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Thermal Degradation of Bacterial Poly(hydroxybutyric acid): Mechanisms from the Dependence of Pyrolysis Yields on Sample Thickness

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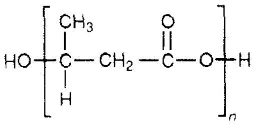
ABSTRACT: The thermal degradation behavior at 350 °C of poly(hydroxybutyric acid), "Biopol", has been studied by pyrolysis–GC using a microthermocouple-controlled filament. The overall pyrolysis mechanism—an array of parallel and consecutive processes—has been elucidated by a novel method. This involves the measurement of product yields as a function of sample thickness, for samples in the microgram range, pyrolyzed for a chosen duration (5 s was used in the present study). This approach provides indirect control of the residence time of primary products in the melt and thereby facilitates the detection of secondary reactions. From quantitative measurements of bonus yields and deficit yields, it is shown, for example, that only *trans* isomers are formed as primary products; *trans–cis* isomerisations then occur as secondary reactions. Moreover, although monomeric, dimeric, and trimeric products are formed by primary processes, there is evidence that a trimeric product is also formed by a consecutive reaction mechanism. Somewhat unexpectedly, the tetrameric products are formed *exclusively* by secondary reactions. This observation casts some doubt on the view that the pyrolysis products from this polymer can be accounted for entirely in terms of random (β-elimination) scissions.

1. Introduction

The synthetic polymers derived from oil and other fossil fuels have received much attention in polymer technology, and they have somewhat overshadowed natural protein and polysaccharide polymers such as wool and cotton. The first reason for this is that the properties of animal proteins and plant fibers, although very appropriate for traditional usage, are not easily varied and controlled and are not suitable for some modern applications. The second reason is that synthetic polymers, in the developed world at least, are sometimes cheaper than natural counterparts. The third, and possibly the most important, reason is the ease with which synthetic polymers can be processed for bulk production.

At the present time, there is increasing concern over the environmental implications of the synthesis and use of synthetic polymers, partly because they consume nonrenewable resources but also because they generally have low natural degradability and their final disposal causes pollution. This has lead to a search for naturally occurring alternatives for these high-tonnage synthetic polymers. One such natural product of considerable interest is poly(D-β-hydroxybutyric acid), known as PHB or by the trade name "Biopol", devised by the manufacturers Zeneca Bioproducts.



$$HO{-}[CH(CH_3){-}CH_2{-}C(=O){-}O]_n{-}H$$

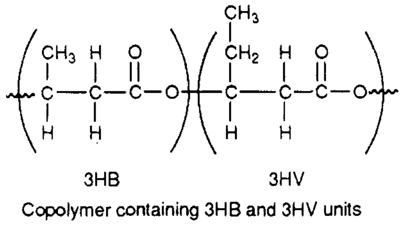
This bacterially-produced polymer was first isolated and characterized by Lemoigne[1] in 1925. Several different microorganisms produce the polyester as discrete, spherical hydrophobic granules[2] which can represent up to 80% of the dry weight of the microbe. The polymer fulfills the role of an energy-storage medium for the microorganism when an amount of food is available which exceeds its immediate energy requirements.[3]

The polymer has additional advantages of being naturally biodegradable by enzymic or hydrolytic degradation processes and also of being thermoplastic, which permits melt processing. With all melt-processed polymers there is the possibility of thermal degradation at temperatures in the region of the melting point (in this case ca. 180 °C), and PHB is no exception in this respect.[4–6]

Melt Processing of Bacterial Polymers. The possibility of melt-processing PHB was studied extensively in the 1950s and 1960s by W. R. Grace and Co.[7] It was considered that the polymer is rather unstable at temperatures close to its melting point, and it was concluded that it is therefore difficult to process by conventional melt routes.[8]

Further work[4–6,9] has confirmed that the polymer can suffer some reduction of molecular weight when maintained even at 170 °C, i.e., about 10 °C below its melting point.

This problem is much less severe for *copolymers* of 3-hydroxybutyric acid because the comonomer influences the physical properties of the polymer. A copolymer of 3-hydroxypentanoic acid (trivially known as 3-hydroxyvaleric acid or 3HV) and 3-hydroxybutyric acid can be produced by adding propionic acid to the nutrient feedstock supplied to the bacteria. The two monomer units in the copolymer are shown below.



$$\sim[CH(CH_3){-}CH_2{-}C(=O){-}O]{-}[CH(CH_2CH_3){-}CH_2{-}C(=O){-}O]\sim$$

Copolymer containing 3HB and 3HV units

Copolymer compositions containing up to 30 mol % 3HV can be produced by controlling the feedstock and the conditions. The mole percentage of valerate in the polymer sample is limited by the toxicity of the propionic acid to the microorganism used, *Alcaligenes eutrophus*. However, polymers with compositions up to 95 mol % 3HV have recently been obtained by adding controlled mixtures of pentanoic acid and butyric acid to the

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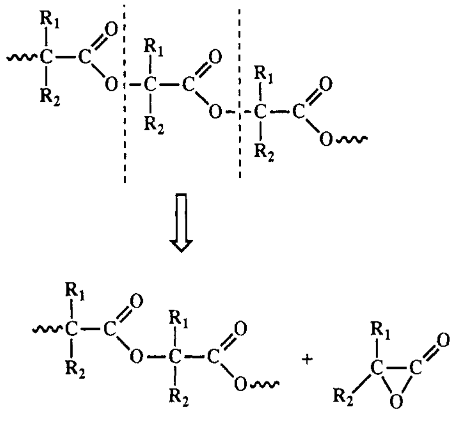
feedstock.[10,11] The copolymer is believed to possess an almost completely random distribution.[12-14]

