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Thermal degradation of poly(lactic acid) oligomer: Reaction mechanism and multistep kinetic behavior

Nao Kameno [a], Shuto Yamada [b], Tomoko Amimoto [c], Kiichi Amimoto [a], Hirohito Ikeda [d], Nobuyoshi Koga [a, *]

[a] *Department of Science Education, Graduate School of Education, Hiroshima University, 1-1-1 Kagamiyama, Higashi-Hiroshima 739-8524, Japan*
[b] *Department of Applied Chemistry, National Defense Academy of Japan, 1-10-20 Hashirimizu, Yokosuka 239-8686, Japan*
[c] *Natural Science Center for Basic Research and Development, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan*
[d] *Faculty of Pharmaceutical Sciences, Fukuoka University, 8-19-1 Nanakuma, Jonan-Ku, Fukuoka 814-0180, Japan*

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ABSTRACT

This study was aimed to reveal the kinetic and mechanistic features of the thermal degradation of linear poly(lactic acid) oligomer (PLAO) by analyzing the evolved gases and overall rate behavior during mass-loss processes. The thermal degradation reaction involved two partially overlapping mass-loss steps. The first mass-loss step started right after the reactant melted and was accompanied with the release of lactides as the main gaseous products while maintaining the microscopic appearance of molten PLAO. The mass-loss rate behavior was controlled by a diffusion process with an apparent activation energy (E_a) of approximately 90 kJ mol^{-1}, with the diffusional transfer of lactides from the reaction sites to the top surface of the molten PLAO being considered as the rate-limiting step. The second mass-loss step became noticeable at reacting system temperatures above the boiling point of lactides. During this dramatically accelerated mass-loss step, carbon oxides, aldehydes, lactides, and cyclic PLAO with large molecular weights were simultaneously evolved with frequent formation and disappearance of gaseous bubbles in the molten reacting system. In this step, the overall rate behavior was largely influenced by the bubbling phenomena for which the E_a value was determined to be approximately 155 kJ mol^{-1}. The changes in the chemical mechanism and the physico-geometrical reaction behavior midway through the thermal degradation reaction were both illustrated by the change in the molten reacting system in view of degradation-polymerization equilibrium via the boiling points of lactides.

1. Introduction

Thermal stability and heat resistance are recognized as some of the most serious issues when considering the potential applications of the aliphatic polyesters. One of these aliphatic polyesters is poly(lactic acid) (PLA), which has received attention because of its biomass-origin and recyclability owing to its relatively high biodegradability and hydrolysis characteristics. Different approaches have been followed to improve the properties of PLA. In this sense, approaches consisting of the enhancement of the thermal stability by cross-linking and end functionalizing along with the blending of polymers and composites with inorganic materials have been described in the literature [1–6]. Detailed understanding of the chemical mechanisms involved in the thermal degradation of PLA based polymers is important for evaluating the thermal stability and for synthesizing improved PLA-based polymers.

Numerous works have been devoted to reveal the thermal degradation mechanism of PLA [7–12], with this process being characterized by a complex chemical mechanism involving intra- and intermolecular trans-esterification, hemolytic chain scissions, and *cis*-elimination reactions releasing a range of gaseous products (e.g., cyclic oligomers, lactides, acetaldehyde, acrylic acid, carbon dioxide, and carbon monoxide). This complex chemical mechanism increases the complexity of the kinetics involved in the thermal degradation of PLA [1,13–21]. Variations in the apparent activation energy (E_a) as the reaction advances were reported in many kinetic studies [1,2,14,16–20], from which a multistep kinetic behavior was proposed to explain the complex chemical mechanism of the reaction. The kinetic rate behavior at constant temperature has been attempted to be determined in connection with some chemical

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* Corresponding author.
E-mail address: nkoga@hiroshima-u.ac.jp (N. Koga).

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mechanisms (e.g., random scission model) in many kinetic studies [1,2,14,16–20], although this simplified physico-chemical model is acceptable in some selected cases. As recently reported, the kinetic rate behavior of the thermal degradation of PLA, typically monitored by thermoanalytical methods such as thermogravimetry (TG), is largely influenced by heterogeneous factors involved in the reaction and measurement processes [21]. In this sense, the molten PLA possibly indicates different thermal degradation reactivities depending on the surfaces (i.e., those exposed to the reaction atmosphere, those in contact with the sample pan, and those in the bulk of the melt). Bubbling is one of the most typical physico-geometrical phenomena observed in PLA degradation reactions, with this process being accompanied by the formation of gases in a viscous liquid. In addition, the properties of the molten PLA (i.e., viscosity and molecular weight) might continuously change with the reaction extent and with temperature [21]. All those physico-geometrical and experimental factors influencing the apparent rate behavior are recorded using thermoanalytical methods and should be considered when interpreting the results of the kinetic analysis associated with the chemical reaction mechanisms.

