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## Precise Depolymerization of Poly(3-hydroxybutyrate) by Pyrolysis

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### 1. Introduction

Poly(3-hydroxybutyrate) (PHB) is a well known microbial and biodegradable polymer, which is accumulated and stored by prokaryotic microorganisms at levels up to 90% of their cellular dry weight (Steinbüchel & Valentin, 1995). PHB has been attracting much interest from researchers not only as an environmentally compatible thermoplastic, but also as a polymeric material obtainable from renewable resources and having a high melting temperature of around 180 °C (Marchessault et al., 1981).

A major problem of PHB when used as a thermoplastic is its thermal instability during melt-processing. Therefore, intense interest has been shown in the thermal degradation of PHB and other related poly(hydroxyalkanoate)s (PHAs). Recently, it has been demonstrated that PHB is a chemically recyclable material with end products such as crotonic acid, linear oligomers having a crotonate end group (Morikawa & Marchessault, 1981), and a cyclic trimer (Melchioris et al., 1996). Melchioris et al. found that cyclic oligomers were obtained via back-biting reactions in a toluene solution with catalysts such as dibutyltin dimethoxide. However, the present review concentrates upon the thermal degradation of PHB in melt.

If plastic materials originating from renewable resources can be efficiently recycled through precise control of their thermal degradation, an ideal recycling system could be constructed for plastic products, in which the resources and production energy of the materials are minimized.

### 2. Accumulative results on thermal degradation behavior

The thermal degradation behavior of PHB, including other PHAs, has been discussed in many reports with the main studies listed in Table 1.

#### 2.1 Analytical procedures

Several thermoanalytical procedures have been used to investigate the thermal degradation behavior of PHB, including thermogravimetry (TG) for the analysis of weight loss behavior (Kopinke et al., 1999; Galego & Rozsa, 1999; Li et al., 2001; He et al., 2001; Lee et al., 2001; Aoyagi et al., 2002; Carrasco et al., 2006; Kim et al., 2006; Kawalec et al., 2007; Liu et al., 2009;

Ariffin et al., 2008, 2010), differential scanning calorimetry (DSC) for monitoring the heat of reaction (Kopinke et al., 1996), fast atom bombardment mass spectrometry (FAB-MS) (Ballistreri et al., 1989), electrospray ionization mass spectrometry (ESI-MS) (Kawalec et al., 2007), pyrolysis-mass spectrometry (Py-MS) (Abate, 1994; Kopinke et al., 1996), pyrolysis-gas chromatography (Py-GC) (Lehrle, 1994), pyrolysis-GC/mass spectrometry (Py-GC/MS) (Kopinke et al., 1996, 1997; Aoyagi et al., 2002; Ariffin et al., 2008, 2010), TG/Fourier transform infrared spectroscopy (TG/FTIR) (Li et al., 2003), NMR (Melchiors et al., 1996; Kopinke et al., 1996; Ariffin et al., 2009), and pyrolysis-GC/FTIR (Li et al., 2003; Gonzalez et al., 2005), for the analysis of volatile products, and size exclusion chromatography (SEC) (Grassie et al., 1984; Kunioka & Doi, 1990; Nguyen et al., 2002; Kim et al., 2006) for the analysis of changes in molecular weight of residual PHB.

Year	First author	Analytical procedure	Heating method	Kinetic parameters		
				$E_a$ (kJ mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$n$ / random $L$
1981	Morikawa, H.	GC, MS, NMR	multiple isothermal heating	-	-	-
1984	Grassie, N.	TG, DSC, TVA, GPC	multiple isothermal heating	247	-	random degradation
1989	Ballistreri, A.	TG, EI-MS, CI-MS, FAB-MS	single constant heating rate	-	-	-
1990	Kunioka, M.	GPC, NMR	multiple isothermal heating	212	-	random degradation
1993	Gogolewski, S.	Injection moulding SEC, DSC	heating at 135 - 160°C	-	-	-
1994	Abate, R.	TG, Py-MS, NMR	single constant heating rate	-	-	-
1994	Hoffman, A.	Mechanical strength, GPC	multiple isothermal heating	-	-	-
1994	Lehrle, R. S.	Py-GC with microthermocouple-controlled filament	isothermal heating at 350°C	-	-	$n = 1$
1995	Lehrle, R.	Py-GC with microthermocouple-controlled filament, MS	isothermal heating at 350°C methanolysis at 84°C	-	-	random degradation + chain-end reactions
1996	Kopinke, F. D.	TG, DSC, Py-MS, Py-GC/MS	single constant heating rate	DSC: 235 Py-GC/MS: 380	$1 \times 10^{19}$	$n = 1, 1.5$
1996	Melchiors, M.	GPC, NMR	multiple isothermal heating, in refluxing solvent	$DG^0_{\text{depoly}} = -70 \text{ kJ mol}^{-1}$ $DH^0_{\text{depoly}} = -43 \text{ kJ mol}^{-1}$		
1997	Kopinke, F. D.	TG, DSC, Py-MS, Py-GC/MS	single constant heating rate	-	-	-
1999	Galego, N.	TG, FTIR	single constant heating rate	PHB: 296 PHBV: 233-311	PHB: $6.36 \times 10^{22}$ PHBV: $10^{22} - 10^{29}$	$n = 1$

Year	First author	Analytical procedure	Heating method	Kinetic parameters		
				$E_a$ (kJ mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$n$ / random $L$
2001	Li, S. D.	TG	multiple constant heating rates	-	-	-
2001	He, J. D.	TG	multiple constant heating rates	-	-	-
2001	Lee, M. Y.	TG/DTA	single constant heating rate	PHB: 296 PHA: 253-378	-	$\beta$ -elimination
2002	Aoyagi, Y.	TG, Py-GC/MS	multiple constant heating rates	111	-	$\beta$ -elimination
2002	Nguyen, S.	NMR, GPC, FAB <sup>+</sup> -MS	Isothermal heating monitoring MW changes	-	-	random degradation
2003	Li, S. D.	TG, TG-FTIR, Py-GC/MS	multiple constant heating rates (Coats-Redfern integral method)	298-307	$4.81 \times 10^{22}$ $- 4.43 \times 10^{25}$	$n=0.6-0.8$
2005	Gonzalez, A.	Py-GC/FTIR, Hi-Res TGA	multiple isothermal heating	-	-	-
2006	Kim, K.-J.	TG, GPC, NMR, Py-GC/MS	multiple constant heating rates isothermal heating	GPC: $182 \pm 23$ $178 \pm 10$ (Ca <sup>+</sup> ) TG: $140 \pm 4$ $119 \pm 2$ (Ca <sup>+</sup> )	-	random chain scission via $\beta$ -elimination reaction nth-order reaction
2006	Carrasco, F.	TG	single constant heating rate	PHB: 304.1 PHBV: 325.4-367.4	PHB: $2.50 \times 10^{27}$ PHBV: $10^{28} - 10^{31}$	nth-order reaction
2007	Kawalec, M.	TG, GPC, NMR, MS	plural isothermal heating	-	-	random chain scission E1cB mechanism random chain scission
2008	Kim, K.-J.	TG, GPC, NMR, Py-GC/MS	multiple constant heating rates isothermal heating	-	-	random chain scission
2008	Ariffin, H.	TG, FTIR, FAB-MS, Py-GC/MS	multiple constant heating rates molecular orbital calculation	$117 \pm 3$ (crude) $135 \pm 4$ (purified)	$3.3 \times 10^8$ $- 1.18 \times 10^9$ $1.9 \times 10^{10}$ $- 3.5 \times 10^{10}$	$n = 0$ unzipping $\beta$ -elimination
2009	Ariffin, H.	TG, FTIR, FAB-MS, Py-GC/MS	multiple constant heating rates	-	-	unzipping $\beta$ -elimination
2009	Liu, Q. S.	TG	single constant heating rate	PHBV: 340 - 550	-	random chain scission
2010	Ariffin, H.	TG, NMR, Py-GC/MS	multiple constant heating rates	$122 \pm 2$ (MgO) $119 \pm 3$ (Mg(OH) <sub>2</sub> )	$2.9 \times 10^{10}$ $1.2 \times 10^{10}$	$n = 0 - 1$ unzipping $\beta$ -elimination

Table 1. List of studies on thermal degradation behaviors of PHB and PHAs.