The effect of the comonomer is to reduce the crystallinity and also the melting point of the homopolymer. Thus the melting point (T_m) of the copolymer decreases from ca. 180 °C with increasing 3-hydroxyvalerate content and reaches a minimum value (ca. 75 °C) at approximately 40 mol % 3HV. As the 3HV content increases toward pure PHV, the melting point increases; thus at 95 mol % 3HV the melting point has increased to 108 °C.[12,15,16]

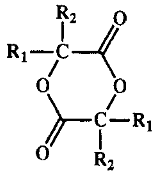
Thermal Degradation Mechanisms of General Polyesters. Condensation-type polymers, by their very nature, cannot be *thermally* degraded to their corresponding hydroxy acids because this would require the provision of one molecule of water at each scission.[17] (Such a process would of course be a hydrolysis reaction.)

A mechanism proposed at an early stage by Carothers[18] could possibly occur in thermal degradation. He showed that some aliphatic polyesters undergo intramolecular ester exchange reactions which result in the formation of monomeric and dimeric cyclic esters. For an R_1, R_2 polyester as shown below, the monomeric cyclic ester would be formed as follows:

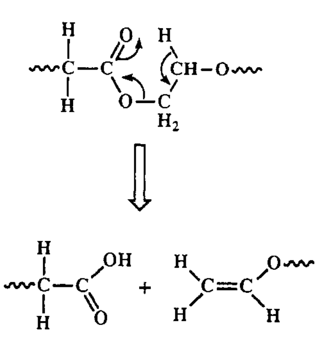


(R_1 and R_2 are alkyl groups or H.)

The comparable elimination of two units would give the following dimeric cyclic ester:



More recently it has been proposed that a more probable polyester degradation mechanism is the abstraction of hydrogen from a β carbon atom ("β-elimination") via a six-membered ring transition state.[19-21] This results in a scission of the chain to give an olefinic end and a carboxyl-terminated end:



This mechanism has been studied in some detail by Pohl.[22]

Product evolution data obtained from poly(isopropylene carboxylate) were examined by Tighe[23] in order to assess various degradation pathways. The following possible mechanisms were considered: (a) random chain scission; (b) depropagation initiated at scissions or at chain ends; (c) inter- or intramolecular ester exchange; (d) molecular decarboxylation (loss of CO_2) or decarbonylation (loss of CO) accompanied by chain recoupling.

Of these mechanisms, the decarboxylation and decarbonylation reactions were thought by Tighe to be unlikely major degradation routes, at least at low temperatures (<400 °C), since they do not give rise to the major observed degradation products. Also, on the basis of molecular weight observations and the absence of any effect by radical scavengers, he concluded that radical depropagation reactions are of little importance. The overall conclusion was that some form of random chain scission (e.g., by β-elimination reactions) appears to fit the observed kinetic behavior and can best account for the degradation products.

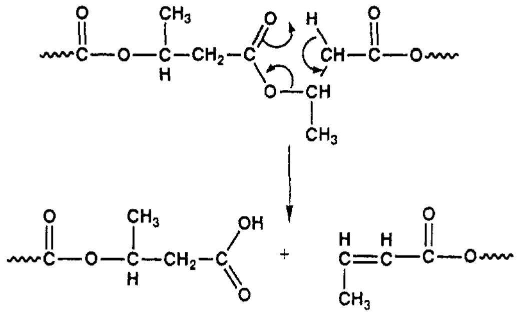
Background to the Present Study of Biopol Degradation. On the basis of the general polyester degradation mechanisms outlined above and from specific experiments on PHB,[24] the thermal degradation of PHB is generally assumed to proceed via the β-elimination reaction. The composition and yields of the degradation products have been studied by various workers,[5,6,9,25,26] who have analyzed the pyrolysis products from the polymer under a range of conditions and temperatures, using several techniques. The results may be summarized under the three headings below.

Low-Temperature Degradation (ca. 170-200 °C). When PHB is maintained at such temperatures, very few, if any, volatile products are observed, but the molecular weight of PHB has been reported[5] to display an initial decrease with time, then to increase slightly, and afterward to continue to fall. It is believed that, in addition to MW reduction caused by chain scissions, condensation of hydroxyl and acidic groups originally present as the end groups of the polymer molecules could lead to the MW increase. When the hydroxyl groups are consumed, the MW again declines.

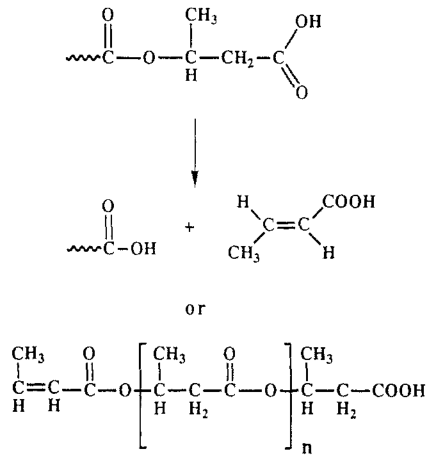
Other evidence for the occurrence of this condensation reaction includes the claim that water is produced during the thermal degradation of PHB.[6]

Moderate-Temperature Degradation (200-300 °C). When the polymer is heated at temperatures up to 300 °C, in addition to scissions leading to a molecular weight reduction, monomeric, dimeric, trimeric, and tetrameric volatile products are observed.[5] β-Elimination mechanisms leading to these are shown in Figure 1. Butenoic acid, commonly known as crotonic acid, is the smallest characteristic degradation product and is usually termed "monomer" although it might be strictly termed the "dehydrated monomer". The oligomers also each possess one olefinic group. Oligomers higher than tetramer are very involatile and at these temperatures would reside within the polymer until further broken down. Oligomers and monomer are principally formed in the *trans* form because the six-membered transition state is sterically more favored for the *trans* configuration. This is shown in Figure 2.

