sn}(\text{Oct})_2$ with Hydroxyl and Carboxyl Groups

The volatility of 2-ethylhexanoic acid (Oct) is far higher than that of STA, since the boiling point of Oct is far lower than that of STA, which are 228 and 383 °C at 101.325 kPa, respectively. PEG is a non-volatile polymer. In the heating process, the double decomposition reactions of $\text{Sn}(\text{Oct})_2$ with the carboxyl and hydroxyl groups of STA and PEG-600 can occur and thus form Sn-carboxylate and Sn-alkoxide, as well as Oct released in the form of gas at high temperatures, as shown in Fig. 1. The reactions were further confirmed using TGA. The TG thermograms of $\text{Sn}(\text{Oct})_2$, STA, PEG-600, $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7) and $\text{Sn}(\text{Oct})_2/\text{PEG}$ -600 (3/7) are shown in Fig. 2. In the main stage of

thermal weight-loss, the weight-loss temperature for STA was higher than that for $\text{Sn}(\text{Oct})_2$ and lower than that for PEG-600 at an identical percentage of weight-loss. In the heating process, the weight-loss was mainly due to the volatilization and decomposition for $\text{Sn}(\text{Oct})_2$, the volatilization for STA, and the decomposition for PEG-600. However, the shape of the TG curves for the blends of $\text{Sn}(\text{Oct})_2$ with STA or PEG-600 can testify the reactions between the blending components. The weight-loss temperatures of the $\text{Sn}(\text{Oct})_2/\text{PEG}$ -600 (3/7) blend or the $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7) blend were between $\text{Sn}(\text{Oct})_2$ and PEG-600 or STA in the initial period of the TG curves but were higher than those for PEG-600 or STA in the middle and later period of the TG curves. The weight-loss temperatures of TG curves for the binary blends were higher than those for any component, indicating that the two components can react to form new products, which were more difficult to volatilize or decompose at higher temperatures. Therefore, the Sn-carboxylate (Oct-Sn-STA and $\text{Sn}(\text{STA})_2$) and the Sn-alkoxide (Oct-Sn-PEG , SnPEG , PEG-Sn-PEG and $(\text{SnPEG})_m$) can be produced through the reactions of $\text{Sn}(\text{Oct})_2$ with STA and PEG at high temperatures (Fig. 1). These Sn salts were more difficult to volatilize or decompose than $\text{Sn}(\text{Oct})_2$.

The thermal weight-loss properties of $\text{Sn}(\text{Oct})_2$, STA, PEG-600, the $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7) blend and the $\text{Sn}(\text{Oct})_2/\text{PEG}$ -600 (3/7) blend are shown in Table 1. The Sn-alkoxide can be produced through the reaction of PEG with $\text{Sn}(\text{Oct})_2$, and the mo-

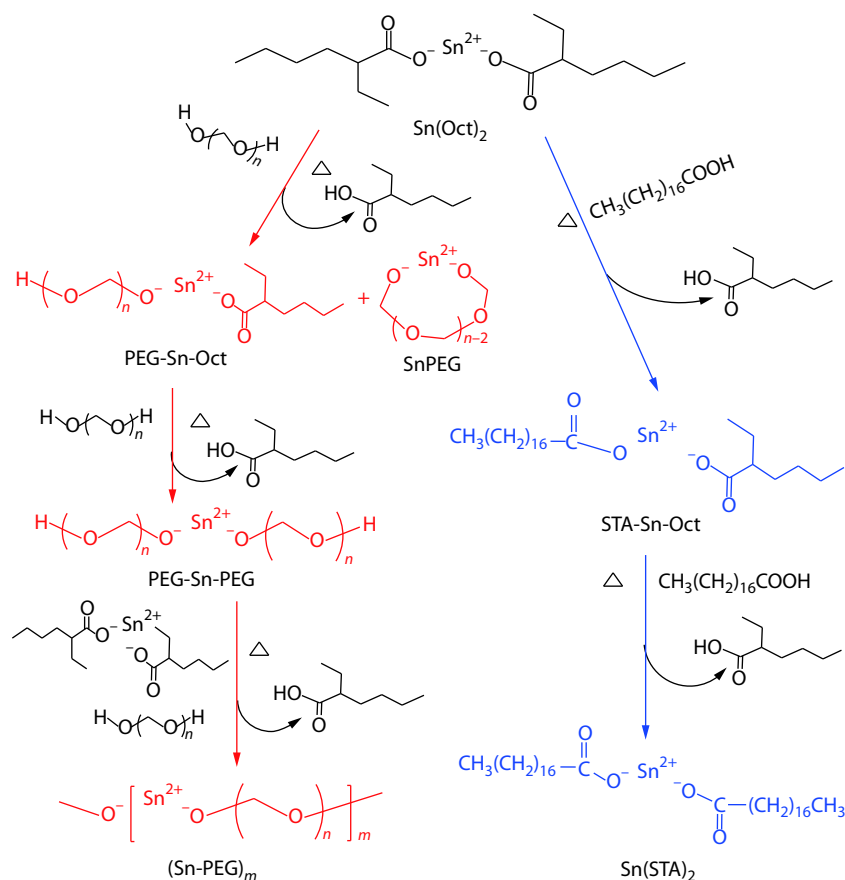


Fig. 1 Possible reactions of $\text{Sn}(\text{Oct})_2$ with hydroxyl and carboxyl groups for PEG and STA.

