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# Crystallization behavior of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) studied by 2D IR correlation spectroscopy

Adchara Padermshoke<sup>a,b</sup>, Harumi Sato<sup>a</sup>, Yukiteru Katsumoto<sup>c</sup>, Sanong Ekgasit<sup>b</sup>, Isao Noda<sup>d</sup>, Yukihiro Ozaki<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, School of Science and Technology, Kwansei-Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan <sup>b</sup>Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand <sup>c</sup>Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan <sup>d</sup>The Procter and Gamble Company, 8611 Beckett Road, West Chester, OH 45069, USA

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## Abstract

Crystallization behavior of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (P(HB-*co*-HHx)) (HHx = 12 mol%) was studied by means of two-dimensional infrared (2D IR) correlation spectroscopy. Three types of crystallization; the gradual cooling from the melt, the isothermal crystallization of the supercooled melt, and the isothermal crystallization of the solution-cast film were investigated. The order of crystal growth steps taking place during the three different types of crystallization processes was analyzed in detail. It was revealed by the asynchronous 2D correlation spectra generated from the dynamic IR spectra in the C=O stretching band region that the development of the highly ordered crystals occurs prior to that of the less ordered crystals for the gradual cooling crystallization. On the other hand, for the supercooled melt and solution-cast film crystallization, the formation of the less ordered crystals takes place before that of the highly ordered crystals. The transition from the amorphous phase to the less ordered crystals is a simultaneous process for all three types of crystallization. © 2004 Elsevier Ltd. All rights reserved.

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# 1. Introduction

Industrial materials derived from petroleum-based synthetic polymers are indispensable for modern human life. These materials, however, cause tremendous environmental problems especially at the waste disposal process. As a consequence, many researchers and manufacturers are driven to move towards materials that can be produced from renewable resources and would not persist in the environment.

Bacterially synthesized poly(3-hydroxyalkanoate)s (PHAs) have received a keen attention as environmentally friendly polymeric materials [1–6]. PHAs are biodegradable

polyesters accumulated as energy-storing inclusion body granules in the cells of certain microorganisms [1-6]. Their chemical structures and physical characteristics are fairly similar to those of certain petroleum-based synthetic polymers [1,4,6]. Due to the high stereoregularity of biologically produced macromolecules, some PHA polymers are highly crystalline and, hence, too rigid, stiff, and brittle [1,6]. Accordingly, many attempts have been made to reduce the crystallinity of PHAs in order to improve their physical and mechanical properties [6]. It has been reported that the copolymerization of a longer side-chain 3-hydroxyhexanoate (3-HHx) comonomer with the highly crystalline 3-hydroxybutyrate (3-HB) units significantly reduces the crystallinity and increases the flexibility of PHB [6]. The resulting P(HB-co-HHx) copolymers possess dramatically improved physical and mechanical properties compared with those of PHB homopolymer [6,7]. The crystallinity and

<sup>\*</sup> Corresponding author. Tel.: +81-79-565-8349; fax: +81-79-565-9077.

E-mail address: ozaki@ksc.kwansei.ac.jp (Y. Ozaki).

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crystallization behavior of PHA polymers are crucial for determining their overall performances and characteristics. The thermal behavior, biodegradation mechanism, and mechanical properties of P(HB-*co*-HHx) were revealed by several research groups [6,8–10].

Infrared (IR) spectroscopy has been successfully employed to investigate the conformational changes and local molecular environments of polymers during their crystallization [11–19]. This is because the technique provides not only sensitivity to changes in molecular interactions and polymer crystallinity but also substantial advantages that allow the dynamic studies at the microscopic molecular level. Two-dimensional (2D) correlation analysis proposed by Noda [20,21] enables a more detailed analysis of the IR spectral variations of polymers. It emphasizes spectral information not readily observable in conventional one-dimensional (1D) spectra. Asynchronous 2D spectra are very powerful in differentiating highly overlapped bands that vary out of phase under the external perturbation [22]. The signs of synchronous and asynchronous cross peaks indicate the successive order of the events taking place in the system of interest under the applied perturbation [19,23]. These features make the technique ideally suitable for the study of polymer crystallization.