Another degradation product observed is β-butyrolactone, which can also be formed from the end of a chain by way of a six-membered ring transition state.[19-21] This is



The β-elimination reaction of PHB, causing a primary scission.



The major volatile degradation products of PHB: crotonic acid and oligomers (n= 0,1,2....)

Figure 1. Scissions of PHB and volatile degradation products.

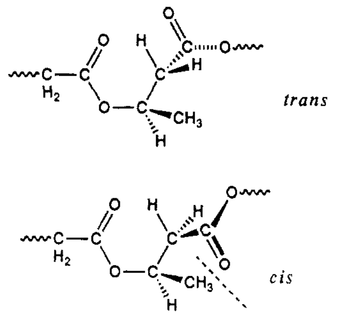


Figure 2. Unfavorable CO/CH$_3$ interactions in the *cis* configuration compared with the *trans*.

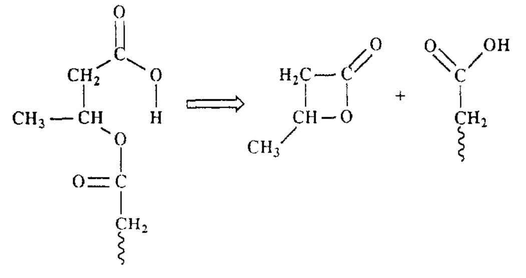
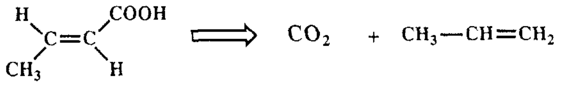


Figure 3. Possible route to the formation of β-butyrolactone.

shown in Figure 3. The strained ring structure of the β-butyrolactone contributes toward its instability at these temperatures; hence, it is more likely to be observed as its breakdown products.

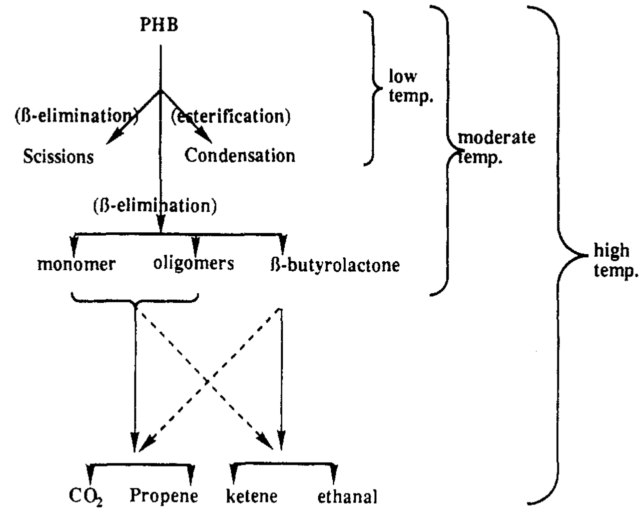
High-Temperature Degradation (ca. 500 °C). When PHB is heated at high temperatures (ca. 500 °C), the degradation product distribution again alters.[5] Propene and carbon dioxide now appear as major products, possibly formed by the secondary decomposition (decarboxylation) of primary degradation products such as crotonic acid:



$$\Longrightarrow CO_2 + CH_3{-}CH{=}CH_2$$

Other minor products are believed to include carbon monoxide, ketene, and ethanal.

A tentative overall scheme for the degradation of PHB, proposed on the basis of speculative mechanisms in the literature, is shown below.



Scope of the Present Work. The present paper sets out to deduce mechanisms of thermal degradation of PHB, in the moderate temperature range, from the way in which volatile product yields and ratios depend on sample thickness. Analysis of the results has been performed using new approaches and principles[27-29] which have been developed in the authors' laboratories as an aid to the elucidation of secondary reactions. The principles used in the study are described in the following section.

2. Degradation Mechanisms from Dependence of Product Yields on Thickness

Unlike solution kinetic studies, in which the *concentration dependence* of rates permits orders of reaction to be evaluated, pyrolysis studies require different approaches for the following reasons.

(1) At the high temperatures at which pyrolyses are carried out, potential solvents would decompose or volatilize. This prevents the use of concentration-dependence studies to explore degradation mechanisms.

(2) Provided certain basic requirements are satisfied, it is expected that the rate of loss of mass from the system will be *first* order with respect to the mass of the remaining material *irrespective* of the degradation mechanism.

The basic requirements referred to in 2 are as follows:

(a) The samples must be small enough to receive uniform heating at the chosen temperature of pyrolysis.

(b) The structure of the residue does not differ greatly from that of the starting material, at least during the initial stages of the pyrolysis.

(c) All the products are formed as a result of *primary processes* in the polymer melt. The term "primary processes" refers to all reactions not involving interaction of primary volatile products.

It should be evident from (c) that the occurrence of secondary reactions (i.e., any subsequent reactions of primary products or the isomerization of primary products) can cause deviations from first-order behavior, and it will be shown that this is revealed from the study of the anomalous dependence of product yields on sample size.

At this point it is appropriate to discuss the normal expectations for such behavior in order that deviations may be subsequently defined.

Consider first the exponential loss of mass associated with the evolution of a volatile product by a first-order process. If the original mass of material is m_0 and the total mass of material evolved after any time t is m, we can write

$$[m_0 - m] = m_0 \exp(-kt) \qquad (1)$$

where k is the first-order rate constant for the process.

