

## Effects of Residual Zinc Compounds and Chain-End Structure on Thermal Degradation of Poly( $\epsilon$ -caprolactone)

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Effects of chain-end structure and residual metal compounds on thermal degradation of poly( $\epsilon$ -caprolactone) (PCL) were investigated by means of thermogravimetric and pyrolysis-gas chromatograph mass spectrometric analyses. Four types of PCL samples with different chain-end structures ( $\alpha$ -carboxylic acid- $\omega$ -hydroxyl-PCL,  $\alpha$ -dodecyl ester- $\omega$ -hydroxyl-PCL,  $\alpha$ -carboxylic acid- $\omega$ -acetyl-PCL, and  $\alpha$ -dodecyl ester- $\omega$ -acetyl-PCL) were prepared by ring-opening polymerization of  $\epsilon$ -caprolactone in the presence of zinc-based catalyst and by subsequent acetylation reaction of polymers with acetic anhydride. PCL samples with different zinc contents were obtained by washing with acetic acid in chloroform solution of polymer. Thermal degradation behaviors of these PCL samples with different chain-end structures were examined under both isothermal and nonisothermal conditions. From both the isothermal and nonisothermal experiments, the thermal degradation of PCL samples containing high amounts of residual zinc compounds from synthesis process revealed the selective unzipping depolymerization step below 300 °C producing  $\epsilon$ -caprolactone exclusively. In contrast, zinc-free PCL samples were stable at temperatures below 300 °C, and the thermal degradation occurred only at temperatures above 300 °C regardless of the chain-end structure. From <sup>1</sup>H NMR analysis of the residual molecules after isothermal degradation of zinc-free PCL, it was confirmed that the  $\omega$ -chain-end of residual molecules was 5-hexenoic acid unit. However, the cyclic monomer and oligomers were detected as the volatile products of zinc-free PCL samples. These results suggest that the dominant reaction of thermal degradation for PCL above 300 °C is a competition between the random chain scission via cis elimination reaction and the cyclic rupture via intramolecular transesterification of PCL molecules.

### Introduction

Recently, there has been a growing demand for biodegradable plastics as a solution to problems concerning the global environment and the solid waste management. Aliphatic polyesters are among the most promising materials for biodegradable fibers and films. Many types of aliphatic polyesters have been prepared by both chemosynthetic and biosynthetic methods. The poly( $\epsilon$ -caprolactone) (PCL) family of polyesters is synthesized by ring-opening polymerization of  $\epsilon$ -caprolactone ( $\epsilon$ -CL), which is an industrially available petrochemical. PCL is known as a biodegradable and biocompatible thermoplastic. The biodegradability of PCL has been investigated in detail by using compost,<sup>1</sup> sludge,<sup>2–4</sup> natural waters,<sup>5</sup> pure cultures of microorganisms,<sup>1,2</sup> and isolated microbial enzymes.<sup>6,7</sup>

Besides intensive studies on the biodegradability of aliphatic polyesters, an understanding of the thermal stability has importance for processing, application, and recycling.

Generally, particular two temperature ranges are important for concerning the thermal stability of polymers. One is the low temperature range, at which polymer decomposition proceeds very slowly, and this range is of primary importance for processing and application of polymers. The other one is the high temperature range, at which the decomposition is completed within a relatively short time period, and this range is important for chemical recycling of polymers.

Several groups investigated the thermal stability of PCL at high-temperature region by using various analytical techniques, but there is no consistency in the mechanism.<sup>8–15</sup> Iwabuchi et al.<sup>8</sup> investigated the thermal degradation behavior under isothermal degradation condition at 220 °C. By monitoring the time-dependent changes in sample weight and viscosity, they proposed a single step degradation mechanism, where the polymer degrades by specific removal of cyclic monomer from the end groups. Aoyagi et al.<sup>13</sup> investigated the thermal degradation of PCL under isothermal and nonisothermal conditions by using gel permeation chromatography, thermogravimetric analyzer, and pyrolysis-mass spectrometry. On the basis of molecular weight measurement and volatile product analysis, the PCL degraded via specific end scission by unzipping of cyclic monomer

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from  $\omega$ -hydroxyl chain-end. Sivalingam and Madras<sup>14</sup> also reported that the thermal degradation of PCL under isothermal conditions at temperatures ranging from 280 to 330 °C progressed by unzipping reaction from  $\omega$ -hydroxyl chain-end. On the other hand, Lüderwald<sup>9</sup> characterized the overall degradation products of PCL during isothermal degradation at 220 °C by using mass spectrometry and reported that the  $\omega$ -hydroxyl and ketene end groups were formed by the cleavage of ester bond. The formation of  $\omega$ -hydroxyl and ketene end groups by thermal degradation of PCL have been confirmed from mass spectrometric analyses of overall degradation products by Garozzo et al.<sup>10</sup> and Plage and Schulten.<sup>11</sup> In addition, Persenaire et al.<sup>12</sup> studied thermal degradation of PCL by high-resolution TGA simultaneously coupled with mass spectrometry and Fourier transform infrared spectrometry. They proposed a consecutive two-step degradation mechanism of random cleavage through cis elimination and specific chain end scission by unzipping from the  $\omega$ -hydroxyl end of the polymers depending on the reaction temperature. Sivalingam et al.<sup>15</sup> also proposed a two-step degradation mechanism of random degradation and specific chain end scission but as parallel steps.

So far, it has been reported that thermal degradation of poly(L-lactide) (PLLA) is influenced by factors such as molecular weight of the sample, moisture, hydrolyzed monomers and oligomers, chain-end structure, and residual metals.<sup>16–19</sup> As a result, thermal degradation of PLLA seems to proceed by a very complicated mechanism which does not give simple activation parameters. It can be expected that these factors also affect on the thermal degradation of PCL molecules.

In this study, we focus on the effects of chain-end structure and residual metal compounds from the synthesis process on the thermal degradation reaction of PCL, and the PCL samples with different chain-end structures and with different amounts of residual metal compounds were prepared. The thermal degradation behaviors of these PCL samples have been characterized under isothermal conditions in addition to conventional thermogravimetric and pyrolysis-gas chromatograph mass spectrometric analyses.

## Experimental Section

**Materials.**  $\epsilon$ -Caprolactone ( $\epsilon$ -CL) (Aldrich Chemical Co.) was dried by  $\text{CaH}_2$  and distilled under reduced pressure. 5-Hexenoic acid was purchased from Aldrich Chemical Co.

