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Communications

Carboxylate-Induced Degradation of Poly(3-hydroxybutyrate)s

Michal Kawalec,† Grażyna Adamus,† Piotr Kurcok,† Marek Kowalczuk,*,† Ismaela Foltran,‡ Maria Letizia Focarete,‡ and Mariastella Scandola*,‡

Centre of Polymer Chemistry, Polish Academy of Sciences, 34, M. Curie-Sklodowska Street, 41-819 Zabrze, Poland, and Department of Chemistry "G. Ciamician", University of Bologna, via Selmi 2, 40126 Bologna, Italy

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This communication shows that thermal degradation of poly(3-hydroxybutyrate)s (PHBs) is induced by carboxylate groups via a newly proposed E1cB mechanism. In PHBs with end groups in the form of carboxylic acid salts with Na^+, K^+, and Bu_4N^+ counterions, the proposed mechanism explains the dependence of thermal stability on the size of the counterion. The degradation via intermolecular α-deprotonation by carboxylate is suggested to be the main PHB decomposition pathway at moderate temperatures. The results of the present study show the ability to control the degradation and stability of poly(3-hydroxybutyrate)s as well as of their blends via chemical structure and concentration of the carboxylate polymer end groups.

Introduction

Poly[(*R*)-3-hydroxybutyrate], n-PHB, which is widely distributed in nature, is a linear polymer of the ketone body (*R*)-3-hydroxybutyric acid. Among the various hypotheses about the origin of life, Seebach and Fritz[1] suggested that the activated polymerizable n-PHB precursor might have been formed prior to proteins under prebiotic conditions. The short-chain complexed polyhydroxybutyrate is present in a wide variety of human tissues and in atherosclerotic plaques.[2] The high molecular weight isotactic n-PHB is a storage material used by bacteria in nutrition-limited environments as an energy and carbon source.[3] Synthetic analogues of this biodegradable natural polymer of potential industrial importance are obtainable by direct copolymerization of epoxides with carbon monoxide[4] and via ring-opening polymerization (ROP) of β-butyrolactone (2-methyl-2-oxetanone) to isotactic,[5,6] atactic (a-PHB)[6−8], and syndiotactic[9] poly-3-hydroxybutyrate. Short-chain PHB, regardless of its tacticity, may be prepared from high molecular weight PHB by high temperature thermal degradation, which proceeds according to a random polymer-chain scission mechanism via intramolecular stereoselective cis-elimination with the formation of oligomers containing trans-crotonate end groups, as the main products.[10,11] The random chain scission by cis-elimination mechanism has been considered as the general pathway of PHB thermal degradation up to now.

In the present communication, a novel thermal degradation of poly(3-hydroxybutyrate)s, operating at moderate temperatures by carboxylate end groups, is reported. Moreover, the respective intermolecular mechanism of this process is proposed. The poly(3-hydroxybutyrate)s used in this study are high molecular weight n-PHBs obtained by biofermentation, isotactic poly(3-hydroxybutyrate)s (i-PHB) prepared by partial saponification of natural precursors,[12] and a-PHBs prepared by anionic ROP.[8]

Experimental Procedures

Materials. β-Butyrolactone, BL, (Aldrich) was distilled over CaH_2, and the fraction boiling at 56 °C (9 mmHg) was collected. Tetrabutylammonium acetate (Bu_4NAc) (Fluka), potassium acetate (KAc) (Aldrich), and sodium acetate (NaAc) (Aldrich) were used as received. 18-Crown-6 ether (18C6) (Aldrich) and 15-crown-5 ether (15C5)

* To whom correspondence should be addressed. Tel: +48322716077. Fax: +48322712969. E-mail: cchpmk@bachus.ck.gliwice.pl (M.K.). Tel: +39-051-2099577. Fax: +39-051-2099456. E-mail: mariastella.scandola@unibo.it (M.S.).

† Polish Academy of Sciences (since January 1, 2007 Centre of Polymer and Carbon Materials).

‡ University of Bologna.