If we define the fractional conversion at time t as m/m_0, we can write eq 1 as

$$m/m_0 = 1 - \exp(-kt) \qquad (2)$$

We therefore see that, for pyrolyses following kinetics of this kind, if they are performed at the *same temperature* (i.e., k = constant), and for the *same duration* (t = constant), then the fractional conversion should be the same, whatever the sample size used, i.e.

$$m/m_0 = \beta \qquad (3)$$

where $\beta = 1 - \exp(-kt)$.

This can be tested by rewriting eq 3 as

$$m = \beta m_0 \qquad (4)$$

whence a plot of m (the product yield) *versus* m_0 (the original sample size) should be a straight line through the origin, for pyrolyses of the same duration. This is the criterion used for normal thickness dependence in the present work.

We may now consider how a consideration of secondary reactions leads to the interpretation of deviations from linearity (Δm) in such a plot. If it is remembered that increasing the thickness of the sample will be associated with increasing the residence time of a primary product in the melt, then two possible deviant trends in the m versus m_0 plot can be envisaged:

(a) Δm Negative and Increasing as Thickness Increases. If a primary product while in the melt shows a tendency to decompose, isomerize, or react with any other product, then its yield will be reduced and the plot will show a negative deviation from the ideal. Since the probability of such events occurring increases with residence time in the melt, the extent of the deviation will increase with sample thickness.

(b) Δm Positive and Increasing as Thickness Increases. A necessary consequence of the decomposition, isomerization, or reaction of a primary product as in a is that the resulting secondary product will be formed in increased bonus yield (positive deviation from linearity) as the sample size is increased. This will be a bonus only if the secondary product from (a) is already being formed as a primary product. If not, the secondary product will appear as a new product, climbing with increased deviation from the x axis in the m versus m_0 plot.

Two further principles may be applied in defining and interpreting the deviations in thickness-dependence plots:

(1) On the assumption that secondary reactions in the melt could not occur if the residence time were zero, it may be assumed that the limiting tangent to the m versus m_0 curve at $m_0 = 0$ defines the ideal line, i.e., the plot which would have been observed in the absence of secondary reactions. On this basis, the magnitude of the deviations can be obtained by measuring Δm as the difference in m between the observed curve and the limiting tangent.

(2) If a particular process (e.g., an isomerization) is proposed as responsible for a particular negative deviation, then there should be an associated positive deviation for the bonus yield of the corresponding (e.g., isomeric) product, and this positive deviation should be of comparable magnitude to the negative deviation.

These principles are applied and extended in the present work to study the mechanisms of PHB pyrolysis.

3. Experimental Section

Materials. Polymer Sample. The purified PHB homopolymer sample, batch number B221901, was manufactured and supplied by Zeneca Bioproducts (Billingham, U.K.).

Solvent. Chloroform (trichloromethane), SLR grade, was supplied by Fisons Scientific Equipment Ltd.

Apparatus. Pyrolysis Unit. Pyrolyses were performed by depositing a range of microgram quantities of polymer from chloroform solution onto a thermocouple-controlled filament pyrolysis unit. The unit, developed in the authors' laboratories,[30] permitted precise control of the temperature and duration of the pyrolysis.

Gas Chromatograph Unit. The gas chromatograph apparatus used for the analysis of pyrolysis products was a Carlo Erba HRGC 5300 Mega series instrument incorporating an FID detector. The instrument was fitted with a 25-m DB1 bonded, nonpolar, fused silica megabore column (internal diameter 0.53 mm), which carried a nitrogen carrier gas with a flow rate of 15.5 $cm^3 min^{-1}$. The temperature of the detector unit was set at 270 °C and that of the pyrolysis chamber at the head of the GC column at 170 °C. Hydrogen and air flow rates for the FID detector were maintained at 25 and 350 $cm^3 min^{-1}$, respectively. The GC column temperature program was 40 °C isothermal for 2 min and then 10 °C/min to 250 °C, where it was maintained for a further 10 min.

Data acquisition was performed using an IBM-compatible PC fitted with Baseline 810 chromatography software (Millipore, Watford, U.K.).

An in-line VG-TS 250 mass spectrometer was used to characterize gas chromatographic peaks. (Mass spectrometric data are available to readers, on request.)

Pyrolysis Procedure. Samples of the PHB homopolymer were deposited uniformly on the thermocouple-controlled filament pyrolyzer from a chloroform solution (1 g dm^{-3}) using a 5-μL microsyringe. Polymer sample sizes of 1, 3, 5, 7, and 10 μg were used. Each sample was pyrolyzed at 350 ± 1 °C for 5 s. Three separate pyrolyses were performed on each sample size, and the areas of each of the product peaks were averaged. These areas are directly related to the mass of each product eluted. Results from these experiments are discussed in the following section.

4. Results and Discussion

Figure 4 shows a pyrogram displaying the products obtained from the pyrolysis of PHB under previously specified conditions.