We have studied the melting behavior of P(HB-co-HHx) (12 mol% HHx) by using the generalized 2D IR correlation spectroscopy [24]. In our previous study, the asynchronous 2D correlation spectrum generated for the C=O stretching band region of P(HB-co-HHx) revealed the coexistence of two crystalline bands at 1731 and 1723  $\text{cm}^{-1}$  [24]. The band at  $1723 \text{ cm}^{-1}$  is possibly ascribed to the highly ordered crystalline component, and that at  $1731 \text{ cm}^{-1}$  may arise from the less ordered crystalline part [24]. The presence of the asynchronous cross peaks between these two crystalline bands suggested that the intensities of the two crystalline bands change successively during the melting process of the copolymer [24]. The vibrational frequencies of bands in the C=O stretching region of P(HB-co-HHx) are identical to those of PHB [25]. The asynchronous 2D correlation spectrum generated for the C=O stretching band region of the PHB homopolymer also showed the coexistence of two crystalline bands at around 1731 and 1723 cm<sup>-1</sup> [25]. The presences of the C=O bands at around 1728 and 1722 cm<sup>-1</sup> in IR spectra of PHB are also reported by Yoshie et al. [26], and they assigned these two C=O bands to the interfacial and crystalline phases, respectively [26].

In general, the formation of an ordered structure during the crystallization of semi-crystalline polymers depends strongly on the crystallization conditions [27]. The present study reveals the mechanism of the crystallization of P(HB*co*-HHx) (12 mol% HHx) under different crystallization conditions by using 2D IR correlation analysis. Three types of crystallization; the gradual cooling from the melt, the isothermal crystallization of the supercooled melt, and the isothermal crystallization of the solution-cast film were performed to verify the differences and similarities of the crystallization behavior among these three processes.

#### 2. Experimental

#### 2.1. Materials

Bacterially synthesized P(HB-*co*-HHx) (12 mol% HHx) was provided by the Procter and Gamble Company, Cincinnati, USA. The glass transition temperature  $(T_g)$ , crystallization temperature  $(T_c)$ , melting temperature  $(T_m)$ , and percentage of crystallinity of the sample are approximately 2.4, 51, 110 °C, and 35%, respectively. Purification of the P(HB-*co*-HHx) sample was performed by dissolving P(HB-*co*-HHx) in hot chloroform (CHCl<sub>3</sub>), re-precipitating in methanol (CH<sub>3</sub>OH), and vacuum-drying at 60 °C for 24 h. Chloroform and methanol were purchased from Wako Pure Chemical Industries, Ltd, Osaka, Japan. Chloroform was used as a solvent for preparing the sample solution. The concentration of the chloroform solution of P(HB-*co*-HHx) was approximately 0.004 g/ml.

## 2.2. IR spectroscopic measurements

#### 2.2.1. Gradual cooling crystallization

A film of P(HB-co-HHx) (12 mol% HHx) for IR measurements was prepared by casting its chloroform solution on a CaF2 window. After chloroform had evaporated, the film was heated to 140 °C and kept for 30 min. IR spectra of the film sample were measured at a  $2 \text{ cm}^{-1}$  spectral resolution by using a Thermo Nicolet Magna-IR<sup>™</sup> 550 spectrometer equipped with a mercury cadmium telluride (MCT) detector. To ensure a high signalto-noise ratio, 512 scans were co-added. The temperature of the sample cell that holds the CaF<sub>2</sub> window with the P(HB-co-HHx) film was controlled by using a temperature controller unit (CHINO, model SU) with an accuracy of  $\pm 1$  °C. The temperature-dependent dynamic IR spectra were collected throughout a temperature range of 140-30 °C with a decrement interval of 10 °C. The cooling rate was 2 °C/min. The sample film was kept at each temperature for 15 min before the measurement.

#### 2.2.2. Supercooled melt crystallization

The sample film was prepared by casting its chloroform solution on a  $CaF_2$  window in the same manner as that for the gradual cooling crystallization. After chloroform had evaporated, the film was heated to 140 °C and kept for 30 min before rapidly quenched to room temperature (25 °C). The time-dependent IR spectra were collected at room temperature with a time interval of 30 min until the crystal growth was completed (i.e., no significant spectral change was observed). The instrumental parameters were the same as those described in Section 2.2.1.

#### 2.2.3. Solvent-cast film crystallization

The sample film was prepared by casting its chloroform solution on a  $CaF_2$  window. After the solvent casting, the sample film was air-dried for 30 min before the measurement. The IR spectrum of the sample film measured after the solvent had evaporated showed no spectroscopic evidence for the presence of chloroform. The time-dependent IR spectra were collected at room temperature with a time interval of 15 min until the crystal growth was completed (i.e., no significant spectral change was observed). The instrumental parameters were the same as those described in Section 2.2.1.