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Table 1. Maximum Degradation Rate Temperature (T_{max}) of PHB Samples

entry	polymer/end group	M_n (g/mol)	T_{max} (°C)
1	n-PHB/COOH	131000	291
2	a-PHB/COOH[a]	36400	291
3	i-PHB/COOH[b]	5800	289
4	a-PHB/COOH[a]	5700	291
5	i-PHB/COONBu$_4$[b]	5600	225
6	a-PHB/COONBu$_4$[a]	36000	252
7	a-PHB/COONBu$_4$[a]	5600	227

[a] The polymer was prepared as described in ref 8[8]. [b] The polymer was prepared as described in ref 12c[12c].

(Aldrich) were dried under vacuum at 50 °C for 72 h. THF (pure, POCh Gliwice) was distilled over potassium−sodium alloy just before use. KAc/18C6 and NaAc/15C5 complexes were prepared by adding the respective crown ether to the solution of the respective acetate in dry methanol. The molar ratio of the acetate to crown ether was 1:1.05. After stirring overnight, methanol was evaporated, and the complexes were dried under vacuum. n-PHB (ICI product − PHB G08) with Ca and Mg content equal to 110 and 11 ppm, respectively,[11b] was used as received.

Polymerization. The β-butyrolactone anionic polymerization experiments were conducted as previously reported.[7a,8] Polymerization initiated with Bu$_4$NAc was carried out in bulk (entries 2 and 6 in Table 1) or in a solution of THF ($[BL]_0 = 3$ mol·dm^{-3}; entries 4 and 7). Polymerization reactions initiated with KAc/18C6 and NaAc/15C5 were carried out in THF ($[BL]_0 = 8$ mol·dm^{-3}). All of the polymerization experiments were conducted at a temperature of 23 °C. Progress of the reaction was measured by FTIR spectroscopy on the basis of the carbonyl carbon signals of BL and the poly(3-hydroxybutyrate) at 1815 and 1735 cm^{-1}, respectively. When the polymerization was complete, the polymer was precipitated in hexane and dried under vacuum. The final product was characterized with ^{1}H NMR and GPC techniques.

Protonation of PHB Carboxylate End Groups. A 10 wt % chloroform solution of polymer sample was acidified with diluted HCl$_{(aq)}$ (Bu$_4$N$^+$/HCl = 1:2), and the mixture was stirred vigorously for 10 min. After phase separation, the organic layer was separated and acidified once more (as described above). Then the polymer solution was washed 10 times with 10 cm^3 of distilled water. Next, the solvent was evaporated, and the polymer was dried under vacuum at room temperature. The final product was characterized with ^{1}H NMR and GPC techniques.

Blend Preparation. The blend components were solubilized in CH_2Cl_2 (5% w/v). The solutions were poured onto Petri dishes, the solvent was allowed to evaporate at room temperature, and the films were additionally dried under vacuum.

Isothermal Degradation Experiments. The degradation of PHBs with carboxylate end groups or carboxylic end groups were isothermally performed at 120 and 150 °C in an oven. At selected degradation times, the nonvolatile residues were analyzed with ^{1}H NMR and GPC techniques as well as by ESI-MS spectrometry.

Measurements. FTIR spectra were recorded with an FTS 40A Bio-Rad spectrometer. ^{1}H NMR spectra were recorded at room temperature in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard using a Varian VCR-300 spectrometer with a 4499 Hz spectral width, an acquisition time of 1.998s, and 64 repetitions. Number of average molecular weight and molecular weight distribution (M_w/M_n) values of polymers were estimated by GPC experiments conducted in chloroform at 35 °C at a flow rate of 1 cm^3·min^{-1} using a Spectra-Physics 8800 solvent delivery system with a set of two PLgel 5 μm MIXED-C ultrahigh efficiency column and a Shodex SE 61 refractive index detector. A volume of 10 μL of sample solution in chloroform (concentration of 1% w/v) was injected. Polystyrene standards with narrow molecular weight distributions were used to generate a calibration curve. Electrospray mass spectrometry analyses were performed using an LCQ ion trap mass spectrometer (Finnigan, San Jose, CA). PHB samples were dissolved in a chloroform/methanol mixture (10/1 v/v). The solution was introduced to the ESI source by continuous infusion by means of the instrument syringe pump at a rate of 3 μL·min^{-1}. The LCQ ESI source was operated at 4.25 kV, and the capillary heater was set to 200 °C. For ESI-MS^n experiments, mass-selected mono-isotopic parent ions were isolated in the trap with an isolation width of 1 m/z and activated by collision with a 30−35% ejection RF amplitude at standard He pressure. The experiments were performed in negative-ion mode. Thermogravimetric measurements (TGA) were carried out using a TA-TGA 2950. The analyses were performed at 10 °C·min^{-1} from room temperature to 600 °C under nitrogen flow. Residual Ca and Mg content in the n-PHB sample was measured with a THERMO Solaar S atomic absorption spectrophotometer.

