Electronic Supplementary Material (ESI) for RSC Advances.

Oxidative degradation of poly(3-hydroxybutyrate). The new method of synthesis the malic acid copolymers

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Fig. S1. The comparison of ^{1}H NMR spectra of product of PHB oxidation with O_3/O_2 mixture (140 °C, 5h), before (a) and after (b) addition of trichloroacetyl isocyanate.

Fig. S2. The ^{13}C NMR spectrum of product of PHB oxidation with O_3/O_2 mixture (140 °C, 5h).

Fig S3. The ESI-MS spectrum of PHB oxidation products after 5h exposure on O_3/O_2 mixture at 140 °C; a) full spectrum, b) representative fragment: *m/z* 500-600, the sequence series correlate with proposed structures presented in Table 2.

Fig S4. The ESI-MS^2 spectrum of ion *m/z* 533.2 (negative ion mode) with theoretical fragmentation for oligomer with α-3HB, ω-3HB end groups and four 3HB units.

Fig. S5. The ESI-MS^2 spectrum of ion *m/z* 563.1 (negative ion mode) and proposed structures of oligomer with α-3HB end groups, four 3HB units and one MA unit.

Fig. S6. The ESI-MS^2 spectrum of ion *m/z* 593.1 (negative ion mode) and proposed structures of oligomer with α-3HB end groups, three 3HB units and two MA units.

Fig. S7. The ESI-MS^2 spectrum of ion *m/z* 347.1 (negative ion mode) corresponding to sequence II and III (identical mass of structures) and proposed structures of oligomer with: α-3HB, ω-LA end groups, and two 3HB (sequence II) and α-mOx end group and three 3HB units (sequence III); both structures without 3-malic acid units

Fig. S8. The original ESI-MS^2 spectrum of ion with *m/z* 579.2 (negative ion mode) (sequence II and III)

Fig. S9. The ESI-MS^2 spectrum of ion *m/z* 419.2 (negative ion mode) (sequence IV) and proposed structures of oligomer with α-mOx, ω-LA end group and three 3HB units.

Fig. S10. The ESI-MS^2 spectrum of ion *m/z* 521.1 (negative ion mode) (sequence V) and proposed structures of oligomer with α-AcAc, ω-LA end groups consisted of three MA units.

Fig S11. Changes in the ^{1}H NMR spectrum of PHB monooxalate ($M_{n\ SEC}$= 1600) during the thermal decomposition study at 140 °C in inert atmosphere; ("croto" – indicate the signals corresponding to protons ascribed to crotonate end group).