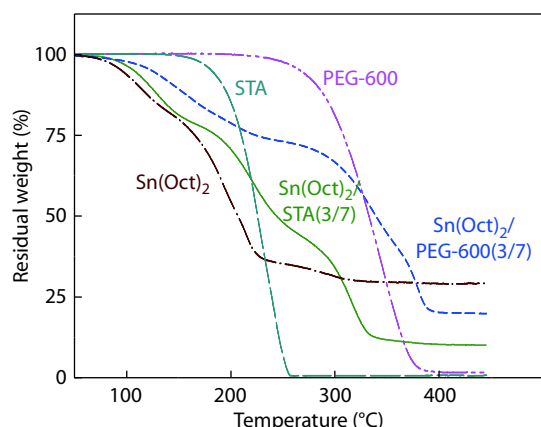


Fig. 2 TG thermograms of $\text{Sn}(\text{Oct})_2$, STA, PEG-600, $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7, W/W), and $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7, W/W) at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

Table 1 Thermal weight-loss properties for $\text{Sn}(\text{Oct})_2$, STA, PEG-600, $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7), and $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7) at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

Sample	Thermal weight-loss temperatures ($^\circ\text{C}$)			Residue (wt%, at 425°C)
	$T_{5\%}$	$T_{50\%}$	T_{max} (onset)	
$\text{Sn}(\text{Oct})_2$	95.1	206.5	313.5	29.1
STA	181.4	225.3	254.9	0.61
PEG-600	266.7	332.2	375.8	1.62
$\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7)	107.3	243.7	332.1	10.2
$\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7)	124.2	338.9	389.0	20.0

lecular chains of PEG can breakdown to produce volatile small molecular fragments at high temperatures under the catalysis of Sn^{2+} . The residual percentages are 29.1 wt%, 0.61 wt%, 1.62 wt%, 10.2 wt% and 20.0 wt% for $\text{Sn}(\text{Oct})_2$, STA, PEG-600, $\text{Sn}(\text{Oct})_2/\text{STA}$ (3/7) blend and $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7) blend respectively, at 425°C . These data indicated that the thermal chemical reaction of $\text{Sn}(\text{Oct})_2$ and PEG-600 was complicated and that the coking and carbonization of the $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7) blend were relatively significant, thus the residual percentage reached 20 wt% for the $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ (3/7) blend at 425°C . Regardless of the products obtained from the reaction of $\text{Sn}(\text{Oct})_2$ and PEG-600, one or several stable Sn salts were formed in the heating process of the $\text{Sn}(\text{Oct})_2/\text{PEG-600}$ blend, thereby effectively inhibiting the volatilization loss of Sn^{2+} at high temperatures.

Pyrolysis Reaction of PLLA

This work aimed to study the pyrolysis process and mechanism of selective lactide elimination for high-molecular-weight PLLA under the catalysis of Sn^{2+} , and to study the effect of extraneous $-\text{OH}$ and $-\text{COOH}$ on the pyrolysis reaction. These PLLAs contained Sn in the range of 65–380 $\text{mg}\cdot\text{kg}^{-1}$, and thus they showed a preceding selective depolymerization step, which produced lactide exclusively according to previous research work.^[3,22,35]

The thermogravimetric and derivative thermogravimetric (TG/DTG) curves are shown in Fig. 3, and the thermal decomposition properties are shown for PLLAs with extraneous $-\text{OH}$, $-\text{COOH}$, and/or Sn^{2+} in Table 2. Compared with raw PLLA, the initial thermal decomposition temperature reduced slightly for $\text{PLLA}(-\text{COOH})$ and $\text{PLLA}(-\text{OH})$ with merely extraneous $-\text{COOH}$ and $-\text{OH}$. However, at the middle and later stages ($\alpha \geq 0.20$), thermal decomposition properties were consistent for raw PLLA, $\text{PLLA}(-\text{COOH})$ and $\text{PLLA}(-\text{OH})$, because their TG/DTG curves coincided roughly. Nevertheless, the thermal decomposition temperature decreased considerably for the PLLAs with higher Sn contents of 349–380 $\text{mg}\cdot\text{kg}^{-1}$, including $\text{PLLA}(\text{Sn}^{2+})$, $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ and $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$, compared with the corresponding PLLAs without extraneous Sn^{2+} , including raw PLLA, $\text{PLLA}(-\text{COOH})$, and $\text{PLLA}(-\text{OH})$. In the starting pyrolysis reaction stage, for the PLLAs with extraneous Sn^{2+} , the temperature for 5% weight-loss ($T_{5\%}$) decreased in the order $\text{PLLA}(\text{Sn}^{2+}) > \text{PLLA}(-\text{OH}, \text{Sn}^{2+}) > \text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$. However, in the main pyrolysis reaction stage, the temperature for 50% weight-loss ($T_{50\%}$) decreased in the order $\text{PLLA}(\text{Sn}^{2+}) > \text{PLLA}(-\text{COOH}, \text{Sn}^{2+}) > \text{PLLA}(-\text{OH}, \text{Sn}^{2+})$. These phenomena indicated that at