Table 2. Influence of the Counterion Type on the Thermal Stability of a-PHB with the Molecular Weight (M_n) in the Range 6−10 kDa

counterion type (Cat$^+$)	Bu$_4$N$^+$	K$^+$/18C6	Na$^+$/15C5	H$^+$
T_{max} (°C)	224	228	231	291

Results and Discussion

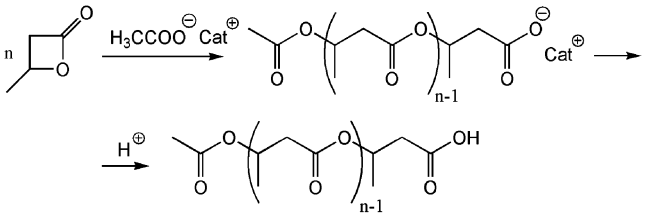
The results of the thermogravimetric experiments presented in Tables 1 and 2 illustrate the effect of the chemical structure of the PHB end group (carboxylate or carboxylic) on the temperature of the maximum degradation rate (T_{max}) of PHBs with different microstructure (isotactic and atactic, Table 1), molecular weight (Table 1), and type of counterion (Table 2).

The presence of either carboxylate or carboxylic end groups significantly influences polymer stability. Thermal stability of PHB with COOH end groups is not influenced by microstructure and molecular weight (Table 1, entries 1−4), which is in agreement with earlier results.[11a] However, when the PHB possesses the terminal groups in the form of carboxylate salt, a significant decrease in T_{max} is observed (Table 1, entries 5−7 vs 1−4). Similarly, a comparison of entries 5 and 7 shows no microstructure effect on thermal stability. However, a comparison of entries 6 and 7 shows a significant difference in T_{max}. This difference in T_{max} is related to the different concentrations of polymer carboxylate end groups (−COONBu$_4$) associated with different molecular weight. Indeed, additional TGA experiments on a-PHBs with different concentrations of carboxylate terminated molecules (obtained by partial acidification of sample 6 in Table 1) have revealed an increase in T_{max} from the initial 252 °C to 265 °C and 281 °C, with decreasing content of carboxylate terminated polymeric chains from 100% to 50% and 20%, respectively.

Furthermore, the type of counterion of the carboxylate end group is found to influence the T_{max} of a-PHB (Table 2). With decreasing cation size, the thermal stability of investigated a-PHB samples (prepared by anionic ROP initiated by either tetrabutylammonium or activated potassium and sodium acetates, Scheme 1) slightly increases as follows: Bu$_4$N$^+$ < K$^+$/18-crown-6 complex < Na$^+$/15-crown-5 complex ≪ H$^+$.

Isothermal degradation experiments were conducted at 120 °C on both a-PHB containing terminal carboxylate groups and tetrabutylammonium counterion (entry 7, Table 1) and a-PHB possessing carboxylic end groups (entry 4, Table 1). After 4 h at 120 °C, a significant decrease in molecular weight is observed in the sample with carboxylate end groups, whereas no change in molecular weight is observed for the sample with carboxylic end groups (Figure 1).