The volatile degradation products consist primarily of the monomer (crotonic acid) and the corresponding dimer, trimer, and tetramer. Due to the presence of olefinic groups in each molecule, the pyrolysis products can exist in two forms, *cis* or *trans*, and as previously discussed, formation of the *trans* species is favored with respect to the *cis* form. (The *cis* and *trans* species, particularly for the trimer and higher oligomers, are not readily resolved chromatographically. This could be due to the structural differences being small compared with the size of the molecules.) A peak (L, Figure 4) between those of the trimers and tetramers has also been detected, but the identity of this species has not yet been established (see

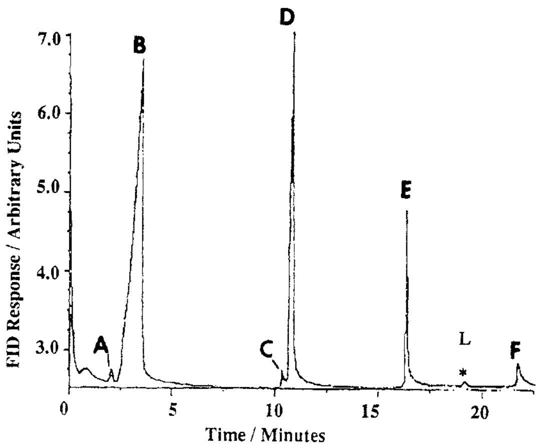


Figure 4. Chromatogram of the products obtained from the pyrolysis of PHB at 350 °C for 5 s: (A) *cis* monomer; (B) *trans* monomer; (C) *cis* dimer; (D) *trans* dimer; (E) trimer; (F) tetramer; (*) position where product L is observed.

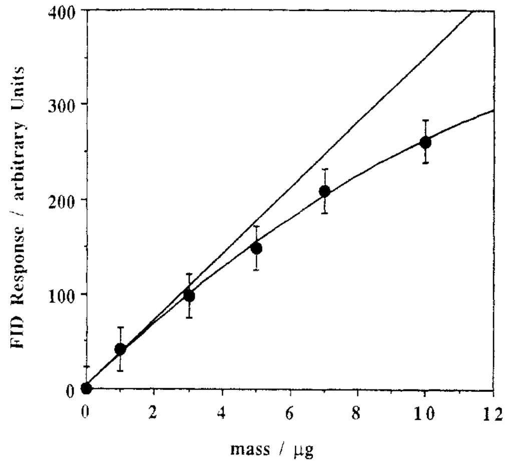


Figure 5. Plot of yield of *trans* monomer versus sample size.

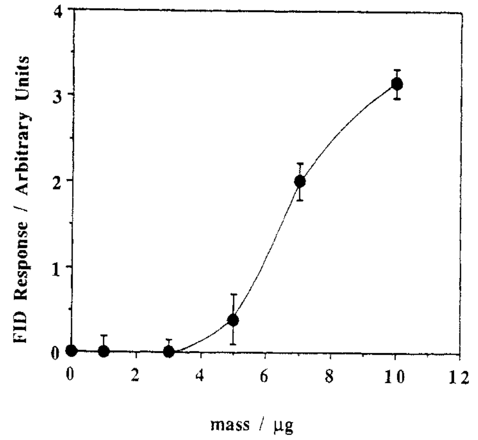


Figure 6. Plot of yield *cis* monomer versus sample size.

section 4.3.b.iv). Species larger than tetramer are not sufficiently volatile to be detected under the specified conditions.

4.1. Product Yields Versus Sample Size. Figures 5–11 show the product yields (expressed in terms of areas of the GC peaks) versus sample size. The plots in Figures 5, 7, and 9 lead off from the origin, indicating that these pyrolysis products are being formed by primary processes, but deviations from the straight line plots as sample thickness increases mean that the overall yields of these products are influenced by secondary reactions.

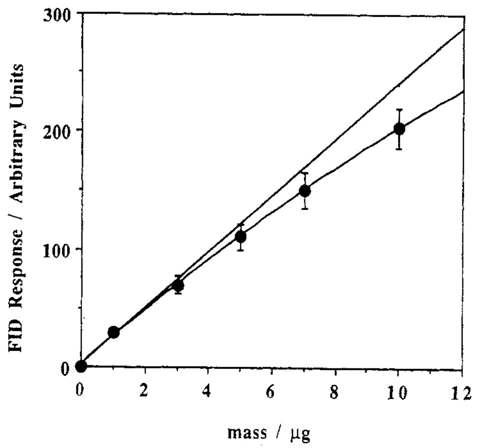


Figure 7. Plot of yield of *trans* dimer versus sample size.

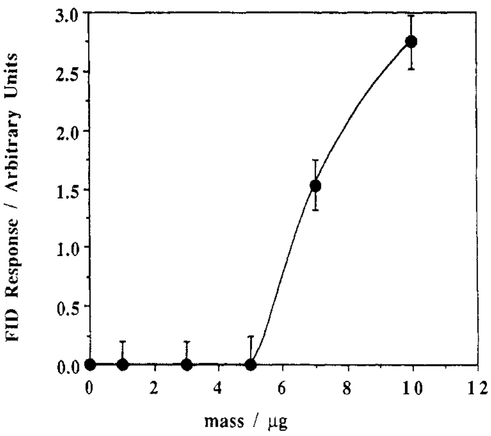


Figure 8. Plot of yield of *cis* dimer versus sample size.

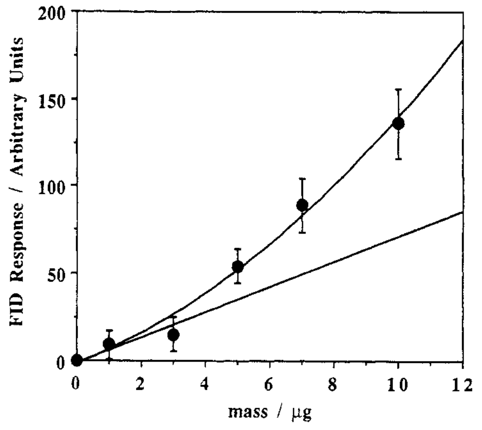


Figure 9. Plot of yield of trimer versus sample size.

