Supplementary Information

Three-step synthesis of a condensation polymer incorporating natural PHB fragments: Structural and physicochemical characterization

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Trichloroacetyl (TAI) derivatization of hydroxy-terminated oligo(3-hydroxybutyrate) (HTOHB) for determination of its oligomeric constituents

As mentioned in the manuscript, the transesterification of PHB with 1,4-butanediol yields two types of oligomers with different chemical structures (see Figure 3 in the main text). The primary products are oligoester diols (denoted as tHTOHB) containing one terminal unit derived from 1,4-butanediol bearing a free primary hydroxyl group and the opposite terminal unit bearing a free secondary hydroxyl group. The secondary products are oligomers (denoted as bHTOHB) containing a bridge derived from 1,4-butanediol and two identical terminal units bearing secondary hydroxyl groups. The secondary hydroxyl units in both tHTOHB and bHTOHB correspond to 1-methyl-1,3-propanediol. TAI was added to such a mixture of oligomers, obtained after an 11-hour reaction in the presence of *p*-toluenesulfonic acid (PTSA), and after brief shaking, the resulting products were analyzed by ^{1}H NMR spectroscopy.

As a result of derivatization with TAI, the hydroxyl groups of HTOHB oligoester diols are converted into *N*-acylcarbamate groups, that is, groups containing an imide proton (–CON*H*CO–) in their structure.[1] The main advantage of such conversion is the position of the imide proton signal in the ^{1}H NMR spectrum. Specifically, the chemical shift of the imide proton formed upon reaction of a hydroxyl group with TAI (that is, the proton in the $–CONHCOCCl_3$ group) appears in the range of 8.2–8.8 ppm, which corresponds to a spectral region where very few proton signals are usually observed.[1] This minimizes accidental signal overlap that could complicate spectral interpretation, making TAI derivatization a highly versatile method. Another advantage of this method is its simplicity: the isocyanate is added directly to the NMR tube containing the sample, and the derivatization reaction proceeds quantitatively at room temperature within a few minutes.[1] Figure S2 presents the reaction scheme for derivatization of tHTOHB and bHTOHB oligoester diols with TAI, together with the ^{1}H NMR spectrum of the resulting products. To make the interpretation clearer and easier to follow, the proton NMR spectrum of the starting oligomers is presented in Figure S1.

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[1] A. Postma, T. P. Davis, A. R. Donovan, G. Li, G. Moad, R. Mulder and M. S. O'Shea, *Polymer (Guildf).*, 2006, **47**, 1899–1911.