## 2.2 Evaluation of degradation kinetics

### 2.2.1 Activation energy, $E_a$

Previous reports have shown that the activation energy ( $E_a$ ) value of the degradation falls within a wide range of 110-550 kJ mol<sup>-1</sup>. This range of values can be classified into three categories: 1) 235-550 kJ mol<sup>-1</sup> calculated with single constant heating rate methods based on weight loss (Kopinke et al., 1996; Galego & Rozsa, 1999; Li et al., 2001; Carrasco et al., 2006; Liu et al., 2009), 2) 111-140 kJ mol<sup>-1</sup> calculated with multiple constant heating rate methods based on weight loss (Aoyagi et al., 2002; Kim et al., 2006; Ariffin et al., 2008, 2010), and 3) 178-247 kJ mol<sup>-1</sup> calculated with non-auto-catalytic random degradation analysis based on changes in molecular weight (Grassie et al., 1984; Kunioka & Doi, 1990; Kim et al., 2006).

### 2.2.2 Single and multiple constant heating rate methods

One reason for the higher values obtained using the single constant heating rate method (e.g., Eq. 1, Kopinke et al., 1996) is probably due to the different reactions proceeding in a mixed and complex manner. If this is true, it is difficult to evaluate the correct  $E_a$  value of each elementary reaction, because the  $E_a$  value is calculated as an apparent value from the slope of the total plot made up of multiple reactions.

$$\begin{aligned} -dw / dt &= k \cdot \exp(-E_a / RT) \cdot (1-w)^n \\ \ln(-dw / dt) - n \cdot \ln(1-w) &= \ln k - E_a / RT \end{aligned} \quad (1)$$

Thus, this method sometimes produces a meaningless value. On the other hand, if the multiple constant heating rate method is used, which is explained in section 3.1, and if the calculated  $E_a$  value is constant in a range of residual weight ( $w$ ), it can be assumed that a constant reaction state is maintained within the range of  $w$ , giving assurance that the obtained  $E_a$  value is significant for the reaction. However, if the plot of the calculated  $E_a$  value against  $w$  shows a slope in the range of  $w$ , it indicates that multiple reactions are proceeding in a mixed manner. By using the multiple constant heating rate method, Aoyagi et al. (Aoyagi et al., 2002), Kim et al. (Kim et al., 2006), and our group (Ariffin et al., 2008, 2010) reported the  $E_a$  value of PHB thermal degradation as being in a relatively narrow range of 111-140 kJ mol<sup>-1</sup>. It was proposed that this small variation in  $E_a$  value was due to the influence of residual metal ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup> and Zn<sup>2+</sup>.

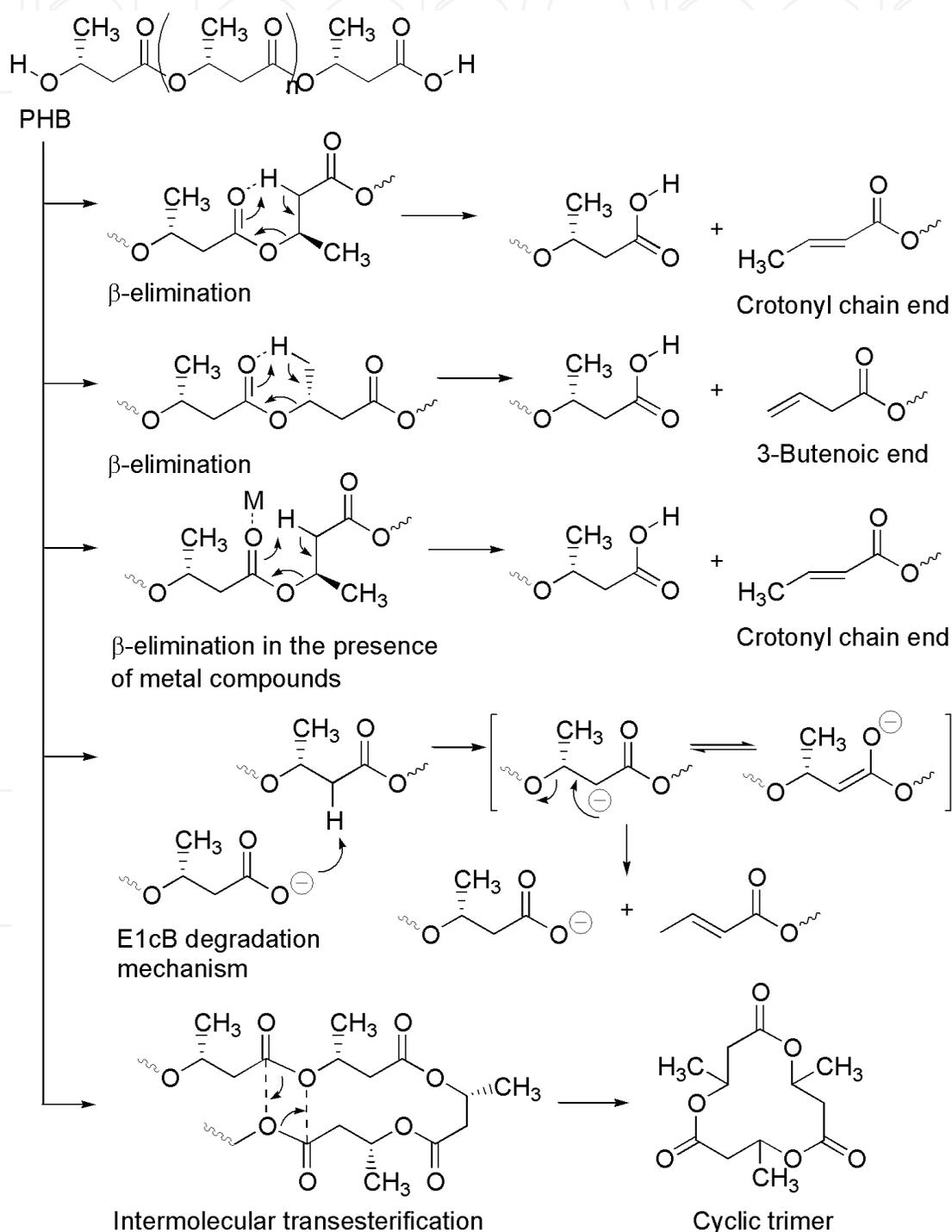
### 2.2.3 Estimation from molecular weight change

In order to avoid the influence of some complex factors on pyrolysis at high temperatures, such as the overlapping of multiple reactions and the occurrence of secondary reactions, the  $E_a$  value of  $\beta$ -elimination has also been calculated from molecular weight changes in a lower temperature range of 170-200 °C. Interestingly, in spite of the same expected degradation mechanism for  $\beta$ -elimination, obtained  $E_a$  values were in a medium range of 178-247 kJ mol<sup>-1</sup>. Kim et al. (Kim et al., 2006) suggested that a discrepancy in the obtained  $E_a$  values, i.e. 140 and 182 kJ mol<sup>-1</sup> from the weight loss and the molecular weight change, respectively, was caused in part by the auto-acceleration effect of low molecular weight compounds.

