Short communication

Dependence of poly(3-hydroxybutyrate) crystal modifications on film thickness as revealed by reflection–absorption infrared spectroscopy

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ABSTRACT

Thickness-dependent ultrathin films of poly(3-hydroxybutyrate) (PHB) were investigated by using infrared reflection-absorption spectroscopy (IRRAS). It was first found that the autogenetic β-form of PHB could be easily obtained through confining the film thickness under 20 nm at room temperature. Moreover, the interphase of PHB simultaneously exists with the β-form of PHB in the films with a thickness less than 10 nm. With the film thickness increasing from several nanometers to about 30 nm, the PHB molecules gradually carry out an orientation shift at the b-axis of PHB crystallite; simultaneously, for the α-form of PHB a conformational rearrangement probably takes place for the growth of helical crystal unit cells in the ultrathin films. The molecular structures and crystal evolutions at sub–100 nm were explained in detail by analyzing the corresponding IRRAS features.

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1. Introduction

The aim of present work is to introduce a strategy for modulating the lamellae crystallite formation and polymorphous transformation at molecular level. With this strategy, the autogenetic β-form of poly(3-hydroxybutyrate) (PHB) film was first obtained at room temperature and shall be shown in this communication. Meanwhile, the characteristic band assignments and thickness-dependent crystal evolution for β and α phases of PHB will be discussed herein via monitoring the grazing-angle IR reflection absorption spectroscopy (IRRAS).

PHB is a nature and biosynthesized semicrystalline polymer attracting much attention as an environment-friendly biodegradable thermoplastic in the last decade [1–4]. However, the inherent features stem from the PHB molecular structure, e.g., high degree of crystallinity; the thermally unstable β-elimination reaction around the melting point (T_m) [5], highly hamper the mechanical processing of PHB polymer. The chemical structure of PHB is shown in Scheme 1. Although the copolymerization of 3-hydroxybutyrate

units with a longer 3-hydroxyhexanoate co-monomer [6,7] or blending PHB with cellulose derivatives [8–10] could significantly affect the mechanical and thermal properties of PHB, the PHB-based copolymers or blenders are hard to fulfill the demands in industrial applications. Recently, Iwata et al. succeeded in developing PHB films suitable for industrial and mechanical applications through producing the ultra-high-molecular-weight PHB (UHMW-PHB) and operating the hot-drawn and two-step drawing method [11,12]. Moreover, the first strong PHB fibers with Young's Modules of 2.9 GPa had been developed with this strategy [13]. Through measuring the time-resolved wide- and small-angle X-ray scattering (WAXD and SAXS), it had been known that the high tensile strength generates from the complicated networks formed by fibrils, i.e., the β-form of PHB (zig-zag conformation) and crystal lamellar stacks, i.e., the α-form of PHB (lamellar helical configuration) in the two-step drawn fibers [14].

Although the β-form of PHB had been proven to mainly contribute to the strong strength and its conformation had been proposed [13–15], the exact molecular information for the β-form of PHB is still largely unclear due to the highly skilled methods for producing the β-form of PHB by drawing α-form crystals. Even though the crystallization process of the PHB polymer had been clarified as a multistep process by measuring SAXS and WAXD [16], however, so far, most of the molecular configuration for the β-form

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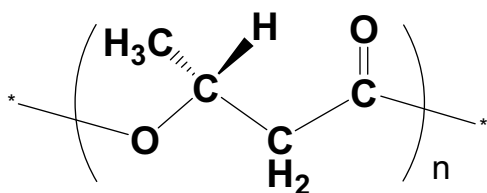
Scheme 1. Chemical structure of the PHB polymer.

of PHB was mainly concluded based on dispersion curve calculation or quantum chemical calculation [17,18]. Accordingly, proposing one way to produce the single β-form of PHB and experimentally exploring the microscopic origin of crystallite lamellar growth at molecular level will be very valuable for improving the processability and for extensively understanding the crystallization of the PHB polymer.

It is well documented that the physical properties of polymers and polymer blends will be profoundly affected due to the spatial confinement including molecular mobility [19,20], crystallization [21–26], when the film thickness is down to nanoscale. For example, based on X-ray diffraction and atomic force microscopy observations, Capitán et al. [23] reported that amorphous PHB thin films on glass could be obtained through spin-coating of PHB films at several tens of nanometers at room temperature; however, such crystallization is highly thickness-dependent. Due to the nano-confinement, we found in the present study that the PHB polymer maintains a highly thickness-dependent modification between α-form and β-form crystals by measuring the infrared spectra of PHB films at a nanoscale dimension (thickness < 100 nm). Under P-polarized infrared beam irradiation, the exact band assignments for the α- and β-form of PHB crystals were given; moreover, the evolution of molecular chain orientation in both forms of crystals are discussed.