Scheme 1. Reaction Scheme for ROP Synthesis of a-PHB with Different Counterions



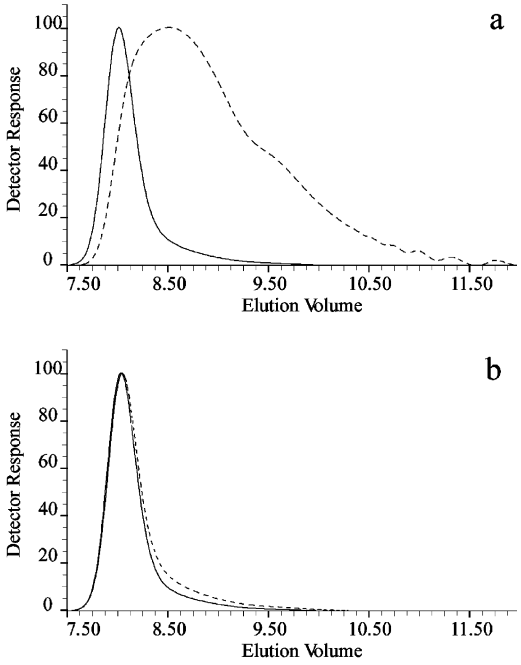


Figure 1. Normalized GPC elugrams of a-PHB with (a) terminal Bu_4N carboxylate groups and (b) carboxylic end groups before (—) and after 4 h of isothermal heating at 120 °C (---).

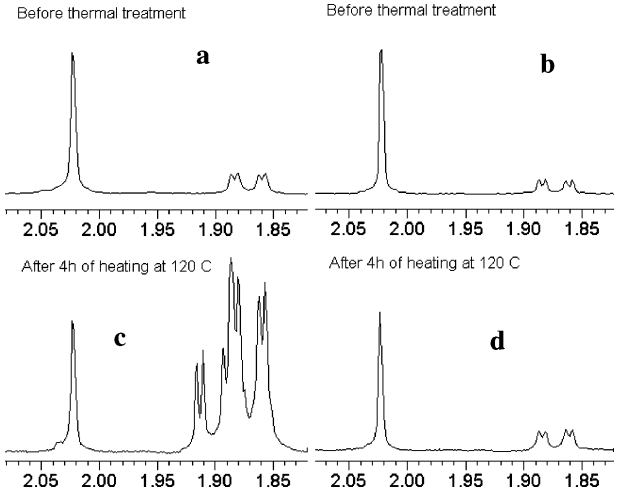


Figure 2. ^{1}H NMR spectra of acetate and crotonate end groups (methyl group protons region) of a-PHB before thermal treatment. (a) COO^- terminated and (b) COOH terminated and a-PHB after 4 h of the isothermal treatment at 120 °C. (c) COO^- terminated and (d) COOH terminated.

The ^{1}H NMR spectra (region between 1.80−2.05 ppm) of the a-PHB samples (entry 4 and 7, Table 1) recorded before and after 4 h of the isothermal treatment at 120 °C are depicted in Figure 2.

In all analyzed samples, the signal of acetate group protons (singlet at $\delta = 2.02$ ppm) originating from the initiator used and the signals of protons of the trans-crotonate group (doublet of doublets centered at $\delta = 1.87$ ppm) have been observed. The small amount of crotonate end groups observed in the a-PHB samples before thermal treatment (a and b in Figure 2) is related to their formation during the polymerization reaction. Indeed, the formation of crotonate end groups in β-butyrolactone polymerization was already reported. They can be formed either in the initiation process[7b,13] or during the propagation, despite alkyl-oxygen or acyl-oxygen bond cleavage.[6,8,14] It was believed that in the polymerization of β-butyrolactone with potassium acetate activated by dibenzo-18-crown-6, the crotonate starting groups were formed because of the chain transfer reaction to the monomer.[14a] Recently, it was found that the crotonate end group formation in anionic ROP of β-butyrolactone can be suppressed by the solvent used in the activation of the carboxylate propagation species.[15]

As depicted in Figure 2 b and d, the relative amount of the crotonate end group with respect to the acetate end group is at the same level before and after isothermal treatment of COOH terminated a-PHB. It clearly demonstrates that the random intramolecular chain scission by cis-elimination mechanism, reported previously for high-temperature PHB degradation, can be neglected in the conditions of the presented study.[10c,d]

However, for the COO^- terminated sample, the substantial increase of the signals of the crotonate end group, which overlaps the signals of crotonic acid, is observed after the isothermal treatment. This result indicates that crotonate-terminated oligomers and crotonic acid are formed as products of degradation under these conditions (compare Figure 2a and c).

