

Higher order conformation of poly(3-hydroxyalkanoates) studied by terahertz time-domain spectroscopy

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Terahertz absorption spectra of poly(3-hydroxyalkanoates) with different conformations were measured by using a terahertz time domain spectrometer. Sharp absorption peaks were observed in the spectrum of crystalline samples. The orientation direction of the transition dipole moment was investigated by the polarization spectra. The peak at 2.92 THz was assigned to a vibration of helical structure along the fiber axis, and the peak at 2.49 THz was attributed to a vibration due to the hydrogen bonding between helix structures. The temperature dependence of the spectra reflects the change in the hydrogen bonding distance and melting process of the crystalline structure. © 2010 American Institute of Physics. [doi:10.1063/1.3358146]

Due to the recent rapid development of spectroscopic techniques in terahertz (THz) range, observation of molecular vibrations in a lower frequency region has become much easier.¹ Terahertz time-domain spectroscopy (THz-TDS) has substantially improved the signal-to-noise ratio in the frequency range between 0.1 to 3 THz. A number of characteristic spectra of organic molecules (so-called fingerprint spectra) have been observed.² Since the origin of those spectra is skeletal motions coupled with intermolecular vibrations,³ information about intermolecular interactions, such as hydrogen bonding, can be effectively probed by the THz spectroscopy. Hydrogen bonding is one of the dominant interactions which determine the higher order conformations of large molecules, such as proteins, DNAs, and polymers. Therefore, THz spectroscopy should help to understand how large molecules form higher order conformation.

In the present study, absorption spectra of poly(3-hydroxybutyrate) (PHB) and its copolymers were obtained by using THz-TDS technique. Poly(3-hydroxyalkanoates) (PHA) have received keen interest as one of biodegradable plastics.^{4,5} Their physical properties, hardness and degradability change with its higher order conformation have been the subject of active study.^{4,6} Figure 1 shows the chemical structure and schematic diagram of the conformation of PHB, which have been determined by wide angle x-ray diffraction measurements.⁷⁻⁹ In the crystalline phase, molecular chains make up the lamellar crystal in which helical structures align along the *c*-axis. In the amorphous phase, the molecular chains tangle randomly. The dashed lines show the hydrogen bonding between the C=O group and the CH₃ group.^{8,10} Previous studies revealed that the direction of the hydrogen bonding in lamellar crystal is parallel to the *a*-axis.⁸⁻¹⁰ Contents of amorphous and crystalline phase, and the thickness of lamellar structure change with the temperature conditions used during the crystal growth.

Figure 2 shows the THz absorption spectra and microscope images of four different types of PHA samples. The spectra were measured by using THz-TDS (Aispec: *pulse* IRS-2300) with the frequency resolution of 0.03 THz. Absorbance was calculated by dividing the thickness of the sample. The microscope image was taken by optical microscope (Keyence VH-Z450). Samples (a) and (b) are isotactic PHB homopolymer (Aldrich Corp.), and sample (c) is a PHA copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) [P(HB-*co*-HHx)] with 2.5 mol % 3-hydroxyhexanoate (HHx) units (Procter & Gamble Co.). The difference of chemical structure between HB and HHx lies in the size of side group, i.e., the CH₃ group of HB is replaced by the C₃H₇ group in HHx. The film samples (a)–(c) with the thickness of about 100 μm were prepared from powder with the following procedures. The PHA powder was melt at 185 °C, pressed (below 0.5 N/mm²), and then cooled down to 40 °C either slowly in 2 h [sample (a) and (c)], or rapidly in 10 min [sample (b)]. Sample (d) is a synthetic amorphous atactic PHB (Procter & Gamble Co.). Since amorphous PHB is a viscous liquid at room temperature, we spread the sample directly to a polypropylene window and measured the spectrum. The absorbance of sample (d) was obtained by using the spectrum of the window as a reference. Because of the

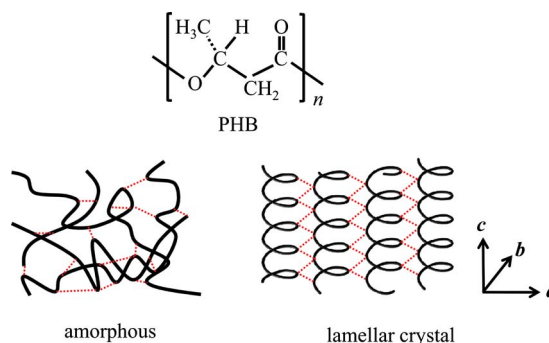


FIG. 1. (Color online) Chemical structure of PHB and schematic diagram of molecular structure in amorphous and lamellar crystal.

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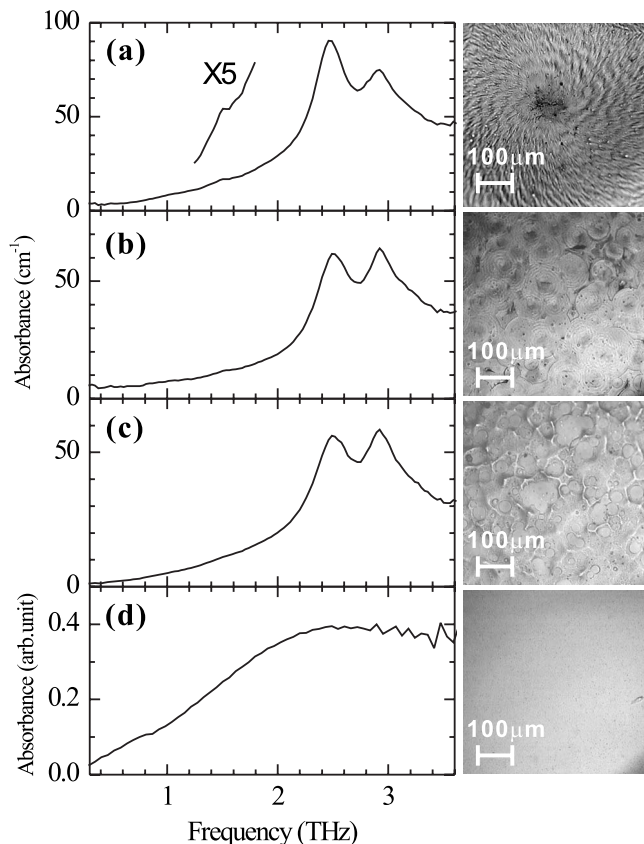


