Electronic Supplementary Material (ESI) for RSC Advances.

Biocompatible terpolyesters containing polyhydroxyalkanoate and sebacic acid structural segments- synthesis and characterization

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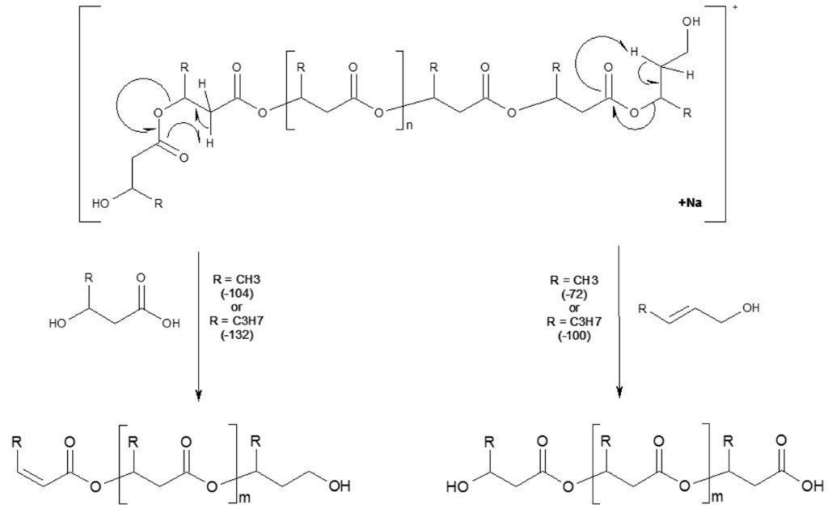
To verify the structure of the individual ions belonging to the clusters, the ESI-MS/MS fragmentation experiments were performed for the selected cluster ions. The ESI-MS/MS product ions spectra, together with theoretical fragmentation pathway for the selected sodium adducts of oligodiols, which not contain HH unit and contain, one HH unit and two HH units, are presented in Figure 1S, 2S and 3S respectively.

The fragmentation of the ions, as a result of the statistical breaking of the ester bonds along the oligo(3-hydroxybutyrate-co-3-hydroxyhexanoate)diols chain, leads to the formation of two types of product ions with a lower value of m/z as presented on Scheme 1S.



Scheme 1S. Fragmentation pathway and structures of the product ions formed during the ESI-MS/MS experiments of the sodium adduct of oligo(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)diols