The presence of oligomers containing crotonate end groups, formed during the thermal treatment of the a-PHB sample with carboxylate end groups, has been confirmed by ESI-MS^n analyses. Two series of singly charged negative mass-resolved $[M - H]^-$ ions with different intensities are present in the mass spectrum depicted in Figure 3a for a-PHB with the terminal Bu_4N carboxylate end group (entry 7, Table 1) after 4 h of the isothermal treatment at 120 °C. The mass differences in the experimental *m*/*z* values between the peaks within both series are equal to 86 Da and correspond to the molar mass of the hydroxybutyrate repeating unit. The most intense series of negative ions observed in the mass spectrum, labeled A, corresponds to the individual a-PHB oligomer chains with crotonate end groups. The second series of negative ions (with low intensity), indicated by B, can be assigned to the a-PHB polyester chains with acetate end groups derived from the initiator used. In order to verify the above structural assignment, MS^2 experiments have been performed for the parent negative ions at *m*/*z* 687 and *m*/*z* 661 selected from series A and B, respectively.

Figure 3b shows the results of the MS^2 experiment of the parent ion at *m*/*z* 687 assigned to the a-PHB oligomer with the crotonate end group. The fragmentation of this negative ion, which may occur from both sides of the molecule (see fragmentation pathway in Figure 3b), produces fragment ions exclusively by the loss of a neutral molecule of crotonic acid.

Figure 4 shows the results of the MS^2 experiment of the molecular ion at *m*/*z* 661, assigned to the oligomer with the acetate end group. The fragmentation of this ion also occurs from both sides of the molecule (see fragmentation pathway in Figure 4) with the formation of two sets of fragment ions with 26 Da spacing. Thus, the fragment ion at *m*/*z* 601 corresponds to the oligomer ion formed by the loss of acetic acid (60 Da),

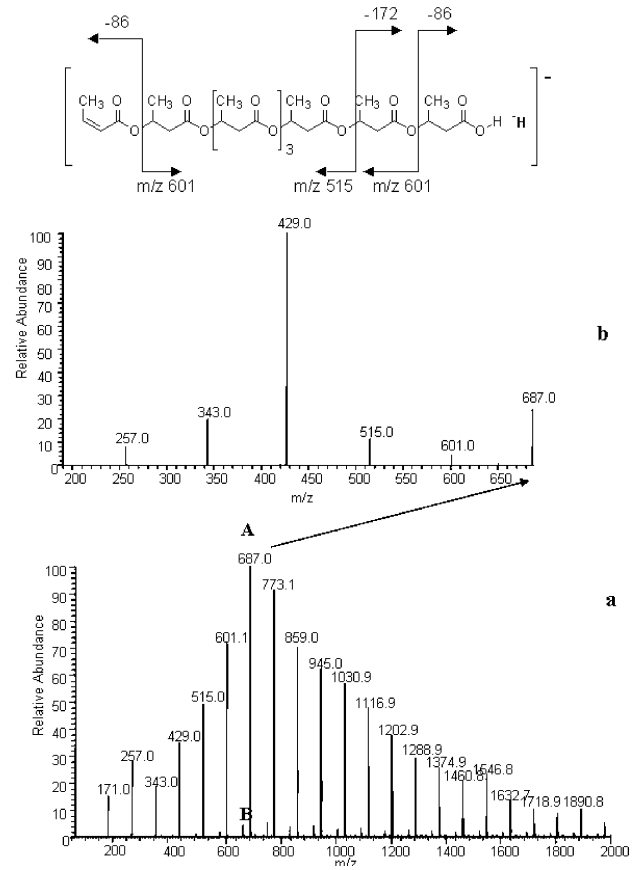


Figure 3. (a) Mass spectrum of a-PHB sample (entry 7, Table 1) after 4 h of isothermal treatment at 120 °C. (b) MS^2 spectrum of the parent ion at *m*/*z* 687 assigned to the a-PHB oligomer with the crotonate end group.