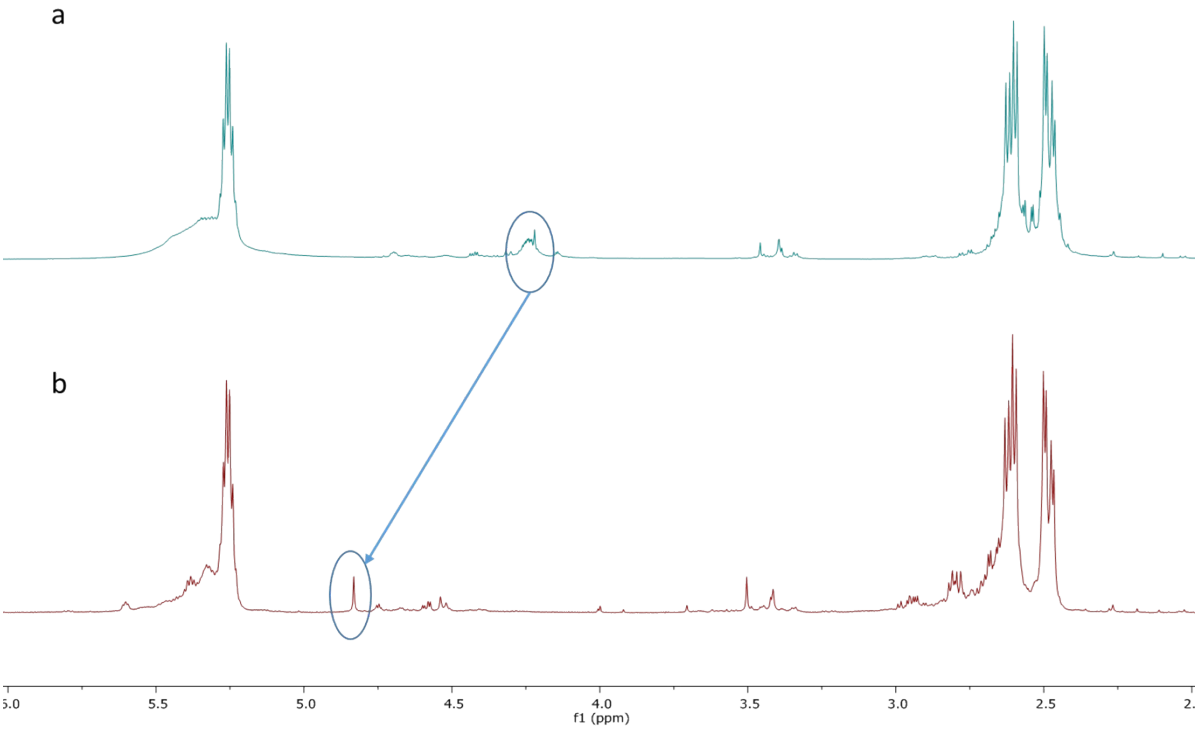


Fig. S1. The comparison of ^{1}H NMR spectra of product of PHB oxidation with O_3/O_2 mixture (140 °C, 