26 H, aliphatic CH_2 and $COOCH_2CH_3$), 0.90 (m, 6 H, aliphatic CH_3).

^{13}C NMR: see Table I.

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Thermal Degradation of Microbial Copolyesters: Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)

Masao Kunioka and Yoshiharu Doi*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan.

Received June 28, 1989

ABSTRACT: Thermal degradation processes of microbial copolyesters were studied in the temperature range 100–200 °C by monitoring the time-dependent changes in molecular weights of melt samples. Two types of copolyesters, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-3HV); 3HV = 0–71 mol %) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3HB-*co*-4HB); 4HB = 0–82 mol %), were used in this study. All copolyester samples used were thermally unstable at temperatures above 170 °C, and their molecular weights decreased rapidly with time. The time-dependent changes in molecular weights during the thermal degradation followed the kinetic model of random chain scission at ester groups. The rates of random chain scission were independent of the compositions of the copolyesters but dependent strongly on temperature. These copolyester samples were thermally stable at temperatures below 160 °C. It has been suggested that the microbial copolyesters with melting temperatures below 160 °C are applicable to conventional plastics processing methods.

Introduction

A wide variety of micoroorganisms produce an optically active polyester, poly(3-(*R*)-hydroxybutyrate) (P(3HB)) as an intracellular storage polymer.[1] P(3HB) is a thermoplastic degradable in the environment, by either hydrolytic or enzymatic degradation processes.[2–5] Industrial-scale fermentation production of P(3HB) has begun,[6–8] and P(3HB) is attractive as an environmentally degradable material that can be processed like conventional commodity thermoplastics. However, P(3HB) is thermally unstable at temperatures above the melting point (around 180 °C), and a drastic reduction in the molecular weight occurs during processing in the temperature range 180–200 °C.[9–11]

This problem has been resolved by the development of a fermentation process to produce microbial copolyesters with lower melting temperatures.[12,13] Imperial Chemical Industries (ICI) has produced commercially a copolyester of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) by the fermentation process in which *Alcaligenes eutrophus* is grown in culture media containning propionic acid and glucose[12] and marketed it as Biopol

0024-9297/90/2223-1933$02.50/0

Table I
Compositions and Properties of Microbial Polyesters

sample	comp,[a] mol % 3HB	3HV	4HB	molec wt[b] $10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_m,[c] °C	ΔH_m,[c] cal·g^{-1}
1	100	0	0	782	1.8	177	20.1
2	76	24	0	291	1.9	138	8.8
3	55	45	0	400	2.4	75	8.6
4	29	71	0	254	2.0	87	13.0
5	89	0	11	223	2.5	160	11.1
6	83	0	17	332	2.4	152	10.4
7	18	0	82	129	2.4	40	4.8

[a] Determined by ^{1}H NMR. [b] Determined by GPC. [c] The melting temperature (T_m) and enthalpy of fusion (ΔH_m) were measured by DSC at 10 °C/min.

in the composition range 0–30 mol % 3HV. We have recently found that the P(3HB-*co*-3HV) with a wide range of compositions from 0 to 95 mol % 3HV is produced by *A. eutrophus* by using pentanoic and butyric acids as the carbon sources.[14,15] In addition, we have developed a fermentation process in which a new copolyester of 3-hydroxybutyrate (3HB) and 4-hydroxybutyrate (4HB) is produced by *A. eutrophus* from 4-hydroxybutyric and butyric acids.[16,17]

The melting temperature (T_m) of P(3HB-*co*-3HV) decreased from 180 °C with increasing the 3HV fraction and reached a minimum value (around 75 °C) at approximately 40 mol % 3HV, followed by a gradual increase to 108 °C at 95 mol % 3HV.[18,19] The T_m value of P(3HB-*co*-4HB) decreased from 180 to 140 °C as the 4HB fraction increased from 0 to 49 mol %.[19] Holmes[13] has studied the melt stabilities of P(3HB) (T_m = 179 °C), P(3HB-*co*-15%3HV) (T_m = 150 °C), and P(3HB-*co*-25%3HV) (T_m = 135 °C) by monitoring the melt flow index during the processing for 10 min in the temperature range 150–200 °C and demonstrated that the P(3HB-*co*-3HV) samples are injection-moldable in practice at or below 165 °C.