**Preparation of Zinc-Based Catalysts.**  $\text{ZnEt}_2/\text{H}_2\text{O}(1/0.6)$  catalyst was prepared as follows.  $\text{ZnEt}_2$  was reacted with deoxygenated water at a molar ratio of 1/0.6 ( $\text{ZnEt}_2/\text{H}_2\text{O}$ ) in dry 1,4-dioxane, followed by freeze-drying of the reaction mixture. A yellow powder was obtained.

Zinc didodecanoxide ( $\text{Zn}(\text{OD})_2$ ) catalyst was prepared as follows.  $\text{ZnEt}_2$  was reacted with *n*-dodecanol at a molar ratio of 1/2 ( $\text{ZnEt}_2/n$ -dodecanol) in 1,2-dichloroethane at room temperature for 5 h, followed by freeze-drying of the reaction mixture. A white powder was obtained.

**Synthesis of Polymers.** Non-end-capped PCL samples were synthesized by the ring-opening polymerization of  $\epsilon$ -CL in the presence of  $\text{ZnEt}_2/\text{H}_2\text{O}$  as a catalyst. The monomer,

$\text{ZnEt}_2/\text{H}_2\text{O}$  catalyst, and dichloromethane were admitted into a reactor under nitrogen atmosphere. The polymerization was carried out at 60 °C for 3 days under nitrogen atmosphere. The polyester produced was dissolved in chloroform and precipitated in methanol. The precipitate was dried in vacuo at room temperature.

PCL samples with a dodecyl ester end at the carboxylic acid terminus were synthesized by the ring-opening polymerization of  $\epsilon$ -CL in the presence of  $\text{Zn}(\text{OD})_2$  as a catalyst. The monomer, catalyst, and 1,2-dichloroethane were admitted into a reactor under nitrogen atmosphere. The polymerization was carried out at 60 °C for 15 h under nitrogen atmosphere.

Obtained PCL samples were acetylated at the  $\omega$ -hydroxyl chain end with acetic anhydride. The chloroform solution of the PCL sample (2.0% (w/v)) was mixed with 1.0% (v/v) of acetic anhydride at room temperature for 24 h. The polyester was precipitated in methanol from chloroform solution.

To prepare PCL samples with different Zn contents, the PCL samples were washed in chloroform solution of polymer (2.0% (w/v)) with 5% (v/v) of acetic acid for 12 h, and then the polymer was precipitated in methanol.

**Thermal Degradation Test.** Thermogravimetric analysis (TGA) and isothermal degradation experiments were performed on a Seiko Instruments TG/DTA 220U using nitrogen as a purge gas. In isothermal degradation experiments, about 5 mg of each sample was preheated from room temperature to the isothermal degradation temperature at a heating rate of 30 °C/min and then maintained isothermally for a given time.

Pyrolysis-gas chromatograph mass spectrometric (Py-GC/MS) analysis was performed on Curie Point Pyrolyzer JHP-5 (Japan Analytical Industry Co., Ltd.) equipped with Shimadzu GCMS QP2010 system. 10  $\mu\text{g}$  of each sample placed on a metal pan was pyrolyzed at a given temperature (280, 358, 386, and 445 °C) for 10 s. The column used for the analysis was a J&W DB-1 (15 m  $\times$  0.25 mm). The column temperature was held at 40 °C for 3 min, then heated to a given temperature at 10 °C/min, and held at a given temperature for 15 min. For the assignment of degradation products, cyclic oligomers of  $\epsilon$ -CL were prepared by refluxing of  $\epsilon$ -CL at 120 °C for 24 h under nitrogen atmosphere.

**Analytical Procedures.**  $^1\text{H}$  NMR analysis of PCL samples was carried out on a JEOL Alpha-400 spectrometer. The 400 MHz  $^1\text{H}$  NMR spectra were recorded at 23 °C in a  $\text{CDCl}_3$  solution of polymer (5 mg/mL) with a 5.5  $\mu\text{s}$  pulse width (45° pulse angle), 5 s pulse repetition, 8000 Hz spectral width, and 16K data points.

All molecular weight data were obtained by gel-permeation chromatography at 40 °C, using a Shimadzu 10A GPC system and 10A refractive index detector with Shodex K-806M and K-802 columns. Chloroform was used as eluent at a flow rate of 0.8 mL/min, and a sample concentration of 1.0 mg/mL was applied. Polystyrene standards with a low polydispersity were used to make a calibration curve. It is known that the actual molecular weight of PCL is apparently different from the values determined from GPC based on polystyrene owing to the difference of the exclusion volume

**Table 1.** Molecular Weights, Thermal Properties, and Residual Zinc Contents of PCL Samples

samples	molecular weight		thermal properties			Zn content (ppm)
	$M_n$	$M_w/M_n$	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	
$\alpha$ -carboxylic acid- $\omega$ -hydroxyl-PCL <sup>a</sup> (C-PCL-H)	113 000	1.47	−69	52	41	2600
C-PCL-H washed with acetic acid <sup>b</sup> (C-PCL-H (W))	113 000	1.55				<3.11
$\alpha$ -carboxylic acid- $\omega$ -acetyl-PCL <sup>c</sup> (C-PCL-A)	95 000	1.66	−70	52	37	6.46
$\alpha$ -dodecyl ester- $\omega$ -hydroxyl-PCL <sup>d</sup> (D-PCL-H)	54 000	1.54	−71	52	40	431
D-PCL-H washed with acetic acid <sup>e</sup> (D-PCL-H (W))	54 000	1.52				<3.11
$\alpha$ -dodecyl ester- $\omega$ -acetyl-PCL <sup>f</sup> (D-PCL-A)	54 000	1.42	−71	52	40	4.65

<sup>a</sup> Synthesized by polymerization of  $\epsilon$ -CL with  $\text{ZnEt}_2/\text{H}_2\text{O}$  as a catalyst. Monomer feed ratio;  $[\epsilon\text{-CL}]/[\text{Zn}] = 200$  (mol/mol). <sup>b</sup> Washed with 5% (v/v) of acetic acid in chloroform solution of C-PCL-H (2% (w/v)) at room temperature for 24 h. <sup>c</sup> Reacted with 1% (v/v) of acetic anhydride in chloroform solution of C-PCL-H (2% (w/v)) at room temperature for 24 h. <sup>d</sup> Synthesized by polymerization of  $\epsilon$ -CL with  $\text{Zn}(\text{OD})_2$  as a catalyst. Monomer feed ratio;  $[\epsilon\text{-CL}]/[\text{Zn}] = 960$  (mol/mol). <sup>e</sup> Washed with 5% (v/v) of acetic acid in chloroform solution of D-PCL-H (2% (w/v)) at room temperature for 42 h. <sup>f</sup> Reacted with 1% (v/v) of acetic anhydride in chloroform solution of D-PCL-H (2% (w/v)) at room temperature for 24 h.

of PCL and polystyrene of the same molar mass. To convert the molecular weight values from GPC to the actual values for PCL, the pertinent correction factor of 0.45<sup>20</sup> was applied in this study.