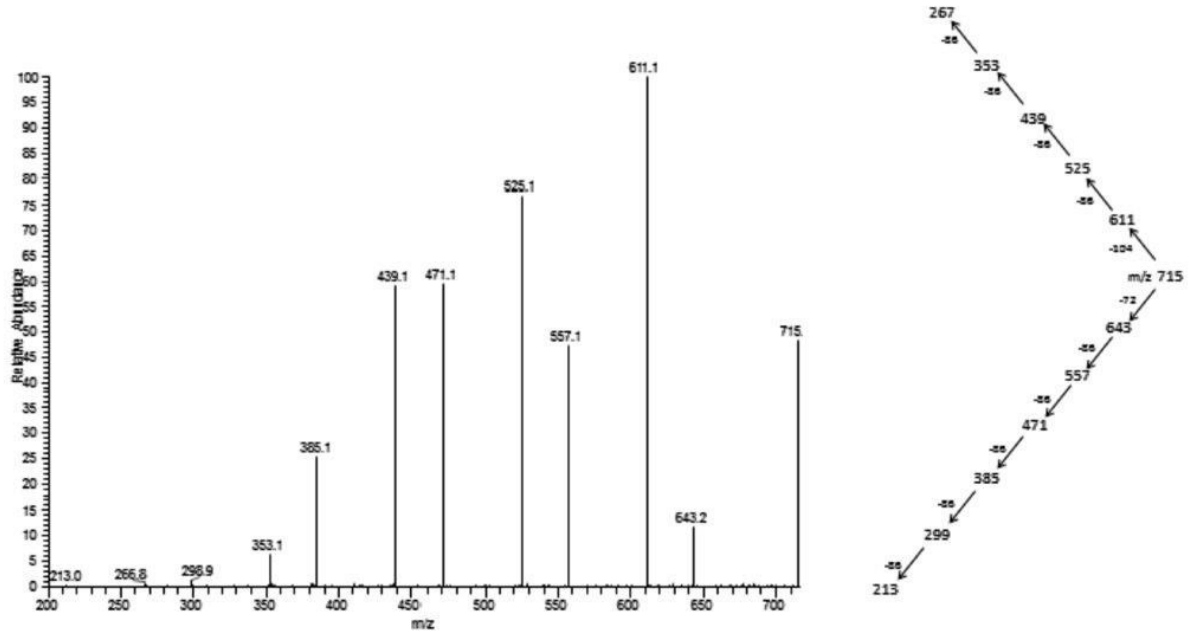


Figure 1S. ESI-MS/MS spectrum of the sodiated precursor ion at m/z 715, selected from the basic ESI mas spectrum (series A) of obtained oligomers via reduction of PHBH biopolyesters.

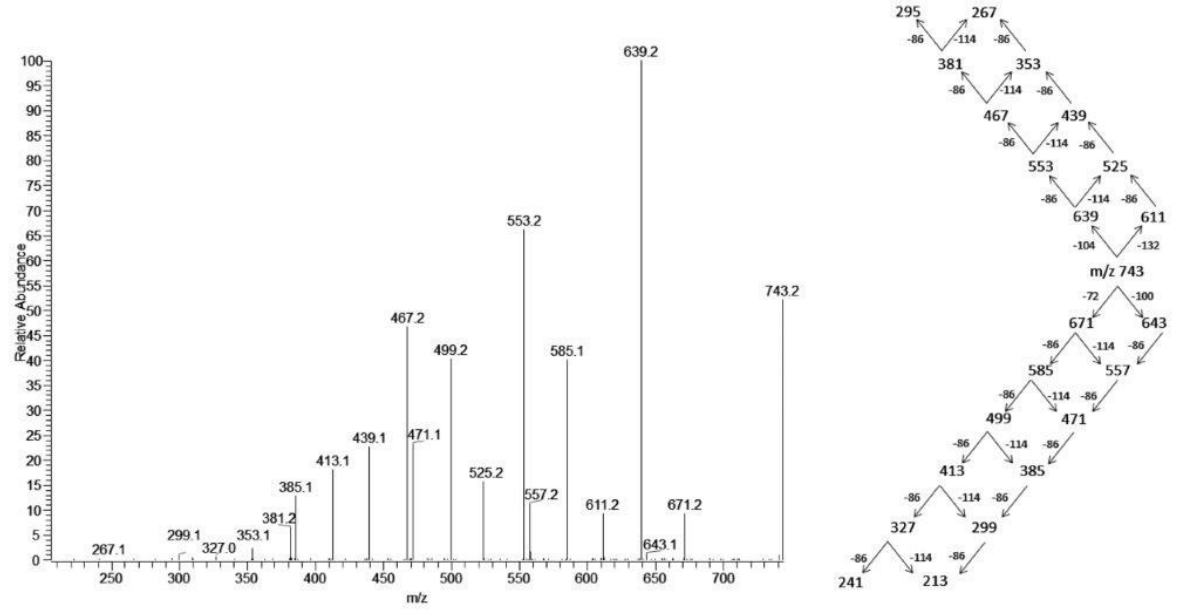


Figure 2S. ESI-MS/MS spectrum of the sodiated precursor ion {HO-[7HB-co-1HH]-OH + Na^+} , m/z 743, selected from the basic ESI mas spectrum (series A) of obtained oligomers via reduction of PHBH biopolyesters. Theoretical fragmentation pathway of the selected ion.

Due to the random distribution of HB and HH co-monomer units, and depending on the content of HH monomer units in oligodiol chains, two or more series of product ions were obtained. As an example of the fragmentation pathway and structures of the product, ions formed in the ESI-MS/MS of the sodium adduct of PHBH oligodiols at m/z 743 containing one HH co-monomer unit (randomly distributed along oligodiols chain or as end groups) are presented in Figure 2S.

