BIOSYNTHESIS AND CHARACTERIZATION OF MEDIUM-CHAIN-LENGTH POLY (3-HYDROXYALKANOATE)S

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Polyhydroxyalkanaotes (PHAs) are biodegradable polyesters produced by bacteria and are recognized as candidate materials for sustainable development. Based on the structure of monomeric units, PHAs are divided into two groups; short-chain-length (scl) PHAs consisting of hydroxyalkanoate units with 3 to 5 carbon atoms, and medium-chain-length (mcl) PHAs containing hydroxyalkanoate with over 6 carbon atoms. In this study, we synthesized the medium-chain-length poly(3-hydroxyalkanoate)s (mcl-P(3HA)s) with different side-chain-length ranging from C3 to C9 carbon atoms and characterized the physical properties and solid-state nano-structure of mcl-P(3HA)s. In addition, the thermal degradation behaviors of mcl-P(3HA)s were examined to focus on 2-alkenoic acids as a recyclable carbon source. Mcl-P(3HA)s with different side-chain length ranging from C3–C9 were synthesized from 2-alkenoic acids of C6–C12 by using a recombinant *Escherichia coli*. All mcl-P(3HA)s formed a chain-packed crystalline structure in the solvent-cast films. Melting temperatures of solvent-cast film of mcl-P(3HA)s first decreased from 59 °C to 45 °C with the change of side-chain from C3 to C4 and thereafter increased to 69 °C with an extension of side-chain to C9. The X-ray diffraction patterns indicate the formation of a layered structure aligned the main-chains in planes involving side-by-side packing of side-chains with a periodic distance of 1.6–2.8 nm for the mcl-P(3HA)s with over C4 side-chain. The interlayer distance increased proportionally to the length of side-chain for the mcl-P(3HA)s with over C4 side-chain, while the corresponding value of mcl-P(3HA) with C3 side-chain was apparently deviated from the extrapolated line plotted the distance against side-chain length. These results indicate that the changeover in crystallization manner occurs between P(3HA)s with under C3 side-chain and with over C4 side-chain. For the mcl-P(3HA)s with side-chain carbon number over C7, two distinct phase transitions were happened during heating process from a melt-quenched amorphous state. At lower temperature region, the mcl-P(3HA) molecules formed a smectic liquid-crystalline structure owing to the side-chain interactions, and the structure was disrupted at temperatures between 20–50 °C. After the disruption of smectic aggregates, the crystallization of mcl-P(3HA) chains immediately occurred with participation of both main- and side-chains. The finding of phase transition from liquid-crystalline to crystalline state promises to use them as thermo-responsive biomaterials. The pyrolysis products of mcl-P(3HA)s were dominantly 2- alkenoic acids used as a carbon

source for the mcl-P(3HA) biosynthesis. This result demonstrates the feasibility of PHA recycling via 2-alkenoic acids, which act as pyrolysis products and raw materials for PHA biosynthesis.