Differential scanning calorimetry (DSC) data of PCL samples were recorded in the temperature range of −100 to +100 °C on a Perkin-Elmer Pyris 1 equipped with a cooling accessory under a nitrogen flow of 20 mL/min. Samples of 3 mg were encapsulated in aluminum pans and heated from 0 to 100 °C at a rate of 20 °C/min. The melting temperature ( $T_m$ ) and enthalpy of fusion ( $\Delta H_m$ ) were determined from the DSC endotherms of the first scan to minimize the effect of the thermal history of the sample during heating treatment and to obtain the accurate values of original samples. The  $T_m$  was taken as the peak temperature. For the measurement of the glass transition temperature ( $T_g$ ), the samples were maintained at 100 °C for 1 min and then rapidly quenched to −100 °C. They were heated from −100 to +100 °C at a heating rate of 20 °C/min. The  $T_g$  was taken as the midpoint of the change in heat capacity.

Residual zinc content in the PCL samples was measured with a Hitachi Z-5000 atomic absorption flame emission spectrophotometer. The adequate amount of PCL samples was degraded by 2% (v/v) nitric acid aqueous solution and then measured. Zinc standard solution (Kanto Kagaku Co., Ltd.) was diluted from 0 to 2 ppb of Zn with a 2% (v/v) nitric acid aqueous solution, and the calibration curve was obtained.

## Results and Discussion

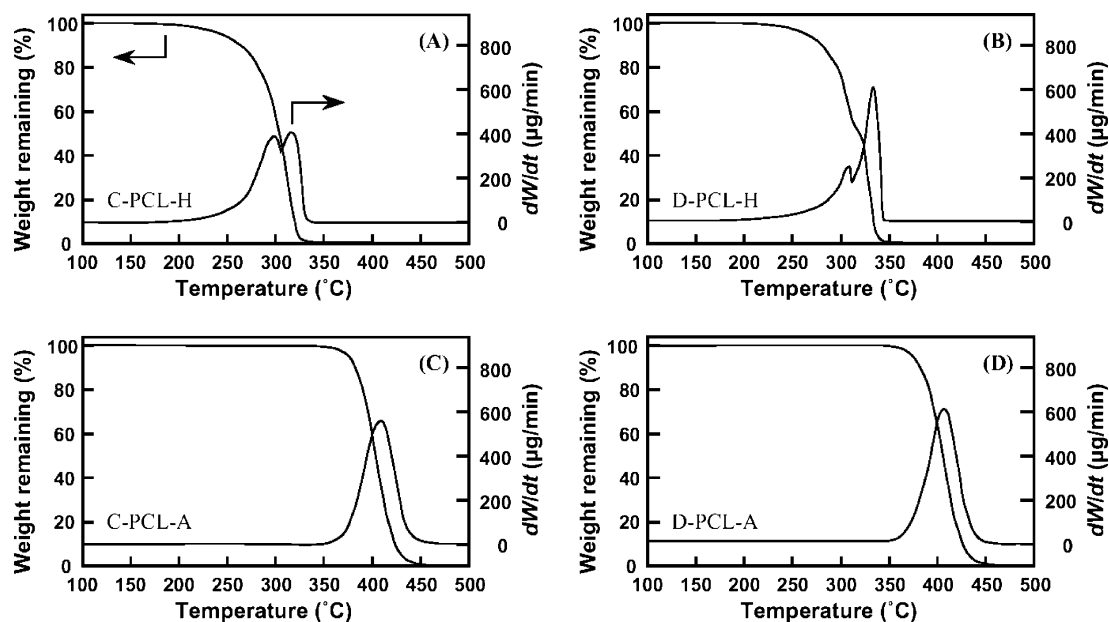
PCL samples with free acid and with dodecyl ester at the  $\alpha$ -carboxyl chain-end were synthesized by ring-opening polymerization of  $\epsilon$ -CL in the presence of  $\text{ZnEt}_2/\text{H}_2\text{O}$  and  $\text{Zn}(\text{OD})_2$  as a catalyst, respectively. The molecular weights of the obtained samples were determined by gel permeation chromatography. Table 1 lists the number-average molecular weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) of PCL samples used in this study. The  $M_n$  values of PCL samples with free acid and with dodecyl ester were 113 000 and 54 000, respectively. Because of such high molecular weights of samples, it was difficult to confirm the chain-end structure of PCL molecules directly. Therefore, PCL samples with low molecular weight ( $M_n = 4000$  (free acid sample) and 5200 (dodecyl ester sample)) were synthesized through the similar procedures by changing the monomer feed ratios and then

characterized by <sup>1</sup>H NMR analysis. In <sup>1</sup>H NMR spectra of both PCL samples with low molecular weights, the methylene proton signals arising from  $\epsilon$ -caprolactone units in main-chain were detected at 1.38, 1.65, 2.32, and 4.06 ppm. For the PCL sample obtained from polymerization with  $\text{ZnEt}_2/\text{H}_2\text{O}$  catalyst, the peaks from the methylene proton of  $\epsilon$ -caprolactone unit at  $\alpha$ -carboxylic acid chain-ends and the methylene proton of  $\epsilon$ -caprolactone unit at  $\omega$ -hydroxyl chain-ends were detected at 2.47 and 3.66 ppm, respectively. On the other hand, the peak at 2.47 ppm was absent in the <sup>1</sup>H NMR spectrum of PCL sample obtained from polymerization with  $\text{Zn}(\text{OD})_2$  catalyst, and the peak from the methyl proton of  $\alpha$ -dodecyl ester was observed at 0.89 ppm. From the peak intensities of the methylene proton at the  $\omega$ -hydroxyl chain-end and the methyl proton of the  $\alpha$ -dodecyl ester, the molar ratio of  $\alpha$ -dodecyl ester end group to the  $\omega$ -hydroxyl chain-end group was calculated as 0.93. From these results, it has been concluded that the majority of the  $\alpha$ -carboxylic acid chain-ends of the PCL molecules obtained from polymerization with  $\text{Zn}(\text{OD})_2$  catalyst were substituted with the dodecyl ester group.

The thermal properties of obtained samples were examined by differential scanning calorimetry. Table 1 also lists the melting temperature and glass-transition temperature of PCL samples. The glass-transition and melting temperatures of nonend-capped PCL ( $\alpha$ -carboxylic acid- $\omega$ -hydroxyl-PCL, C-PCL-H) were −69 °C and 52 °C, respectively. Both the melting and glass-transition temperatures of PCL with  $\alpha$ -dodecyl ester ends ( $\alpha$ -dodecyl ester- $\omega$ -hydroxyl-PCL, D-PCL-H) were almost same with those of C-PCL-H. This result suggests that the  $\alpha$ -dodecyl ester end hardly affects the thermal properties of PCL.