## 2.3 Thermal degradation mechanisms

In Scheme 1, previously reported mechanisms of the thermal degradation of PHB and PHAs are illustrated. Even though many approaches have been taken on the subject of PHB

thermal degradation, a clear explanation for the wide variation in  $E_a$  value has yet to be provided. Despite this uncertainty, the random  $\beta$ -elimination scission has been widely held as the exclusive degradation mechanism of PHB based on typical structures of pyrolysis products, i.e. crotonic acid and oligomers with a crotonate end-group (Morikawa & Marchessault, 1981; Ballistreri et al., 1989). Recently, an E1cB mechanism proceeding via  $\alpha$ -deprotonation by a carboxylate anion to produce the same products was proposed (Kawalec et al., 2007).



Scheme 1. Reported thermal degradation mechanisms of PHAs.

## 2.4 Suggestions of other degradation mechanisms

There have been suggestions that some other reactions may be occurring in the course of PHB thermal degradation. Lehrle et al. reported that the analytical results of partial pyrolysis of PHB showed some deviations from theoretical predictions of random scission statistics (Lehrle et al., 1994, 1995). These deviations were probably due to reactions induced by the end groups. Kopinke et al. found that the isothermal degradation curve at 270 °C did not agree with the model curves of random degradation reactions, and that non-isothermal thermogravimetric (TG) and differential TG (DTG) curves of PHB seemed to better fit a first-order degradation reaction curve (Kopinke et al., 1996). However, they also commented that the high  $E_a$  value of 380 kJ mol<sup>-1</sup> obtained by using a single heating rate method was not chemically meaningful and may have been due to an auto-catalytic reaction. Finally, they suggested that the observed degradation behavior was characteristic of a chain reaction with a short kinetic chain length. Galego and Rozsa (Galego & Rozsa, 1999) came to similar conclusions to those of Kopinke et al. (Kopinke et al., 1996). Nguyen et al. (Nguyen et al., 2002) also suggested the occurrence of auto-acceleration in the PHB thermal degradation at 190 °C based on the changes in molecular weight.

## 3. Precise depolymerization of PHB

Based on abovementioned results, three features are noteworthy in relation to PHB thermal degradation, i.e. 1) during the pyrolysis of PHB, other kinds of degradation mechanisms in addition to  $\beta$ -elimination proceed at the same time, making the kinetics analysis complicated; 2) obtained plausible  $E_a$  values may incorporate some parameters of other reactions; and 3) the thermal degradation of PHB may be auto-accelerated.

### 3.1 Kinetic analysis by a multiple constant heating rate method

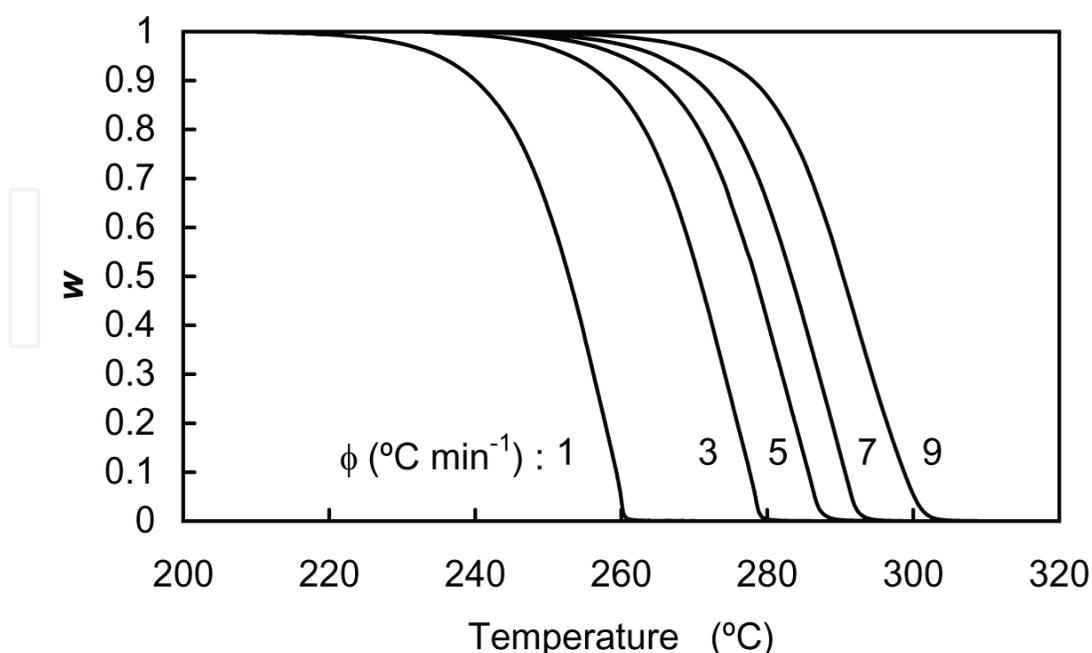


Fig. 1. TG curves of PHB degradation at multiple heating rates ( $\phi=1, 3, 5, 7$  and  $9\text{ °C min}^{-1}$ ) in a constant  $\text{N}_2$  flow ( $100\text{ mL min}^{-1}$ ).

In order to analyze the thermal degradation kinetics by the multiple constant heating rate method (Nishida et al., 2000), thermograms at heating rates varying from 1 to 9 °C min<sup>-1</sup> are illustrated in Fig. 1, in which each thermogram showed smooth and one-step decomposition from the beginning to almost completion. The TG traces are shifted up the temperature scale with increase in the rate. If the pyrolysis of PHB proceeds by the same degradation process with fixed apparent parameters,  $E_a$  and  $A$ , over the examined temperature range, the thermogravimetric curves can be superposed by shifting them along the abscissa as shown by Eq. 2 (Qzawa, 1965).

$$1/T_1 = 1/T_2 + (R/bE_a)(\log \phi_2 - \log \phi_1) \quad (2)$$

where  $T$ ,  $R$  and  $\phi$  are temperature in degrees Kelvin, the molar gas constant and heating rate, respectively, and  $b$  is a constant value for Doyle's approximation (Doyle, 1961, 1962) as follows:

$$\log p(y) \cong -a - bE_a/RT \quad (3)$$

where  $y = Ea/RT$ . If  $y > 20$  in the function  $p(y)$ , values of constants  $a$  and  $b$  are 2.315 and 0.4567, respectively.

Where the thermogravimetric curves are given as plots of fractional weight ratio,  $w$ , versus the right-hand side in Eq. 2, superposition produces a single master curve. This master curve means that the thermogravimetric curves of PHB pyrolysis can be analyzed as a single degradation process with fixed apparent parameters,  $E_a$  and  $A$  (Flynn & Wall, 1966a).