5h), before (a) and after (b) addition of trichloroacetyl isocyanate.

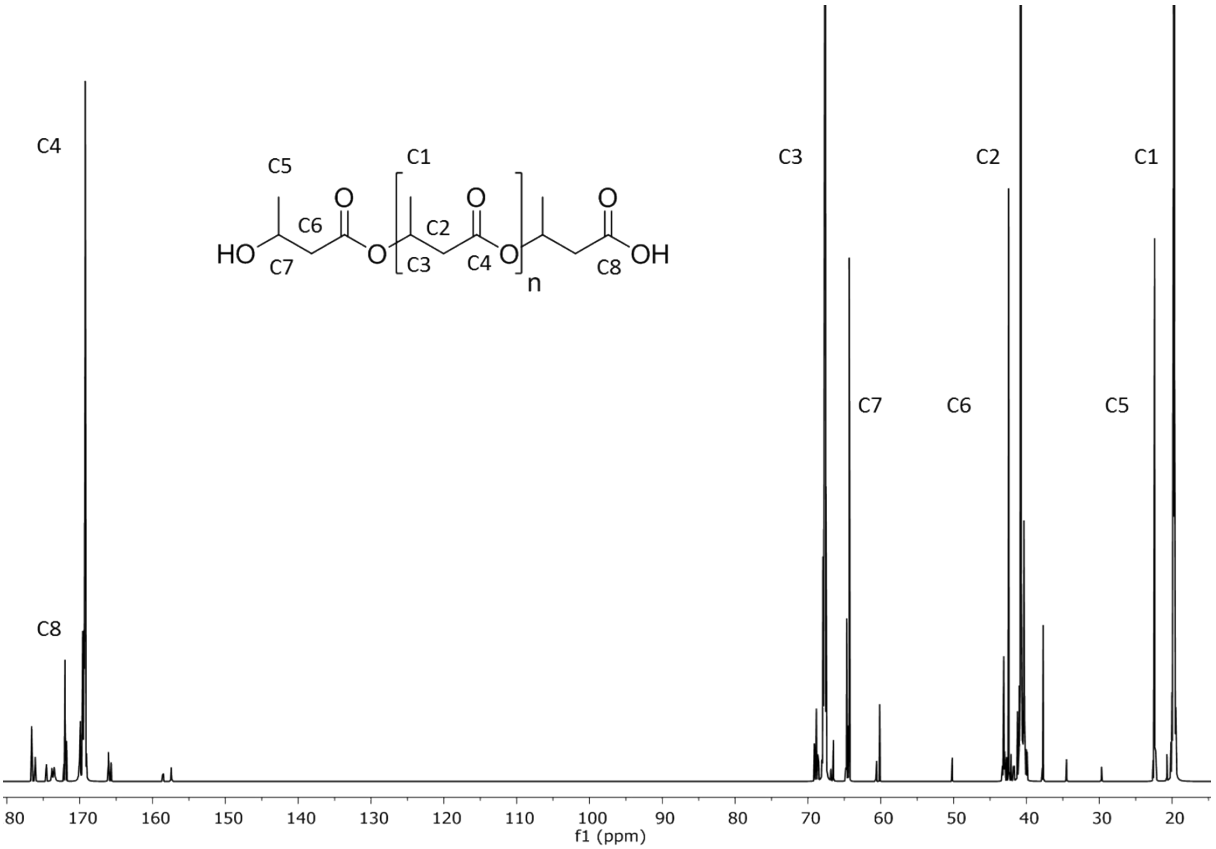
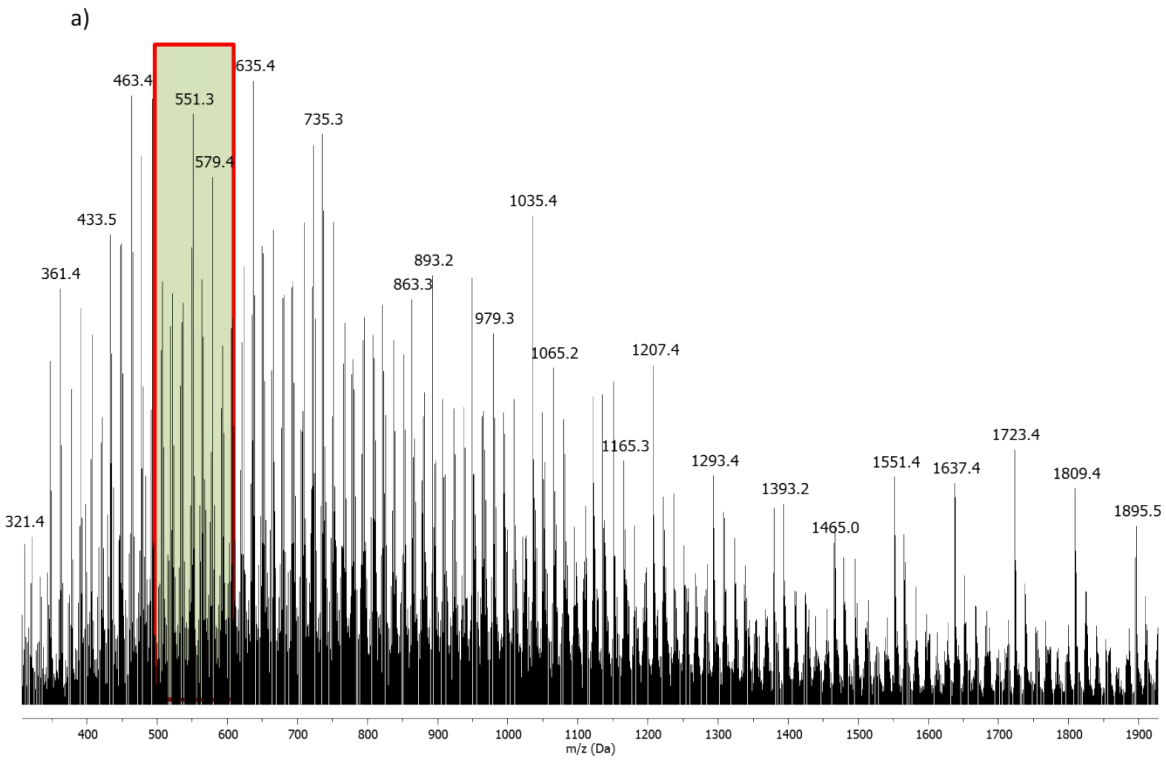