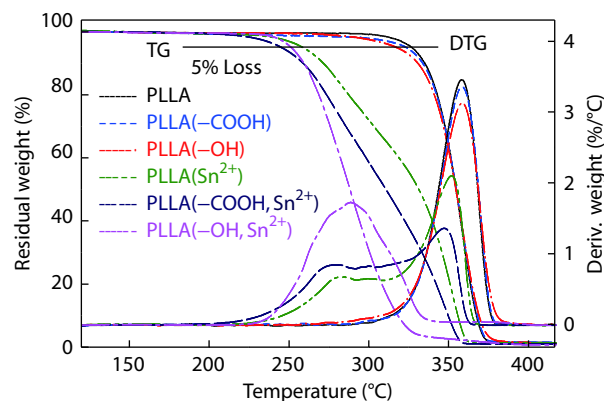


Fig. 3 TG/DTG thermograms of PLLAs with extraneous $-\text{OH}$, $-\text{COOH}$, and/or Sn^{2+} at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

Table 2 Thermal-decomposition properties for PLLAs with extraneous $-\text{OH}$, $-\text{COOH}$, and/or Sn^{2+} at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

Sample	Sn ($\text{mg}\cdot\text{kg}^{-1}$)	Extraneous $-\text{OH}/-\text{COOH}^*$		Thermal decomposition temperatures ($^\circ\text{C}$)			Residue (wt%, at 425°C)
		$\text{mmol}\cdot\text{kg}^{-1}$	wt%	$T_{5\%}$	$T_{50\%}$	T_{max} (onset)	
Raw PLLA	65	—	—	326.8	354.4	369.4	1.31
$\text{PLLA}(-\text{COOH})$	70	100	2.8	323.3	354.5	370.2	1.47
$\text{PLLA}(-\text{OH})$	68	100	3.0	317.3	354.3	371.5	1.18
$\text{PLLA}(\text{Sn}^{2+})$	349	—	—	257.1	330.7	360.0	0.98
$\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$	368	100	2.8	245.2	310.4	356.1	0.94
$\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$	380	100	3.0	251.2	287.9	314.7	0.72

* $\text{PLLA}(-\text{OH})$ and $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$ contained only extraneous $-\text{OH}$, whereas $\text{PLLA}(-\text{COOH})$ and $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ contained only extraneous $-\text{COOH}$.

lower Sn levels of 65–70 mg·kg⁻¹, exogenous hydroxyl and carboxyl groups can slightly affect the reaction rate of PLLA thermal decomposition. However, the pyrolysis reaction rate of PLLA increased appreciably in the presence of extraneous Sn²⁺, —COOH/Sn²⁺, or —OH/Sn²⁺. According to the DTG curves, PLLA(Sn²⁺) and PLLA(—COOH, Sn²⁺) contained at least two steps of decomposition, given that the double or multiple peaks of DTG curves appeared evidently, but the decomposition process was relatively simple for raw PLLA, PLLA(—COOH), PLLA(—OH) and PLLA(—OH, Sn²⁺) due to the single peak of DTG curves.

The thermal analysis kinetics for PLLAs was evaluated by the KAS method. The TG thermograms of the PLLAs with exogenous —OH, —COOH and/or Sn²⁺ at different heating rates are shown in Fig. S1 (in the electronic supplementary information, ESI). The relationships of E_a and lg A versus α of the pyrolysis reactions for these PLLAs are shown in Fig. 4. The evaluation plots for E_a and the relationships of lg A versus α are shown in Figs. S2–S7 (in ESI) and Fig. S8 (in ESI). The E_a values of the thermal degradation of the PLLAs with exogenous —OH, —COOH, and/or Sn²⁺ varied in the range of 65–160 kJ·mol⁻¹ at $\alpha=0.05$ –0.95, which were consistent with the reported E_a values (70–270 kJ·mol⁻¹).^[3,8,23,36–38] The E_a values of the thermal degradation of the PLLAs decreased in the order of PLLA(—COOH)>PLLA>PLLA(—OH)>PLLA(Sn²⁺)≈PLLA(—OH, Sn²⁺)>PLLA(—COOH, Sn²⁺) at the initial stage ($\alpha=0.05$ –0.10), PLLA(—COOH)>PLLA(—OH)>PLLA>PLLA(Sn²⁺)>PLLA(—OH, Sn²⁺)>PLLA(—COOH, Sn²⁺) at the intermediate stage ($\alpha=0.40$ –0.70), and PLLA(—COOH)≈PLLA(—OH)>PLLA>PLLA(Sn²⁺)>PLLA(—COOH, Sn²⁺)>PLLA(—OH, Sn²⁺) at the later stage ($\alpha=0.50$ –0.95).