Figures 6, 8, 10, and 11 show plots of sample size versus product yield in which the curves do not extrapolate through the origin. Before any of these pyrolysis products are observed in any detectable quantities, the polymer sample size has to exceed a certain mass which corresponds to a limiting polymer thickness. This implies that these products are totally formed via secondary reactions, in which their precursors require different residence times in order that measurable quantities of these secondary degradation products are formed.

This "minimum sample size effect" has not been previously observed in studies of the thickness dependence of product yields. Such observations may be used as a new and additional criterion for consecutive reactions.

These results have major implications with respect to the overall degradation mechanism of PHB, not least because no tetramers were detected at the lowest sample sizes investigated. (This is evident from Figure 10, where

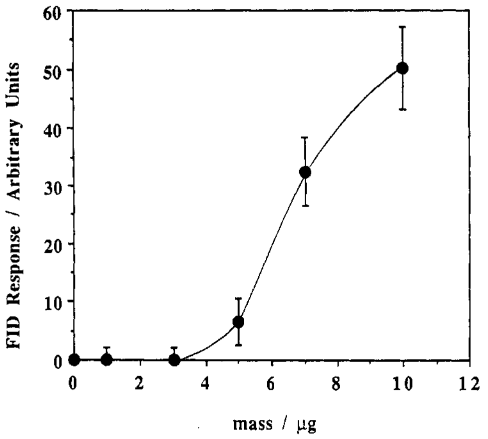


Figure 10. Plot of yield of tetramer versus sample size.

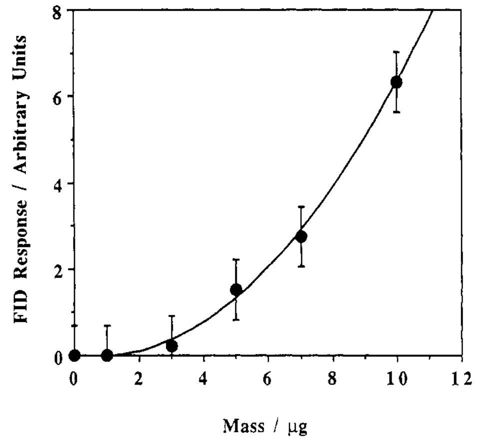


Figure 11. Plot of yield of product L versus sample size.

Table 1. Yields (in Terms of Relative Mass) of the Products from PHB Degradation at 350 °C for 5 s[a]

	primary product?	primary product (ideal) yield at 10 μg/arbit. mass units	bonus (+) or deficit (−) yield/arbit. mass units
trans monomer	yes	355	−95
cis monomer			+4.4 (−1.3)
trans dimer	yes	240	−30
cis dimer			+3.8 (−1.0)
trimer	yes	70	+65
tetramer			+70 (−20)
L		?	6 total

[a] Bonus and deficit yields are shown in terms of relative mass. Where two figures are given for bonus or deficit yield, the first corresponds to its yield as a secondary product and the second (in parentheses) corresponds to its loss in a tertiary reaction. In the case of product L it was not possible to deduce the extent to which the total yield consisted of primary products.

it is clear that no line with a gradient through the origin can be drawn through the points.)

4.2. Bonus and Deficit Yields. With reference to Figures 5, 7, and 9, the limiting tangent at zero sample size is defined by the linear term in a general polynomial curve fitted to the points. The ΔM values are then calculated as the difference between the observed yields and those calculated on the basis of the linear term in the equation.

In order to compare the orders of magnitude of the bonus and deficit yields, values of these were calculated for the sample size of 10 μg in all cases, and the results are listed in Table 1. The values correspond to gas chromatographic peak areas, which are closely proportional to component masses.

In those plots (Figures 6, 8, 10, and 11) which do not pass through the origin, the products are totally formed by secondary reactions and hence the observed total yields of these consequences are themselves bonus yields. In addition to this, these plots show further deviations at ca. 10 μg, possibly caused by the occurrence of tertiary reactions.

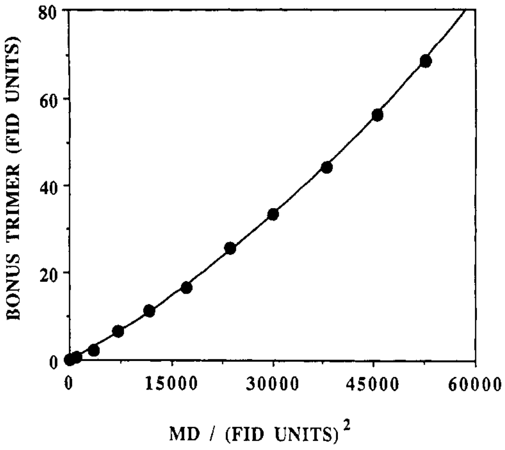


Figure 12. Plot of bonus trimer versus MD.

4.3. An Interpretation of the Results Which Accounts for Bonus and Deficit Yields. (a) Primary Pyrolysis Products. Because the plots in Figures 5, 7, and 9 extrapolate through the origin, it is evident that *trans* monomer, *trans* dimer, and trimer are primary products, and all of these are obtained in substantial yield. From the curvature it can be deduced that all of these products are participating in secondary reactions, but whereas the *trans* monomer and *trans* dimer display negative deviations, the trimer displays a net positive deviation.