In this paper we study the thermal degradation properties of P(3HB-*co*-3HV) (3HV = 0–71 mol %) and P(3HB-*co*-4HB) (4HB = 0–82 mol %) by monitoring the time-dependent changes in the molecular weights of melt samples in the temperature range 100–200 °C. The composition effects on the melt stability of microbial copolyesters are reported. In addition, the mechanism of chain scission at ester groups is investigated by analysis of the 500-MHz ^{1}H NMR spectrum of thermally degraded P(3HB) oligomers.

Experimental Section

Microbial Polyester Preparation. We prepared seven microbial polyester samples of P(3HB), P(3HB-*co*-3HV), and P(3HB-*co*-4HB). Sample 1 of P(3HB) homopolyester was produced by *A. eutrophus* from fructose. Samples 2, 3, and 4 of P(3HB-*co*-3HV) copolyesters (3HV = 24, 45, and 71 mol %) were produced by *A. eutrophus* from pentanoic and butyric acids.[15] Samples 5 and 6 of P(3HB-*co*-4HB) copolyesters (4HB = 11 and 17 mol %) were produced by *A. eutrophus* from 4-hydroxybutyric and butyric acids.[16,17] Sample 7 of P(3HB-*co*-4HB) (4HB = 82 mol %) was an acetone-soluble fraction of the mixture of P(3HB-*co*-4HB) copolyesters produced from γ-butyrolactone and butyric acid by *A. eutrophus*. The compositions of microbial copolyesters were measured by ^{1}H NMR spectroscopy.[15,17] Table I shows the compositions, molecular weights, melting temperatures, and enthalpies of fusion of polyester samples used in this study.

Thermal Degradation. The powders of polyester samples were dried at room temperature under vacuum before the experiments of thermal degradation. Thermal degradation studies of polyesters were performed by using the differential scanning calorimetry (Shimadzu DSC-30) equipment under a nitrogen flow of 30 cm^3·min^{-1}. Polyester samples of 3 mg were encapsulated in aluminum pans, heated from ambient to isothermal temperature at 10 °C·min^{-1}, and degraded isothermally under nitrogen for a given time.

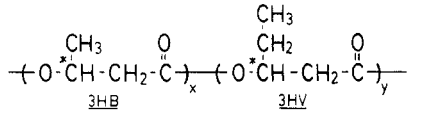
Analytical Procedures. All molecular weight data of the polyester samples were obtained at 40 °C by using a Shimadzu 6A GPC system and a 6A refractive index detector with a Shodex 80M column. Chloroform was used as eluant at a flow rate of 0.5 cm^3·min^{-1}, and a sample concentration of 1.0 mg·cm^{-3} was used. Polystyrene standards with a low polydispersity were used to make a calibration curve.

The ^{1}H NMR analyses of polyester samples were carried out on a JEOL GX-500 spectrometer. The 500-MHz ^{1}H NMR spectra were recorded at 27 °C in $CDCl_3$ solution of polyester (5 mg·cm^{-3}) with 45° pulses (5 μs), 5-s pulse repetetion, 5000-Hz spectral width, 32K data points, and 100 accumulations.

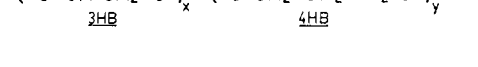
The melting temperatures of polyester samples were recorded on a Seiko DSC-10. The as-isolated powder samples of 3 mg were encapsulated in aluminum pans and heated at 10 °C·min^{-1} up to 200 °C. The heat of fusion of indium (6.80 cal·g^{-1}) was used as a calorimetric calibration.

