

New Aspect of Poly(3-hydroxybutyrate) Pyrolysis Mechanisms

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Abstract The thermal degradation behavior of poly (3-hydroxybutyrate), PHB was studied kinetically and by characterization of the PHB pyrolyzates using $^1\text{H}/^{13}\text{C}$ NMR, FTIR, and FAB-MS. From the kinetics analysis of weight loss behavior, it is proposed that there are some kinetically favored scissions occurring at the chain ends, which were assumed to be unzipping reactions occurring at ester groups neighboring the crotonate end groups. Newly proposed thermal degradation pathways of PHB bring new aspect to the PHB pyrolysis mechanisms.

Introduction Random chain scission by β -elimination has been considered as the dominant mechanism in PHB thermal degradation based on typical structures of pyrolysis products, *i.e.* crotonic acid and oligomers with a crotonate end-group. Recently, Lehrle *et al.*^{1,2} reported that the analytical results of partial pyrolysis of PHB showed some deviations from the theoretical predictions of random scission statistics due to reactions induced by the end groups. However, a clear confirmation has not yet been reported. In this paper, we propose an expected thermal degradation pathway of PHB based on the kinetics analysis of weight loss behavior.

Materials and Methods Dynamic pyrolysis of PHB film samples was conducted using TG and Py-GC/MS. In the TG analysis, the sample was heated at prescribed multiple heating rates of 1, 3, 5, 7 and 9 $^\circ\text{C min}^{-1}$ in the range of 60–400 $^\circ\text{C}$ under a steady N_2 flow of 100 mL min^{-1} . For pyrolysis in Py-GC/MS, the sample was heated from 40 $^\circ\text{C}$ to a prescribed temperature at a heating rate of 9 $^\circ\text{C min}^{-1}$. Isothermal pyrolysis was took place in a glass tube oven at 260 $^\circ\text{C}$ for 30 min. Pyrolyzates obtained were analyzed using ^1H and ^{13}C NMR, FTIR and FAB-MS.

Results and Discussion

PHB pyrolysis at multiple heating rates. TG curves of PHB film degradation, which were normalized in accordance with sample weight = 1, are illustrated in Figure 1. All the TG curves showed a smooth decomposition from the beginning until completion, with TG traces shifted up the temperature scale by an increase in the heating rate. Calculation of activation energy E_a value showed that thermal degradation of PHB has a constant E_a value in the range of $117 \pm 3 \text{ kJ mol}^{-1}$. This suggests that the weight loss over the whole period resulted mainly from one main reaction.

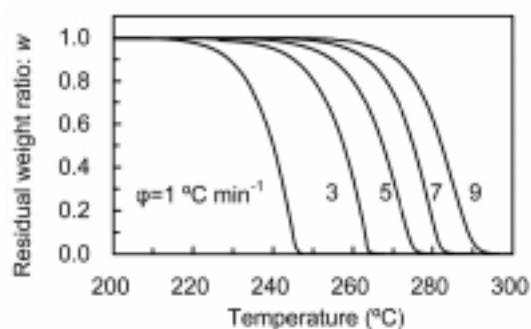


Figure 1. TG curves of PHB degradation.

Composition of pyrolyzates. Isothermal degradation of PHB in a glass tube oven was conducted at 260 $^\circ\text{C}$ *in vacuo* to determine the components of distilled pyrolyzates. Pyrolysis products were characterized and categorized as major and minor products. Major pyrolysis product was seen as crystals, whereas the minor product was an oily liquid. From ^1H NMR analysis, it was found that the

major component was *trans*-crotonic acid, which contributed to 67.7 % of the total PHB pyrolyzates. Minor components were *cis*-crotonic acid and its derivatives (3.1 %) and oligomers (29.2 %) having crotonyl end groups. ^{13}C NMR spectrum of the minor component showed at least four kinds of carbonyl carbons detected at 175.5, 170, 166, 161 ppm (Figure 2), which were assigned as carbonyl carbons of 3HB units (a)^{3,4}, chain-end carboxyl (a') and crotonyl (a'', a''') groups. As one minor component having the crotonyl end group, crotonic anhydride was assigned to the signal at around 161 ppm. This was evident by the ^{13}C NMR and FTIR analyses.

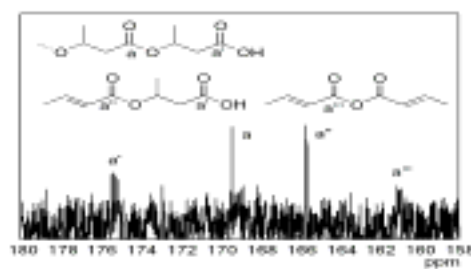


Figure 2. 125MHz of ^{13}C NMR spectrum of PHB pyrolyzates.

Kinetics analysis of PHB pyrolysis. Plots in Fig. 3 show the integral simulation analysis of the observed TG data ($9\text{ }^\circ\text{C min}^{-1}$) and model reaction plots with parameter values: E_a : 118 kJ mol^{-1} and A : $1.18 \times 10^9\text{ s}^{-1}$. Interestingly, the observed plot 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 0th-order simulation plot⁵.

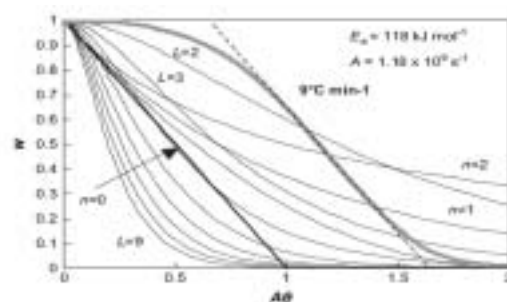
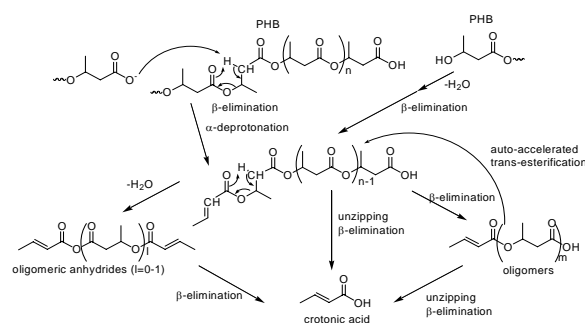


Figure 3. Plots of w vs $A\theta$ for TG data of PHB at heating rate $9\text{ }^\circ\text{C min}^{-1}$

Expected thermal degradation pathways of PHB. Based on the above results, it was considered that there are some kinetically favored scissions occurring near the ends of the molecules, which proceeded by a 0th-order weight loss process in the middle stage. This reaction is identified as unzipping reaction occurring at ester groups neighboring the crotonate end groups.



Scheme 1. Expected thermal degradation pathways of PHB

Apart of the initial random degradation and following unzipping reaction, crotonic anhydride and its oligomers were detected as minor products from condensation reactions between carboxyl groups. The anhydrides production must be one out of conforming to the random degradation statistics and contribute to the complexity of the PHB pyrolysis. By considering all these, expected thermal degradation pathways of PHB are proposed in Scheme 1.

References

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