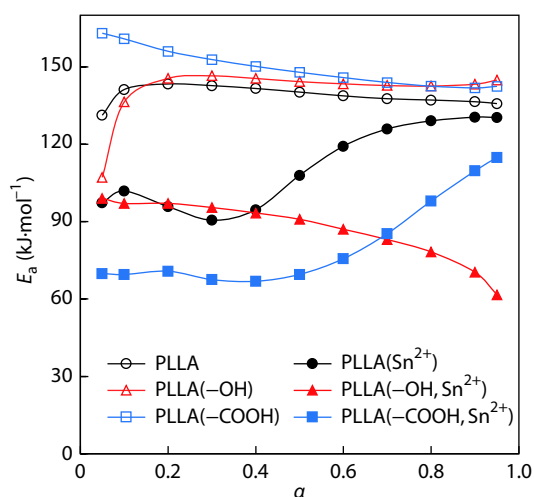


Fig. 4 Relationship of E_a versus α of pyrolysis reactions for PLLAs containing exogenous —COOH, —OH, and/or Sn²⁺ by the KAS method.

In our previous work,^[22] we found that the low-molecular-weight PLAs (L-PLA) containing merely carboxyl or hydroxyl end-groups (R-L-PLA-COOH with $M_w=13.6$ kg·mol⁻¹ or R-L-PLA-OH with $M_w=18.8$ kg·mol⁻¹) had an approximately identical E_a value of pyrolysis reactions at a certain conver-

sion for $\alpha=0.1$ –0.40 under the catalysis of Sn²⁺ (497 and 461 mg·kg⁻¹). R-L-PLA-COOH and R-L-PLA-OH can form Sn-carboxylate and Sn-alkoxide chain-ends. Thus, the pyrolysis reaction of the L-PLAs can selectively produce lactide through the backbiting reaction caused by the Sn-carboxylate and Sn-alkoxide chain-ends. The E_a values were equal for the pyrolysis reactions that PLA selectively produce lactide through backbiting reactions from the carboxyl and hydroxyl end-groups. In the present work, the exogenous —OH, —COOH, and/or Sn²⁺ from PEG-600, STA, and/or Sn(Oct)₂ were introduced into the PLLA matrix, and the formed Sn-carboxylate and Sn-alkoxide were located outside the molecular chains of PLLAs. Thus, they can produce different effects on the pyrolysis reaction of PLLA, compared with those located at the chain-ends of PLLAs.

For raw PLLA, PLLA(—COOH), and PLLA(—OH) with lower Sn levels of 65–70 mg·kg⁻¹, the E_a values of pyrolysis reactions decreased in the order of PLLA(—COOH)>PLLA>PLLA(—OH) at the initial stage ($\alpha=0.05$ –0.10) because the Sn²⁺ was located at the end of the PLLA molecular chains (PLLA-O-CO-CH(CH₃)-O-Sn-X), and the depolymerization of PLLA primarily occurred through the backbiting reaction. The —COOH introduced from STA could snatch Sn²⁺ located at the end of the PLLA molecular chains and generate a small amount of STA-Sn-X. Then, STA-Sn-X formed an activated complex transition state with PLLA. Finally, the depolymerization of PLLA occurred, slightly increasing the pyrolysis activation energy. The —OH introduced from PEG can also snatch Sn²⁺ located at the end of the PLLA molecular chains and generate PEG-Sn-X, but the snatching Sn²⁺ competitiveness for —OH was weaker than that for —COOH. Thus, the generated trace PEG-Sn-X had no significant effect on the activation energy of thermal degradation. The reduced activation energy of PLLA(—OH) with PEG content of 100 mmol·kg⁻¹ (3.0 wt%) was primarily due to the pyrolysis effect of PEG in PLLA. $T_{50\%}$ s of PEG and PLLA are 266.7 and 326.8 °C, respectively (Tables 1 and 2), and thus PEG could decompose at lower temperature than PLLA. The activation energy of PEG should be further lower than that of PLLA, thus might reducing the activation energy of pyrolysis reaction of PLLA(—OH).