(b) Secondary Products. (i) *Cis* Isomers. The "intercepts" in Figures 6 and 8 show that the *cis* monomer and *cis* dimer are formed *exclusively* as secondary products under specified degradation conditions. Since, as mentioned above, the corresponding *trans* products both show deficits at larger sample sizes, it is reasonable to propose that *trans–cis* isomerizations are occurring. Presumably the rates of the two processes are sufficiently slow to require the longer residence time of the *trans* species which would arise with thicker samples. It is possible that there is a tendency to establish an equilibrium between the *cis* and *trans* isomers, and increased residence time is allowing movement toward this situation. The inflection in the growth curves indicates in each case the occurrence of a tertiary reaction, which will be discussed later. We can thus define the first two secondary reactions as:

$$\textit{trans}\ \text{monomer} \rightarrow \textit{cis}\ \text{monomer} \qquad \text{(I)}$$

$$\textit{trans}\ \text{dimer} \rightarrow \textit{cis}\ \text{dimer} \qquad \text{(II)}$$

The measured yields of the *cis* products (Table 1) can easily be accommodated within the observed deficits of the *trans* products. Indeed the deficits in *trans* monomer and *trans* dimer are so large that they must be involved in other secondary reactions in a far more substantial way.

(ii) Trimer. Initially, on the basis of the previous paragraph, it was considered that the formation of trimer might be accounted for by the secondary interaction of monomer and dimer in a direct process. On this basis, a plot of bonus trimer versus the product of the monomer and dimer yields was drawn (Figure 12), on the assumption that these yields are proportional to the concentrations of the corresponding products in the melt.[27-29] The curvature in this plot casts some doubt on this mechanistic proposal; moreover, it will be shown in the next section that the

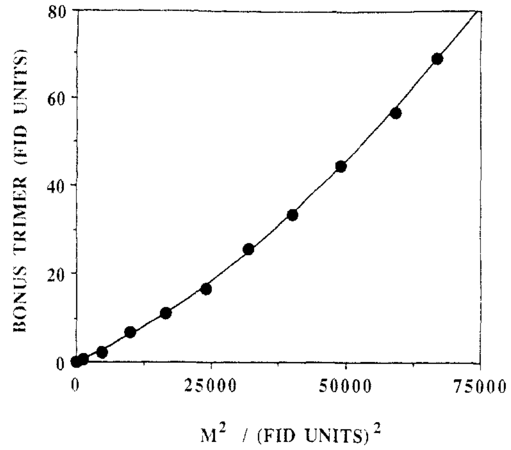


Figure 13. Plot of bonus trimer versus M^2.

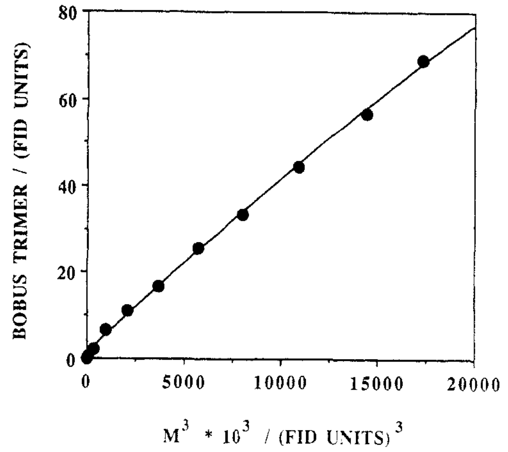


Figure 14. Plot of bonus trimer versus M^3.

actual yield of tetramer cannot be accounted for if the dimer is consumed in trimer formation. The mechanisms III and IV have therefore been proposed as the simplest explanations of the formation of trimer by secondary reactions.

$$\left.\begin{array}{l} M + M \rightleftarrows D^* \\ D^* + M \rightarrow Tri \end{array}\right\} \qquad \text{(III)}$$

$$\left.\begin{array}{l} M + M \rightarrow D^* \\ D^* + M \rightarrow Tri \end{array}\right\} \qquad \text{(IV)}$$

The kinetic implications of these involve the suggestion that in IV the proposed dimeric species D* is an unstable intermediate, whereas in III it is an entity which can exist in pseudo equilibrium with monomer. It can be shown that, for mechanism IV, the rate of trimer formation is proportional to M^2; but for III the rate is expected to be proportional to M^3. Plots to test these are shown in Figures 13 and 14, from which it can be seen that mechanism III is to be preferred. Since the proposed mechanism III requires that all of the bonus trimer comes from the monomer, from Table 1 we see this will account for a substantial proportion of the 95 mass units of monomer yield deficit.

(iii) Tetramer. It might seem plausible to suggest that tetramer might be formed by mechanisms involving:

$$\text{monomer} + \text{trimer} \rightarrow \text{tetramer} \qquad \text{(V)}$$

or

$$\text{dimer} + \text{dimer} \rightarrow \text{tetramer} \qquad \text{(VI)}$$

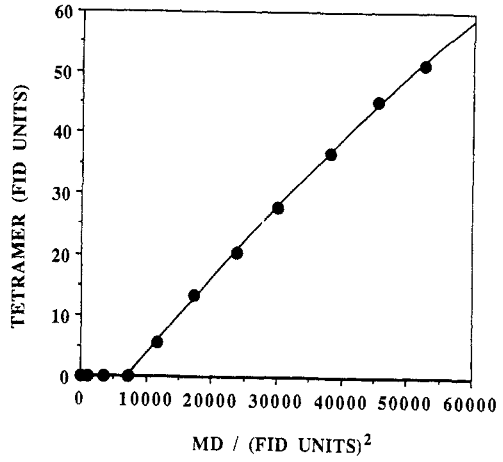


Figure 15. Plot of bonus tetramer versus MD.

