Thermal degradation of poly[(R)-3-hydroxybutyrate], poly[ε-caprolactone], and poly[(S)-lactide]

Yoshihiro Aoyagi,a,b, Koichi Yamashitaa,*, Yoshiharu Doia,c

aPolymer Chemistry Laboratory, RIKEN Institute, Hirosawa 2-1, Wako-shi, Saitama 351-0198, Japan
bAkebono Brake R&D Centre, Ltd., 5-4-71 Higashi, Hanyu-shi, Saitama 348-8501, Japan
cDepartment of Innovative and Engineered Materials, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Received 29 September 2001; accepted 1 November 2001

Abstract

Thermal degradations of poly[(R)-3-hydroxybutyrate] (PHB), poly[ε-caprolactone] (PCL), and poly[(S)-lactide] (PLA) were investigated under both isothermal and non-isothermal conditions. In isothermal degradation experiments, the three polyesters showed quite different time-dependent profiles of weight loss and the number-average degree of polymerization, reflecting their different degradation mechanisms. Thermogravimetric analysis and pyrolysis coupled with GC/MS suggest that PHB is degraded by a random chain scission (cis-elimination), while PCL is degraded by an unzipping depolymerization from the hydroxyl end of the polymer chains. In contrast, the thermal degradation behavior of PLA was very complex because various reactions occurred concurrently. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Thermal degradation; Thermoanalysis; Pyrolysis; Poly(3-hydroxybutyrate); Poly(ε-caprolactone); Poly(lactide); Biodegradable polymer

1. Introduction

Polyhydroxyalkanoates (PHAs) have attracted a great deal of attention because of their biodegradability and thermoplastic properties. Poly[(R)-3-hydroxybutyrate] (PHB), poly[ε-caprolactone] (PCL), and poly[(S)-lactide] (PLA) are well known as typical biodegradable polyesters in practical applications. Besides intensive studies on their biodegradability, understanding of their thermal stability and thermal degradation behavior has importance for processing, application, and thermal recycling.

Thermal degradations of PHB [1–13], PCL [14–16], and PLA [10,17–29] have been studied by many researchers. Thermal degradation of PHB has been suggested to occur almost exclusively by a non-radical random chain scission reaction (cis-elimination) involving a six-membered ring transition state, as shown in Scheme 1 [1–3]. On the other hand, PCL has been suggested to decompose by a two-step mechanism [16]. The first step is a polymer chain cleavage via cis-elimination and the consecutive second step is an unzipping depolymerization from the hydroxyl end of the polymer chain (Scheme 2). For PLA, thermal degradation seems to proceed by a very complicated mechanism which does not give simple activation parameters [22,27]. Moisture, hydrolyzed monomers and oligomers, molecular weight and residual metals can affect thermal stability of PLA [19,24]. Thus, the thermal degradation mechanism of PHAs varies according to the structure of each polymer. Despite the extensive data reported in the literature, some aspects are, however, still not completely understood.

In most cases, thermal decomposition of polymers has been investigated by non-isothermal techniques like differential thermogravimetry and differential scanning calorimetry. Volatile products have been analyzed by pyrolysis–GC/MS (Py–GC/MS) techniques, NMR, and/or IR. However, thermogravimetric analysis (TGA) and volatile product analysis essentially give information concerning degradation which produces volatile species. Non-isothermal analysis tends to reflect phenomena at higher temperature. Therefore, investigation of isothermal degradation and analysis of residual materials needs to be integrated into the study of thermal degradation of PHAs.

In this study, thermal degradation of PHB, PCL, and PLA has been studied under isothermal conditions in addition to conventional TGA and Py–GC/MS analyses.
as a method to compare thermal properties of PHAs
with different degradation mechanisms.

2. Experimental

PHB and PLA were purchased from ICI and Poly-
science Inc., respectively. PCL was prepared by ring-
opening polymerization of ε-caprolactone in the presence
of a poly(methylaluminoxane) catalyst at 60 °C. All
polyester samples were purified by reprecipitation in
methanol from chloroform solution and dried in vacuo.

TGA and isothermal degradation experiments were
performed on a Seiko TG/DTA 220U using helium as a
purge gas. In isothermal degradation experiments,
about 2.5 mg of each polyester sample was preheated
from ambient to the isothermal temperature at a heating
rate of 10 °C min⁻¹, and then degraded isothermally for
a given time.

All molecular weight data of the polyesters were eval-
uated on a Shimadzu LC-10A GPC system equipped
with a 10A refractive index detector and joint columns
of Shodex 80M and K802 at 40 °C. Chloroform was
used as eluent at a flow rate of 0.8 ml/min. Polystyrene
standards were used for calibration.