### 3.1.1 Activation energy, $E_a$

The logarithms of the heating rates,  $\log \phi$ , are plotted against  $1/T$  based on Eq. 2. Straight lines for each fraction  $w$  are drawn by the method of least squares. From the slopes of these lines, tentative  $E_a$  values are calculated using the tentative  $b$  value, 0.4567. With an average tentative  $E_a$  value, the function  $y$  is calculated in the corresponding temperature range. For this range of function  $y$ , more accurate values of constants,  $a$  and  $b$ , were recalculated. The recalculated values of  $a$  and  $b$  are then used to re-determine a more accurate  $E_a$  value. The  $E_a$  value can also be determined from the slope of the plots of  $\ln(T^2/\phi)$  versus  $1/T$  using the same fractional  $w$  based on Eq. 4.

$$E_a = R \{ \ln(T_1^2/\phi_1) - \ln(T_2^2/\phi_2) \} / (1/T_1 - 1/T_2) \quad (4)$$

Eq. 4 was proposed by Reich (Reich, 1964). The method is based on taking the exponential integral in  $p(y)$  as approximately equal to the sum of the first two terms of the asymptotic expansion (Doyle, 1961). These two differently derived  $E_a$  values are compared to each other to select a plausible  $E_a$  value.

### 3.1.2 Order of reaction, $n$ , and pre-exponential factor, $A$

The general rate equation of decomposition can be written as follows:

$$-dw/dt = k_d g(w) \quad (5)$$

where  $k_d$  is the apparent specific rate constant of the decomposition reaction. The specific form of  $g(w)$  depends on the type of kinetic process but usually takes the form  $w^n$ , where  $n$  is the order of reaction. The temperature dependence of the rate constant is obtained by the

application of the Arrhenius equation. Considering the relationship  $dT/dt = \phi$ , Eq. 5 becomes as below (Flynn & Wall, 1966b).

$$-dw/dT = (A/\phi)\exp(-E_a/RT)g(w) \quad (6)$$

In the differential method, to evaluate the reaction order  $n$  for pyrolysis,  $-dw/dT$  is plotted against  $(1-w)$  based on Eq. 6. Experimental plots are then compared with the plots for the model reactions, *i. e.*, zero, half, 1st, and 2nd order reactions, and random degradation (Qzawa, 1965).

Although the differential value,  $-dw/dT$ , is effective for determining  $n$ , as shown above, it is ineffective in the lower range of  $(1-w)$  during the beginning period. To examine the behavior of the reaction in this early period for variation, especially, in comparison with a random degradation process, the integration method is examined. For some typical kinetic processes, the integral,  $-\int dw/g(w)$  has been given by Simha and Wall (Simha and Wall, 1952) and Ozawa (Ozawa, 1965), *e. g.*,  $-\int dw/g(w) = 1-w, 2(1-w^{1/2}), -\ln w, (1/w) - 1$ , and  $-\ln\{1-(1-w)^{1/2}\}$  for zero, half, 1<sup>st</sup>, 2<sup>nd</sup> order reactions and random degradation. The integral is expressed as follows:

$$-\int dw/g(w) = (AE_a/\phi R)p(y) = A\theta \quad (7)$$

where  $\theta = E_a/\phi R p(y)$  was demonstrated as the "reduced time" (Ozawa, 1965). In the integral method, the residual weight value  $w$  is plotted against  $A\theta$  with model reaction plots.

Consequently, the reaction-order:  $n$  and the pre-exponential factor:  $A$ , can be determined properly by comparing with the plots for  $n^{\text{th}}$ -order model reactions.

### 3.1.3 Random degradation: $L$ parameters

When a random degradation process is suggested to proceed, it is analyzed on the basis of the linear relation:  $\ln[-\ln\{1-(1-w)^{1/2}\}]$  vs.  $1/T$  for TG data (Nishida et al., 2000). However, the exact linear relation is only applicable to the random degradation ( $L = 2$ ), where  $L$  is the least number of repeating units of oligomer not volatilized.

The general relation between  $L$  and  $w$  for all random reactions was derived as Eq. 8 (Nishida et al., 2002).

$$\ln\{1-(1-w)^{1/2}\} = -\frac{L}{2}A\theta + \ln\left\{e^{\frac{L}{2}A\theta} - (e^{LA\theta} - Le^{A\theta} + L - 1)^{1/2}\right\} \quad (8)$$

When  $L=2$ ,

$$\ln\{1-(1-w)^{1/2}\} = -A\theta \quad (9)$$

$$\ln\left[-\ln\{1-(1-w)^{1/2}\}\right] = \ln A\theta = \ln \frac{AE_a}{\phi R} - a' - b' \frac{E_a}{RT} \propto \frac{1}{T} \quad (10)$$

where  $a'$  and  $b'$  are constants.

The  $n^{\text{th}}$ -order model-reactions' plots converge and indicate a linear relation in the beginning period, after which the reaction plots separate as the reaction progresses. On the other hand, all random degradation model reactions can be plotted linearly and in parallel over the

whole period. The linear parts in the beginning period of the group of  $n^{\text{th}}$ -order model reaction curves and the random degradation model reaction curves do not converge. Slopes of the beginning plots are obviously different between the  $n^{\text{th}}$ -order and random degradation model reactions. Therefore, by analyzing the plots, the random degradation and the  $n^{\text{th}}$ -order reactions can be distinguished even in the beginning period.

### 3.2 Products during PHB thermal depolymerization

In the dynamic degradation process of PHB in Py-GC/MS (EI), the total ion current (TIC) chromatograms of the evolved gas show two or three peaks attributable to crotonic acid monomer, related dimer and trimer.

Isothermal degradation of PHB in a glass tube oven was conducted at 260 °C *in vacuo* to determine the components of distilled pyrolyzates. The pyrolyzates were collected and analyzed by  $^1\text{H}$  NMR and  $^1\text{H}$ - $^1\text{H}$  COSY measurements with the major component: *trans*-crotonic acid, making up 67.7 % of the total PHB pyrolyzates. Other components were *cis*-crotonic acid and its derivatives (3.1 %) and oligomers having crotonyl end groups 29.2 %.

In order to examine the selective transformation of PHB during the catalytic thermal degradation, compositions of pyrolyzates generated in various temperature ranges were analyzed from the peak area in Py-GC/MS chromatograms and integrated with the fractional weight loss values from the TG data (Ariffin et al., 2010). The products from PHB/Mg compounds showed maximum values for monomeric acid composition at a temperature range of 230–240 °C, which was lowered by 40–50 °C in comparison with the non-catalytic pyrolysis. Especially, products from PHB-H/Mg(OH)<sub>2</sub> gave the highest selectivity for monomeric acids of ~100 %. These results indicate that Mg(OH)<sub>2</sub> is the most effective catalyst for the selective transformation of PHB. As a general tendency, it is noted that the lower the temperature, the higher the monomers' composition, indicating that the catalytic reaction is more favorable for monomer formation at lower temperatures.

### 3.3 Kinetic analysis of PHB thermal degradation

In order to analyze the thermal degradation behavior of PHB precisely, kinetic analysis of PHB degradation is carried out by using the improved random degradation analytical method (Nishida et al., 2002) and integral method (Ozawa, 1965; Nishida et al., 2000). The result of the improved random degradation analysis is illustrated in Fig. 2, in which the kinetics parameters:  $E_a = 120 \text{ kJ mol}^{-1}$  and  $A = 1.0 \times 10^9 \text{ s}^{-1}$  were employed for the model reactions: zero ( $n=0$ ), half ( $n=0.5$ ), 1<sup>st</sup> ( $n=1$ ), 2<sup>nd</sup>-order ( $n=2$ ), and random degradations (random  $L=2-6$ ).

The degradation of PHB (1 °C min<sup>-1</sup>) is initially faithful to a simulation plot of random degradation ( $L=2$ ). The  $L$  value was actually measured to be around 2 (crotonic acid) or 3 (dimer) by Py-GC/MS analysis. Thereafter, the observed curve gradually diverges from the random ( $L=2$ ) simulation with an associated rise in  $L$  value ( $L\sim 6$ ) (Fig. 2).