Results and Discussion

Table I summarizes compositions, molecular weights, melting temperatures (T_m), and enthalpies of fusion (ΔH_m) of microbial polyester samples used in this study. Sample 1 is a P(3HB) homopolyester, which shows the highest T_m (177 °C) among all samples. Samples 2, 3, and 4 are copolyesters of 3-hydroxybutyrate and 3-hydroxyvalerate, P(3HB-*co*-3HV). The T_m value



of P(3HB-*co*-3HV) samples decreased from 177 to 75 °C as the 3HV fraction increased from 0 to 45 mol %. As reported in a previous paper,[19] a minimum value (around 75 °C) of the T_m was observed at approximately 40 mol % 3HV. The T_m value of P(3HB-*co*-71%3HV) sample 4 was 87 °C. Samples 5, 6, and 7 are copolyesters of 3-hydroxybutyrate and 4-hydroxybutyrate, P(3HB-co-4HB). The T_m value of P(3HB-*co*-4HB) sam-



ples decreased monotonously to 40 °C as the 4HB fraction increased up to 82 mol %.

Thermal degradation studies on a series of microbial copolyesters were carried out for 20 min at temperatures above the respective T_ms. Table II lists the changes in the number-average molecular weights ($\bar{M}_n$) and polydispersities ($\bar{M}_w/\bar{M}_n$) of microbial polyesters during thermal degradation in the temperature range 100–200 °C under nitrogen. At temperatures below 160 °C, the $\bar{M}_n$ values of copolyester samples decreased very slowly with time. The $\bar{M}_n$ values of P(3HB-*co*-3HV) samples 3 and 4 were almost unchanged over a period of 20 min at 100 °C. In contrast, at temperatures above 170 °C, the $\bar{M}_n$ values of all polyester samples decreased rapidly with time. For example, the $\bar{M}_n$ values of P(3HB) and P(3HB-*co*-17%4HB) samples decreased to only 2% of the initial $\bar{M}_n$ values after 20 min at 200 °C. For all polyester samples the molecular weight distributions were unimodal and the polydispersities ($\bar{M}_w/\bar{M}_n$) remained relatively narrow during thermal degradation. There was no appreciable weight loss of polyester samples for 20 min in the temperature range 100–200 °C.

In a previous paper,[10] Grassie et al. found that the degradation reaction of P(3HB) in the temperature range 170–200 °C was a random chain scission process. Provided that the chain scission is completely random and no volatilization occurs during the thermal degradation of copolyester samples, the number-average degree of polymerization $\bar{P}_{n,t}$ at time t is given

Table II
Changes in Molecular Weights of Microbial Polyesters during Thermal Degradation at Different Temperatures

degrad temp, °C	sample	$10^{-3}\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) 0 min	1 min	2 min	5 min	10 min	20 min
100	3. P(3HB-*co*-45%3HV)	347 (2.9)	353 (2.9)	341 (3.0)	337 (3.0)	347 (2.9)	327 (3.1)
	4. P(3HB-*co*-71%3HV)	310 (1.8)	264 (2.4)	258 (2.4)	263 (2.4)		295 (2.3)
140	3. P(3HB-*co*-45%3HV)	318 (3.0)	321 (3.0)	296 (3.2)	303 (3.1)	296 (3.1)	245 (3.5)
	4. P(3HB-*co*-71%3HV)	231 (2.8)	236 (2.6)	283 (2.5)	197 (2.8)	230 (2.7)	174 (2.8)
160	3. P(3HB-*co*-45%3HV)	366 (2.6)	357 (2.6)	364 (2.5)	340 (2.5)	317 (2.3)	
	6. P(3HB-*co*-17%4HB)	351 (2.1)	344 (2.1)	319 (2.0)	333 (1.9)	292 (2.0)	
170	6. P(3HB-*co*-17%4HB)	379 (2.0)	315 (2.3)	308 (2.3)	296 (2.3)		170 (2.5)
175	1. P(3HB)	564 (2.1)	502 (2.2)	417 (2.2)			146 (1.9)
180	1. P(3HB)	477 (2.2)	432 (2.0)	434 (1.8)	312 (2.0)	169 (2.0)	93 (2.1)
	2. P(3HB-*co*-24%3HV)	234 (1.9)	235 (1.8)	234 (1.8)	183 (1.8)	145 (1.8)	89 (2.1)
	3. P(3HB-*co*-45%3HV)	274 (2.8)	229 (2.9)	160 (3.5)	122 (3.4)	103 (3.0)	54 (3.6)
	4. P(3HB-*co*-71%3HV)	263 (2.2)	158 (2.4)	120 (2.3)	107 (2.6)	60 (2.4)	46 (2.2)
	5. P(3HB-*co*-11%4HB)	195 (2.4)	208 (2.4)	198 (2.4)		182 (1.8)	78 (2.5)
	6. P(3HB-*co*-17%4HB)	283 (2.3)	305 (2.1)	208 (2.3)	229 (1.9)	171 (1.9)	134 (1.8)
	7. P(3HB-*co*-82%4HB)	71 (2.1)	68 (2.3)	71 (2.2)	68 (2.2)		51 (2.0)
190	1. P(3HB)	402 (2.1)	192 (2.9)	136 (3.3)		52 (2.4)	
	4. P(3HB-*co*-71%3HV)	126 (2.8)	110 (2.9)	90 (2.5)		42 (2.3)	
200	1. P(3HB)	282 (2.0)	121 (2.2)	121 (2.0)	37 (2.4)		7 (3.9)
	6. P(3HB-*co*-17%4HB)	172 (2.3)	173 (2.1)	92 (2.2)	50 (2.4)	12 (4.5)	5 (3.2)