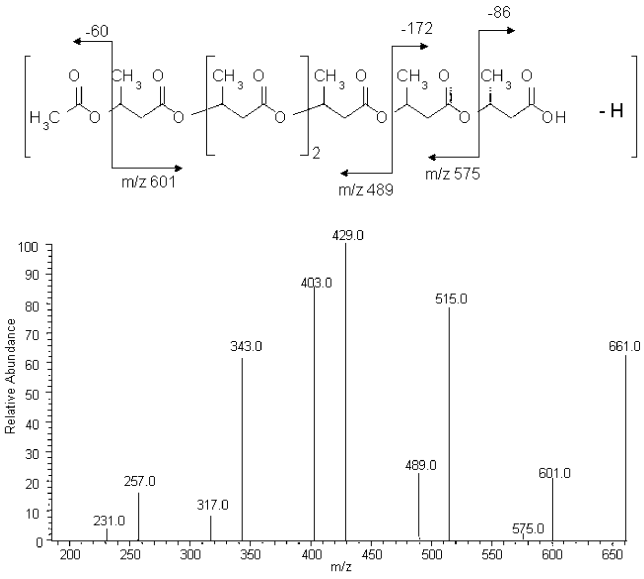


Figure 4. MS^2 experiment of the molecular ion at *m*/*z* 661 assigned to the oligomer with the acetate end group.

and the ion at *m*/*z* 575 corresponds to the oligomer ion formed by the expulsion of crotonic acid (86 Da).

The results of the ESI-MS^2 experiments confirm that a-PHB oligomers containing predominantly crotonic end groups are formed after the isothermal treatment of COO^- terminated a-PHB at moderate temperature (120 °C). Small amounts of oligomers containing acetate end groups derived from the initiator have been also observed.

Additional isothermal degradation experiments have been performed at 150 °C on samples prepared by adding to a protonated a-PHB sample (entry 4, Table 1) an equimolar amount of acetate salts with different counterions: Bu_4N^+, K^+/18C6, and K^+. A significant decrease in molecular weight combined with weight loss has been observed in all analyzed blends during isothermal treatment at 150 °C (Figure 5); it was most pronounced for the protonated a-PHB sample blended with tetrabutylammonium acetate. The results confirm that the thermal degradation of protonated a-PHB is induced by the added acetates and that the size of the acetate counterion affects thermal stability.

The results of the studies presented above indicate, noticeably, that at moderate temperatures, the degradation of PHB is induced by carboxylates. This phenomenon may be explained by the E1cB mechanism proposed in this work for the degradation of poly(3-hydroxybutyrate)s possessing a hydrogen atom at the C2 carbon (Scheme 2), where a crucial role is played by the carboxylate terminal groups.