Fragmentation of this precursor ion at *m/z* 743 (Figure 4) takes place as a result of random breakage of ester bonds along the oligomer chain a (see the fragmentation pathway in Scheme 1S). Thus, the product ion at *m/z* 671 corresponds to the oligomer formed by the loss of 2-buten-1-ol (72 Da) derived from the terminal group in the case when the reduced HB unit is the last co-monomer unit in oligodiol chain. Whereas, the product ion at *m/z* 643 corresponds with the oligomer formed by the loss of 2 hexen-1-ol (100 Da) derived from the terminal group if the last co-monomer unit in oligodiol is the reduced HH unit. The formation of the product ion at *m/z* 639 and m/z 611 is associated with the loss of 3-hydroxybutyric acid (104 Da) or 3-hydroxyhexanoic acid (132 Da), in the cases when the first co-monomer unit in the oligdiol chain is HB or HH unit, respectively.

On the other hand, if the HH unit does not constitute the end groups but is randomly distributed in the middle of the oligodiol chain, the product ions formed by the loses of neutral molecule crotonic acid (86 Da) or 2-hexenoic acid (114 Da) are observed in the ESI-MS/MS spectrum.

All theoretically predicted product ions are present in the ESI-MS/MS spectrum in Figure 2S, which is in good agreement with the theoretical fragmentation pathways we proposed. Moreover, such a fragmentation pathway indicates that the HH co-monomer unit is randomly distributed along the oligomer chain.

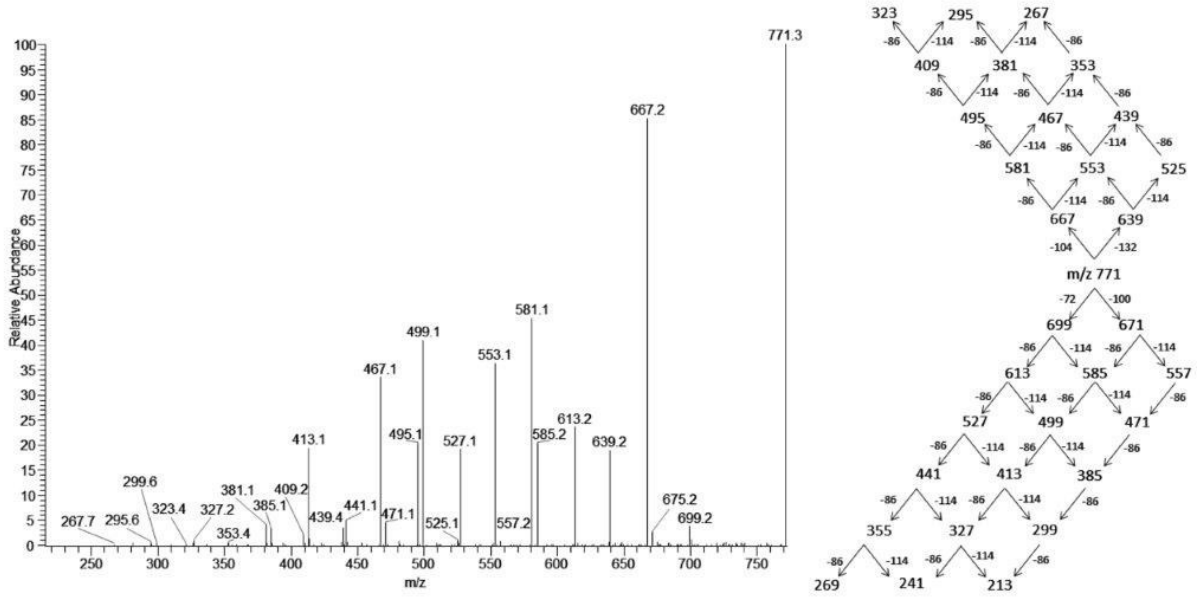


Figure 3S. ESI-MS/MS spectrum of the sodiated precursor ion at m/z 771, selected from the basic ESI mas spectrum (series A) of obtained oligomers via reduction of PHBH biopolyesters.