#### 2.3. 2D correlation analysis

The IR spectra were preprocessed to minimize the effect of baseline instability prior to the 2D correlation analysis. The spectral region of interest  $(1800-1660 \text{ cm}^{-1})$  was subjected to a linear baseline correction, followed by offsetting to the zero absorbance value. The calculations of 2D correlation spectra were performed by using the 2D-Pocha software composed by Daisuke Adachi (Kwansei-Gakuin University, Japan). Temperature-averaged and time-averaged IR spectra in the selected wavenumber region were used as the reference spectra for the 2D correlation calculations of the temperature and timedependent IR spectra, respectively.

# 3. Results and discussion

# 3.1. Gradual cooling crystallization

Fig. 1 shows temperature-dependent IR spectra of P(HBco-HHx) (12 mol% HHx) in the 1780–1680 cm<sup>-1</sup> region, where bands due to the C=O stretching modes appear. A broad band at 1740 cm<sup>-1</sup> decreases while a sharp band at 1723 cm<sup>-1</sup> gradually increases in intensity during the



Fig. 1. IR spectra of P(HB-co-HHx) (12 mol% HHx) in the C=O stretching vibration region measured during the crystallization from the melt over a temperature range of 140–30 °C.

course of temperature decrease. The sharp band at  $1723 \text{ cm}^{-1}$  arises from the crystalline part of P(HB-*co*-HHx), and the broad band at 1740 cm<sup>-1</sup> is attributed to the amorphous component [24]. These spectral variations reflect the crystallization process of P(HB-*co*-HHx).

To extract more detailed information about the spectral variations induced by the gradual cooling crystallization process, 2D correlation analysis was employed. Fig. 2(A) and (B) shows the synchronous and asynchronous 2D correlation spectra in the spectral region of 1790–1670 cm<sup>-1</sup> generated from the temperature-dependent IR spectra. A pair of negative cross peaks developed at (1745, 1723) cm<sup>-1</sup> in the synchronous spectrum (Fig. 2(A)) indicates the opposite directions of the intensity variations in these two



Fig. 2. Synchronous (A) and asynchronous (B) 2D IR correlation spectra of P(HB-co-HHx) (12 mol% HHx) in the C=O stretching vibration region generated from the temperature-dependent IR spectra measured over a temperature range of 140–30 °C.

correlated bands. In the asynchronous spectrum (Fig. 2(B)), two pairs of cross peaks appear at (1745, 1723) and (1728, 1723) cm<sup>-1</sup>. The band at around 1728 cm<sup>-1</sup> revealed by the asynchronous 2D correlation spectrum may arise from the less ordered crystalline component of P(HB-co-HHx) [24]. The presence of asynchronous cross peaks indicates the out-of-phase changes in the intensity of the correlated bands. Fig. 2(B) suggests that, during the crystallization process, the decrease in intensity of the amorphous C=O band at  $1745 \text{ cm}^{-1}$  and the increase in intensity of the crystalline C=O band at  $1723 \text{ cm}^{-1}$  do not occur simultaneously. Of note in Fig. 2(B) is that the two crystalline C=O bands at 1728 and 1723  $\text{cm}^{-1}$  share asynchronous cross peaks. This observation indicates that the development of the highly ordered crystalline component and that of the less ordered crystalline component take place out of phase. The negative sign of the asynchronous cross peak at (1728, 1723)  $\text{cm}^{-1}$  and the positive sign of the corresponding synchronous spectral intensity reveal that the formation of the highly ordered crystalline component proceeds prior to that of the less ordered crystalline structure during the course of the gradual cooling crystallization.

#### 3.2. Supercooled melt crystallization

Fig. 3 shows time-dependent IR spectra of P(HB-*co*-HHx) (12 mol% HHx) in the C=O stretching band region measured during the isothermal crystallization of the supercooled melt. The representative spectra shown in Fig. 3 were collected at 0 (start), 540, 900, 1020, 1140, 1380, 1560, 1740, 1920, 2100, and 2220 min after the initiation of the isothermal crystallization. Because the crystallization rate of P(HB-*co*-HHx) is slow, one can supercool the system away from the thermal equilibrium, and an amorphous sample can be obtained well below its  $T_{\rm m}$ . The time-dependent crystal growth of the supercooled melt was clearly revealed by the changes in intensity of the amorphous C=O band at 1739 cm<sup>-1</sup> and the crystalline C=O band at 1724 cm<sup>-1</sup>. The trend of the supercooled



Fig. 3. IR spectra of P(HB-*co*-HHx) (12 mol% HHx) in the C=O stretching vibration region measured during the crystallization of the supercooled melt at room temperature.