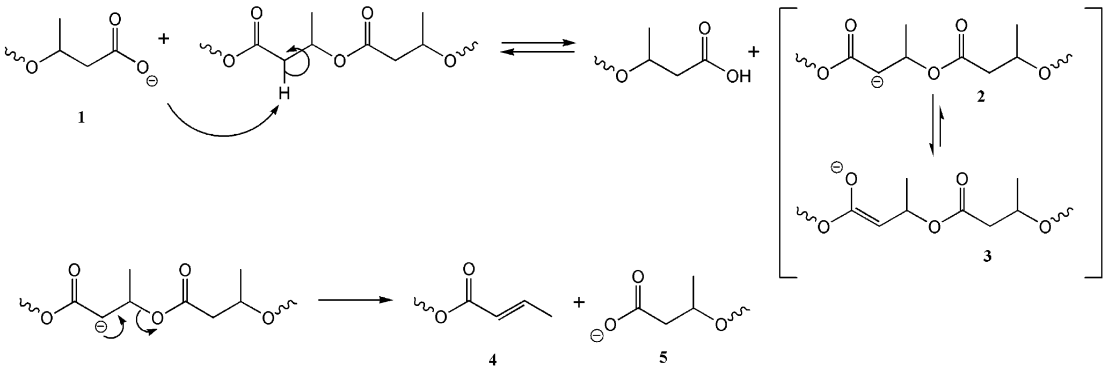
According to the E1cB mechanism of the degradation reaction (see Scheme 2), the carboxylate end group of PHB **1** abstracts the acidic proton at C2 of PHB with the generation of carbanion **2**, which can tautomerise to an enolate form **3**. The carbanion **2** undergoes the elimination reaction, leading to chain scission with the generation of the trans-crotonate terminal group in one polymer chain fragment **4** and to the replication of carboxylate end group (leaving group **5**) in the other fragment. As reported by Mulzer et al.,[16] the decomposition to trans-crotonate of the enolate derived from the α-deprotonation of 3-hydroxyacid diester takes place even at low temperature, indicating the relatively low activation energy of such a reaction. Thus, the PHB degradation induced by carboxylate end groups can proceed at moderate temperatures via the E1cB mechanism. The proposed mechanism of PHB degradation explains the peculiar thermal stability of PHB containing carboxylic acid salts as end groups and the dependence of PHB stability on the counterion type. In the present mechanism, the intermolecular character of the reaction is shown; however, the intramolecular reaction cannot be excluded.

The intermolecular character of carboxylate-induced PHB degradation by the E1cB mechanism has been additionally proved by TGA experiments (Figure 6) investigating the thermal stability of a 50/50 w/w blend of a-PHB containing carboxylate end groups with -COOH terminated n-PHB (Table 1, entries 7 and 1, respectively). The TGA analysis of such a blend revealed only one degradation step at T_{max} = 241 °C, that is, in between the T_{max} of the two blend components.

The TGA indicates a significant decrease in T_{max} of the more stable component and an increase in T_{max} of the less stable one when the carboxylate anions are present in such a system. The observed decrease in n-PHB T_{max} results from the intermolecular α-deprotonation of its molecules by the carboxylate end groups of a-PHB (through the E1cB mechanism). Conversely, the apparent increase in a-PHB stability is connected with the fact that in the 50/50 blend, the total concentration of a-PHB carboxylate end groups is two times lower than that in the plain $-COONBu_4$-terminated a-PHB. The same effect is also observed in a mirror image reverse experiment (Figure 7) on a 50/50 w/w blend of a-PHB containing carboxylic end groups (entry 4, Table 1) with i-PHB possessing carboxylate terminal groups (entry 5, Table 1). Again, only one T_{max} is observed at 241 °C, that is, in between the T_{max} of plain protonated a-PHB and i-PHB bearing the Bu_4N^+ counterion, thus proving the intermolecular character of the PHB degradation reaction.

CDV

Scheme 2. E1cB Degradation Mechanism of PHB[a]



[a] In order to be brief, the counterion is omitted.

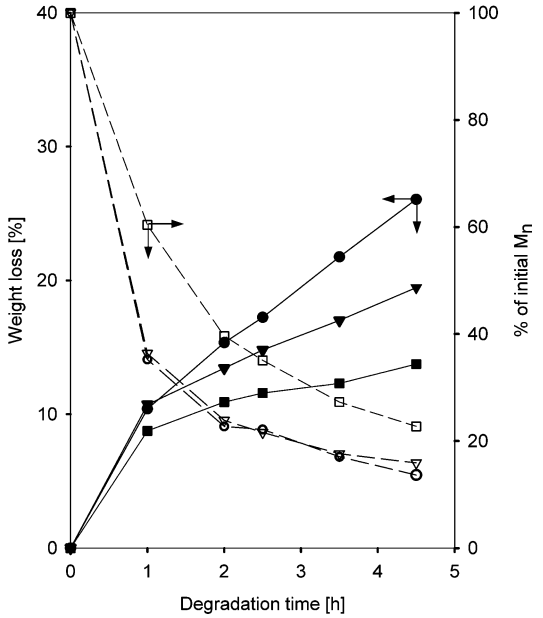


Figure 5. Sample weight loss (filled symbols) and molecular weight changes (as a percent of initial M_n; open symbols) during the isothermal degradation (150 °C) of a-PHB (entry 4, Table 1) mixed with equimolar amounts of acetates. (○,●) Bu_4N^+; (▽,▼) K^+/18C6; (□, ■) K^+.