Plots in Fig. 3 show the integral analysis of the observed data (1 °C min<sup>-1</sup>) and the model reaction plots with parameter values:  $E_a=120 \text{ kJ mol}^{-1}$  and  $A=1.0 \times 10^9 \text{ s}^{-1}$ . Interestingly, the observed plots gradually decreased in weight similar to the random degradation process in the initial period, and thereafter the weight loss curve showed a linear relationship between  $w$  and  $A\theta$  in parallel to the 0<sup>th</sup>-order simulation plot.

According to Flynn and Wall (Flynn & Wall, 1966a), if the total material may be volatilized by two alternative degradation paths, for which the respective Arrhenius parameters are  $E_{a1}$

and  $A_1$  for path 1, and  $E_{a2}$  and  $A_2$  for path 2, and if the two paths are expressible by a combined function  $f(w)$ , then the integral function will be given by Eq. 11.

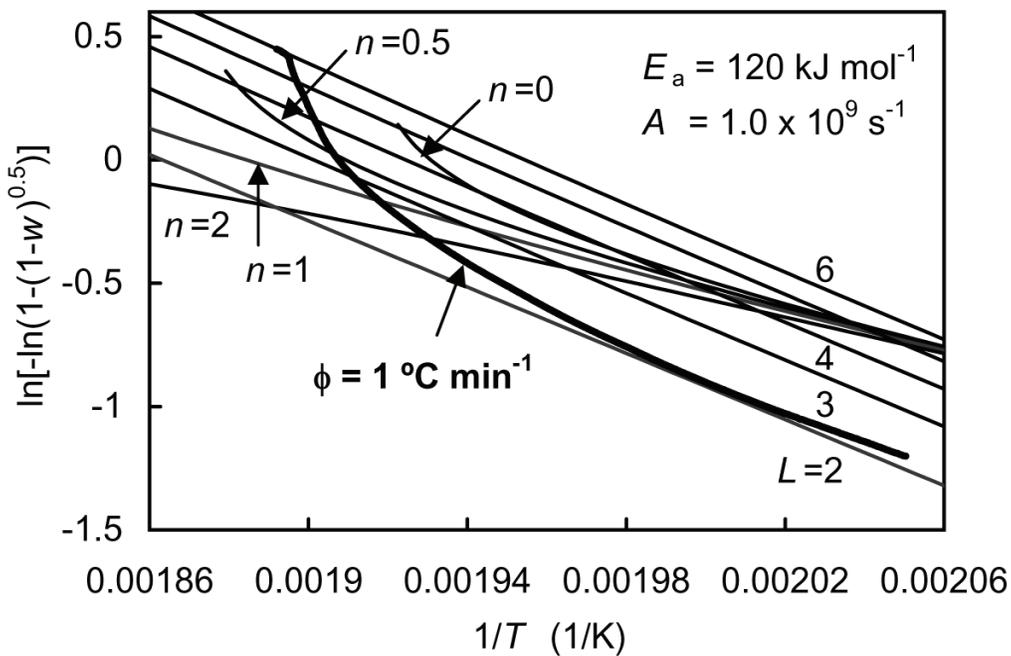


Fig. 2. Plots of  $\ln[-\ln\{1-(1-w)^{0.5}\}]$  vs.  $1/T$  for thermogravimetric data of PHB at a heating rate of  $1\text{ }^{\circ}\text{C min}^{-1}$  ( $E_a=120\text{ kJ mol}^{-1}$ ,  $A=1.0\times 10^8\text{ s}^{-1}$ ), and for model reactions. Model reactions: zero ( $n=0$ ), half ( $n=0.5$ ), 1<sup>st</sup> ( $n=1$ ), 2<sup>nd</sup>-order ( $n=2$ ), and random degradations (random  $L=2-6$ ).

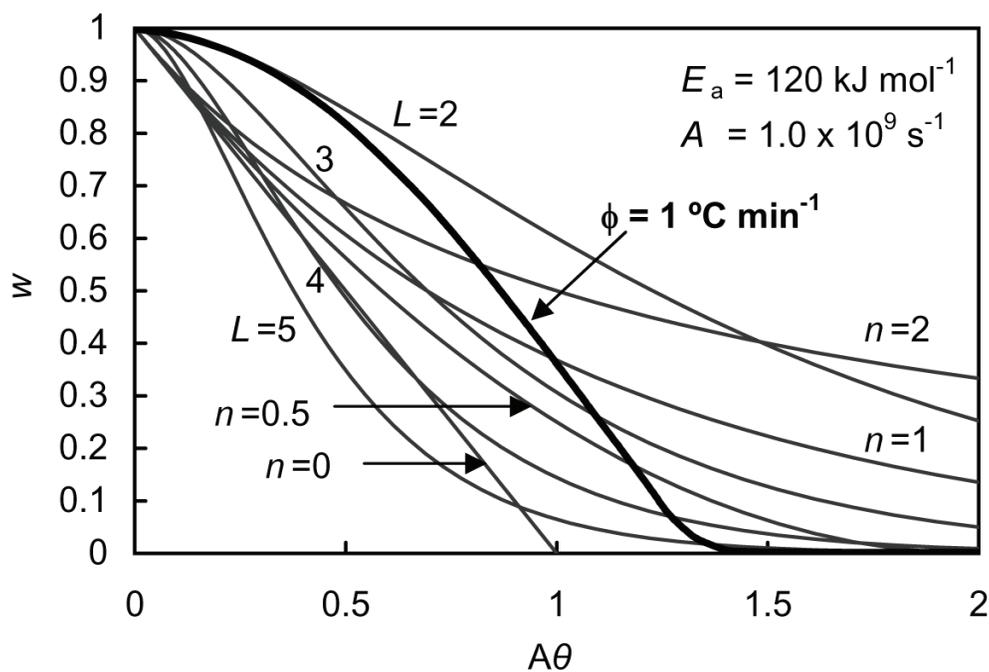


Fig. 3. Plots of  $w$  vs.  $A\theta$  for thermogravimetric data of PHB at a heating rate of  $9\text{ }^{\circ}\text{C min}^{-1}$  ( $E_a=120\text{ kJ mol}^{-1}$ ,  $A=1.0\times 10^9\text{ s}^{-1}$ ), and for model reactions. Model reactions: zero ( $n=0$ ), half ( $n=0.5$ ), 1<sup>st</sup> ( $n=1$ ), 2<sup>nd</sup>-order ( $n=2$ ), and random degradations (Random  $L=2-5$ ).

$$\begin{aligned}
 -\int \frac{dw}{f(w)} &= \frac{A_1}{\phi} \int \exp(-E_{a1}/RT) + \frac{A_2}{\phi} \int \exp(-E_{a2}/RT) \\
 &= \frac{A_1 E_{a1}}{\phi R} p(x_1) + \frac{A_2 E_{a2}}{\phi R} p(x_2) = A_1 \theta_1 + A_2 \theta_2
 \end{aligned}
 \tag{11}$$

where  $x_1$ ,  $x_2$ ,  $\theta_1$ ,  $\theta_2$ , and  $p(x)$  are  $E_{a1}/RT$ ,  $E_{a2}/RT$ ,  $(E_{a1}/\phi R)p(x_1)$ ,  $(E_{a2}/\phi R)p(x_2)$ , and function  $p(x)$  (Nishida et al., 2003). If each path occurs within an isolated temperature range, the two paths may appear as consecutive reactions. Eq. 11 suggests that the linear relation parallel to the 0<sup>th</sup>-order simulation plot, which appeared as one of the consecutive processes, should be regarded as a 0<sup>th</sup>-order reaction. Thus, the time lag,  $A_1\theta_1$ , between the linear part of the observed plot and the 0<sup>th</sup>-order simulation plot in Fig. 3 can be regarded as a retardation time or induction period needed to shift from the initial random degradation ( $L=2$ ) process as shown in Fig. 2 into the 0<sup>th</sup>-order weight loss process in the middle stage.