2. Experimental

2.1. Materials and samples preparation

Bacterially produced PHB ($M_w = 4.3 \times 10^5$) was purchased from Sigma-Aldrich Corp. and was used as received. Ultrathin PHB films were prepared by first dissolving predetermined PHB powder into hot chloroform. After completely dissolving, the chloroform solution was cooled down to room temperature and was spun-cast onto a gold-coated ultra-flat glass wafer on a KW-4A spin-coater (Institute of Microelectronics of Chinese Academy of Sciences, China) at 4000 rpm for 1 min. After then, the wafer was quickly put into a vacuum oven at room temperature, ca. 20 °C for 2 h to remove any residual solvent. The obtained ultrathin film at 20 °C was named as-prepared PHB film hereafter. Conversely, a bulk film was prepared via evaporation of a 1% chloroform solution on a KBr window as reference. However, to completely remove the solvent, the bulk film was maintained at ~100 kPa for at least 12 h at room temperature after the majority of the solvent had evaporated.

The gold-coated glass wafers were obtained by sputtering chromium (2 nm) and gold (80 nm) in sequence onto a glass surface at rates of 0.1 nm s^{-1} in a diffusion-pumped chamber. Prior to use, the wafers were successively cleaned with pure ethanol, piranha solution (concentrated H_2SO_4 (98%)/H_2O_2 (30%) = 2:1), ultrapure water, and dried in a stream of nitrogen.

2.2. IRRAS spectroscopy measurements and analysis

The IRRAS spectra were recorded by a Bruker Tensor 27 spectrometer equipped with a MCT detector. Normal transmission mode and grazing incidence reflection-absorption mode in combination with a Polarization Modulation Accessory (PMA50) at an incident angle of 85° together with P-polarized irradiation were employed for the measurements of bulk and ultrathin films, respectively. Each spectrum was collected at a spectral resolution of 2 cm^{-1} with 32 scans co-added for an acceptable S/N ratio. Thicknesses of the ultrathin films were immediately measured on a step-profilometer (Model P10, KLA Tencor Cooperation, USA) after the spectral measurements. The intensity of infrared bands was calculated herein with a numerical data processor for vibrational spectroscopy, Spina (version 3.×23), which was developed by Yukiteru KATSUMOTO in the Ozaki group of Kwansei Gakuin University, Japan. In the present study, all spectra were pretreated with a linear baseline correction before starting the automatic intensity calculation to minimize the baseline instability and other non-selective effects.

3. Results and discussion

3.1. Thickness-dependent IRRAS spectral changes of ultrathin PHB films as-prepared at room temperature

Fig. 1 shows the measured IRRAS spectra in the regions of 3100–2800 cm^{-1} and 1800–850 cm^{-1} of ultrathin PHB films with different thickness as prepared at room temperature (RT), ca. 20 °C. To easily observe the spectral variances, the normal transmission FTIR spectrum of a bulk PHB film collected at RT was added into Fig. 1 (red trace). Comparing with the bulk film, as shown in Fig. 1, several new spectral features appear in the IRRAS spectra of ultrathin films. For example, this is obvious for bands in the region of 1800–1700 cm^{-1} assigned to the C=O stretching vibration [27–30]: the band at 1726 cm^{-1} that can be associated with the ν(C=O) of α-form of PHB increases relatively versus the band at 1749 cm^{-1}, assigned to ν(C=O) of the amorphous form with an increase in film thickness. In addition to the remarkable changes related to C=O group, the characteristic bands associated with CH$_2$, C—O—C, C—O and C—C vibrations also show distinct differences between the ultrathin and bulk PHB films [30–34]. Two strong bands at 1297 and 1264 cm^{-1}, present in the IRRAS spectra of ultrathin films, are dominant instead of the highly overlapped bands associated with CH bending and C—C—O stretching centered at 1300 cm^{-1} in the bulk specimen spectrum. Furthermore, several bands, i.e., at 1135 cm^{-1} and 1047 cm^{-1}, relatively decrease in intensity with an increase in film thickness under a P-polarized infrared beam.

Surprisingly, several remarkably strong bands, i.e., at 1264 cm^{-1}, 1135 cm^{-1} and 1047 cm^{-1}, are present in the spectrum of a PHB film with a thickness of ~7 nm. According to the calculation of phonon dispersion using a Urey-Bradley force field as executed by Chaturvedi et al. [17], these bands stem from the zig-zag conformation of the β-form of PHB. The unusual intensity of these bands indicate that the as-prepared ultrathin film with a thickness ~7 nm holds a large fraction of the β-form of PHB. On the other hand, the single band centered at 1222 cm^{-1} (marked with a red asterisk) confirms that the helical α-form crystal configuration does not exist within this film. The helical configuration of the α-form of PHB, characterized by a characteristic band at 1229 cm^{-1}, gradually forms into the as-prepared ultrathin films as the film thickness increases, which is especially true, when the film thickness is larger than 20 nm. In the spectrum of the PHB ultrathin film with a thickness of ~7 nm, a novel band that had been hardly mentioned before clearly appears at 1358 cm^{-1}, gradually disappearing with an increase in film thickness. Although the exact assignment for this band is still not clear, it is reasonable to assign this single band to the β-form of PHB. Interestingly, the noted ν(C=O) band assigned to the interphase of