Py–GC/MS analysis was performed on Curie Point
Pyrolyzer JHP-5 (Japan Analytical Industry Co., Ltd.)
equipped with JEOL Automass 5890 series II. 100 mg of
each sample placed on aluminum pan was pyrolyzed at
280 °C for 10 s. The column used for the analysis was a
J&W DB-1 (15×0.25 mm i.d.). The column temperature
was held at 40 °C for 3 min, and then heated to 280 °C
at 10 °C/min, and held at 280 °C for 15 min.

3. Results and discussion

3.1. Isothermal degradation

Isothermal degradations of PHB, PCL, and PLA were
carried out under N₂ atmosphere at 170, 250, and 290 °C,
respectively. Fig. 1A and B show the changes in weight
and the number–average degree of polymerization (Pₙ)
of the polyesters during isothermal degradation. For
PHB, only slight weight loss was observed in contrast to
rapid decrease of the Pₙ value with time. The fact indi-
cates that less volatile products were produced by iso-
thermal degradation of PHB at 170 °C. Both weight and
the Pₙ value of PCL decreased linearly with degradation
time. A linear relationship between the Pₙ value and
time is consistent with depolymerization from the ends
of polymer chains via an unzipping mechanism (see

![Diagram](https://via.placeholder.com/150)

Scheme 1.

![Diagram](https://via.placeholder.com/150)

Scheme 2.

![Graph](https://via.placeholder.com/150)

Fig. 1. (A) Weight changes during isothermal degradation of PHB at
170 °C (●), PCL at 250 °C (▲), and PLA at 290 °C (■). (B) Changes
in number–average degrees of polymerization during isothermal
degradation of PHB at 170 °C (●), PCL at 250 °C (▲), and PLA at
290 °C (■).
Scheme 2). Substantial decrease in weight and the $P_n$ value was observed at the early stage of isothermal degradation of PLA.

Nonlinear relationships between the $P_n$ values and time for isothermal degradation of PHB and PLA suggest that unzipping is not a major process in their isothermal degradation. As an alternative mechanism, a random chain scission reaction has been proposed for PHB [1–3]. When the chain scission is completely random, a linear relationship between the inverse of $P_n$ and time is predicted as Eq. (1) [4,30].

$$\frac{1}{P_{n,t}} = k_d t + \frac{1}{P_{n,0}}$$

(1)

where $P_{n,0}$ and $P_{n,t}$ are the number-average degrees of polymerization at time 0 and $t$, respectively, and $k_d$ is the rate constant of degradation. In Fig. 2, the $1/P_n$ values are plotted against reaction time for isothermal degradation of PHB and PLA. The plots for PHB give a linear relationship in accordance with random scission mechanism. The rate constant of isothermal degradation of PHB is calculated to be $k_d = (1.84 \pm 0.17) \times 10^{-6}$ s$^{-1}$ from the slope of the linear plots in Fig. 2. On the other hand, the plots for PLA are convex, suggesting that thermal degradation of PLA does not proceed via simple random scission of the polymer chain.

Since the thermal degradation behaviors of PHB, PCL, and PLA are different, initial rates ($V_{ini}$) of the weight loss and the $P_n$ decrease were evaluated for their isothermal degradation at various temperatures to compare their thermal stability (Figs. 3–5).

Fig. 3 shows the initial rates observed for isothermal degradation of PHB at 160–220 °C. Interestingly, the $P_n$ values decreased very fast even at temperatures lower than the melting point (~180 °C). Decrease of the $P_n$ values indicates that scission of the polymer chain proceeds efficiently at these temperatures. However, weight loss of the polymer was very slow even at 220 °C, indicating less production of volatile species by chain scission. When the thermal degradation of PHB occurs almost exclusively via random chain scission reaction, the probability of production of volatile species is lower than the probability of chain scission. Thus, the results shown in Fig. 3 clearly reflect random chain scission mechanism.

For isothermal degradation of PCL, the profile of temperature dependence for the rates of the weight loss overlaps with the rates of the $P_n$ decrease as shown in Fig. 4. This result strongly suggests that the species
produced by thermal degradation of PCL immediately volatilize. In other word, thermal chain scission of PCL produces almost exclusively small molecules with low boiling points. Unzipping depolymerization from the ends of the polymer chains would lead to efficient formation of volatile species like ε-caprolactone as illustrated by Scheme 2.

Surprisingly, the rate of the $P_n$ decrease in isothermal degradation of PLA did not change with the reaction temperature, while the weight loss rate was accelerated with degradation temperature (Fig. 5). Slower weight loss as compared with the $P_n$ decrease at temperatures below 320 °C indicates that the degradation products contain species with the boiling points higher than the reaction temperature. The weight loss rates were two times faster than the $P_n$ decrease at 340 °C. These phenomena can not be explained by a simple degradation mechanism.