To prepare the PCL samples with  $\omega$ -acetyl chain-ends, both  $\omega$ -hydroxyl-PCL samples (C-PCL-H and D-PCL-H) were reacted with acetic anhydride. The degree of substitution with the acetyl group at the  $\omega$ -hydroxyl chain-end was estimated from the <sup>1</sup>H NMR spectra of PCL samples with low molecular weights. After the reaction with acetic anhydride, the methylene proton signal at 3.66 ppm arising from the  $\epsilon$ -caprolactone unit at  $\omega$ -hydroxyl chain-ends completely disappeared in the <sup>1</sup>H NMR spectra, and the peak from the methyl proton of the acetyl group was observed at 2.05 ppm. From this result, it was confirmed that the  $\omega$ -hydroxyl chain-ends of the PCL molecules were substituted with the acetyl group by the acetylation treatment. The molecular weight data and thermal properties of  $\omega$ -acetyl-





**Figure 1.** TGA and DTA curves of thermal degradation of PCL samples with different chain-ends structures at a heating rate of 10 °C/min. (A)  $\alpha$ -Carboxylic acid- $\omega$ -hydroxyl-PCL (C-PCL-H), (B)  $\alpha$ -dodecyl ester- $\omega$ -hydroxyl-PCL (D-PCL-H), (C)  $\alpha$ -carboxylic acid- $\omega$ -acetyl-PCL (C-PCL-A), and (D)  $\alpha$ -dodecyl ester- $\omega$ -acetyl-PCL (D-PCL-A).

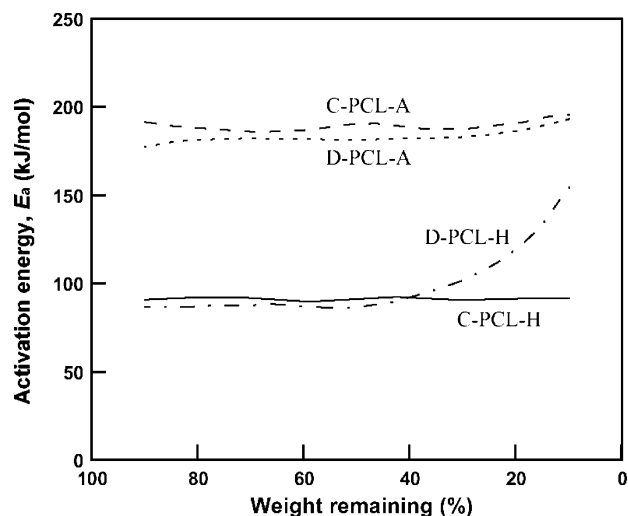
PCL samples ( $\alpha$ -carboxylic acid- $\omega$ -acetyl-PCL, C-PCL-A and  $\alpha$ -dodecyl ester- $\omega$ -acetyl-PCL, D-PCL-A) are also shown in Table 1. The molecular weight of C-PCL-A was slightly smaller than that of C-PCL-H. The decrease in molecular weight for the C-PCL-A sample may be due to the hydrolysis reaction by acetic acid produced during acetylation treatment. The D-PCL-A samples had same molecular weight with that of D-PCL-H. Both the melting and glass transition temperatures of the  $\omega$ -acetyl-PCL samples were also identical with those of PCL with  $\omega$ -hydroxyl chain-ends.

First, the thermal degradation behaviors of PCL samples were examined by the conventional thermogravimetric analysis under nonisothermal conditions. Figure 1 shows the TGA and DTA curves of PCL samples with different chain-end structures at a heating rate of 10 °C/min under nitrogen atmosphere. As shown in Figure 1A, the weight loss of non-end-capped PCL (C-PCL-H) started at around 200 °C under nitrogen atmosphere, and the sample weight decreased with a rise in temperature. The weight remaining of the sample reached zero at around 330 °C. The DTA curve of C-PCL-H revealed two peaks at 290 °C and at 310 °C. When the TGA measurements were carried out at different heating rates ranging from 3 to 20 °C/min, different two types of DTA profiles were observed depending on the heating rate. In the DTA curves recorded at heating rates ranging from 3 to 7 °C/min, only one peak was detected at the temperature region below 290 °C. In contrast, two peaks were observed in the DTA curves recorded at heating rates above 10 °C/min. The peak temperature for the higher temperature region increased with an increase in heating rate, and the peak intensity became to be large. These results indicate that the thermal degradation of C-PCL-H proceeds in a two-stage degradation under nonisothermal condition depending on the reaction temperature and heating rate. In the case of a slow heating rate, the C-PCL-H sample was completely degraded at the temperature regions of the first degradation stage before

reaching the second stage. On the other hand, the C-PCL-H sample was degraded incompletely at a fast heating rate, and the residual fraction was degraded at the second stage. As a result, two peaks were detected in the DTA curve of C-PCL-H recorded at a fast heating rate under nonisothermal condition.

For the PCL sample with  $\alpha$ -dodecyl ester chain-ends (D-PCL-H), the weight loss started at around 240 °C, and the weight remaining of the sample reached zero at around 340 °C. The TGA curve of D-PCL-H apparently exhibited two phases, and the DTA curve gave a peak at 325 °C in addition to the peak at 300 °C (Figure 1B). The TGA curves of both  $\omega$ -acetyl-PCL samples (C-PCL-A and D-PCL-A) significantly shifted toward the higher temperature region compared with  $\omega$ -hydroxyl-PCL samples (C-PCL-H and D-PCL-H). Both the TGA and DTA curves of  $\omega$ -acetyl-PCL samples revealed the identical profiles regardless of the  $\alpha$ -chain-end structure of the PCL molecules. The weight loss of the  $\omega$ -acetyl-PCL samples started at around 360 °C under nitrogen atmosphere, and no carbonaceous residue was left at around 440 °C (Figure 1, parts C and D).

