STRUCTURAL AND THERMAL CHARACTERIZATION OF BLUEPHA® BIOPOLYESTERS: INSIGHTS INTO MOLECULAR ARCHITECTURE AND POTENTIAL APPLICATIONS

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Introduction

Polyhydroxyalkanoates (PHAs) are a class of biodegradable and biocompatible polyesters synthesized by various microorganisms as intracellular carbon and energy reserves [1,2]. Owing to their thermoplasticity, tunable mechanical properties, and environmental degradability, PHAs are considered promising alternatives to conventional petroleum-based plastics [3]. Their structure and properties can be tailored through biosynthetic or chemical modifications, affecting crystallinity, degradation rate, and processability [4,5].

This study presents an in-depth molecular and structural characterization of novel biopolyesters developed under the trademark Bluepha®. The primary aim was to elucidate the relationship between chemical structure, chain architecture, and material properties of these biopolyesters to define their potential applications across various sectors. Proton nuclear magnetic resonance (^{1}H NMR) analysis identified the biopolyesters as poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate] (PHBH) copolymers, containing 4% and 10% molar content of hydroxyhexanoate (HH) units, respectively. Mass spectrometry analysis of PHBH oligomers, produced via controlled thermal degradation, further confirmed the chemical structure and molecular architecture of the PHBH samples. Additionally, multistage electrospray ionization mass spectrometry (ESI-MS/MS) provided insights into the chemical homogeneity and arrangement of comonomer units within the copolyester chains, revealing a random distribution of hydroxyhexanoate (HH) and hydroxybutyrate (HB) units along the PHBH chains. X-ray diffraction (XRD) patterns demonstrated partial crystallinity in the PHBH samples. The thermal properties, including glass transition temperature (Tg), melting temperature (Tm), and melting enthalpy (ΔHm), were found to be lower in PHBH than in poly(R)-3-hydroxybutyrate (PHB), suggesting a broader application potential for the tested PHBH biopolyesters [6].

Aim of work

To uncover structure–property relationships in Bluepha® PHBH biopolyesters by integrating molecular-level characterization with thermal analysis, enabling rational design of biodegradable materials for eco-friendly and biomedical applications.

🧪 Analytical Strategy:

^{1}H NMR → comonomer composition
ESI-MS/MS → sequence distribution & molecular architecture
DSC & XRD → crystallinity and thermal transitions

❓ Key Questions:

- How does HH content affect structure and crystallinity?
- Can mass spectrometry reveal deeper insights than NMR?
- Do these structure changes improve application potential?

Table 1. Number average molar mass (M_n), weight average molar mass (M_w), dispersity (M_w/M_n), composition of the PHBH4 and PHBH10 copolymers and respective oligomers obtained via thermal degradation.

Sample Name	M_n *	M_w *	M_w/M_n *	Composition ** mol%HB/mol%HH
PHBH4	412,000	863,000	2.09	96/4
PHBH10	305,000	665,00	2.18	90/10
PHBH4T	1100	2200	2.00	96/4
PHBH10T	1300	2900	2.22	90/10

* Estimated by GPC; ** chemical composition of PHBH in mol% estimated from ^{1}H NMR, HB (hydroxybutyrate) and HH (hydroxyhexanoate).

Table 2. DSC results of the PHBH4 and PHBH10 biopolyesters and resulting PHBH4T and PHBH10T oligomers obtained via thermal degradation.

Sample Name	T_g (II Run) [°C]	T_m (I Run) [°C]	ΔH_m (J g^{-1})
PHBH4	3.7	122.4/149.7	68.2
PHBH10	1.3	114.0	48.8
PHBH4T	−10.0	89.1/108.2/125.5	57.7
PHBH10T	−7.4	94.8/113.7/122.2	46.1

T_g—glass transition temperature, T_m—melting temperature, ΔH_m—melting enthalpy.

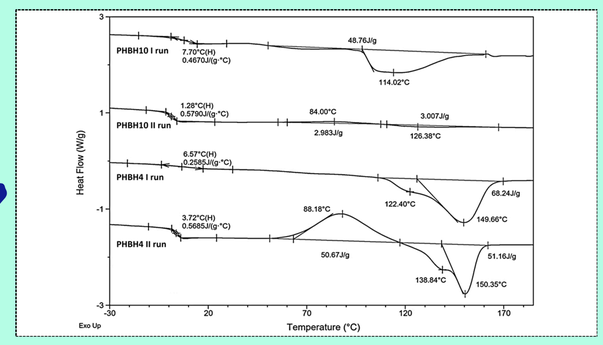


Figure 1. The DSC traces (first and second runs) of the PHBH4 and PHBH10 biopolyesters.

