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題目(和文)	3-ヒドロキシ-2-メチル酪酸含有ポリエステル生合成および諸物性に関する研究
Title(English)	Study on Biosynthesis and Properties of 3-Hydroxy-2-Methylbutyrate-Containing Polyesters
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

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（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質科学創造	専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（ 工学 ）
学生氏名： Student's Name	古舘 祥		指導教員（主）： Academic Supervisor(main)	柘植 丈治	
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Polyhydroxyalkanoates (PHAs) are carbon-storage polymers accumulated in various bacteria. Poly(3-hydroxybutyrate) [P(3HB)], the most wide-spread PHA in nature, is a semi-crystalline bio-based thermoplastic polymer and has similar thermal properties to polypropylene. Some companies attempted to commercialize P(3HB) or its copolymers in past. However, most of their fermentation plants were closed because of the P(3HB)'s poor crystallization speed and thermal stability. The crystallization speed is the important factor in converting plastics to products because it is directly linked to the cost, the energy consumption, and the emission of CO_2. Exploring a new PHA monomer unit with the improved crystallization and thermal resistance is required. 3-Hydroxy-2-methylbutyrate (3H2MB) is a monomer biosynthesized by bacteria from activated sludge in sewage farm, and recently our group found that PHA containing this monomer exhibits different thermal behavior from the other PHAs. Thus, the aim of this study is to investigate the performance of 3H2MB monomer in crystallization and thermal behavior by biosynthesizing the homopolymer and the copolymers of 3H2MB.

In Chapter 1, the general introduction about the bio-based plastics, PHAs produced in the activated sludge, and the crystallization of polymer is presented.

In Chapter 2, the biosynthesis of P(3H2MB) homopolymer by recombinant *Escherichia coli* are presented. The expression of propionyl-CoA transferase led to the considerable improvement of P(3H2MB) biosynthesis. The extracted and purified P(3H2MB) homopolymer was consisted of one enantiomer judging from the ^{13}C nuclear magnetic resonance (NMR) spectra. The methyl ester of 3H2MB was obtained by methanolysis of P(3H2MB) homopolymer, and its optical rotation was investigated. The thermal properties were evaluated by differential scanning calorimetry (DSC) and the equilibrium melting point (T_m^o) of P(3H2MB) was higher than the those of PHAs previously reported. The glass transition temperature (T_g) of P(3H2MB) was also higher than other PHAs. In addition, P(3H2MB) exhibits very fast crystallization speed when compared to the conventional polyesters, like P(3HB) or polylactic acid. To quantify the crystallization speed of P(3H2MB), the melting point (T_m) and crystallization temperature (T_c) were measured. The difference of P(3H2MB)'s T_m and T_c was close to commodity plastics, which means the crystallization behavior of P(3H2MB) is more like commodity plastics than P(3HB). The smaller difference ($\Delta T = T_m - T_c$) reflects faster crystallization speed. Moreover, the higher thermal degradation temperature than P(3HB) was observed in P(3H2MB) by thermogravimetry-differential thermal analysis-mass spectrometry. The molecules generated during the thermal degradation were analyzed, and this suggested the thermal degradation process of P(3H2MB) proceeds via *cis*-elimination, which is the same process as P(3HB). The α-methyl group in 3H2MB could be considered to interfere the deprotonation of α position. Consequently, 3H2MB polymer is found to exhibit the higher processability and thermal resistance than the conventional PHAs.

In Chapter 3, poly(3-hydroxy-2-methylbutyrate-*co*-3-hydroxyhexanoate) [P(3H2MB-*co*-3HHx)], the analogue copolymer of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH), which is the PHA currently available commercially, was biosynthesized by recombinant *E. coli* and the thermal properties were evaluated. This was the first report of P(3H2MB-*co*-3HHx) synthesis in both chemical synthesis and biosynthesis approaches. As a result, the fast crystallization behavior of 3H2MB was found to be maintained even in copolymerized with 3HHx. It was found that softening by copolymerization can be adapted also in 3H2MB-containing polyesters.

In Chapter 4, to investigate the potential of 3H2MB polymers, poly(3-hydroxy-2-methylbutyrate-*co*-3-hydroxybutyrate) [P(3H2MB-*co*-3HB)] was biosynthesized by recombinant *E. coli* with the support of 3HB-supplying enzymes and the thermal properties were analyzed. Combining the monomer supplying enzymes, the 3H2MB fraction in P(3H2MB-*co*-3HB) could reach higher levels with high PHA content. The extracted and purified polymer was subjected to methanolysis reaction and the molecular weight of P(3H2MB-*co*-3HB) was significantly reduced. The terminal of these P(3H2MB-*co*-3HB) oligomer was methoxy group confirmed by NMR analysis. The oligomers were mixed with PHA and the cast-film of PHA/oligomers were obtained. The PHA film containing a small amount of oligomer exhibited higher crystallization temperature and faster crystallization speed than raw PHA. This indicates the potential of P(3H2MB) oligomers as the nucleating agents against the 3HB-based copolymers.

In conclusion, the 3H2MB monomer was reveal to possess the high crystallization speed, high thermal resistance, and even the possibility of biodegradation. This suggests 3H2MB could be the alternative building block to 3HB. In addition, the application of P(3H2MB) as the nucleating agent can be expected.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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