melt is similar to that induced by the gradual cooling crystallization shown in Fig. 1. The amorphous C=O band at  $1739 \text{ cm}^{-1}$  decreases while the crystalline C=O band at  $1724 \text{ cm}^{-1}$  gradually increases in intensity during the crystallization process. However, the details of spectral features for the supercooled melt crystallization are substantially different from those of the gradual cooling process. The crystalline band observed during the gradual cooling crystallization is more sharp and intense than that observed during the supercooled melt crystallization. This observation implies that the crystallinity of the gradually cooled sample is much higher than that of the sample crystallized from the supercooled melt at room temperature. In addition, the crystalline band observed during the gradual cooling process (Fig. 1) appeared very clearly as a wellseparated band at 1723 cm<sup>-1</sup> below the  $T_{\rm m}$  of the sample and developed down to room temperature. On the other hand, the crystalline band observed during the isothermal crystallization of the supercooled melt developed very slowly.

Fig. 4(A) and (B) shows the synchronous and asynchronous 2D correlation spectra in the spectral region of 1790- $1670 \text{ cm}^{-1}$  generated from the time-dependent IR spectra shown in Fig. 3. Two autopeaks developed at 1745 and  $1724 \text{ cm}^{-1}$  reflect the spectral variations of the amorphous and crystalline C=O bands, respectively. A pair of negative cross peaks appeared at (1745, 1724) cm<sup>-1</sup> indicates the opposite directions of the intensity variations in these two bands. The asynchronous spectrum (Fig. 4(B)) shows two pairs of asynchronous cross peaks at (1745, 1723) and (1728, 1723) cm<sup>-1</sup> similar to that for the gradual cooling crystallization case. This result indicates that the disappearance of the amorphous component does not proceed simultaneously with the appearance of the crystalline component during the supercooled melt crystallization. The two crystalline C=O bands at 1728 and 1723 cm<sup>-1</sup> for the supercooled melt crystallization also share asynchronous cross peaks, indicating the time lag between the increase in intensity of these two crystalline C=O bands. However, the signs of the asynchronous cross peaks shown in Fig. 4(B) are opposite to those shown in Fig. 2(B). The positive sign of the asynchronous cross peak at (1728, 1723)  $cm^{-1}$  and the corresponding positive synchronous spectral intensity suggest that the increase in intensity of the band at  $1728 \text{ cm}^{-1}$  occurs before that of the band at  $1723 \text{ cm}^{-1}$ , i.e., during the supercooled melt crystallization, the formation of the less ordered crystalline component proceeds before that of the highly ordered crystalline component. In other words, the order of crystal growth steps is different from that for the gradual cooling crystallization process.

#### 3.3. Solvent-cast film crystallization

Fig. 5 shows time-dependent IR spectra of P(HB-co-HHx) (12 mol% HHx) in the C=O stretching band region measured during the isothermal crystallization of the



Fig. 4. Synchronous (A) and asynchronous (B) 2D IR correlation spectra of P(HB-co-HHx) (12 mol% HHx) in the C=O stretching vibration region generated from the time-dependent IR spectra measured during the crystallization of the supercooled melt at room temperature.



Fig. 5. IR spectra of P(HB-*co*-HHx) (12 mol% HHx) in the C=O stretching vibration region measured during the crystallization of the solvent-cast film at room temperature.

solution-cast film. The representative spectra shown in Fig. 5 were collected at 0 (start), 75, 210, 240, 285, 315, 375, 420, 480, 660, and 1080 min after the initiation of the isothermal crystallization. The time-dependent crystal growth of the sample was also observed for the solution-cast film as indicated by the changes in intensity of the amorphous C=O band at  $1740 \text{ cm}^{-1}$  and the crystalline C=O band at  $1724 \text{ cm}^{-1}$ . The spectral variations shown in Fig. 5 are very similar to those for the supercooled melt crystallization shown in Fig. 3. The development of the crystalline C=O band proceeded slowly, and the band shape is not sharp and intense.

Fig. 6(A) and (B) shows the synchronous and asynchronous 2D correlation spectra in the spectral region



Fig. 6. Synchronous (A) and asynchronous (B) 2D IR correlation spectra of P(HB-co-HHx) (12 mol% HHx) in the C=O stretching vibration region generated from the time-dependent IR spectra measured during the crystallization of the solvent-cast film at room temperature.

of 1790–1670 cm<sup>-1</sup> generated from the time-dependent IR spectra shown in Fig. 5. The 2D correlation spectra shown in Fig. 6(A) and (B) are very similar to those generated for the supercooled melt crystallization shown in Fig. 4(A) and (B). Two pairs of asynchronous cross peaks appear at (1745, 1723) and (1728, 1723) cm<sup>-1</sup>. The signs of the asynchronous intensity reveal that the formation of the less ordered crystalline component proceeds before that of the highly ordered crystalline component during the crystallization of the solution-cast film. This order of crystal growth steps is the same as that for the supercooled melt crystallization.

