

Effects of (R)-3-hydroxyhexanoate units on thermal hydrolysis of poly((R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate)s

ABSTRACT

In order to clarify effects of (R)-3-hydroxyhexanoate (HHx) unit on the hydrothermal degradation of poly((R)-3-hydroxybutyrate-co-(R)-3-hydroxyhexanoate) (PHBHHx), two PHBHHxs: P(HB-co-6%-HHx) and P(HB-co-11%-HHx), and poly((R)-3-hydroxybutyrate) (PHB) as a reference were treated by superheated steam at 130e190 °C. Interestingly, despite having contents of the HHx unit nearby, contrastive degradation property: the contradictory scission behavior of HB-HHx sequence was confirmed. From analysis of chain-end structures, it was confirmed that HHx unit basically suppressed the hydrolysis of HB-HHx sequence and the formation of crotonoyl chain-end groups rapidly increased at higher temperatures, suggesting the shift to thermal degradation from hydrolysis as a main reaction. On thermal degradation, the contrary upper and lower E_a values: 138 ± 1.9 and 121 ± 1.8 kJ mol⁻¹ for P(HB-co-6%- HHx) and P(HB-co-11%-HHx), respectively, compared to E_a value: 126 ± 5.3 kJ mol⁻¹ of PHB were obtained. The HHx unit basically acts as suppressing factor of the thermal degradation from T_{d50} and $T_{d50} - T_m$ values; however, the increase in flexibility of polymer sequence must promote the thermal chain cleavage. Thus, the complex hydrothermal degradation behaviors were considered to be combined results of the suppression effects by hydrophobicity and steric hindrance of propyl group in HHx unit and the promotive effects of lower crystallinity and easier steam diffusion into more flexible amorphous region of PHBHHx.

Keyword: Microbial polyester; PHBHHx; Thermal hydrolysis; Diad sequence distribution; Chain-end structure; Alkenyl group; Crotonoyl group; b-elimination