It is considered that the 0<sup>th</sup>-order weight loss process may be due to an unzipping degradation from chain ends. Kopinke et al. (Kopinke et al., 1996) also suggested the presence of a chain reaction with a short kinetic chain length during the PHB degradation. Thus, the above kinetically analyzed results based on the weight loss demonstrate that the PHB degradation proceeds by at least two-steps: the initial random degradation and a subsequent 0<sup>th</sup>-order weight loss process.

### 3.4 Theoretical calculation of activation energy of $\beta$ -elimination

Kopinke et al. (Kopinke et al., 1996) discussed in their report that the decomposition rate of PHB is very sensitive to the reactivity of the  $\beta$ -C-H bonds. They speculated that, if carboxyl groups at chain ends of fractured molecules accelerate the scission of neighboring ester groups faster than the original ester groups, the decomposition results would be equivalent to a chain reaction. Nguyen et al. (Nguyen et al., 2002) also suggested that the conjugation of an unsaturated group with an ester group generates an inductive effect, increasing the scission rate of the neighboring ester linkages.

To confirm these suggested acceleration reactions, the activation energy,  $E_a$ , value of the  $\beta$ -elimination via a pseudo-six-membered transition structure was estimated by well-known molecular orbital calculation methods (Table 2) (Ariffin et al., 2008). To calculate the  $E_a$  value, various model compounds are employed. The equilibrium geometries of these model compounds are calculated by the Hartree-Fock/3-21G\* method and the reaction coordinate systems of the  $\beta$ -elimination were derived from the energy profile obtained by using the PM3 Hamiltonian. Estimated results indicated that the lowest  $E_a$  value (253.91 kJ mol<sup>-1</sup>) was associated with the reaction of an internal ester group of a trimer model molecule, supporting the observed internal random scission as the initial reaction. The reaction at the chain-end neighboring crotonyl group produced a slightly high  $E_a$  value of 260.46 kJ mol<sup>-1</sup>, but this is considerably lower than the 365.22 kJ mol<sup>-1</sup> at carboxyl chain-ends. The reaction at the chain-end must be accelerated by the chain-end's higher mobility when compared to that at internal chain units. Moreover, it is clearly indicated that for the cases where  $R_2 = H$  in Table 2, the crotonyl group has a fundamental acceleration effect for  $\beta$ -elimination on the neighboring ester group.

Thus, this acceleration effect at the crotonyl chain-end induces the generation of a crotonic acid and a new crotonyl chain-end, repeating the same reaction in the same manner as the unzipping reaction.

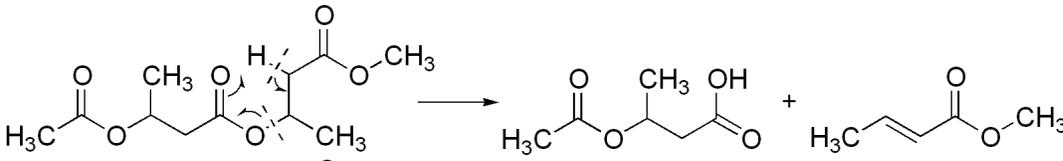
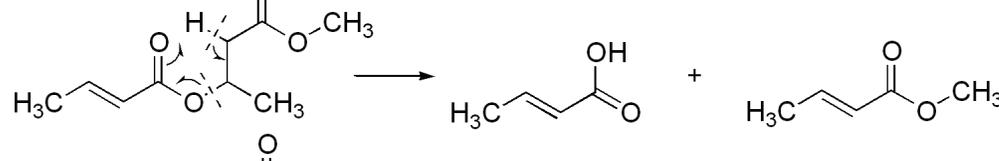
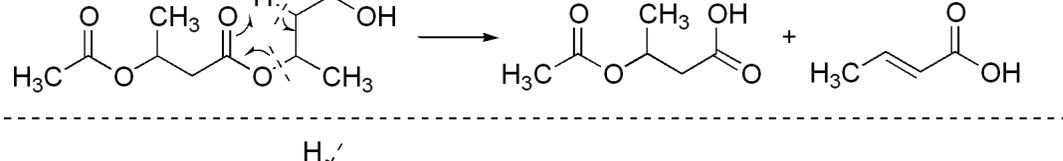
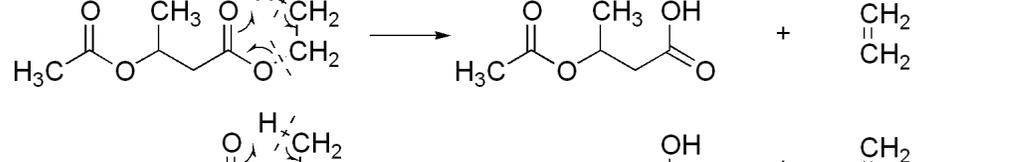
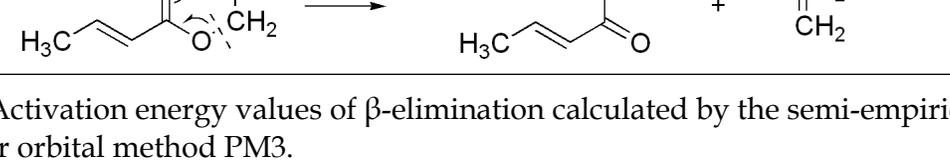
Model reactions		$E_a$ (kJ mol <sup>-1</sup> )
		253.91
		260.46
		365.22
<hr/>		
		339.04
		287.40

Table 2. Activation energy values of  $\beta$ -elimination calculated by the semi-empirical molecular orbital method PM3.

### 3.5 Effects of alkali earth compounds as depolymerization catalysts

In order to transform PHB into a specific monomer, precise control of the thermal degradation is crucial. In spite of the wealth of previous studies, there are few reports thus far which focus on the selective depolymerization of PHB into the monomer. In cases of PHB pyrolysis without a catalyst, net yield of all butenoic acids (*trans/cis*-crotonyl acids (CAs) + 3-butenic (BA)) as main pyrolysis products ranged from 39.5 wt.-% using thermal volatilization analysis (Grassie et al., 1984) to 87 total ion count % (TIC-%) using Py-GC/MS analysis (Gonzalez et al., 2005). Recently, it was reported that <sup>1</sup>H NMR analysis of PHB pyrolyzates at 260 °C revealed the ratio *trans*-CA:*cis*-CA:oligomers = 67.7:3.1:29.2 (monomeric unit-%) (Ariffin et al., 2008). Kopinke et al. (Kopinke et al., 1996) also reported on the production of a large amount of oligomers during the PHB pyrolysis, with the recovered monomer fraction being composed of *trans*-CA:*cis*-CA:BA = 100:10:2 (GC-area-%). When pyrolysis catalysts were used in PHB pyrolysis, Kim et al. (Kim et al., 2006, 2008) reported the enhancement of PHB depolymerization by CaCl<sub>2</sub> or MgCl<sub>2</sub>. This enhancement was explained as being due to the Lewis acidity of Ca<sup>2+</sup> and Mg<sup>2+</sup> facilitating the formation of a double bond by the elimination of  $\beta$ -hydrogen. Kawalec et al. (Kawalec et al., 2007) also reported on the enhancement of the thermal degradation of PHB by Na<sup>+</sup>, K<sup>+</sup>, and Bu<sub>4</sub>N<sup>+</sup> counter cations at chain-ends, proposing an E1cB mechanism. However, there was no discussion on the selectivity of pyrolyzates.