To evaluate the activation energies ( $E_a$ ) of thermal degradation for PCL samples, thermogravimetric analysis was carried out at different heating rates ranging from 3 to 20 °C/min. According to Ozawa's method,<sup>21</sup> apparent activation energies of thermal degradation were calculated from TGA data. Figure 2 shows the apparent activation energies ( $E_a$ ) of thermal degradation for PCL at different residual weight fractions of samples. The apparent  $E_a$  values for C-PCL-H were almost constant during weight changes in TGA measurements, and the value was calculated to be  $91 \pm 3$  kJ/mol. For  $\omega$ -acetyl-PCL samples (C-PCL-A and D-PCL-A), constant  $E_a$  values of  $180 \pm 10$  kJ/mol were obtained throughout the degradation process. The  $E_a$  values of  $\omega$ -acetyl-PCL samples were much higher than that of C-PCL-H, indicating that the reaction mechanism differs between nonend-capped PCL and  $\omega$ -acetyl-PCL. For the



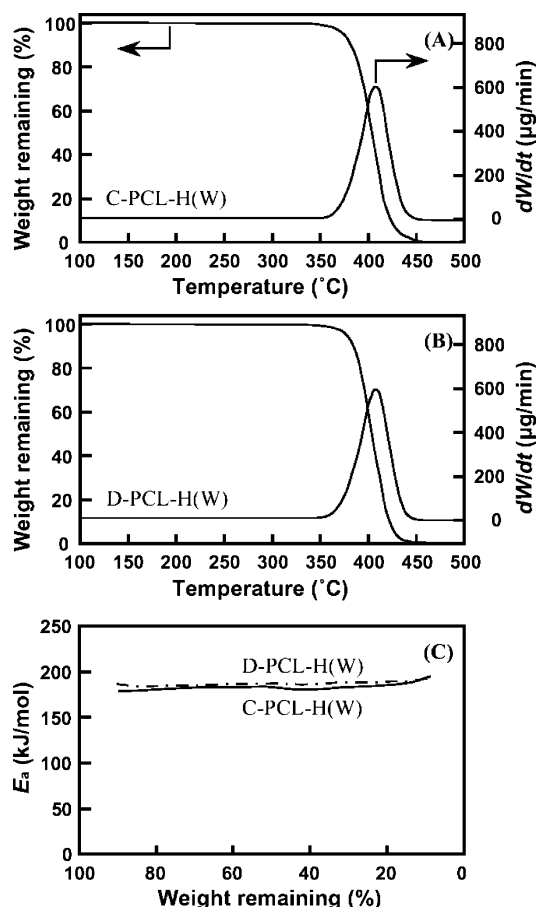
**Figure 2.** Apparent activation energies ( $E_a$ ) at various residual weight fractions evaluated for PCL samples with different chain-end structures.

D-PCL-H sample, the apparent  $E_a$  value calculated significantly changed with the residual weight fraction as shown in Figure 2. The  $E_a$  value of the D-PCL-H sample revealed a constant value of about 87 kJ/mol at the initial stage of degradation but then increased to 154 kJ/mol with progress of degradation. The change in the  $E_a$  value of thermal degradation of D-PCL-H indicates that the reaction mechanism changes with temperature. The  $E_a$  values of C-PCL-H and D-PCL-H at the initial stage are relatively similar to the values reported by Persenaire et al. of 92 kJ/mol<sup>12</sup> and Aoyagi et al. of 74 kJ/mol.<sup>13</sup> On the other hand, the  $E_a$  values of the  $\omega$ -acetyl-PCL samples are comparable to the values reported by Madras groups of 201<sup>14</sup> and 229–259 kJ/mol.<sup>15</sup>

From these results, it has been concluded that the thermal degradation of PCL dominantly progresses from the  $\omega$ -hydroxyl chain-end by the unzipping reaction and that the end-capping with the acetyl group at the  $\omega$ -hydroxyl chain-end of PCL molecules depresses the unzipping reaction.

Recently, Nishida et al.<sup>19</sup> reported that the Sn compounds of residual synthesis catalyst play an important role in the thermal degradation reaction of poly(L-lactide) (PLLA), and that the thermal degradation temperature of PLLA is strongly depending on the content of Sn compounds. For PLLA samples with high Sn contents, the thermal degradation took place at  $\omega$ -hydroxyl chain-ends via the unzipping reaction by the function of Sn compounds. However, the PLLA samples with low Sn contents were randomly degraded in PLLA chains.

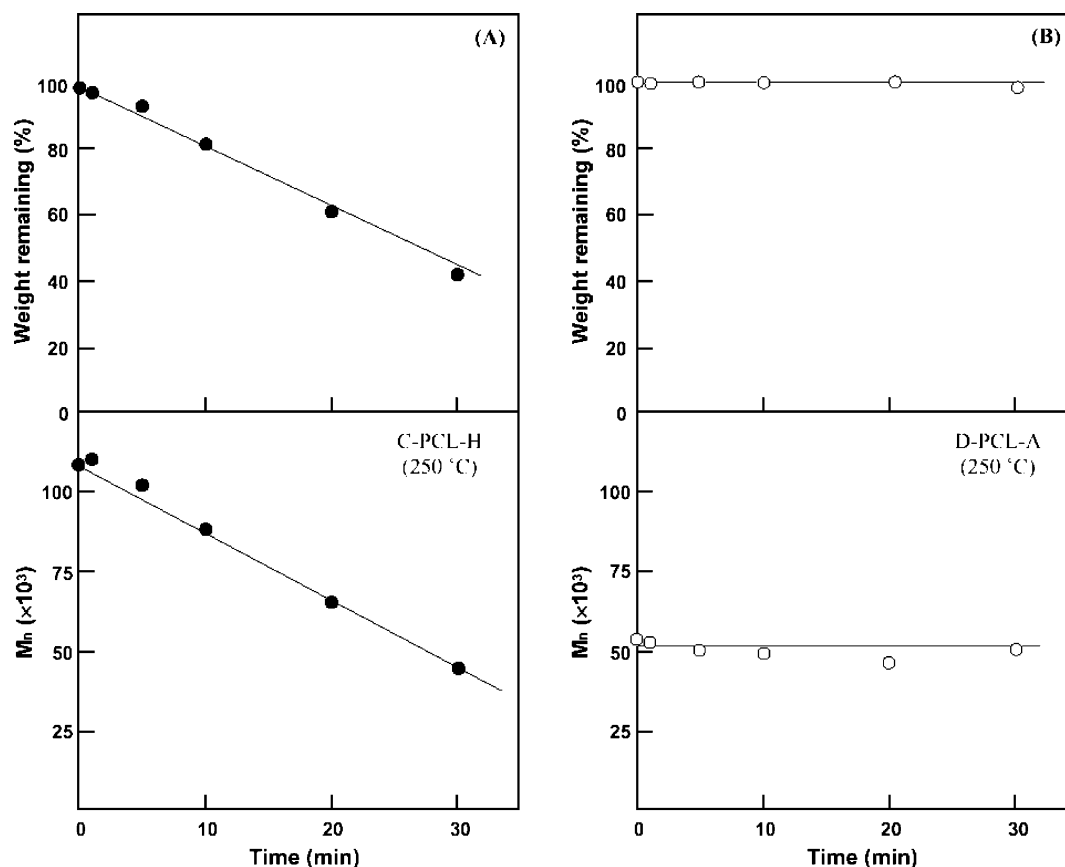
In this study, we prepared the PCL samples by using Zn-based catalysts. The contents of Zn residues in PCL samples were determined by atomic absorption spectrometry, and the results are shown in Table 1. As shown in Table 1, Zn contents of PCL samples were varied from 4.65 to 2600 ppm. The Zn contents of the  $\omega$ -acetyl-PCL samples were much lower than those of the  $\omega$ -hydroxyl-PCL samples. To remove the Zn residues in the samples, the  $\omega$ -hydroxyl-PCL samples were washed in a chloroform solution of polymer with 5% of acetic acid. On the basis of <sup>1</sup>H NMR analysis for PCL samples with low molecular weights, it was confirmed that the  $\omega$ -hydroxyl chain-ends of the PCL molecules were