So far, it has been reported that thermal stability of PLA is influenced by factors such as moisture, hydrolyzed monomers and oligomers, molecular weight, and residual metals [19,24]. Cam and Marucci reported that low molecular weight compounds such as moisture, monomers, oligomers associated with the polymer can be removed by preheating [24]. In this study, the sample was preheated at a heating rate of 10 °C min$^{-1}$ from room temperature to the isothermal conditions to release volatile impurities. As can be seen from the considerable rate of the $P_n$ decrease at 240 °C, the polymer chains are degraded during the preheating process. For example, the $P_n$ of PLA was reduced to 4600 from 6200 during the preheating process from room temperature to 240 °C at a heating rate of 10 °C min$^{-1}$. The negligibly slow rate of weight loss at 240 °C suggests accumulation of the degraded product in the sample during the preheating process. As a result, drastic weight loss might be observed in the initial stage of the isothermal reaction at higher temperature as shown in Fig. 1.

As can be seen from Figs. 3–5, the degradation rate of PHB is faster than those of PCL and PLA at a given temperature, indicating lower thermal stability of PHB. The chemical structure of the monomeric unit in PHB is characterized by an activated C–H bond neighboring a carbonyl group, which can participate in the cis-elimination reaction. Although a PCL unit also possesses an activated C–H bond, it can not participate in a six-membered cyclic transition state. In the case of PLA, the tertiary C–H bond is acidified by the two neighboring ester groups. However, only the non-activated C–H bond of the methyl group can form a six-membered cyclic transition state. Thus, availability of cis-elimination in thermal degradation would determine thermal stability of the polyesters.

### 3.2. Thermogravimetric and Py-GC/MS analyses

Thermal degradation behaviors of PHB, PCL, and PLA were also studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) under helium. The TGA and DTA curves of PHB, PCL, and PLA samples are respectively summarized in Figs. 6–8. From the TGA data shown in Figs. 6A, 7A, and 8A, the apparent activation energies ($E_a$) of thermal degradation of the polyesters were calculated according to Ozawa's method [31]. In Fig. 9, the estimated $E_a$ values are plotted against the residual weight fraction of the samples.

Fig. 6A and B show TGA and DTA curves obtained for PHB at heating rate of 3, 5, 7, and 10 °C min$^{-1}$. The TGA curves monotonously decreased with temperature and no carbonaceous residue was left. A single peak observed in each DTA curve indicates a single step degradation reaction of PHB polymer chains. The apparent activation energies for PHB were almost constant during weight changes in TGA measurements (Fig. 9). The average $E_a$ value for PHB was calculated to be $111 \pm 7 \text{ kJ mol}^{-1}$. These facts indicate that the reaction mechanism does not change with temperature and/or conversion.

The volatile products of PHB were analyzed by Py–GC/MS at 280 °C. As shown in Fig. 10, three major peaks were separated by the gas chromatograph. Mass spectra of three peaks are shown in Fig. 11. For the peak 1, the characteristic signals of crotonic acid were recorded at $m/z = 39, 41, 68, 69,$ and $86$. The additional signals at $m/z = 103, 154, 155, 171, 172,$ and $173$ in Fig. 11B and C can be attributed to oligomers of crotonic acid. Thus, the peaks 2 and 3 can be assigned to the dimers Fig. 6. (A) TGA and (B) DTA curves of thermal degradation of PHB at heating rates of 3, 5, 7, 10 °C/min.
and trimers of crotonic acid as suggested by Kopinke et al. [8,10].

These observations are in accordance with the thermal degradation mechanism of PHB which almost exclusively involves a random chain scission (cis-elimination) reaction of the ester groups to form crotonic acid and its oligomers [1–3,8,10].

