



Effects of composition and sequential structure on thermal properties for copolymer of 3-hydroxybutyrate and lactate units



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ABSTRACT

Copolymers of (*R*)-3-hydroxybutyrate (3HB) and (*R*)-lactate ((*R*)-2-hydroxypropionate: 2HP) units were synthesized by polycondensation reaction from methyl esters of 3HB and 2HP in the presence of titanium-based catalyst. Mixing of two monomers from the beginning of polymerization yielded random copolymers of 3HB and 2HP units. On the other hand, by controlling the time of mixing of two monomers, copolymers with blocking tendency were obtained. The structure and thermal properties of the obtained copolymers were characterized by ¹H and ¹³C NMR, X-ray diffraction, differential scanning calorimetry, and optical microscopy. Glass-transition temperature of the copolymers was mainly governed by the copolymer composition, and the values varied linearly with the composition. In contrast, the melting temperature was strongly depending on the sequential length of crystallizable monomeric unit, and the values were in inverse proportion to the number-averaged sequential length of crystallizable monomeric unit. The crystallinity of the copolymer samples was affected by both the composition and sequential length of crystallizable monomeric unit. The finding is valuable for design of copolymer molecules with desirable thermal properties by controlling both the copolymer composition and sequential structure.

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1. Introduction

Poly(hydroxyalkanoate)s (PHAs) are naturally occurring polyesters synthesized by a wide variety of bacteria and accumulated as an intracellular carbon and energy storage material [1–4]. PHAs are biodegradable and biocompatible thermoplastics and have attracted industrial attention as an environmentally degradable material for a wide range of agricultural, marine and medical applications [4].

Poly[(*R*)-3-hydroxybutyrate], P(3HB), is the most studied polymer material in the family of PHAs. P(3HB) isolated from microorganisms has a melting temperature around 180 °C and a glass transition temperature around 4 °C [3]. To meet a variety of demands for a usage of PHA materials in a wide range of application fields, copolymerization of P(3HB) with other PHA monomer units has been attempted. Copolymers containing 3HB as a constituent and other PHA monomer units such as (*R*)-3-hydroxyvalerate (3HV) [5–

9], 4-hydroxybutyrate (4HB) [10–14], and (*R*)-3-hydroxyhexanoate (3HHx) [15–17] have been produced from various carbon substrates by a variety of bacteria. The structure and properties of random copolymers containing 3HB units have been examined, and it has been found that the physical and thermal properties of P(3HB)-based copolymers be regulated by varying their molecular structure and copolymer compositions.

Homopolymers of lactates (PLAs) are also known as biodegradable and biocompatible thermoplastics chemically synthesized from either lactates or its cyclic dimers [18–22]. PLAs have been investigated as a material for medical devices such as controlled drug release matrixes, degradable sutures, and implanted for bone fixation [21,23–25]. Optically pure PLA has a melting temperature around 180 °C and a glass transition temperature around 60 °C [21].

Recently, Taguchi's group succeeded in construction of biosynthetic system of copolymers consisting of (*R*)-lactate ((*R*)-2-hydroxypropionate; 2HP) and 3HB units (P(3HB-*co*-2HP)), and the copolymers with a wide range of composition have been produced [26–29]. Among the microbial PHAs containing 3HB units, P(3HB-*co*-2HP) copolymers are quite interesting due to their glass transition temperatures ranging from below room temperature to above body temperature. By applying the relaxation phenomenon

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of glass-transition, it is expected that the P(3HB-co-2HP) copolymers have a potential to be an intelligent material, e.g., matrixes for controlled release of drug or fertilizer in response to temperature.

It has been reported that the bacterially produced PHA copolymers have broad distributions in randomness, resulting from various factors controlled by changing bacterial strains, carbon substrates, pH, in the fermentation medium, and so on during the cultivation [30–32]. Most recently, Ochi et al. have succeeded in production of P(3HB-co-7 mol% 2HP) copolymer with blocking tendency by using recombinant *Escherichia coli* harboring the point-mutated PHA synthase [33]. The variation in sequential distribution of monomeric units for copolymers will certainly expand the properties and functions of PHAs and their applications. In comparison with random copolymers containing 3HB units, the investigation on the copolymers with blocking tendency is still few. Understanding the relationship between sequential distribution and properties is valuable to design the copolymer molecules with desirable properties. In this study, the effects of copolymer composition and sequential structure on thermal properties of P(3HB-co-2HP) copolymers were investigated. The P(3HB-co-2HP) copolymers with wide ranges of composition and sequential distributions were prepared by chemosynthetic methods, and their thermal properties and structure were examined.