Fig. S2. The ^{13}C NMR spectrum of product of PHB oxidation with O_3/O_2 mixture (140 °C, 5h).



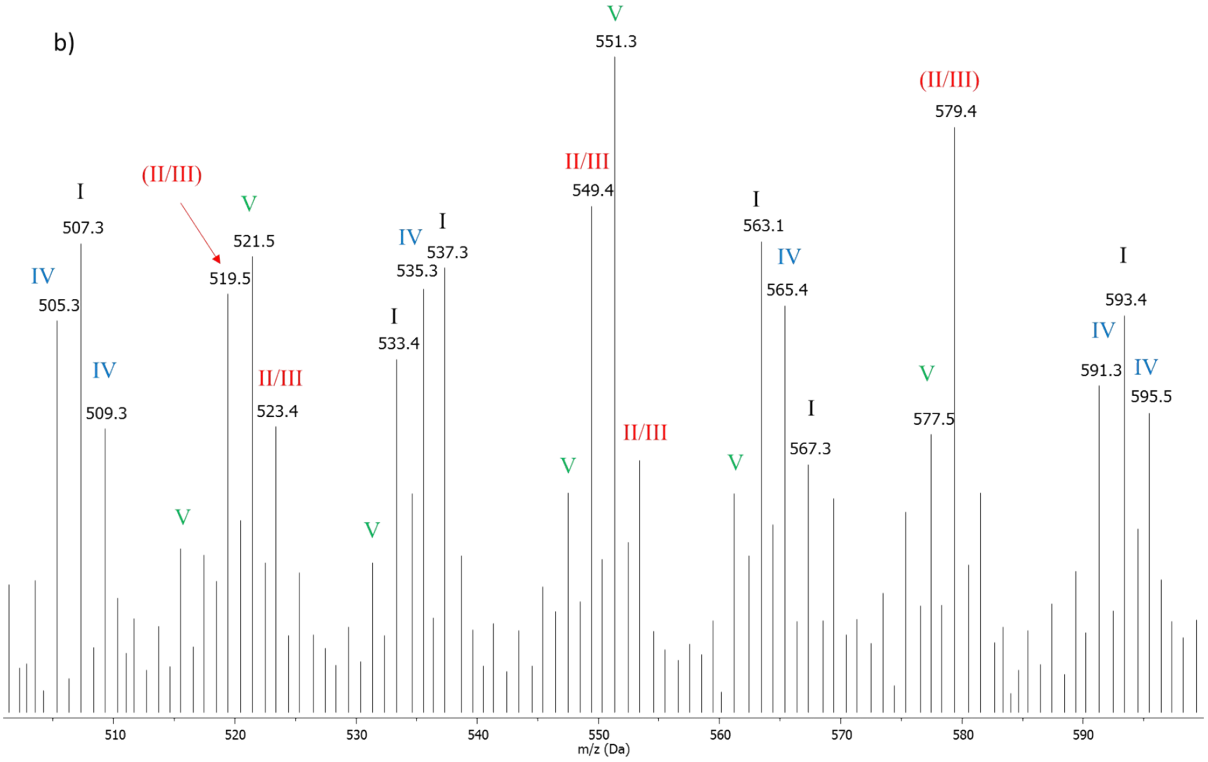
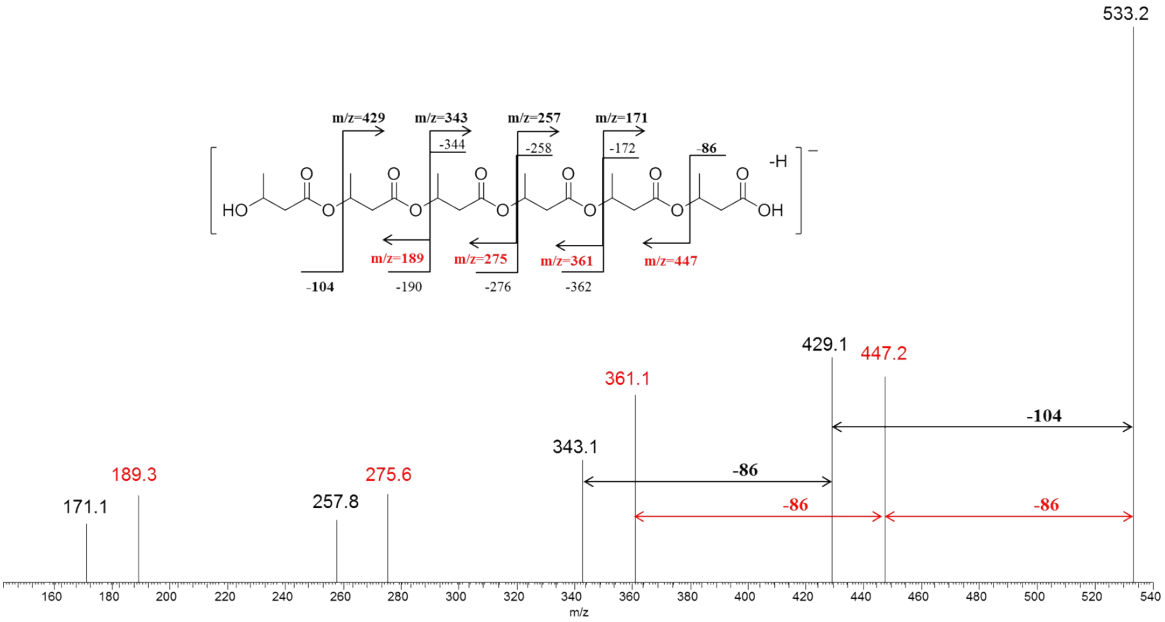


Fig S3. The ESI-MS spectrum of nPHB oxidation products after 5h exposure on O_3/O_2 mixture at 140°C; a) full spectrum, b) representative fragment: *m/z* 500-600, the sequence series correlate with proposed structures presented in Table 2.



