論文 / 著書情報
Article / Book Information

題目(和文)	連鎖構造制御による脂肪族共重合ポリエステルの材料設計に関する研究
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（博士課程）
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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　）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Bio-based polyesters have attracted industrial attention and as environmentally friendly polymeric materials to be used for a wide range of applications to date. In order to fulfill the demands in practical and specialized applications, the research on synthesis of bio-polyesters has been established to obtain high-performance and specific functional bio-plastic materials. Thus, to achieve this target, the present thesis has focused on construct the methodology of molecular design for bio-plastics to predict their properties and functions, and efficient and precise bio-plastic synthesis technology. This thesis, focused on the structure and physical properties of copolymers of 3-hydroxybutyrate (3HB) and lactate (2-hydroxypropionate: 2HP) units. The structure and physical properties of random, block tendency, and alternating copolymers were characterized. The relationships among the molecular structure, thermal property, crystalline structure and sequential structure in copolymers were investigated.

In chapter 1, the general introduction about the significance of bio-based polymer, aliphatic polyesters, polyhydroxyalkanoates (PHAs), and current polymerization techniques were described. From the viewpoint of environmental protection, bio-based polymers have attracted considerable attention. In addition, the two important classes, α- and β-hydroxyalkanoate in their polymers were taken, and the aim of this study, including methodology about the polymer design, was presented.

In chapter 2, copolymers of (*R*)-3HB and (*R*)-2HP units ([(*R*)-3HB-*co*-(*R*)-2HP]) were synthesized by polycondensation reaction from methyl esters of (*R*)-3HB and (*R*)-2HP in the presence of titanium-based catalyst. Mixing of two monomers from the beginning of polymerization yielded random copolymers of (*R*)-3HB and (*R*)-2HP units. On the other hand, by controlling the time of mixing of two monomers, copolymers with blocking tendency were obtained. According to the results of physical properties of copolymer samples, the relationship between the compositional and sequential structure and the physical properties of copolymers are discussed. The effects of copolymer composition and sequential structure on the thermal properties of P[(*R*)-3HB-*co*-(*R*)-2HP] copolymers were investigated. The obtained results indicate that the T_g of copolymers varies in accordance with the copolymer composition, while that the T_m is predominantly determined by the averaged sequential length of crystallizable monomer units. It means that we can produce the copolymers with various T_m values and a constant T_g value by varying the sequential length of monomers at the fixed copolymer composition. Unfortunately, since the synthesized copolymers had relatively low molecular weights, it is difficult to prepare films being subjected to biodegradation test. It has been demonstrated that the rate of biodegradation for PHA materials is strongly dependent both on the chemical structure of monomeric unit and on the solid-state structure of samples. In the aspect of the solid-state structure of PHA materials, the crystallinity and lamellar crystal sizes play a decisive role in degradation process. The lamellar thickness of P[(*R*)-3HB-*co*-(*R*)-2HP] copolymers is regulated by the averaged sequential length of crystallizable monomer units, and the crystallinity is versatile with the combination of copolymer composition and averaged sequential length of monomers. Therefore, it is expectable that the biodegradation rate of P[(*R*)-3HB-*co*-(*R*)-2HP] copolymers is also controlled desirably by selecting the copolymer composition and averaged sequential length of monomers.

In chapter 3, novel alternating copolymers of (*R*)-3HB and 2HP units (P[(*R*)-3HB-*alt*-2HP]) were synthesized by the polycondensation reaction of pre-prepared dimeric monomers, (*R*)-3HB-(*R*)-2HP and (*R*)-3HB-(*S*)-2HP, in the presence of condensation agent. On the basis of the results of physical properties of alternating copolymer samples, the relationship between the stereocompositional and sequential structure and the properties of copolymers are discussed. The effects of enantiomeric structure of 2HP units and stereocomposition of dimeric monomers on the thermal properties and crystalline structure of alternating copolymers were investigated. In contrast to random copolymers of (*R*)-3HB and 2HP units, the repeating sequence of alternately connected (*R*)-3HB and 2HP units formed crystalline region. The crystalline structure and thermal properties was different from each other between the alternating copolymers obtained from two types of stereoisomeric macromonomers. The melting of the crystalline region for alternating copolymers varied in the wide range of temperatures depending on both the enantiomeric structure of 2HP units and stereocomposition of dimeric monomers. In particular, the melting temperature of P[(*R*)-3HB-*alt*-(*R*)-2HP] was reached to 233 °C, and the copolymers was one of the aliphatic polyesters with highest melting temperature.

In chapter 4, by means of transmission electron microscopy, single crystal for the alternating copolymer is resolved. The unit cell of P[(*R*)-3HB-*alt*-(*R*)-2HP] alternating copolymer was determined as a monoclinic form with the lattice constants of a = 0.933 nm, b = 0.904 nm, c (chain axis) = 2.138 nm, and β = 82 °. It was concluded that the density of P[(*R*)-3HB-*alt*-(*R*)-2HP] alternating polymer was increased by sequential control of alternating, as a result, melting temperature of P[(*R*)-3HB-*alt*-(*R*)-2HP] alternating polymer higher than homopolymer of 3HB and 2HP.

On the basis of the above results, it may be concluded that the thermal properties of polyesters can be improved by sequential structure and stereosequence, which can be lead to a variety of useful properties. This study would provide an alternative way for polyesters applications and industrial production, and a platform for material design.

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).