

NANO-STRUCTURE AND PROPERTIES OF BIOSYNTHEZIZED MEDIUM-CHAIN-LENGTH POLY(3-HYDROXYALKANOATE)S

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Polyhydroxyalkanoates (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 investigated the effect of side-chain length on the physical properties and solid-state nano-structure of mcl-P(3HA)s.

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 metabolically engineered strain of *Escherichia coli*. Thermal properties and crystallization behaviors of synthesized mcl-P(3HA)s was examined by DSC and X-ray analyses.

All mcl-P(3HA)s formed a chain-packed crystalline structure in the solvent-cast films. As shown in Figure 1, 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 (see Figure 1). 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 (Figure 2). At lower temperature region, the mcl-P(3HA) molecules formed a smectic liquid-crystalline structure from a melt-quenched amorphous state 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. In the crystallization process of mcl-P(3HA)s, the main-chains are arranged with helical conformation, and the packing of alkyl side-chains progresses to play a role in stabilization of the crystalline. The finding of phase transition from liquid-crystalline to crystalline state for mcl-P(3HA)s with over C7 side-chain promises to use them as thermo-responsive biomaterials.

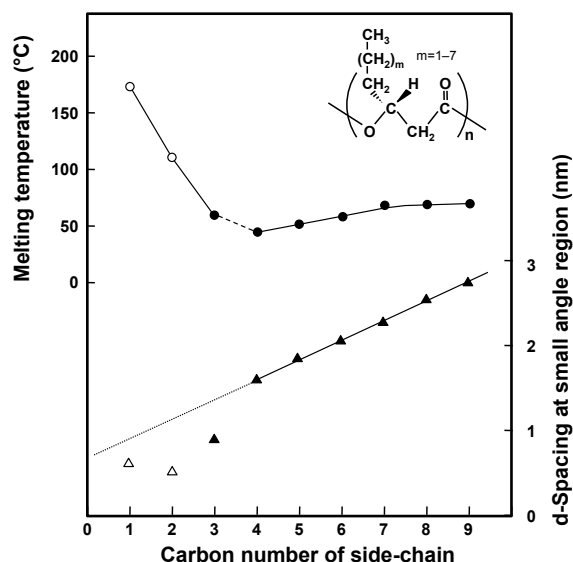


Figure 1. Melting temperature and distance of reflection detected at small angle region for mcl-P(3HA)s.

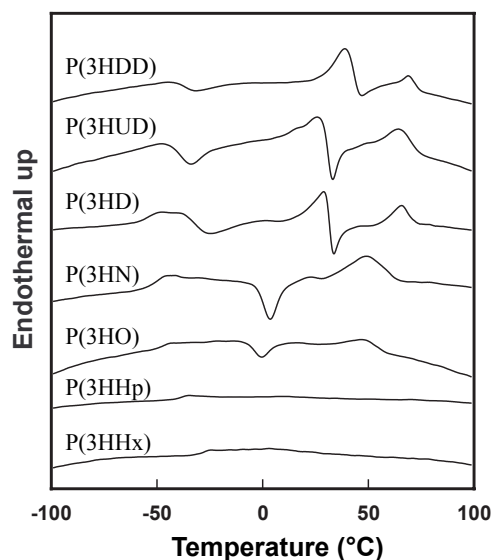


Figure 2. DSC thermograms of mcl-P(3HA)s recorded at second heating scan after melt-quenching.