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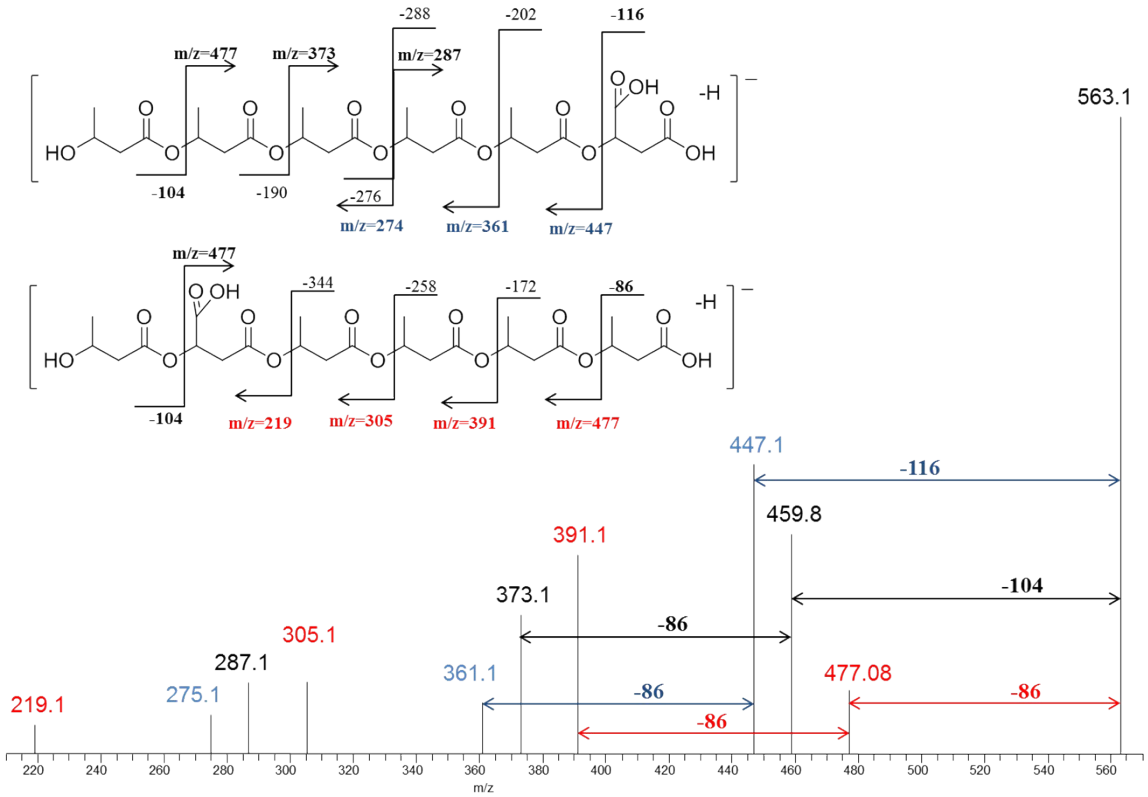


Fig. S5. The ESI-MS^2 spectrum of ion *m/z* 563.1 (negative ion mode) and proposed structures of oligomer with α-3HB end groups, four 3HB units and one MA unit.

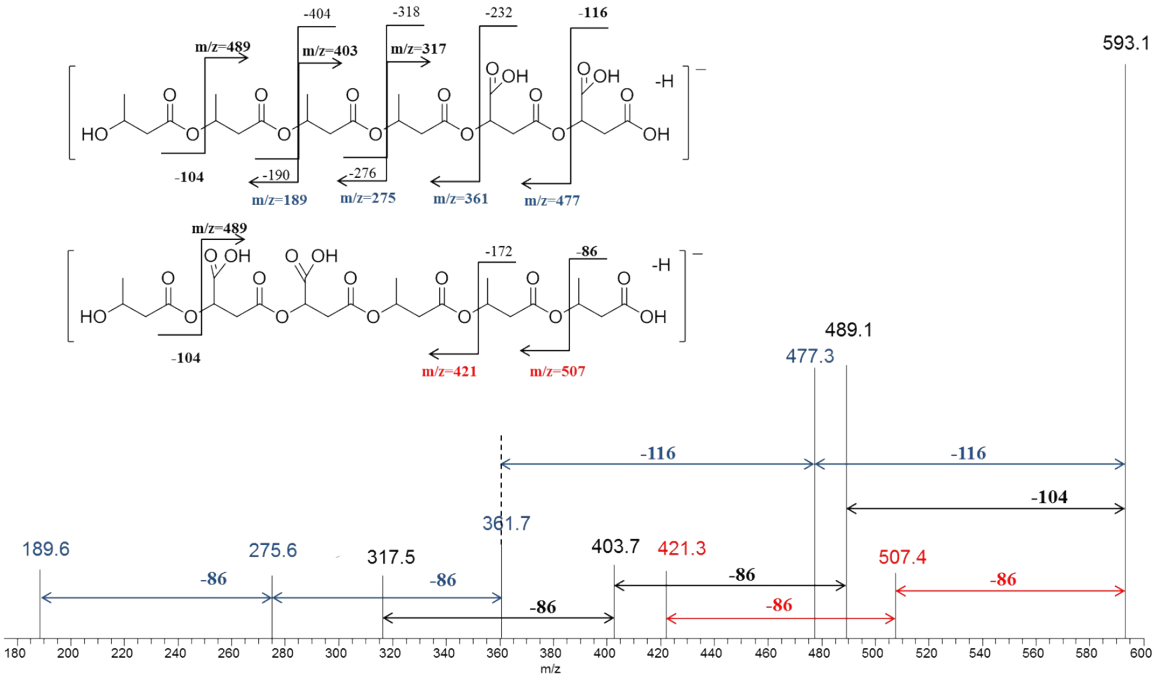


Fig. S6. The ESI-MS^2 spectrum of ion *m/z* 593.1 (negative ion mode) and proposed structures of oligomer with α-3HB end groups, three 3HB units and two MA units.