**Figure 3.** TGA and DTA curves of thermal degradation of C-PCL-H(W) (A) and D-PCL-H(W) (B) samples. Apparent activation energies ( $E_a$ ) at various residual weight fractions evaluated for these samples were shown in part C.

retained after the washing with acetic acid. After the washing with acetic acid, the Zn contents in PCL samples were decreased to less than 3.11 ppm.

Figure 3 shows the typical TGA curves of PCL samples after washing with acetic acid. The TGA curves of  $\omega$ -hydroxyl-PCL samples after washing (C-PCL-H(W) and D-PCL-H(W)) significantly shifted toward the higher temperature region compared with  $\omega$ -hydroxyl-PCL samples before washing (C-PCL-H and D-PCL-H), and the curves revealed identical profiles with  $\omega$ -acetyl-PCL samples (see in Figures 1 and 3). The apparent activation energies of thermal degradation for  $\omega$ -hydroxyl-PCL samples after washing were calculated from TGA data. Figure 3C shows the apparent activation energies ( $E_a$ ) of thermal degradation for  $\omega$ -hydroxyl-PCL samples after washing at different residual weight fraction of samples. The apparent  $E_a$  values for  $\omega$ -hydroxyl-PCL samples after washing were calculated to be  $180 \pm 7$  kJ/mol, and these values were also identical with those of  $\omega$ -acetyl-PCL samples. These results suggest that the shift toward the higher temperature region of TGA curves for  $\omega$ -acetyl-PCL samples is caused by the removal of the residual Zn compound and not by the end-capping treatment of the  $\omega$ -hydroxyl chain-ends. The residual Zn compounds should catalyze the depolymerization reaction of PCL molecules. As a result, the activation energy of thermal degradation for PCL molecules reduced in the presence of



**Figure 4.** Sample weight and number-average molecular weight ( $M_n$ ) changes during isothermal degradation of PCL at 250 °C. (A) C-PCL-H and (B) D-PCL-A.

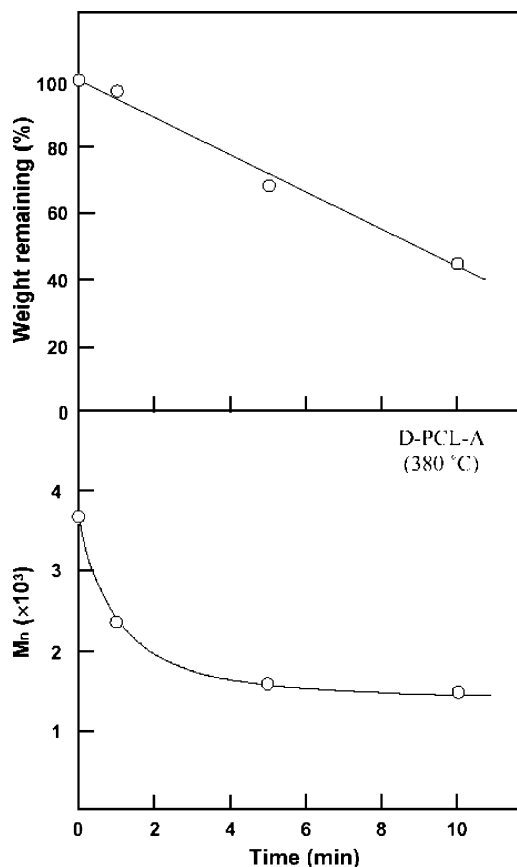
Zn compounds, and the thermal degradation started from the lower temperature region.

Isothermal degradations of PCL samples were carried out under nitrogen atmosphere at 250 and 380 °C. Figure 4 shows the time-dependent changes in sample weight and number-average molecular weight ( $M_n$ ) during isothermal degradation at 250 °C. Both the sample weight and  $M_n$  of C-PCL-H were unchanged during the preheating process from room temperature to 250 °C at a heating rate of 30 °C/min. As shown in Figure 4A, after the temperature reached at 250 °C, both the sample weight and  $M_n$  of C-PCL-H decreased linearly with degradation time. The rate of decrease in the  $M_n$  value was almost consistent with the rate of weight loss. A linear relationship between the  $M_n$  and time is accounted for in terms of a depolymerization from the ends of polymer chains via an unzipping mechanism. The thermal chain scission of C-PCL-H produces almost exclusively small molecules with low boiling points. On the other hand, the sample weight and  $M_n$  value of D-PCL-A sample remained unchanged during isothermal treatment at 250 °C for 30 min (Figure 4B).

Figure 5 shows the time-dependent changes in sample weight and  $M_n$  of D-PCL-A sample during isothermal degradation at 380 °C. The  $M_n$  value of the D-PCL-A sample was reduced to 3700 from 54 000 during the preheating process from room temperature to 380 °C, while the sample weight was unchanged. During the isothermal degradation process at 380 °C, the sample weight of D-PCL-A decreased linearly with degradation time. In contrast, the  $M_n$  of D-PCL-A decreased nonlinearly with time. Substantial

decrease in  $M_n$  was observed at the initial stage of isothermal degradation at 380 °C. The rate of decrease in  $M_n$  was 5-fold faster than the weight loss of PCL in the initial stage at 380 °C. The nonlinear relationship between  $M_n$  and time suggests that unzipping is not a major process in the isothermal degradation at 380 °C. When the chain scission is completely random, a linear relationship between the inverse of  $M_n$  and time is predicted. The plots of inverse  $M_n$  against time for PCL are convex (data not shown), suggesting that thermal degradation of PCL does not proceed via simple random scission of the polymer chain.