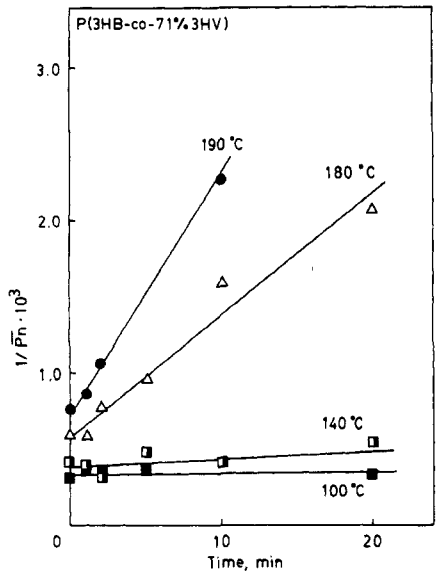


Figure 1. Relationship between $1/\bar{P}_n$ and time t of heating for sample 4, P(3HB-*co*-71%3HV), at different temperatures: (■) 100 °C; (□) 140 °C; (△) 180 °C; (●) 190 °C.

by[20]

$$\frac{1}{\bar{P}_{n,t}} - \frac{1}{\bar{P}_{n,0}} = k_d t \qquad (1)$$

where $\bar{P}_{n,0}$ is the initial number-average degree of polymerization and k_d is the rate constant of thermal degradation.

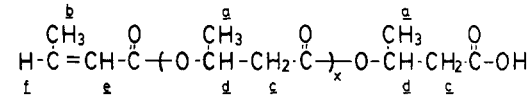
Figure 1 shows a linear relationship between $1/\bar{P}_{n,t}$ and time t for the representative copolyester sample 4, P(3HB-*co*-71%3HV) at different temperatures. This result confirms that the decrease in $\bar{P}_n$ during thermal degradation is due to random chain scission. Table III lists the values of degradation rate constant k_d for all polyester samples in the temperature range 100–200 °C, determined from the slopes of the plots of eq 1. At temperatures below 140 °C the values of k_d for copolyester samples 3 and 4 were less than 1×10^{-6} min^{-1}.

The temperature dependence of the rate constants k_d for seven polyester samples is shown in Figure 2. For comparison, Figure 2 shows also the k_d values (●) of P(3HB) determined in the temperature range 170–200 °C by Grassie et al.[10] The k_d values of all microbial polyester samples are distributed on the same line in the temperature range 160–200 °C, which indicates that the rate of random chain scission is not influenced by the compositions of microbial copolyesters P(3HB-*co*-3HV) and P(3HB-*co*-4HB). The activation energy of random chain scission was determined as 212 ± 10 kJ·mol^{-1} from the slope of the Arrhenius plot in Figure 2.