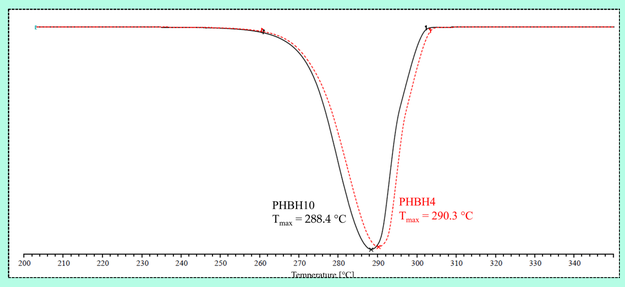
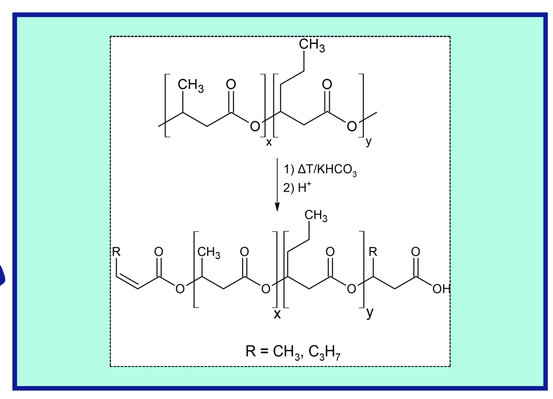
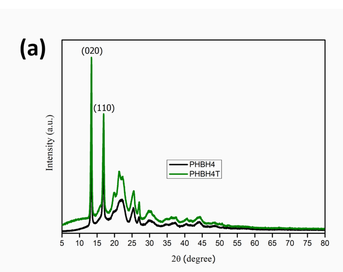


Figure 2. First-order derivative (DTG) of thermal decomposition (TGA) curves of the PHBH10 (solid black line) and PHBH4 (dotted red line).



Scheme 1. Thermal degradation of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) biopolyester.

RESULTS



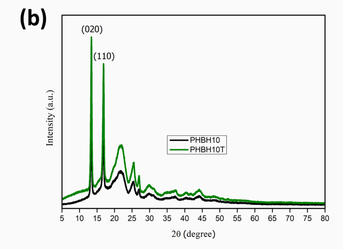


Figure 3. X-ray diffraction patterns of the biopolyesters and respective oligomers obtained via thermal degradation (a) PHBH4 and PHBH4T and (b) PHBH10 and PHBH10T.

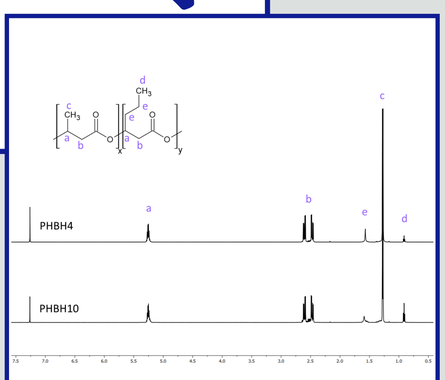


Figure 4. ^{1}H NMR spectrum of (a) PHBBH4 and (b) PHBH10 biopolyesters.

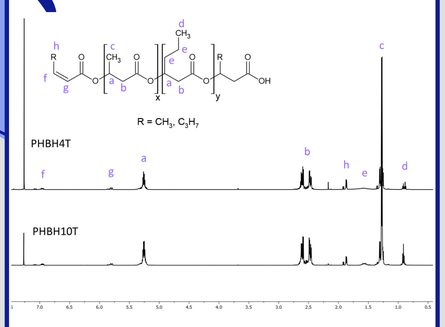


Figure 5. ^{1}H NMR spectrum of (a) PHBBH4T and (b) PHBH10T oligomers obtained via thermal degradation.

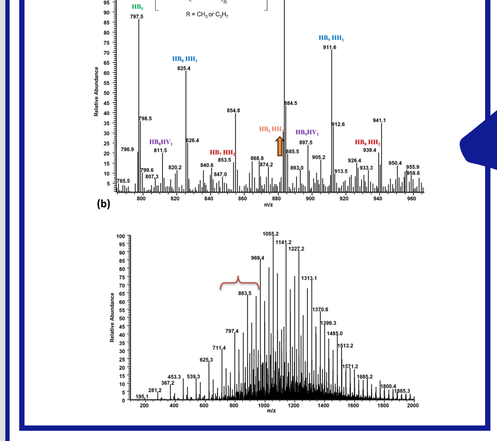


Figure 6. ESI-mass spectra (positive ion-mode) of PHBH10T low molecular weight oligomers (a) and expanded ESI-MS spectra (positive-ion mode) in the mass range 785 < m/z < 965 (b); The bracketed area represents an enlargement of the ESI-MS spectrum (a), providing an extended view of specific spectral details (b).

Conclusions

- **Advanced structural characterization using ESI-MS/MS provided detailed insight into the molecular architecture and random comonomer distribution in PHBH copolymers, beyond the capabilities of NMR alone.**
- **Even small changes in comonomer composition (4–10 mol% HH) had a notable impact on polymer structure, confirming the value of mass spectrometry in material design.**
- **The presence of HH units reduced crystallinity and increased flexibility, improving thermal behavior and processing potential of PHBH compared to PHB.**
- **These findings support the development of next-generation biodegradable materials with tunable properties for use in sustainable packaging, biomedical applications, and eco-friendly consumer products.**

LITERATURE

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