For PLLA(Sn²⁺), PLLA(—COOH, Sn²⁺) and PLLA(—OH, Sn²⁺), the chemical environment of Sn²⁺ was located as follows: Sn(Oct)₂, Sn(Oct)₂/Oct-Sn-STA/Sn(STA)₂ and Sn(Oct)₂/Oct-Sn-PEG/SnPEG/PEG-Sn-PEG/(SnPEG)_m (Fig. 1). In the early stage of pyrolysis, the produced Oct-Sn-PEG, SnPEG, PEG-Sn-PEG, and (SnPEG)_m were very little for PLLA(—OH, Sn²⁺), which had no evident effect on the activation energy. In addition, $T_{50\%}$ of PLLA(—OH, Sn²⁺) was 251.2 °C, less than that of PEG (266.7 °C), so the pyrolysis of PEG (3 wt%) has little contribution to the E_a values of the blend. Therefore, PLLA(Sn²⁺) and PLLA(—OH, Sn²⁺) had approximately identical E_a values at the initial stage of pyrolysis. The initial activation energy for PLLA(—COOH, Sn²⁺) was relatively lower than that of PLLA(Sn²⁺), because Oct in Sn(Oct)₂ contained the α -substituted branched structure, which could produce a steric hindrance to the formation of activated complex between Sn²⁺ and PLLA. However, in the presence of STA, Sn(Oct)₂ could be partially converted into Oct-Sn-STA and Sn(STA)₂.

STA is a linear molecule, and the generated Oct-Sn-STA and Sn(STA)_2 could reduce the steric hindrance to the formation of activated complex between Sn^{2+} and PLLA. Therefore, the activation energy of pyrolysis reaction was much lower for $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ than that for $\text{PLLA}(\text{Sn}^{2+})$. In the later stage of pyrolysis reaction, the loss of Sn^{2+} in $\text{PLLA}(\text{Sn}^{2+})$ and $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ increased with increasing temperature. Thus, the activation energy increased in the later stage of the reaction. However, the loss of Sn^{2+} in $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$ was the lowest because the formed Oct-Sn-PEG, SnPEG, PEG-Sn-PEG and $(\text{SnPEG})_m$ were more difficult to volatilize and decompose. Moreover, PEG has no branched structure, and the steric hindrance to the formation of activated complex between Sn^{2+} and PLLA was lower for Oct-Sn-PEG, SnPEG, PEG-Sn-PEG, and $(\text{SnPEG})_m$ than that for $\text{Sn}(\text{Oct})_2$; thus, the activation energy decreased.

Pyrolysis Kinetic Model

PLA can selectively produce lactide under the catalysis of Sn^{2+} , and the most probable kinetic model can be identified by the Malek method. The plots of the standard model functions for common kinetic models, $y_{\text{Std}}(a)$, and the experimental curves, $y_{\text{Exp}}(a)$, versus conversion (a) for PLLAs are shown in Fig. 5. The differential and integral forms [$f(a)$ and $G(a)$] of the common mechanism models for pyrolysis processes are shown in the supplementary data of the reference.^[22] When a pyrolysis process can be described by a single kinetic model, $y_{\text{Exp}}(a)$ should be overlapped with $y_{\text{Std}}(a)$. However, when a pyrolysis process is controlled by two or multiple mechanism functions, the experimental curve must deviate from any standard model function. $y_{\text{Exp}}(a)$ for raw PLLA, $\text{PLLA}(-\text{COOH})$, and $\text{PLLA}(-\text{OH})$ overlapped roughly with $y_{\text{Std}}(a)$ of Nos. 10–20 at $a < 0.95$. However, $y_{\text{Exp}}(a)$ for $\text{PLLA}(\text{Sn}^{2+})$, $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$, and $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$ was away from all the standard model functions. These phenomena indicated that the pyrolysis processes of PLLA, $\text{PLLA}(-\text{COOH})$ and $\text{PLLA}(-\text{OH})$ with the Sn

content of $65\text{--}70 \text{ mg}\cdot\text{kg}^{-1}$ tended to be described by a single kinetic model. However, the pyrolysis processes of $\text{PLLA}(\text{Sn}^{2+})$, $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ and $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$ with the Sn content of $349\text{--}380 \text{ mg}\cdot\text{kg}^{-1}$ must be controlled by not less than two processes. For $\text{PLLA}(\text{Sn}^{2+})$, $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ and $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$, the initial Sn contents were very high, and in the pyrolysis processes, the Sn contents evidently decreased with temperature due to the volatilization of $\text{Sn}(\text{Oct})_2$ (boiling point 228°C at 101.325 kPa). Moreover, the Sn^{2+} in the PLLAs had different losses due to the different volatility of Sn^{2+} under different chemical environments. According to the previous section, the reduction in Sn content was maximum for $\text{PLLA}(\text{Sn}^{2+})$ and minimum for $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$. Thus, the pyrolysis mechanism and processes were more complicated in the later stage of the decomposed reactions for $\text{PLLA}(\text{Sn}^{2+})$, $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ and $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$. However, the pyrolysis processes were unaffected in the initial stage of the reactions, so the pyrolysis mechanism could be investigated for the polymers in the presence of Sn^{2+} , $-\text{COOH}/\text{Sn}^{2+}$, and $-\text{OH}/\text{Sn}^{2+}$.