After isothermal degradation at 380 °C for 5 min, the molecular structure of the residual D-PCL-A sample ( $M_n = 1600$ ) was characterized by  $^1\text{H}$  NMR analysis. In the  $^1\text{H}$  NMR spectrum of the residual D-PCL-A sample, the methylene and methine proton signals arising from the 5-hexenoic acid chain-end were detected at 4.99 and 5.78 ppm. In addition, the peak from the methylene proton of the  $\epsilon$ -caprolactone unit at the  $\alpha$ -carboxylic acid chain-ends was detected at 2.47 ppm. The molecular weight of the residual PCL sample was determined from the peak intensities of the methylene proton at the 5-hexenoic acid chain-ends and the main-chain methylene proton in the  $^1\text{H}$  NMR spectrum. The calculated value ( $M_n = 1800$ ) was almost consistent with the value from GPC ( $M_n = 1600$ ). This result indicates that most of the chain-ends for the residual PCL sample were 6-hydroxyhexanoic acid (ring-opening structure of  $\epsilon$ -caprolactone) and 5-hexenoic acid as the  $\alpha$ - and  $\omega$ -chain-end, respectively. The formation of 5-hexenoic acid chain-ends indicates that the chain scission of PCL molecules during



**Figure 5.** Sample weight and number-average molecular weight ( $M_n$ ) changes during isothermal degradation of D-PCL-A at 380 °C.

the thermal degradation at 380 °C progresses by a random cis elimination reaction at ester bonds, as shown in Figure 6.

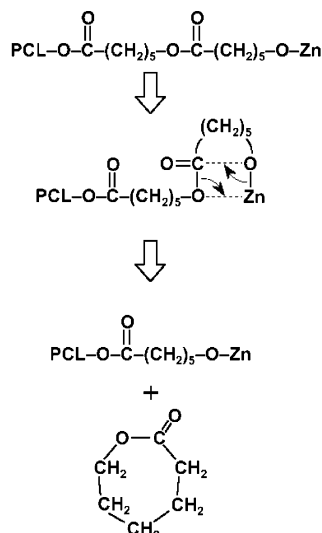
The volatile products of PCL samples were analyzed by Py-GC/MS at 280, 358, 386, and 445 °C, respectively. In the Py-GC curve of C-PCL-H at 280 °C, three peaks were detected at retention time ( $t_R$ ) of 10.2, 18.4, and 25.7 min as shown in Figure 7A. Figure 8 shows the mass spectra of three peaks detected as volatile products. For the first peak,

the characteristic signals of  $\epsilon$ -caprolactone were recorded at  $m/z$  (mass-to-charge ratio) = 28, 42, 56, 70, 84, and 114. The additional signals at  $m/z$  = 73, 97, 128, 141, 207, and 229 can be attributed to the cyclic dimer and trimer of  $\epsilon$ -caprolactone. In the Py-GC curve of D-PCL-A at 280 °C, there were no peaks corresponding to the volatile products of PCL. As shown in Figure 7B–D, three peaks corresponding to the monomer, dimer, and trimer of  $\epsilon$ -caprolactone were also detected in Py-GC curves of D-PCL-A at 358, 386, and 445 °C. Surprisingly, the signal corresponding to 5-hexenoic acid ( $t_R$  = 7.8 min) and its oligomers were rarely detected in all of the Py-GC/MS spectra. These results indicate that the weight loss during thermal degradation of D-PCL-A is mainly caused by the formation of small cyclic molecules.

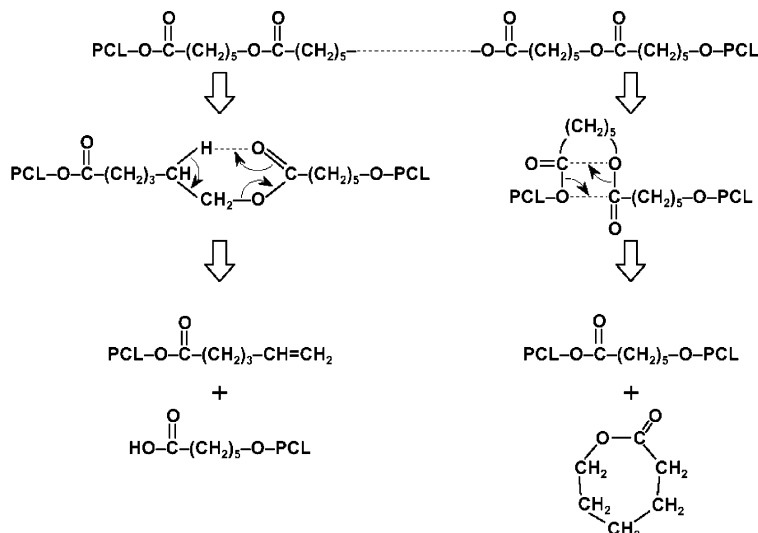
Persenaire et al.<sup>12</sup> studied thermal degradation of PCL by high-resolution TGA simultaneously coupled with mass spectrometry and Fourier transform infrared spectrometry. Two well-resolved degradation peaks were observed in high-resolution DTA curves. Based on the evolved gas analysis, they concluded that thermal degradation of PCL proceeded in a two-stage degradation mechanism. That is, the first step is a random rupture of the PCL chains via a cis elimination reaction which produces  $H_2O$ ,  $CO_2$ , and 5-hexenoic acid, and the second step is an unzipping depolymerization process at the chain-ends with hydroxyl end groups to form  $\epsilon$ -caprolactone. In this study, we could detect only the  $\epsilon$ -caprolactone and its cyclic oligomers, whereas 5-hexenoic acid and its oligomers were not detected.

On the basis of  $^1H$  NMR analysis of residual samples after isothermal degradation at 380 °C, most of the residual PCL molecules were found to have the  $\alpha$ -carboxylic acid and  $\omega$ -olefinic (5-hexenoic acid) chain-ends. It is expected that the cyclic monomer and oligomers of  $\epsilon$ -caprolactone cannot be generated from  $\omega$ -olefinic chain-ends. The cyclic monomer and oligomers of  $\epsilon$ -caprolactone may be formed by the intramolecular transesterification of PCL molecules and/or unzipping reaction from  $\alpha$ -carboxylic acid chain-ends. If the cyclic monomer and oligomers of  $\epsilon$ -caprolactone produce