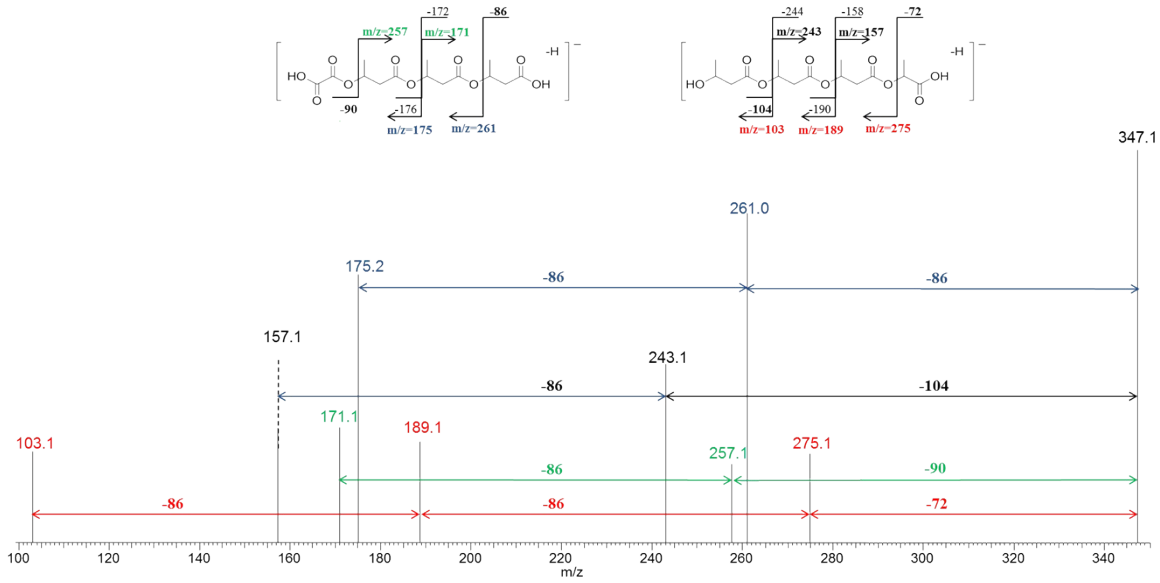
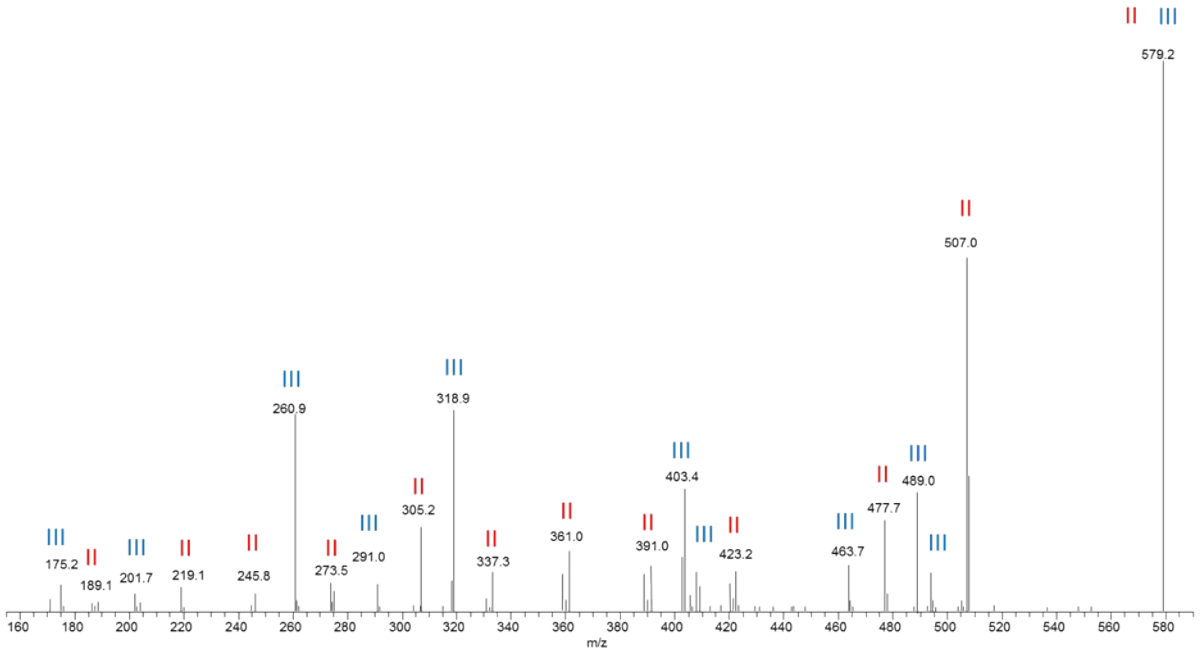