Table III
Rate Constants k_d of Thermal Degradation at Different Temperatures

degrad temp, °C	sample	k_d, min^{-1}
100	3. P(3HB-*co*-45%3HV)	$\ll 1 \times 10^{-6}$
	4. P(3HB-*co*-71%3HV)	$\ll 1 \times 10^{-6}$
140	3. P(3HB-*co*-45%3HV)	$< 1 \times 10^{-6}$
	4. P(3HB-*co*-71%3HV)	$< 1 \times 10^{-6}$
160	3. P(3HB-*co*-45%3HV)	$(3.9 \pm 1.0) \times 10^{-6}$
	6. P(3HB-*co*-17%4HB)	$(4.4 \pm 1.0) \times 10^{-6}$
170	6. P(3HB-*co*-17%4HB)	$(1.3 \pm 0.1) \times 10^{-5}$
175	1. P(3HB)	$(2.2 \pm 0.5) \times 10^{-5}$
180	1. P(3HB)	$(3.8 \pm 0.1) \times 10^{-5}$
	2. P(3HB-*co*-24%3HV)	$(3.2 \pm 0.1) \times 10^{-5}$
	3. P(3HB-*co*-45%3HV)	$(6.6 \pm 1.0) \times 10^{-5}$
	4. P(3HB-*co*-71%3HV)	$(8.3 \pm 1.0) \times 10^{-5}$
	5. P(3HB-*co*-11%4HB)	$(3.2 \pm 0.5) \times 10^{-5}$
	6. P(3HB-*co*-17%4HB)	$(1.7 \pm 0.5) \times 10^{-5}$
	7. P(3HB-*co*-82%4HB)	$(2.0 \pm 0.5) \times 10^{-5}$
190	1. P(3HB)	$(1.4 \pm 0.1) \times 10^{-4}$
	4. P(3HB-*co*-71%3HV)	$(1.5 \pm 0.1) \times 10^{-4}$
200	1. P(3HB)	$(6.2 \pm 0.5) \times 10^{-4}$
	6. P(3HB-*co*-17%4HB)	$(8.6 \pm 1.0) \times 10^{-4}$

In order to investigate the mechanism of chain scission at ester groups, the 500-MHz ^{1}H NMR spectrum of the thermal degradation product of P(3HB) was recorded. Figure 3 shows the ^{1}H NMR spectrum of the P(3HB) oligomer ($\bar{M}_n$ = 2000 and $\bar{M}_w/\bar{M}_n$ = 2.8 by GPC) obtained by thermal degradation under nitrogen for 70 min at 200 °C. The chemical shift assignments of proton resonances are shown in Figure 3 together with the expanded spectrum at 4.7–7.4 ppm. The strong proton resonances a, c, and d are assigned to the methyl, methylene, and methine proton resonances in 3-hydroxybutyrate units, respectively. The weak resonances e (δ 5.8) and f (δ 6.9–7.1) are assignable to the resonances of olefinic protons in the chain end unit of the P(3HB) oligomer, and the weak resonance b at δ 1.9 is assigned to the resonance of the methyl proton in the chain end unit.



From the intensity ratio of signals b, e, and f of the protons in the chain end units to those a, c, and d of protons in the 3-hydroxybutyrate units, the number-average molecular weight $\bar{M}_n$ was estimated to be 1800. This value is in good agreement with the $\bar{M}_n$ value (2000) determined by GPC measurement,