# 3.4. Comparison among the three types of crystallization processes

2D IR correlation spectroscopy suggests that the order of crystal growth steps for the gradual cooling crystallization is different from that for the supercooled melt and solutioncast film crystallization. For the gradual cooling process, the development of the highly ordered crystals occurs prior to the formation of the less ordered crystals. On the other hand, for the supercooled melt and solution-cast film crystallization, the formation of the less ordered crystals takes place first, and the highly ordered crystals develop later.

In general, being kinetically controlled, structures formed during the crystallization of partially crystalline polymers are strongly affected by the thermal history and preceding processes. In the gradual cooling condition, the sample is slowly cooled from the melt to a temperature below the  $T_{\rm m}$ . At each temperature, the sample is allowed to reach the equilibrium state. Consequently, the crystallization occurs by nucleation and growth of spherulites [27]. The highly ordered crystals develop first and fill the specimen volume with a skeletal structure of crystalline lamellae. The inter crystalline regions, which remained amorphous, still have the potential to crystallize upon further cooling. The secondary crystallization follows at lower temperatures. The formation of the less ordered crystals proceeds via insertion into the original stack of the crystalline lamellae. The reduction of the order of these secondary crystals arises from the spatial constraint. The crystalline lamellae generated in the secondary crystallization are geometrically strained because they are sandwiched in the narrow space between the already existing lamellae. Clearly, the additional lamellae formed at lower temperatures are generally thinner, less uniform, and include more internal disorder [27].

For the supercooled melt crystallization, the sample is quenched rapidly from 140 to 25 °C. In this state, the crystallization is substantially retarded due to the reduced segmental mobility of the polymer when approaching the  $T_g$ . Under such a condition, the transition from the disordered phase to the higher ordered structure proceeds through a continuous sequence of states rather than building up a two-phase structure from the very beginning. The

increase in the crystallinity of the supercooled melt sample is very slow. The crystal growth occurs as the formation of numerous less ordered crystallites. The apparent reduction of the order in these crystallites arises from the interfacial effect of the very small size of crystals. The radius of curvature is too small to have a well-developed crystal. The interfacial effect is different from the effect of the over crowding by the volume filling crystal lamellae already existing as in the case of the gradual cooling crystallization. Once these tiny crystallites are formed, the additional growth of the highly ordered crystals, which is characterized by the band at  $1723 \text{ cm}^{-1}$ , will occur. In other words, for the isothermal crystallization of the amorphous solid at room temperature, the geometrically strained nuclei change to more ordered crystallites. This process, however, is very slow. The system is hardly at the crystal volume filled stage during the crystallization period. The solution-cast P(HBco-HHx) film exhibits similar crystallization behavior to that of the supercooled melt P(HB-co-HHx). The crystallization was carried out starting from the state in which the mobility of the entanglements is suppressed. The crystallization takes a long time to proceed. The very slow ongoing increase in the crystallinity with long times indicates the difficulty in approaching the perfect fully crystalline state of the sample. This lack of crystal growth results in the very weak intensity of the crystalline band observed for the supercooled melt and solution-cast film crystallization.

For all three types of crystallization, there is no asynchronous cross peak between the bands at 1745 and  $1728 \text{ cm}^{-1}$  in the 2D correlation spectra. This observation suggests that the transition from the amorphous state to the small crystallites with a less ordered structure is a one step transformation.

# 4. Conclusion

2D IR correlation spectroscopy was employed to study the crystallization behavior of P(HB-co-HHx) (12 mol% HHx). The order of crystal growth steps for the three different types of crystallization, i.e., the gradual cooling, supercooled melt, and solution-cast film crystallization, was investigated. The C=O stretching band region showed the coexistence of two crystalline bands, which might be assignable to the differently ordered crystalline parts of the polymer. The 2D IR correlation spectra generated for the C=O stretching band region suggested that, for the gradual cooling crystallization, the development of the highly ordered crystalline component proceeds prior to that of the less ordered crystalline component. On the other hand, for the supercooled melt and solution-cast film crystallization, the formation of the less ordered crystalline component occurs before that of the highly ordered crystalline component. The transition from the amorphous state to the less ordered crystalline component is a one step transformation for all three types of crystallization.

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