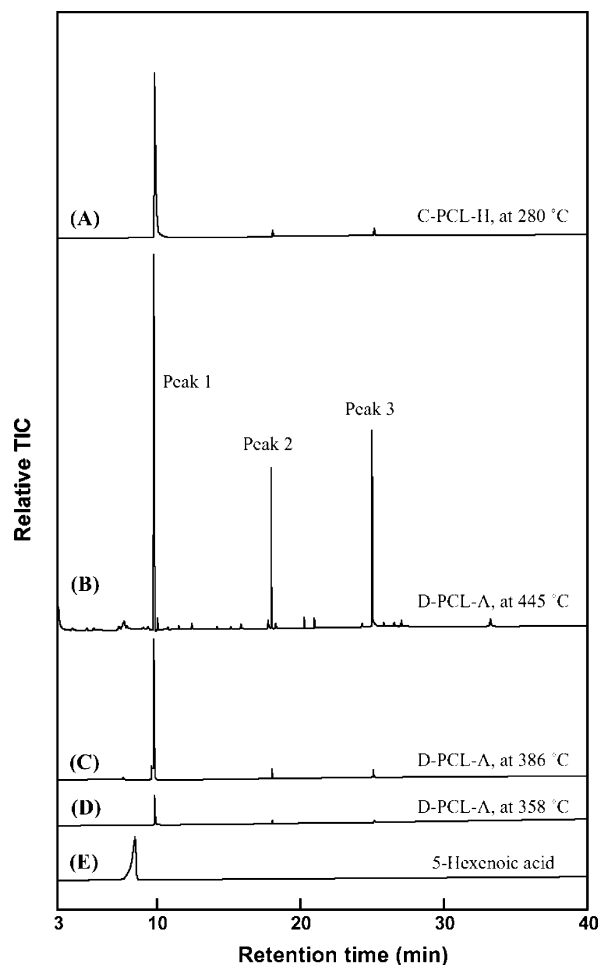
**A) Unzipping reaction catalyzed by Zn residue at temperatures below 300 °C**



**B) cis-Elimination reaction with intramolecular transesterification at temperatures above 300 °C**



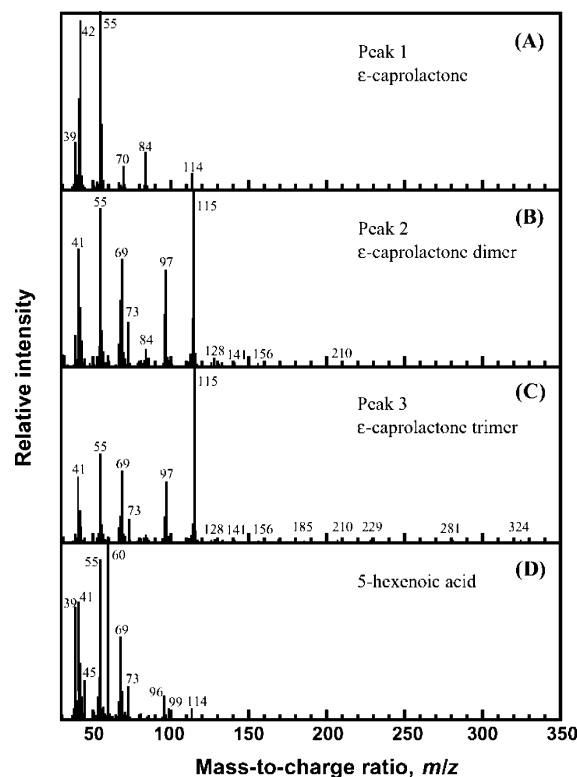
**Figure 6.** Schematic illustrations of thermal degradation reactions of PCL molecules.



**Figure 7.** Total ion chromatogram (TIC) of Py-GC/MS for PCL at various temperatures. (A) C-PCL-H degraded at 280 °C, (B) D-PCL-A degraded at 445 °C, (C) D-PCL-A degraded at 386 °C, (D) D-PCL-A degraded at 358 °C, and (E) 5-hexenoic acid.

by the unzipping reaction from  $\alpha$ -carboxylic acid chain-ends, the rate of weight loss should be accelerated with time during isothermal degradation process. However, the weight loss of PCL during isothermal degradation at 380 °C progressed proportionally with reaction time as shown in Figure 5. This result indicates that the formation of cyclic compounds is dominantly formed by the intramolecular transesterification of PCL molecules. It is concluded that the thermal degradation of PCL molecules occurs by competitive reactions between the random chain scission via a cis elimination reaction and the cyclic rupture via intramolecular transesterification of PCL molecules at temperature region above 300 °C, as shown in Figure 6.

It is known that the cis elimination reaction occurs for the thermal degradation reaction of poly( $\beta$ -propiolactone) (PPL).<sup>10,22</sup> The DTA curve of PPL recorded at a heating rate of 10 °C/min under nitrogen atmosphere showed one peak at 230 °C, and the acrylic acid and its oligomers were detected as the volatile products. In this study, the single peak was observed at around 410 °C in DTA curves of metal-free PCL samples. The degradation temperature for PCL was much higher than that for PPL, although both the degradation reactions progress through the cis elimination reaction. In both cases of PPL and PCL, the carbon atom at the  $\beta$ -position to the ester oxygen is methylene, and the  $\beta$ -C–H bond



**Figure 8.** Mass spectra of PCL pyrolysis products. (A) Peak 1 ( $\epsilon$ -caprolactone), (B) peak 2 (dimer of  $\epsilon$ -caprolactone), (C) peak 3 (trimer of  $\epsilon$ -caprolactone), and (D) 5-hexenoic acid.

participates in the cis elimination reaction. The  $\beta$ -C–H bond of the methylene group for PPL may be activated by the neighboring carbonyl group. As a result, the thermal degradation of PPL takes place at the lower temperature region via cis elimination reaction. In contrast for PCL, the methylene group at the  $\beta$ -position may be hardly activated by the neighboring methylene group at the  $\gamma$ -position to the ester oxygen at lower temperature region. Therefore, the cis elimination reaction of PCL can be detected at the higher temperature region. In addition, due to such low activity of the  $\beta$ -C–H bond in PCL, the intramolecular transesterification reaction occurs in competition with the cis elimination reaction at higher temperature region.

## Conclusions

Thermal degradation behaviors of these PCL samples with different chain-end structures were examined under both isothermal and nonisothermal conditions. The thermal degradation of metal free PCL samples occurred at temperatures above 300 °C regardless of the chain-end structure, giving rise to the formation of cyclic monomer and oligomers of  $\epsilon$ -caprolactone. In addition, 5-hexenoic acid units were detected in the residual polymer samples as main  $\omega$ -chain-end. These results suggest that the dominant reaction of thermal degradation for PCL at a temperature above 300 °C is a combination of the random chain scission via a cis elimination reaction and the cyclic rupture via intramolecular transesterification of PCL molecules. In contrast, the thermal degradation of PCL samples containing high amounts of residual zinc compounds from the synthesis process revealed



the selective unzipping depolymerization step at temperatures below 300 °C producing  $\epsilon$ -caprolactone exclusively.

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