Chemical syntheses of P(3HB) have been achieved by both the ring-opening polymerization of β -butyrolactone and the polycondensation reaction of 3HB derivatives [34–37]. In contrast to microbial syntheses of P(3HB), most cases of chemosynthetic methods hardly yielded P(3HB) polymers with high molecular weights. It has been merely found that the distannoxane catalysts were very active for the ring-opening polymerization of β -butyrolactone to afford P(3HB) with high molecular weights ($M_n > 100,000$ g/mol) [35]. By using the same tin-based catalyst, the copolymers of 3HB and 2HP units with relatively high molecular weights ($M_n > 50,000$ g/mol) were synthesized by ring-opening polymerization of a mixture of β -butyrolactone and lactide [38]. However, it was reported that the obtained copolymers had a statistically random distribution of 3HB unit and dimeric units of 2HP since the 2HP comonomers were inserted as in units of lactide into the propagating polymer chains. Although the molecular weights of products by polycondensation reaction are less than those by ring-opening polymerization, the polycondensation reaction yields the copolymers incorporating 2HP comonomer as monomeric units and varies the composition and sequential distribution, extensively, by controlling the mixing conditions of two monomers. Therefore, we presumed to adopt the polycondensation reaction for preparation of P(3HB-co-2HP) copolymers in this study.

2. Experimental

2.1. Materials

Basic chemicals were purchased from Kanto Chemical Co. (Japan). Methyl (*R*)-3-hydroxybutyrate (3HB-M) and methyl (*R*)-lactate (methyl (*R*)-2-hydroxypropionate; 2HP-M) were used as received.

2.2. Synthesis of random copolymers of 3HB and 2HP units

P(3HB-co-2HP) random copolymers were prepared by polycondensation reaction of 3HB-M and 2HP-M in the presence of titanium tetraisopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$) as a catalyst. First, copolymerization of 3HB-M and 2HP-M with $\text{Ti}(\text{O}^i\text{Pr})_4$ was carried out at 140 °C under atmospheric pressure for 24 h. Then, the pressure was gradually reduced to less than 0.1 mbar, and the reaction was continuously

progressed for 66 h. The product was dissolved into chloroform and precipitated in cold methanol. The precipitate was dried in vacuo at room temperature.

2.3. Synthesis of copolymers with blocking tendency

P(3HB-co-2HP) copolymers with blocking tendency were synthesized by two-step polycondensation reaction. 3HB oligomers were prepared by pre-condensation reaction of 3HB-M with $\text{Ti}(\text{O}^i\text{Pr})_4$ at 140 °C. The reaction was first carried out under atmospheric pressure for 24 h, and then the pressure was reduced to about 1 mbar. The degree of oligomerization of 3HB was controlled by varying the reaction time for 1–6 h under the reduced pressure. Copolymerization was started by adding the 2HP-M monomer into the 3HB oligomers. After the initial copolymerization reaction at 140 °C for 12 h under atmospheric pressure, the pressure of reactor was gradually reduced to less than 0.1 mbar. After the additional polymerization reaction for 66 h, the product was cooled to room temperature and dissolved into chloroform. The copolymer precipitated in cold methanol was dried in vacuo at room temperature.

2.4. Analytical procedures

All molecular weight data were obtained by gel-permeation chromatography at 40 °C, using a Shimadzu 10A GPC system and 10A refractive index detector with Shodex K-806M and K-802 columns. Chloroform was used as an eluant at a flow rate of 0.8 mL/min, and sample concentration of 1.0 mg/mL was applied. Polystyrene standards with a low polydispersity were used to make a calibration curve.

^1H and ^{13}C NMR analyses of copolymer samples were carried out on a Varian NMR System 500 spectrometer. The samples (2 mg/mL) were dissolved in CDCl_3 and the 500 MHz ^1H NMR spectra were recorded at 25 °C with a 5.45 μs pulse width (45° pulse angle), 3.2 s pulse repetition, 8000 Hz spectral width, and 16K data points. The 125 MHz ^{13}C NMR spectra were recorded at 25 °C in a CDCl_3 solution of polymer (30 mg/mL) with a 4.15 μs pulse width (45° pulse angle), 1.3 s pulse repetition, 30,000 Hz spectral width, 32K data points. Data were analyzed by JEOL ALICE 2 software.

Differential scanning calorimetry (DSC) data of copolymer samples were recorded in the temperature range of –100–200 °C on a Perkin Elmer DSC 8500 equipped with a liquid nitrogen cooling accessory under a helium flow of 20 mL/min. Samples of 3–5 mg were encapsulated in aluminum pans and heated from –50–200 °C at a rate of 20 °C/min (first heating scan). The melting temperature (T_m) and enthalpy of fusion (ΔH_m) were determined from the DSC endotherms of first heating scan. The T_m was taken as the peak temperature of the main endothermal peak. For measurement of the glass-transition temperature (T_g), the samples were maintained at 200 °C for 1 min, and then rapidly quenched at –100 °C. They were then reheated from –100 to 200 °C at a heating rate of 20 °C/min (second heating scan). The T_g was taken as the midpoint of the heat capacity change.

The copolymer spherulitic morphologies were observed with an Olympus optical microscope equipped with crossed polarizers and a Linkham hot stage. The copolymer samples (2 mg) were first heated on a hot stage from room temperature to 200 °C at a rate of 30 °C/min. Samples were maintained at 200 °C for 30 s, and then the temperature was rapidly lowered to a given crystallization temperature (T_c). The samples were crystallized isothermally at a given T_c to monitor the growth of the spherulites as function of time. The radial growth rate of spherulites was calculated as the slope of the line obtained by plotting the spherulite radius against time with more than ten data points. For each crystallization

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