Unlike the thermal degradation of higher molecular weight PLA that has been the focus of very comprehensive experimental studies on the mechanisms and kinetics, less attention has been paid to the thermal degradation of lower molecular weight PLA, also known as poly(lactic acid) oligomers (PLAO). PLAO have been synthesized and subsequently used as starting materials for the synthesis of functionalized PLA-based polymers while also being applied to biomedical fields [22–26]. PLAO were also used for investigating the degradation mechanisms and kinetics in aqueous media [27]. In this sense, PLAO are considered to be the precursors of higher molecular weight PLA while also being involved as intermediates in the thermal degradation of PLA. PLAO have been reported to change their molar mass distribution and chemical heterogeneity characteristics upon a heat treatment at 473 K in a closed nitrogen atmosphere as a result of simultaneous thermal degradation and recombination processes [28]. Therefore, the elucidation of the reaction mechanisms and kinetic behavior of the thermal degradation of PLAO is expected to provide fundamental and useful information for the research and development of PLA and PLAO polymers while also further providing a detailed understanding of the reaction mechanism and kinetic behavior of the thermal degradation of PLA. A PLAO reactant supplied as a health supplemental food was used as a sample herein. After characterizing the sample in terms of the molecular structure and molecular weight distribution, the PLAO thermal degradation process was investigated using different thermoanalytical techniques. In this sense, the chemical reaction mechanisms were deduced from the evolved gas analyses, while the overall kinetic behavior was characterized on the basis of the mass-loss curves obtained during thermal degradation. The experimentally resolved multistep kinetic behavior was analyzed using the kinetic deconvolution method, which has been recently used to study complex heterogeneous kinetic processes [29–36]. The kinetic results were interpreted by considering both the physico-chemical and physico-geometrical characteristics of the reaction and subsequently compared with previously reported kinetic studies describing the thermal degradation of higher molecular weight PLA.

2. Experimental

2.1. Sample and characterization

A commercially available PLAO (health supplements, produced using 100% pure L-lactic acid) was purchased and used as a sample. With the aim to confirm the influence of the contaminant ions possibly introduced during preparation, a portion of the sample was subjected to a purification treatment [9,13] after being dissolved in dichloromethane (Wako Chem.). Liquid–liquid extraction was performed with a separatory funnel by adding aqueous hydrochloric acid (3 wt%) to the solution. This treatment was applied to remove possible ionic species introduced during the polymerization process. After repeating the liquid–liquid extraction three times, the dichloromethane layer was separated, and the PLAO precipitated upon evaporation of the organic solvent. The precipitate was washed with methanol and vacuum-dried in a desiccator at room temperature for 24 h.

The original and purified samples were characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetry–differential thermal analysis (TG–DTA). The FTIR spectra were recorded using a spectrophotometer (FTIR8400s, Shimadzu) by diffuse reflectance method after diluting the samples with KBr. Each sample ($m_0 = ca.$ 5.0 mg) was weighed in a platinum pan (5 mm in diameter and 2.5 mm in height). TG–DTA measurements (TG/DTA220, SII) were performed by heating the weighed samples at a heating rate (β) of 5 K min^{-1} under flowing N_2 (300 cm^3 min^{-1}).

The sample was further characterized by electrospray ionization–mass spectrometry (ESI–MS) and ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR). The ESI–MS spectra were obtained in the positive-ion mode using a LTQ Orbitrap XL mass spectrometer (Thermo Fisher Scientific). The ESI–MS samples (dissolved in $CDCl_3$ and further diluted with methanol) were infused into the ESI source by a syringe pump at a flow rate of 5 μL min^{-1} and subsequently analyzed using a spray voltage of 5 kV. The ^{1}H NMR spectrum was recorded using a JEOL NMR 500 MHz spectrometer after dissolving the sample in $CDCl_3$ and adding tetramethylsilane (TMS) as an internal standard.

2.2. Monitoring of the thermal degradation process

The gaseous products released upon thermal degradation of the sample were identified by pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS). The device consisted of a double-shot pyrolyzer (PY-2020D, Frontier Lab.) coupled with a GC/MS instrument (GC/MS-QP2010, Shimadzu). The samples ($m_0 = ca.$ 0.1 mg) were weighed in a stainless steel sample holder (50 mm^3) and subsequently heated at a constant β of 10 K min^{-1} from 323 K to 573 K, 603 K, or 723 K under flowing He (50 cm^3 min^{-1}). Some measurements were also carried out by pyrolyzing the sample at 723 K for 6 s. The gases evolved upon each heat treatment were introduced into a GC column (UA5-30M-0.25F, 30 m in length and 0.25 mm inner diameter). The GC column was initially held at 343 K, subsequently heated to 573 K at 20 K min^{-1}, and finally, held at this temperature for 15 min. The outlet gas from the GC column was introduced into the mass spectrometer via a GC–MS interface heated at 573 K. Mass spectra were recorded by scanning in the range from 18 to 700 m/z at an electron impact ionization energy of 70 eV.

The changes in the composition of the evolved gas with the reaction extent were followed by TG/differential scanning calorimetry (DSC) coupled with an FTIR system (TG–DSC: STA6000, FTIR: Frontier, PerkinElmer) by a stainless steel tube (2 mm inner diameter and 1000 mm in length). Both the transfer line and the FTIR gas cell were heated at 523 K while performing the measurements. Approximately 20.0 mg of the sample was weighed in a platinum pan (7 mm in diameter and 5 mm in height), and TG–DSC measurements were subsequently performed by heating the sample at a β of 10 K min^{-1} under flowing N_2 (80 cm^3 min^{-1}). The outlet gas from the TG–DSC instrument was continuously introduced into the gas cell for repeatedly FTIR measurements (wavenumber range: 450–4000 cm^{-1}, resolution: 4 cm^{-1}).