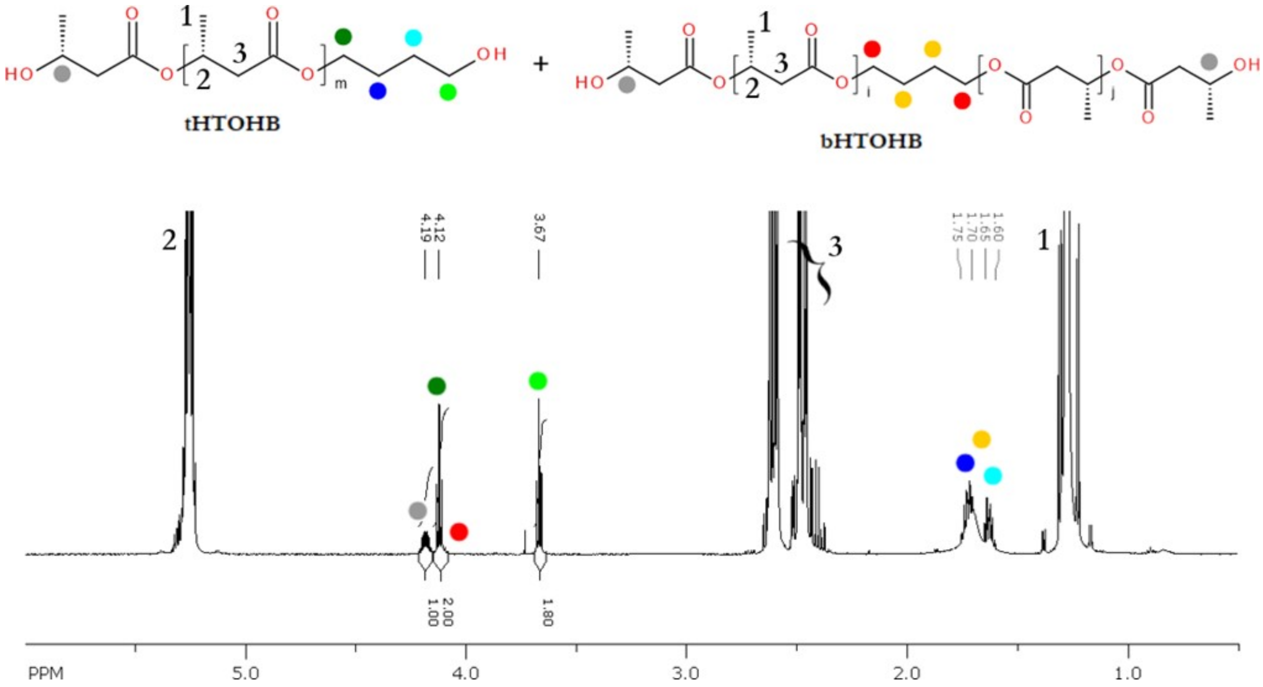

Figure S1. ^{1}H NMR spectrum of tHTOHB and bHTOHB oligoester diols prior to derivatization with TAI.

The method employing TAI is based on the conversion of the hydroxyl groups of oligoester diols into functional groups containing an imide proton (–CON*H*CO–). As a result of this conversion, two types of oligomers terminated with *N*-acylcarbamate groups are obtained: oligoesters containing a 1,4-butanediol bridge (bCTOHB) and oligoesters without such a bridge (CTOHB). TAI derivatization of the primary hydroxyl group of tHTOHB oligoester diols leads to the formation of an imide proton signal appearing at 8.65 ppm (indicated by the boxed yellow star in Figure S2). In turn, derivatization of the secondary hydroxyl group results in an imide proton signal at 8.87 ppm (marked with a pink star). Both signals appear as singlets. Based on the intensities of the aforementioned imide proton signals, the mole fraction of oligoester diols containing a 1,4-butanediol bridge (X_{bHTOHB}) can be calculated as follows:

$$X_{\mathbf{bHTOHB}} = I_{\text{★}} - I_{\text{☆}} / I_{\text{★}} + I_{\text{☆}}$$

In the above equation, $I_{\text{★}}$ is the relative integral area of the signal appearing at 8.87 ppm, whereas $I_{\text{☆}}$ represents the relative integral area of the signal at 8.65 ppm. The mole fraction of bHTOHB oligoester diols calculated according to the above equation is 5.8%.