The TGA and DTA curves for thermal degradation of PCL at heating rate of 3, 5, 7, and 10 °C/min are shown in Fig. 7A and B. Smooth changes in the TGA curves and a single peak in each DTA curve are observed. As shown in Fig. 9, a constant $E_a$ value of 74 ± 4 kJ mol$^{-1}$ is obtained, indicating that the degradation mechanism remains unchanged throughout degradation. Although these results suggest a single step degradation of PCL, a two-step degradation mechanism has been proposed by Persenaire et al. [16]. They studied thermal degradation of PCL by high-resolution TGA simultaneously coupled with mass spectrometry and Fourier transform infrared spectrometry. Two well-resolved degradation peaks were observed in high-resolution DTA curves. Based on the evolved gas analysis, they concluded that thermal degradation of PCL proceeded in a two-stage degradation mechanism. That is, the first step is a random rupture of the polyester chains via cis-elimination reaction which produces H$_2$O, CO$_2$, and 5-hexanoic acid, and the second step is an unzipping depolymerization process at the chain-ends with hydroxyl end groups to form ε-caprolactone. In the present study, kinetics of isothermal degradation of PCL obeyed an unzipping depolymerization mechanism from the polymer-chain ends. The TGA and DTA curves also suggest a single-step degradation of PCL. The constant $E_a$ value obtained during weight loss in TGA suggests rather a simple degradation mechanism. Furthermore, only production of ε-caprolactone was detected by Py–GC/MS analysis at 280 °C as shown in Fig. 12A and B. However, these results do not exclude the possibility of a random rupture of the polyester chains via a cis-elimination reaction. Persenaire et al. have pointed out that the cis-elimination reaction and the unzipping depolymerization proceed...
consecutively at very close temperatures [16], so that these two steps may not be resolved by a conventional DTA technique used in this study.

The TGA and DTA patterns of PLA in Fig. 8 were considerably different from those of PHB and PCL. As shown in Fig. 8A and B, the TGA curves exhibited two phases and the DTA curves gave shoulders at ca. 300 °C in addition to the peaks at 340–360 °C. The apparent $E_a$ values calculated for PLA drastically change with the residual weight fraction as shown in Fig. 9. The $E_a$ values decreased with weight loss at initial stage of degradation, but then increased remarkably with progress of degradation. The drastic change in the $E_a$ values of thermal degradation indicates that the reaction mechanism changes with temperature and/or conversion. In Py–GC/MS analysis, we obtained one broad peak as shown in Fig. 13A. The mass spectrum of this peak shown in Fig. 13B indicated that the peak is the mixture of at least acetaldehyde ($m/z = 43, 45$), lactide monomer ($m/z = 43, 56$) and oligomers of lactide ($m/z = 43, 45, 56, 100$) [28].

Thus, all results suggest that thermal degradation of PLA involves more than two mechanisms.

The complexity of the thermal degradation of PLA has been reported by previous workers [19,22,24–26]. Kopinke et al. have suggested that degradation at temperatures above 200 °C includes intramolecular transesterification leading to lactide and cyclic oligomers, cis-elimination leading to acrylic acid acrylic oligomers, and fragmentation leading to acetaldehyde and CO$_2$ [22]. In addition to these degradation mechanisms, residual metals which stem from the polymerization catalyst can catalyze depolymerization of PLA to form exclusively lactide. The drastic effects of metals on thermal stability of PLA were studied by Cam and Marucci [24]. Since the PLA sample used in this study contains residual aluminum catalysts, thermal degradation at ca. 300 °C in the
DTA curves might be attributable to the aluminum-catalyzed depolymerization. Metal-catalyzed depolymerization at lower temperatures seems to be one origin of the drastic changes in the $E_a$ values during thermal degradation.

However, the $E_a$ values obtained in this study are considerably larger than the values reported by McNeil and Leiper of 120 kJ mol\(^{-1}\) \cite{18} and Kopinke et al. of 110 kJ mol\(^{-1}\) \cite{22}. Recently, Babanalbandi et al. have also reported a change of activation energies with weight loss \cite{27}. The range of the change was between 70–100 kJ mol\(^{-1}\) which is much smaller than the present result of 80–160 kJ mol\(^{-1}\). Since the origin of discrepancy is unclear at present, further investigation by using carefully prepared samples and analytical systems would be necessary.

Lower thermal stability of PHB is indicated by the TGA and DTA curves in Figs. 6–8 in accordance with the results obtained under isothermal conditions. The peak temperatures of the DTA curves for PHB are about 50 °C lower than those of PCL and PLA. However, the $E_a$ values estimated by the TGA curves are inconsistent with these results. The apparent activation energy in thermal degradation of PHB is higher than that of PCL, and corresponds to that of PLA. Since the TGA mainly reflects reactions which form volatile products, the $E_a$ values in Fig. 9 might not directly indicate the activation parameters of thermal degradation. Especially, thermal degradation of PHB which produces less volatile products would not be assessed appropriately by a conventional TGA technique alone. Consequently, development of other techniques to evaluate the activation parameters of the reaction in melt states would be needed for further investigation.

Acknowledgements

This work was supported in part by a grant for Eco-molecular Science Research provided by RIKEN Institute and by the SORST (Solution Oriented Research for Science and Technology) grant from Japan Science and Technology Corporation (JST).

References

\[5\] Mitomo H, Ota E. Sen-i Gakkaishi 1991;47:89–94.
\[24\] Cam D, Marucci M. Polymer 1997;38:1879–84.