Completely selective transformation of poly[(*R*)-3-hydroxybutyric acid] (PHB) into *trans*-crotonic acid was achieved by thermal degradation using Mg compounds: MgO and

Mg(OH)<sub>2</sub> as catalysts (Ariffin et al., 2010). Through catalytic action, not only were the temperature and  $E_a$  value of degradation lowered by 40-50 °C and 11-14 kJ mol<sup>-1</sup>, respectively, but also significant changes in the selectivity of pyrolyzates were observed. Notably, Mg(OH)<sub>2</sub> and MgO showed nearly complete selectivity (~100%) to *trans*-crotonic acid.

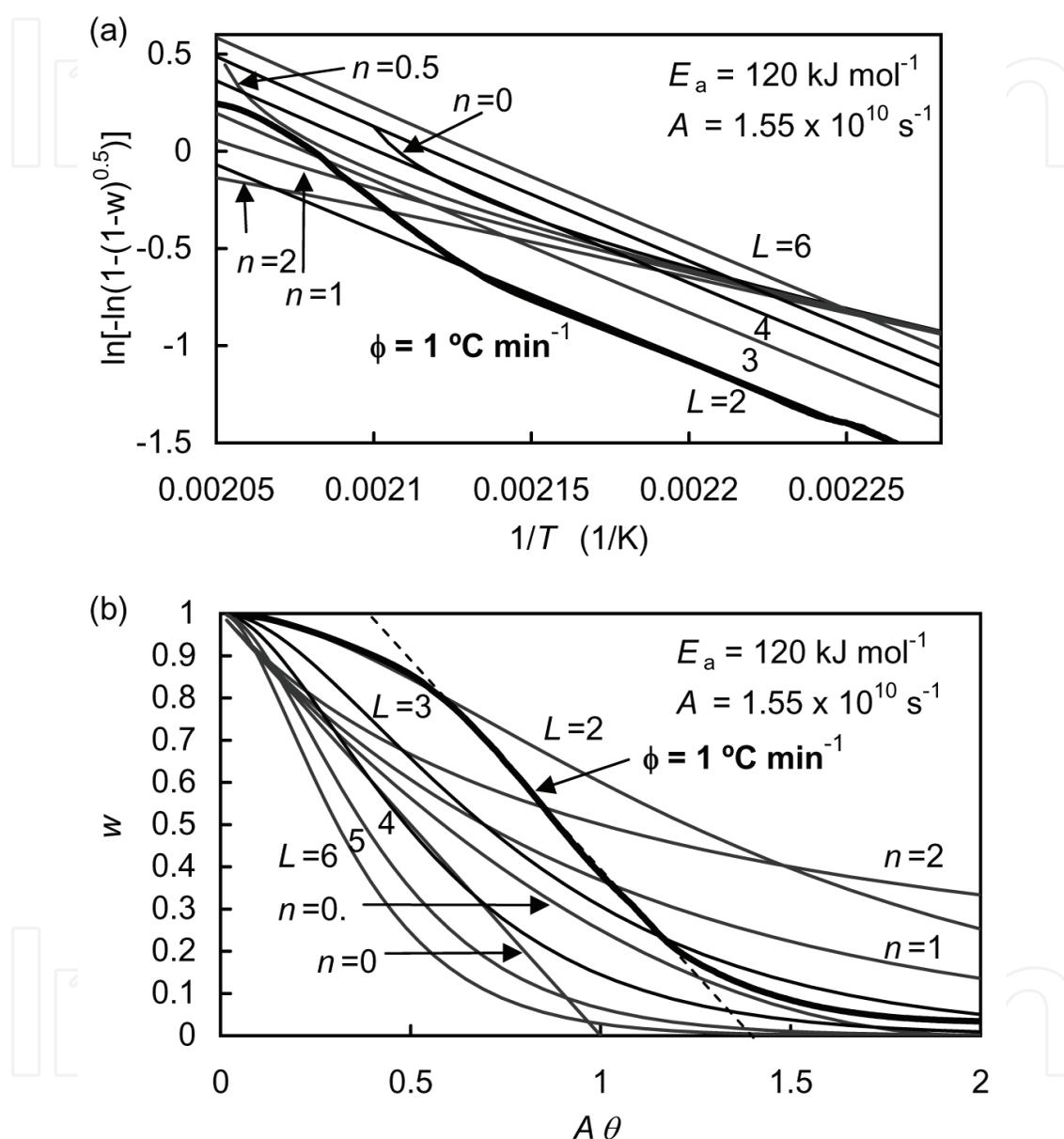


Fig. 4. Plots of (a)  $\ln[-\ln\{1-(1-w)^{0.5}\}]$  vs.  $1/T$  and (b)  $w$  vs.  $A\theta$  for thermogravimetric data of PHB/MgO (100:5 wt/wt) at a heating rate of  $1 \text{ °C min}^{-1}$  ( $E_a=120 \text{ kJ mol}^{-1}$ ,  $A=1.55 \times 10^{10} \text{ s}^{-1}$ ), and for model reactions. Model reactions: zero ( $n=0$ ), half ( $n=0.5$ ), 1<sup>st</sup> ( $n=1$ ), 2<sup>nd</sup>-order ( $n=2$ ), and random degradations (random  $L=2-6$ ).

In Fig. 4, the random degradation and the integral analyses of PHB/MgO (100:5 wt/wt) are illustrated. The pyrolysis of PHB-H/MgO was shown to start by a random degradation ( $L=2$ ), and gradually shift into an  $n^{\text{th}}$ -order weight loss behavior. PHB/Mg(OH)<sub>2</sub> also showed the same kinetics. These results show that the thermal degradation mechanisms of