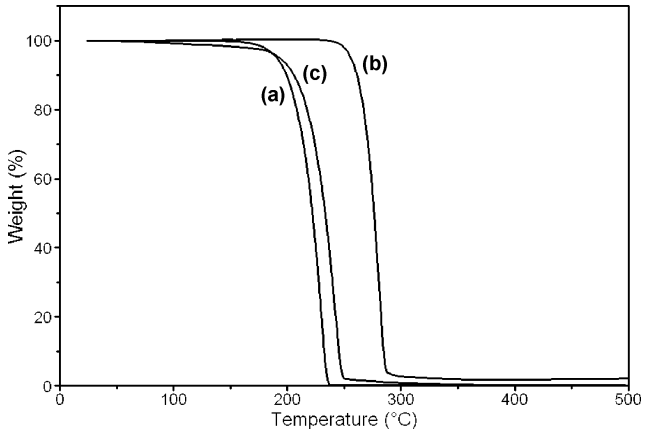


Figure 6. Thermogravimetric curves of (a) a-PHB/$COONBu_4$ (entry 7, Table 1), (b) n-PHB/COOH (entry 1, Table 1), and (c) their 50/50 (wt %) blend.

The novel degradation mechanism may be competitive to cis-elimination at higher temperatures. However, it is hardly expected that the type of terminal group can affect the known

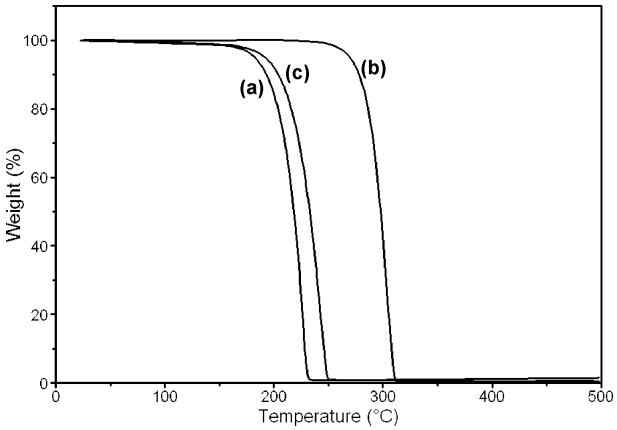


Figure 7. Thermogravimetric curves of (a) i-PHB/$COONBu_4$ (entry 5, Table 1), (b) a-PHB/COOH (entry 4, Table 1), and (c) their 50/50 (wt %) blend.

cis-elimination mechanism that occurs as non-ionic random intramolecular chain scission.

Conclusions

In conclusion, the carboxylate-induced degradation of poly(3-hydroxybutyrate)s by the E1cB mechanism is proposed. The new mechanism explains the dependence of PHB thermal stability on the chemical structure of its end groups in the form of carboxylic acid salts. The degradation via α-deprotonation is suggested to be the main PHB decomposition pathway at moderate temperatures. The intermolecular nature of the proposed mechanism has been proved, though proton abstraction at C2 of the same macromolecule that bears the active end group cannot be excluded. The E1cB mechanism elucidates the influence of the size of the counterion.[17] The results of the present study indicate the possibility of controlling the thermal degradation and stability of poly(3-hydroxybutyrate)s as well as their blends by changing (i) the chemical structure of PHB terminal groups (carboxylic or carboxylate bearing the counterion with the desired size) and/or (ii) the concentration of the polymer carboxylate end groups. Ongoing experiments at our laboratories show the general character of the E1cB mechanism in poly(3-hydroxyalkanoate)s containing the hydrogen atom at C2 (e.g., poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), PHBH; data not shown), thus demonstrating a facile method of production of PHA oligomers well defined at the molecular level.[18]

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