Evaluation of Random Scission

The cleavage of bonds in random scission processes and the n^{th} -order model reactions (half-, zero-, first-, and second-order reactions) of PLLA were evaluated using the plots of $\ln\{-\ln[1 - (1 - w)^{0.5}]\}$ versus $1/T$ for the experimental data from TG with model reactions, as shown in Fig. 6. For random degradation, the least number of repeating units of the residual polymer (L) should be variable for the model simulations.^[39] Compared with the model reactions, the degradation behavior of these PLLAs did not present an n^{th} order ($n=0.5, 0, 1$, and 2) weight-loss process and a random scission process ($L=2\text{--}10$) in the initial stage ($w=0.99\text{--}0.85$). Therefore, the random main-chain scission for raw PLLA, $\text{PLLA}(-\text{COOH})$, $\text{PLLA}(-\text{OH})$, $\text{PLLA}(\text{Sn}^{2+})$, $\text{PLLA}(-\text{OH}, \text{Sn}^{2+})$ and $\text{PLLA}(-\text{COOH}, \text{Sn}^{2+})$ did not occur in the initial pyrolysis stage. Therefore, under the catalysis

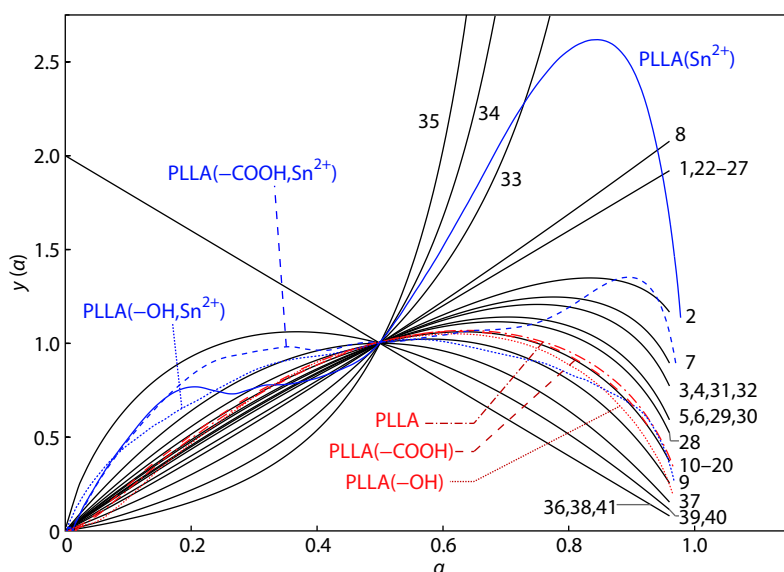


Fig. 5 Standard model functions for common kinetic models and the experimental curves versus a for PLLAs obtained from TG data at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$.