Fig. S7. The ESI-MS^2 spectrum of ion *m/z* 347.1 (negative ion mode) corresponding to sequence II and III (identical mass of structures) and proposed structures of oligomer with: α-3HB, ω-LA end groups, and two 3HB (sequence II) and α-mOx end group and three 3HB units (sequence III); both structures without 3-malic acid units



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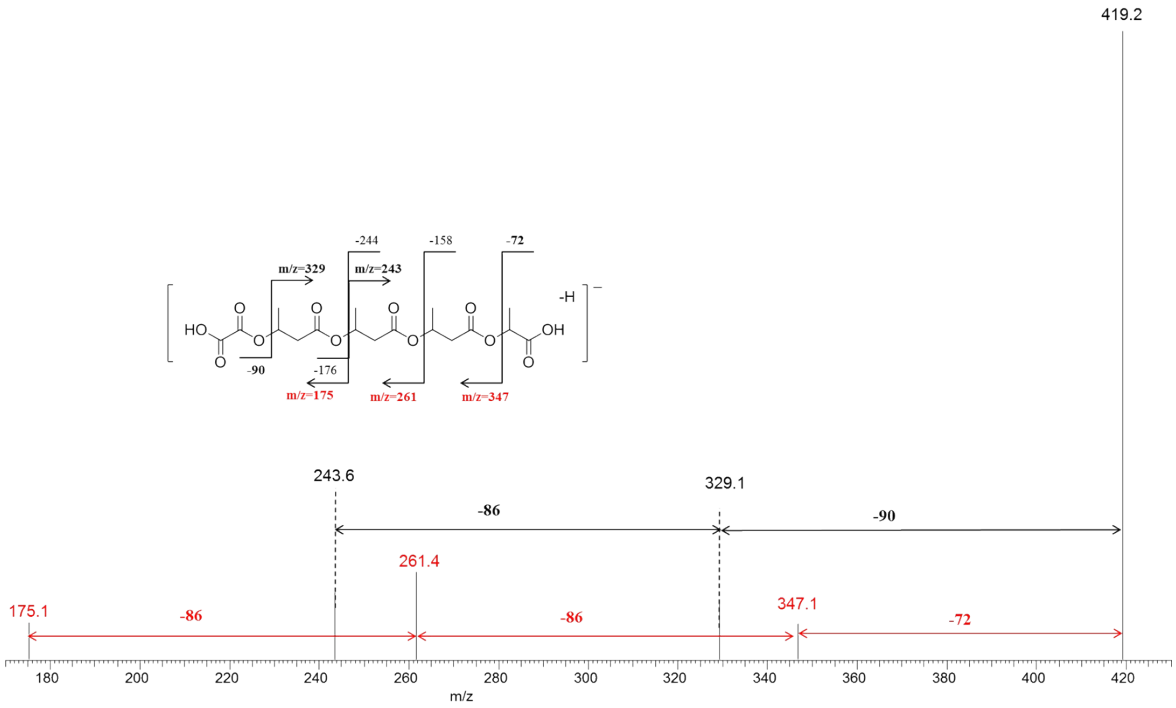


Fig. S9. The ESI-MS^2 spectrum of ion *m/z* 419.2 (negative ion mode) (sequence IV) and proposed structures of oligomer with α-mOx, ω-LA end group and three 3HB units.