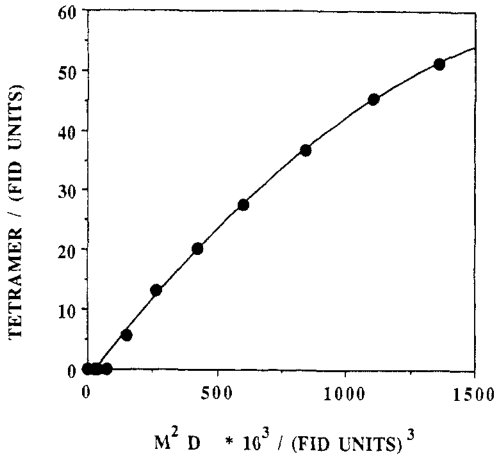


Figure 16. Plot of bonus tetramer versus M^2D.

However, neither of these is consistent with quantitative yields listed in Table 1. There is no deficit in the trimer yield, and indeed trimer is formed in substantial bonus yield; hence, mechanism V is not probable. With respect to mechanism VI there is insufficient dimer deficit to account for the tetramer yield, and thus this mechanism must be discarded. Since a quaternary interaction of four monomer molecules to form tetramer seems totally unacceptable, even when in the melt, the authors propose VII or VIII as the simplest mechanism for tetramer formation.

$$\left.\begin{array}{l} M + D \rightarrow Tri^* \\ Tri^* + M \rightarrow Tet \end{array}\right\} \qquad \text{(VII)}$$

$$\left.\begin{array}{l} M + D \rightleftarrows Tri^* \\ Tri^* + M \rightarrow Tet \end{array}\right\} \qquad \text{(VIII)}$$

These mechanisms were tested in a way similar to those in the previous section, i.e., by plotting tetramer yield versus the product of monomer and dimer yields (Figure 15) and tetramer yield versus M^2D (Figure 16). In the case of tetramer, the better linearity of Figure 15 suggests that mechanism VII applies. Thus, in this mechanism, the trimeric intermediate, Tri*, is an unstable species compared with the D* species in the previous section.

The mass yield of tetramer, 70 arbitrary units, can be very largely accounted for in terms of the 30 mass units deficit of dimer plus the remaining 25.6 mass units of monomer [95 minus 4.4 (to give *cis* monomer) minus 65 (to give trimer) equals 25.6].

(iv) Product L. From Figure 11, it is evident that either this product is not a primary product or its primary formation is negligible.

It has not yet been possible to characterize the structure of product L, because of its small yield and the fact that it is eluted at a late stage in the chromatography temperature program where the noise has become significant. It is therefore difficult to propose a realistic chemical mechanism for its formation. Furthermore, no precursor for it can be deduced from examination of Table 1. Since its retention time lies between that for trimer and that for tetramer, it could be an oligomer with intermediate structure. Alternatively, it could be a discrete oligomer with different structure, e.g., a lactonic form of the trimer or tetramer.

One important characteristic of the product is that its bonus yield with sample thickness becomes very large for thicker samples; it is therefore possible that it is formed by a tertiary reaction, as discussed below.

(c) Tertiary Reactions. The inflections shown in Figures 6, 8, and 10 indicate that *cis* monomer, *cis* dimer, and tetramer are all involved in tertiary reaction processes. The inflection occurs in each case when the sample size is on the order of 7 μg; this means that the tertiary products resulting must be evident as an abnormal bonus for samples above this size. Of all the products detected, only product L falls into this category. We therefore propose that the following two tertiary reactions are possible:

$$\textit{cis}\text{ monomer} + \textit{cis}\text{ dimer} \rightarrow \text{L} \qquad \text{(IX)}$$

$$\text{tetramer} + \text{monomer/oligomer} \rightarrow \text{Y} \qquad \text{(X)}$$

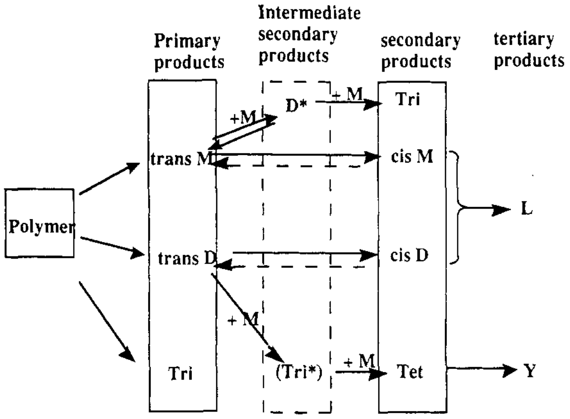
The assumption is that the product Y from mechanism X is so involatile that its GC retention time lies outside the time of the temperature program. It is thought that products of this kind are formed because it has been found to be necessary to periodically reverse the carrier gas flow in the column in order to remove such materials of very low volatility.

5. Conclusions

Principles have previously been applied in the authors' laboratories for deducing pyrolysis mechanisms from the dependence of product yields on sample thickness. These have now been extended in the present study of the thermal degradation of PHB by the interpretation of intercepts on the sample size axis as a definitive indication that the corresponding components are formed exclusively as secondary products. Applying all of these principles, the complete results for the pyrolysis of PHB at 350 °C can now be interpreted in terms of an array of primary, secondary, and tertiary reactions, with evidence for the participation of some intermediates. The overall situation is displayed in Scheme 1, which shows the sequence of reactions from left to right.

One interesting feature of the present work, evident in Scheme 1, is that tetramer is not detectable as a primary product but appears to be formed as a result of the addition of two monomer molecules consecutively to dimer. This throws some doubt on the widely-held view that PHB pryolysis products can be accounted for exclusively in terms of β-elimination scissions.

Scheme 1. Proposed Thermal Degradation Mechanism of PHB



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