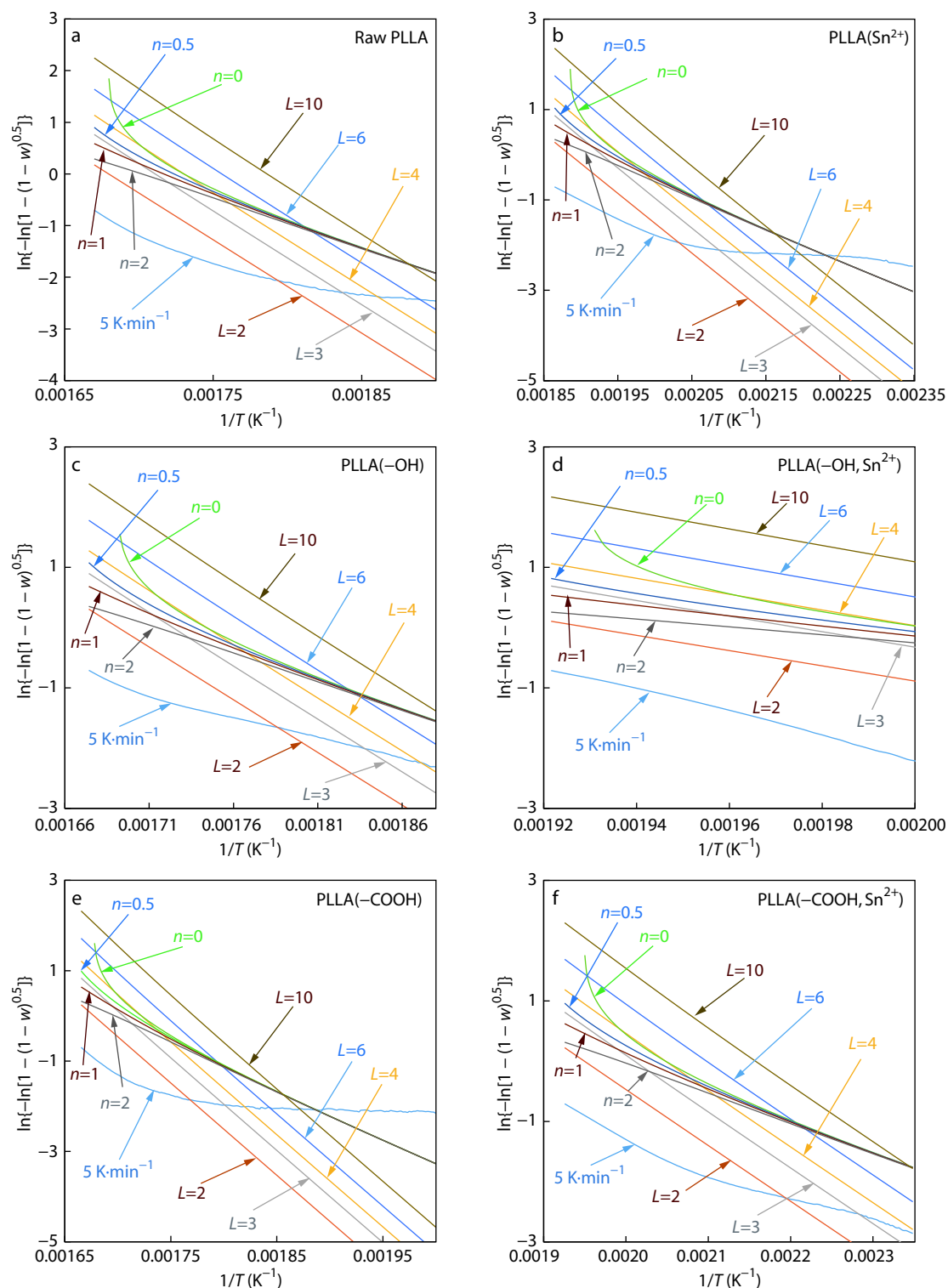


Fig. 6 Plots of $\ln\{-\ln[1 - (1 - w)^{0.5}]\}$ versus $1/T$ for TGA data of PLLAs with $w=0.99-0.85$ at $\beta=5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and model reactions with kinetic parameters at $w=0.90$: (a) $E_a=141.2\text{ kJ}\cdot\text{mol}^{-1}$ and $A=6.24\times 10^{11}\text{ min}^{-1}$ for raw PLLA, (b) $E_a=101.8\text{ kJ}\cdot\text{mol}^{-1}$ and $A=2.52\times 10^9\text{ min}^{-1}$ for PLLA(Sn^{2+}), (c) $E_a=136.4\text{ kJ}\cdot\text{mol}^{-1}$ and $A=2.81\times 10^{11}\text{ min}^{-1}$ for PLLA($-\text{OH}$), (d) $E_a=97.1\text{ kJ}\cdot\text{mol}^{-1}$ and $A=1.43\times 10^9\text{ min}^{-1}$ for PLLA($-\text{OH}, \text{Sn}^{2+}$), (e) $E_a=160.9\text{ kJ}\cdot\text{mol}^{-1}$ and $A=3.58\times 10^{13}\text{ min}^{-1}$ for PLLA($-\text{COOH}$), and (f) $E_a=69.5\text{ kJ}\cdot\text{mol}^{-1}$ and $A=2.12\times 10^6\text{ min}^{-1}$ for PLLA($-\text{COOH}, \text{Sn}^{2+}$).

of Sn^{2+} , an activated complex center could be formed between PLLA and Sn^{2+} , a lactide molecule was eliminated selectively at a random position of PLLA molecular chains, and the PLLA

molecular chain was not broken but regenerated into forming a new PLLA with the molecular weight reduced by $144\text{ g}\cdot\text{mol}^{-1}$ (molecular weight of lactide).

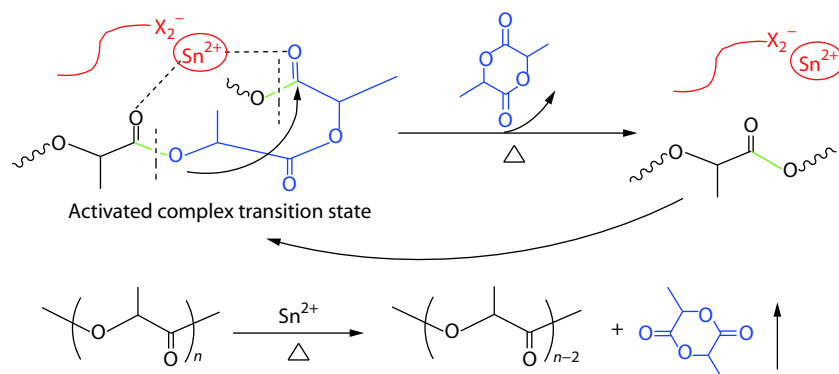


Fig. 7 Possible pyrolysis mechanism of high-molecular-weight polylactide for producing lactide under the catalysis of Sn^{2+} .