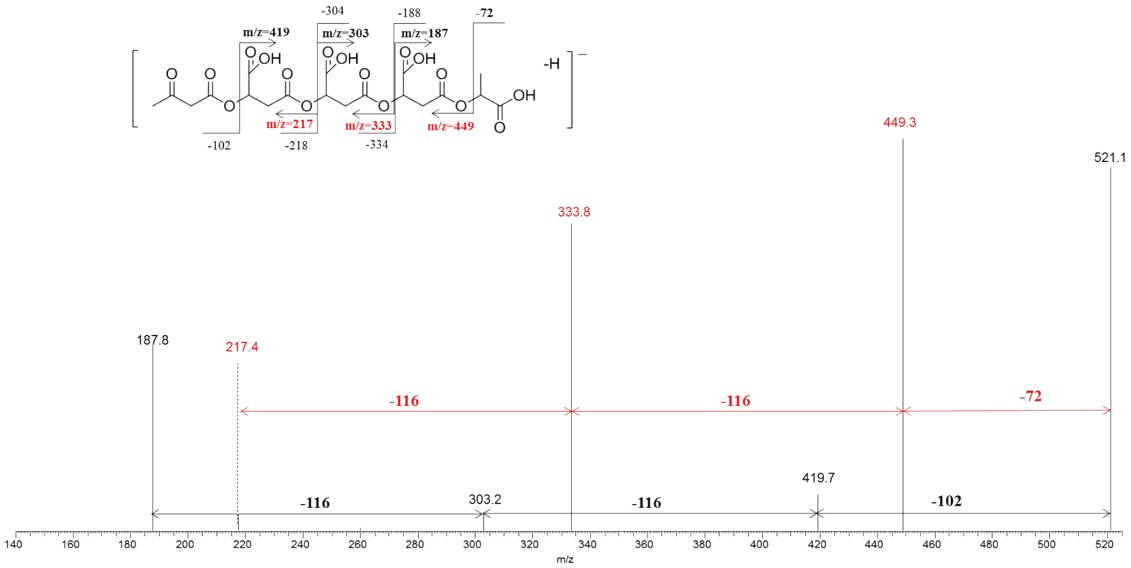
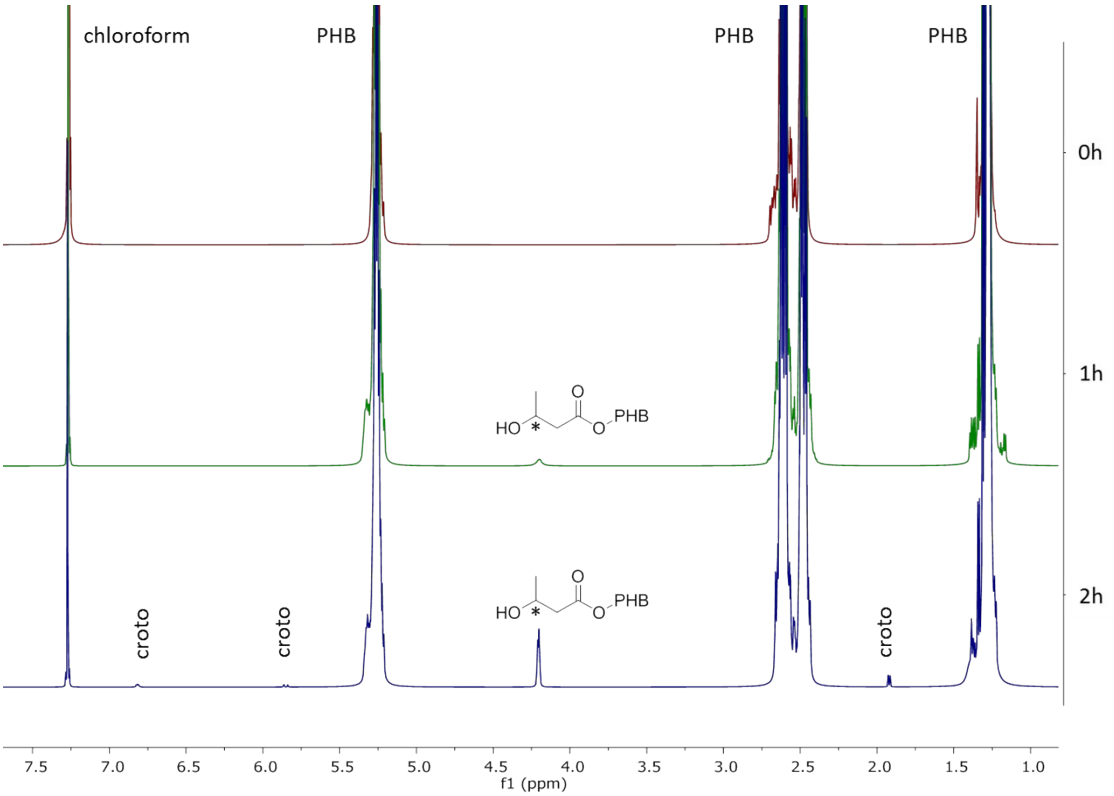


Fig. S10. The ESI-MS^2 spectrum of ion *m/z* 521.1 (negative ion mode) (sequence V) and proposed structures of oligomer with α-AcAc, ω-LA end groups consisted of three MA units.



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