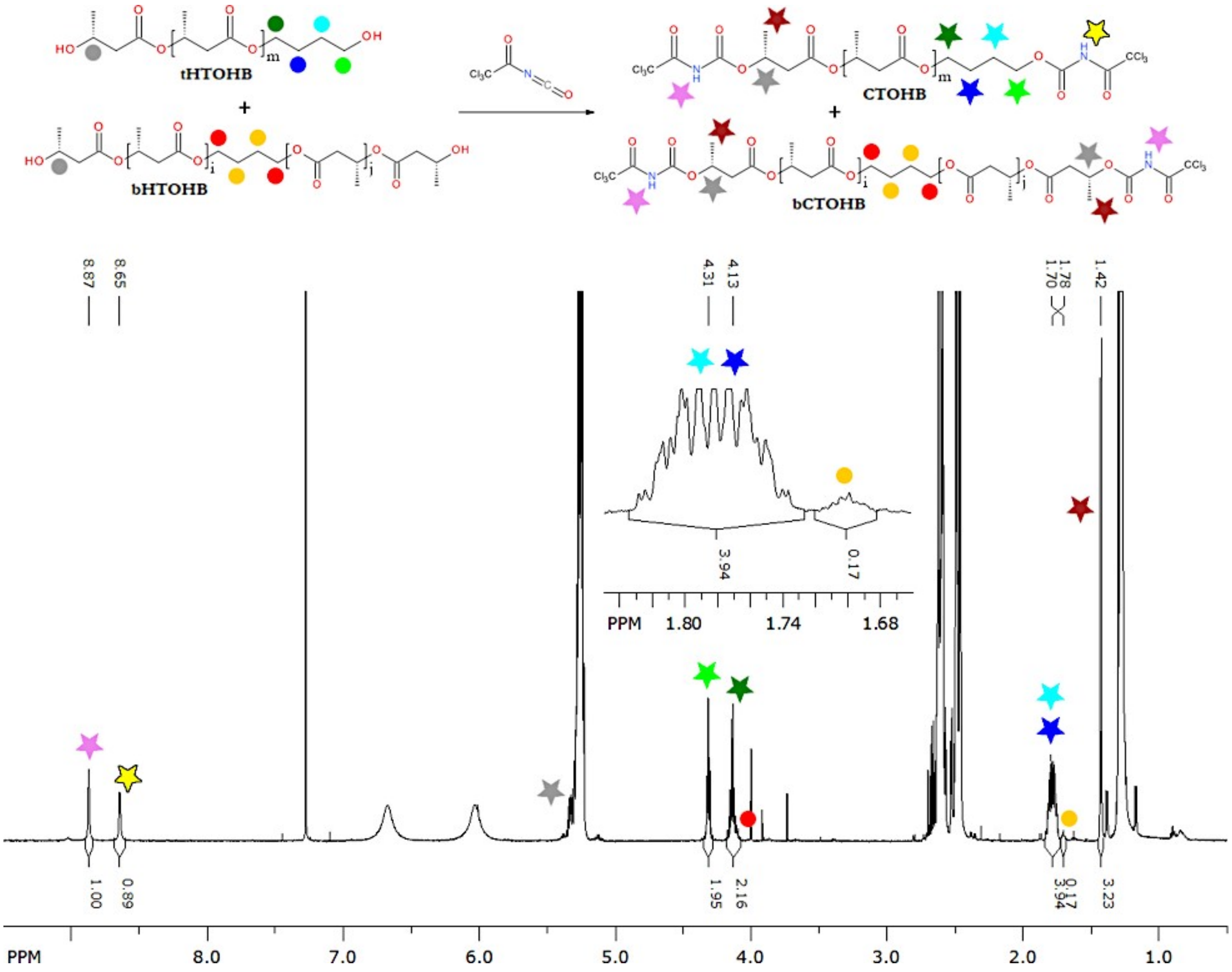

Figure S2. Reaction scheme for the derivatization of tHTOHB and bHTOHB oligoester diols with TAI (top), and the ^{1}H NMR spectrum of the resulting products (bottom).

It is worth noting that the N-acylcarbamate group derived from TAI (that is, the group with the structure –CONHCOCCl$_3$) is a strongly electron-withdrawing substituent, as evidenced by the pronounced downfield shift of signals from specific end-group protons of the oligoester diols. For example, the signal of the CH$_2$ group adjacent to the primary hydroxyl group appears at 3.67 ppm, whereas that adjacent to the CONHCOCCl3 group appears as a multiplet centered at 4.31 ppm (this signal is marked with a light green star in Figure S2). This corresponds to a downfield shift of approximately 0.64 ppm. The strongly electron-withdrawing nature of the –CONHCOCCl$_3$ substituent is further demonstrated by the fact that the spectrum of CTOHB and bCTOHB oligoesters exhibits a well-resolved signal for the methyl protons of their secondary end-groups (CCl$_3$CONHCO–OCH(CH_3)CH$_2$–). These protons appear as a doublet at 1.42 ppm (marked with a brown star). In contrast, in the spectrum of tHTOHB and bHTOHB oligoester diols (Figure S1), the corresponding methyl signal appears further upfield (at 1.28 ppm), overlapping with the doublet originating from the CH$_3$ protons of the PHB constitutional unit, designated as 1 in the structural formulas of the oligoester diols (see Figure S1). Naturally, the chemical shifts of the 1,4-butanediol bridge protons are not affected by the derivatization.

In conclusion, the ^{1}H NMR spectra presented in Figures S1 and S2 confirm that the products of the transesterification of PHB with 1,4-butanediol are oligoester diols with the chemical structure shown in Figure S1. Furthermore, the appearance of these spectra and the integral values of the corresponding signals indicate that these oligoester diols are characterized by a very high purity of functional groups, with end groups consisting almost exclusively of hydroxyl groups. Such high purity is desirable for macromonomers intended for use in polycondensation reactions.