Mechanism of PLLA Pyrolysis

Under the catalysis of Sn^{2+} , PLLA can be decomposed for producing lactide. According to previous research results, PLLA can form Sn-carboxylate and Sn-alkoxide from the PLLA molecular chain end-groups. Thus, it can continuously generate lactide through the backbiting reaction or directly eliminate a lactide molecule at a random position of PLLA molecular chains. However, to this day, when a lactide molecule is eliminated directly at a random position of PLLA molecular chains, whether the molecular chains of PLLA were broken remains unknown. We found that after the selective lactide elimination at a random position of PLLA molecular chains, the molecular chain of PLLA could neither break nor form two PLLA fragments at the elimination site of lactide but could be regenerated into a new PLLA molecule with the molecular weight reduced by $144 \text{ g}\cdot\text{mol}^{-1}$ (molecular weight of lactide), as shown in Fig. 7.

CONCLUSIONS

Exogenous hydroxyl, carboxyl groups, and/or Sn^{2+} were introduced into high-molecular-weight PLLA by solution blending with PEG-600, STA, and/or $\text{Sn}(\text{Oct})_2$. Thus, the obtained PLLA films, including raw PLLA, PLLA(–COOH), PLLA(–OH), PLLA(Sn^{2+}), PLLA(–COOH, Sn^{2+}) and PLLA(–OH, Sn^{2+}), were depolymerized by TGA to obtain the kinetic parameters and mechanism of the pyrolysis reaction in which high-molecular-weight PLLA provided lactide in the presence of exogenous –COOH, –OH, and/or Sn^{2+} . The pyrolysis reaction rate of PLLA was affected slightly by exogenous hydroxyl and carboxyl groups at lower Sn levels of $65\text{--}70 \text{ mg}\cdot\text{kg}^{-1}$, but increased appreciably in the presence of extraneous Sn^{2+} , –COOH/ Sn^{2+} , or –OH/ Sn^{2+} (Sn contents of $349\text{--}380 \text{ mg}\cdot\text{kg}^{-1}$). The E_a values for the pyrolysis reactions of the PLLAs with higher Sn^{2+} contents decreased appreciably, compared with those with lower Sn^{2+} contents. The E_a values for the pyrolysis reactions of the PLLAs with higher Sn^{2+} contents differed with each other because the newly formed Sn-carboxylate (Oct-Sn-STA and $\text{Sn}(\text{STA})_2$) and Sn-alkoxide (Oct-Sn-PEG, SnPEG, PEG-Sn-PEG and $(\text{SnPEG})_m$) with the exogenous carboxyl (STA) and hydroxyl (PEG) groups were different in steric hindrance for the formation of activated complex between Sn^{2+} and PLLA. In the early stage of pyrolysis, PLLA(Sn^{2+}) and PLLA(–OH, Sn^{2+}) had approximately identical E_a values, given that the produced Oct-Sn-PEG,

SnPEG, PEG-Sn-PEG, and $(\text{SnPEG})_m$ were very little for PLLA(–OH, Sn^{2+}) and had little effect on the activation energy. However, the E_a value was much lower for PLLA(–COOH, Sn^{2+}) than that for PLLA(Sn^{2+}) because Oct in $\text{Sn}(\text{Oct})_2$ contained the α -substituted branched structure, which could produce the steric hindrance to the formation of activated complex between Sn^{2+} and PLLA. However, in the presence of STA, $\text{Sn}(\text{Oct})_2$ could be partially converted into Oct-Sn-STA and $\text{Sn}(\text{STA})_2$, thereby reducing the steric hindrance to the formation of activated complex between Sn^{2+} and PLLA. The pyrolysis processes of PLLA, PLLA(–COOH), and PLLA(–OH) with lower Sn levels of $65\text{--}70 \text{ mg}\cdot\text{kg}^{-1}$ tended to be described by a single kinetic model. However, the pyrolysis mechanism and processes of PLLA(Sn^{2+}), PLLA(–COOH, Sn^{2+}), and PLLA(–OH, Sn^{2+}) with higher Sn contents of $349\text{--}380 \text{ mg}\cdot\text{kg}^{-1}$ were complicated in the later stage of the decomposed reactions because Sn^{2+} had significant losses when heated. Under the catalysis of Sn^{2+} , a lactide molecule can be directly eliminated selectively at a random position of PLLA molecular chains. In addition, the molecular chain of PLLA cannot form two PLLA fragments at the elimination site for lactide but was regenerated into a new PLLA molecule with the molecular weight reduced by $144 \text{ g}\cdot\text{mol}^{-1}$.

Electronic Supplementary Information

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