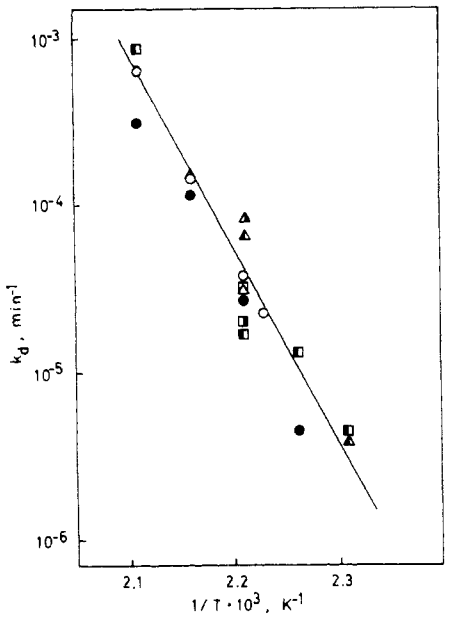


Figure 2. Arrhenius plot for the rate constants k_d of random chain scission of various microbial polyesters. (○) P(3HB) sample 1; (△) P(3HB-*co*-24%3HV) sample 2; (▲) P(3HB-*co*-45%3HV) sample 3; (▲) P(3HB-*co*-71%3HV) sample 4; (□) P(3HB-*co*-11% 4HB) sample 5; (■) P(3HB-*co*-17%4HB) sample 6; (■) P(3HB-*co*-82%4HB) sample 7; (●) Grassie et al.'s data in ref 10.

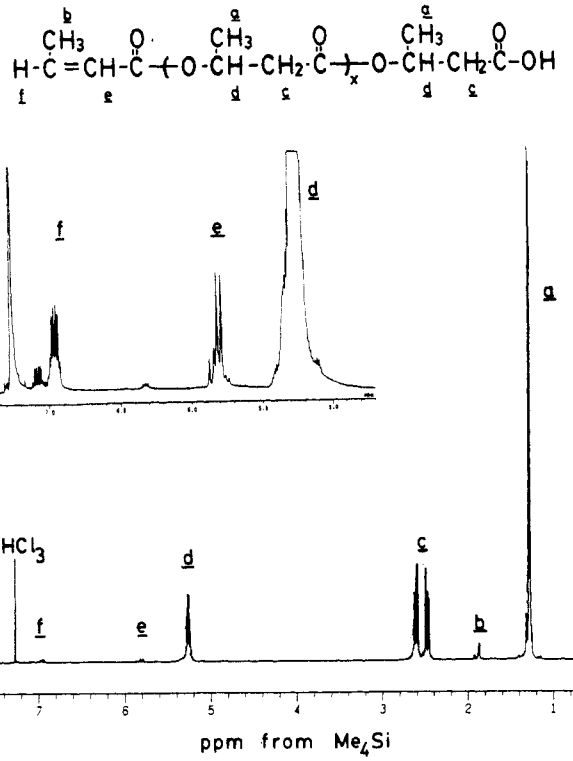


Figure 3. 500-MHz ^{1}H NMR spectrum of the P(3HB) oligomer obtained by thermal degradation under nitrogen at 200 °C. Chemical shifts are in parts per million from Me_4Si.

indicating that the random chain scission at ester groups occurs by the widely accepted six-membered ring ester decomposition process as represented by eq 2.[11,21]

Conclusion

All copolyester samples of P(3HB-*co*-3HV) and P(3HB-*co*-4HB) studied were thermally unstable at temperatures above 170 °C, and the molecular weights of melt samples decreased drastically for 20 min. The time-dependent changes in molecular weights of these copolyesters followed kinetic model (1) of random chain scission at ester groups. The rate constant k_d of random chain scission was not influenced by the compositions of copolyesters but was dependent strongly upon temperature. The activation energy of random chain scission was as large as 212 ± 10 kJ·mol^{-1} in the temperature range 170–200 °C. The 500-MHz ^{1}H NMR analysis of the thermally degraded P(3HB) oligomer confirmed that the chain scission occurs by the widely accepted six-membered ring ester decomposition process.

All copolyester samples were thermally stable at temperatures below 160 °C, and their molecular weights decreased at a very slow rate for 20 min. These results suggest that the microbial copolyesters with melting temperatures below 160 °C are injection moldable in practice and applicable to blown-film processing.

Acknowledgment. This work is supported in part by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture in Japan.

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