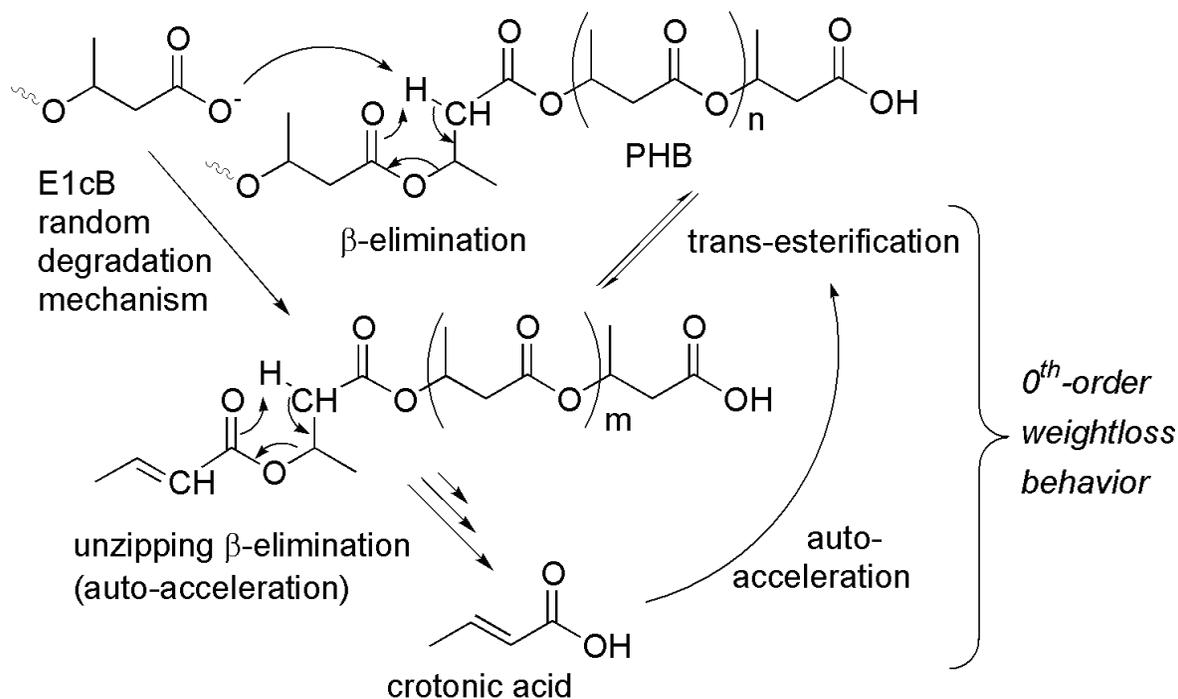
all the samples are similar to each other, *i.e.* random  $\beta$ -elimination and/or E1cB mechanisms as the initial processes followed by the unzipping  $\beta$ -elimination accelerated by the chain-end crotonate group as the main process.

### 3.6 Degradation mechanisms

Under the pyrolysis conditions without any other reactant from the outside, the auto-catalytic or auto-accelerated random degradation may be induced by a large number of carboxyl compounds, which self-generate as the reaction progresses. The carboxyl compounds randomly attack ester groups on polymer chains to induce the transesterification, resulting in the reproduction of carboxyl groups and a remarkable decrease in molecular weight as demonstrated by Nguyen et al. (Nguyen et al., 2002).

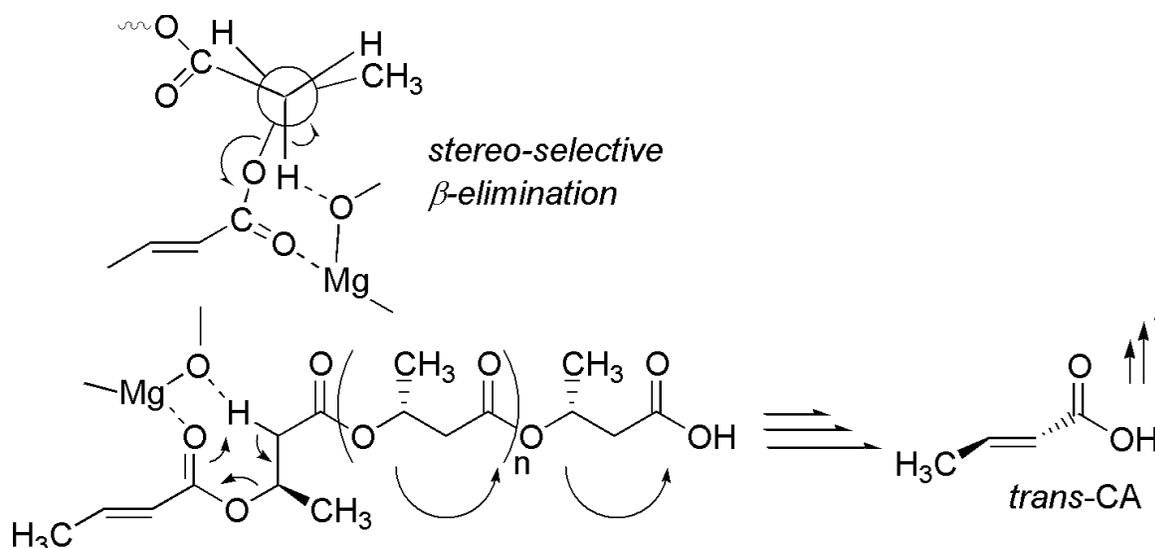
In order to induce the auto-accelerated random degradation, carboxylic groups have to be self-proliferated in bulk. The unzipping reaction occurring at the end of molecules, which was suggested to be the 0<sup>th</sup>-order reaction by the kinetic analysis and the theoretical calculation in the above sections, is just a kinetically favored scission of polymer chains that repeatedly generate a large number of crotonic acids. This is an ideal self-proliferation reaction of carboxyl compounds and is the key factor in the auto-accelerated random degradation.

According to predictions based on the above measured and analyzed results, an expected overall thermal degradation pathway of PHB is illustrated in Scheme 2.



Scheme 2. Expected overall thermal degradation pathway of PHB.

The Mg compounds as catalysts may accelerate both the  $\beta$ -elimination reactions in the beginning and main stages and/or the E1cB mechanism by carboxyl anions as Lewis acids and counter cations, respectively. Thereby the initial random degradation was promoted as shown by the increases in *A* values, consequently increasing the crotonate chain-end groups, resulting in the acceleration of the main unzipping  $\beta$ -elimination (*cis*-elimination) as shown in Scheme 3.



Scheme 3. *Trans*-form preferential depolymerization of PHB.

#### 4. Conclusions

The thermal degradation of PHB was investigated by various kinetic analysis methods in detail to clarify its complex degradation behavior, resulting in a finding of mixed mechanisms comprising at least a thermal random degradation with subsequent auto-accelerated trans-esterification, and a kinetically favored chain reaction from crotonate chain ends.

From the kinetic analysis of changes in molecular weight, it was found that a random degradation proceeding in the initial period was followed by an auto-accelerated reaction in the middle period. From the kinetic analysis of weight loss behavior, it was proposed that there were some kinetically favored scissions occurring at the chain ends, where the degradation proceeded by a 0<sup>th</sup>-order weight loss process in the middle stage. The observed 0<sup>th</sup>-order weight loss process was assumed to be an unzipping reaction occurring at ester groups neighboring the crotonate end groups.

The completely selective transformation of PHB into *trans*-crotonic acid was achieved by thermal degradation using catalysts: MgO and Mg(OH)<sub>2</sub>. Through catalytic action, not only were the temperature and  $E_a$  value of degradation lowered, but also significant changes in the selectivity of pyrolyzates were observed. Notably, Mg(OH)<sub>2</sub> showed nearly complete selectivity (~100%) to *trans*-crotonic acid. It was suggested that the Mg catalysts promote the totality of the  $\beta$ -elimination reactions by acting throughout the beginning and main processes, resulting in a lowering in the degradation temperature and the completely selective transformation of PHB.

By the above approaches, some complicated problems on the thermal degradation mechanisms of PHB have been solved, and the controlled depolymerization of PHB into *trans*-crotonic acid, which is a versatile monomer for many applications, has been achieved.

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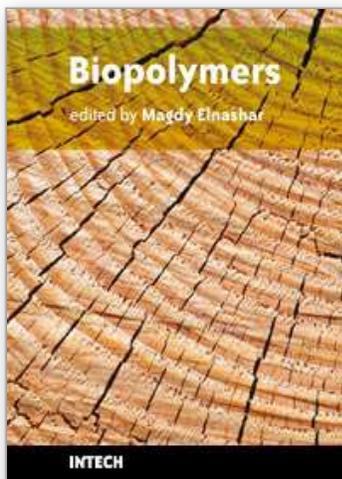
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