Thermal stability of the synthesized PHBBGD terpolyesters

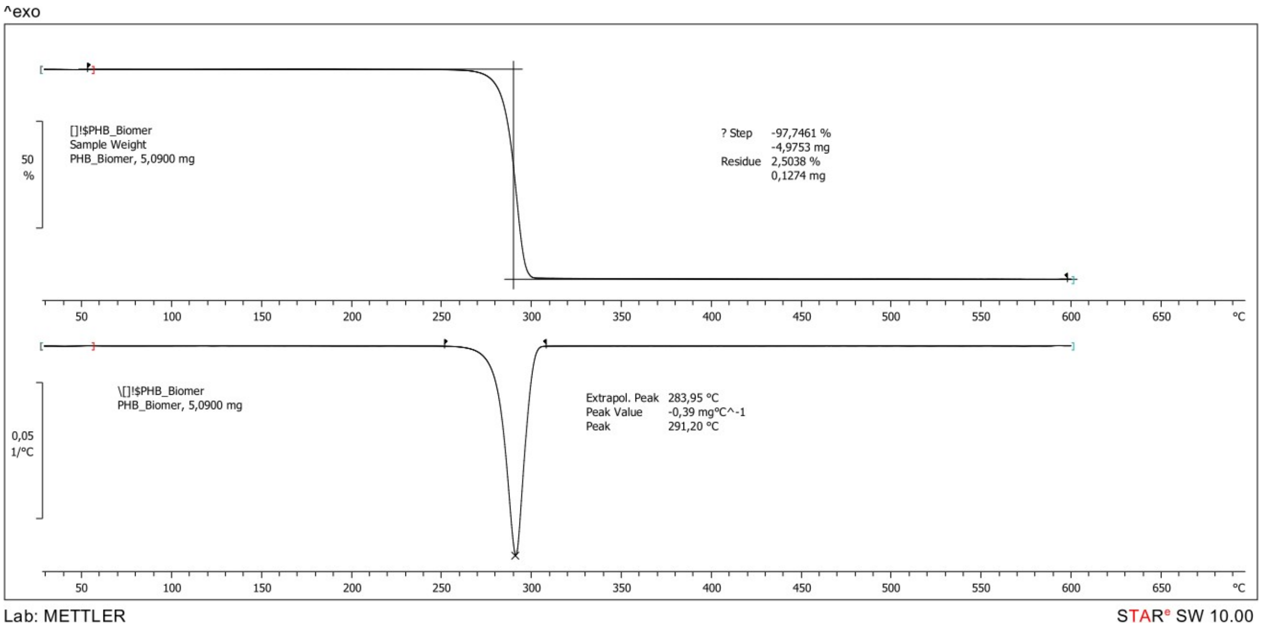

Figure S3. TGA and DTG curves of native PHB.

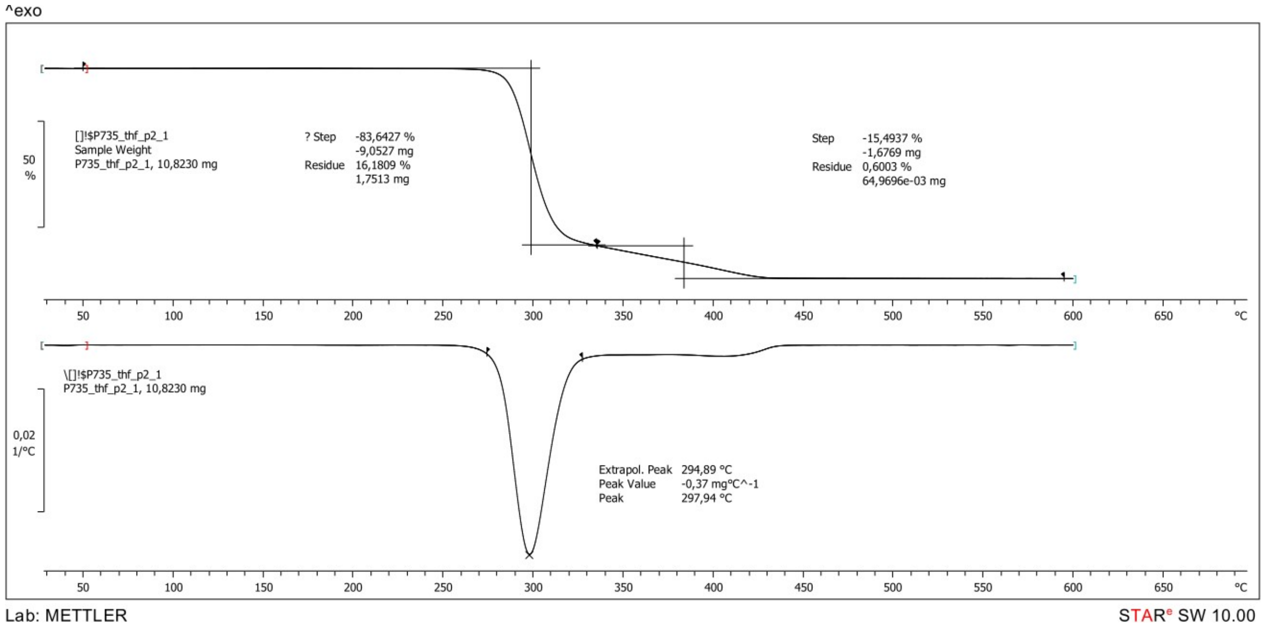

Figure S4. TGA and DTG curves of the PHBBGD terpolyester (sample PHBBGD-23k).