FIG. 2. THz absorption spectra and microscope images of four different types of PHA: (a) slowly crystallized PHB, (b) rapidly crystallized PHB, (c) slowly crystallized P(HB-co-HHx), and (d) amorphous atactic PHB. The insertion in the spectrum of sample (a) shows an expanded spectrum by five times.

difficulty in measuring the precise thickness, absorbance of sample (d) in Fig. 2 is given in an arbitrary unit. To reduce the spectral artifacts due to the multireflection in the samples, the samples were placed at 55° angled to the THz propagation direction, which is the Brewster's angle when the refractive index of the samples is about 1.4.

Factors affecting the morphological properties of semicrystalline polymers, such as size of spherulite structures shown in the microscope images, are of both scientific and practical interest. The spherulite structure is the aggregation of crystal lamellae which grow from the center of the sphere toward the outside. The size of spherulite structures of sample (a) is more than five times larger than those of sample (b), probably because of the slow cooling of the sample helping the unhindered crystal growth. In the microscope image of sample (c), the spherulite structure is much smaller than sample (b). Due to the large size of its side group, the HHx unit breaks the crystal structure of the polymer, and the size of crystal lamellae in P(HB-co-HHx) becomes smaller and amount of amorphous phase increases.⁴ The microscope image of sample (d) is flat and has no spherulite structure due to the lack of the crystalline structure. From the microscope images, the degree of unhindered spherulite growth is determined as (a) > (b) > (c) > (d).

In the THz spectra of crystalline PHB [sample (a)], two major peaks are found at 2.49 and 2.92 THz, and a weak absorption peak is observed around 1.5 THz. In contrast, the amorphous PHB shows only a broad absorption feature in the entire spectrum region. This broad feature is attributed to

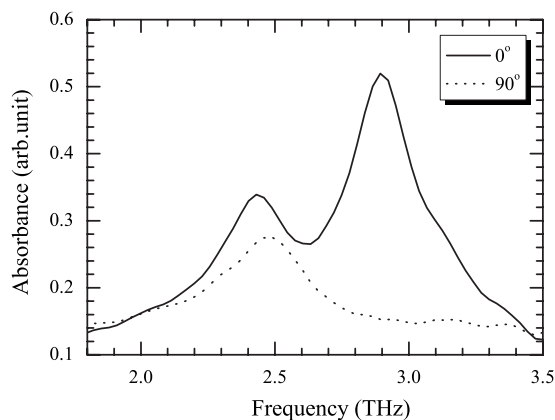


FIG. 3. Polarized THz absorption spectra of highly stretched PHB. The angle between stretched direction and electric field of the THz wave was set to 0° and 90° .

the libration band of polymer chain, which has been observed in the THz spectra of various polymers.¹¹ It can be seen that the absorbance in the 1–2 THz region of sample (c) is slightly higher than that of sample (a) and (b), which is probably due to the increase in the amorphous phase in P(HB-co-HHx). However, the rise of the baseline in the spectra appears not only due to the absorption by the amorphous phase but also due to the Mie scattering by the spherulite structure of the sample. It is difficult to estimate the amount of amorphous phase quantitatively by the spectra. According to the sharpness of the linewidth and the increase in the absorbance with the crystallinity, the peaks at 2.49, 2.92, and 1.5 THz can be assigned to the lattice vibrations of the lamellar crystal of PHA. The relative intensity of the peak at 2.49 and 2.92 THz changes with the speed of the crystal growth [sample (a) and (b)] and the contamination of HHx units [sample (a) and (c)]. The intensity of the 2.49 THz peak increases with the size of spherulite structure and the degree of crystallinity.

To make an assignment of those peaks, polarization spectra of highly stretched PHB was measured. The stretched PHB was prepared by drawing a sheet of PHB up to 1000% at 165°C and annealing for 2 h at 100°C . Under such high level of drawing, the *c*-axis of PHB is known to align in the direction of stretching.¹² Figure 3 shows absorption spectra of stretched PHB measured by changing the angle between the stretching direction and the polarization of THz radiation. Of note is that the peak at 2.92 THz completely disappears when the electric fields of THz radiation is oriented perpendicular to the *c*-axis, which means that the vibrational dipole transition moment of this peak must be oriented in the direction parallel to the *c*-axis. Most probably, this mode is a spring like motion of helical structure. On the other hand, the peak around 2.5 THz remains when the THz polarization is perpendicular to the *c*-axis. It is not clear at this moment whether the peak around 2.5 THz truly shifts by the orientation angle or two modes are overlapped in this frequency. It is, however, very clear that the absorption around 2.5 THz is due to the vibrational dipole transition moment which is not parallel to the *c*-axis. Given the fact that hydrogen bonding interaction in the PHA crystal lamellae exists along the *a*-axis, the peak around 2.5 THz may well be a vibrational mode due to the hydrogen bonding. As shown in Fig. 2, the intensity of the peak at 2.49 THz increases when the crystal-

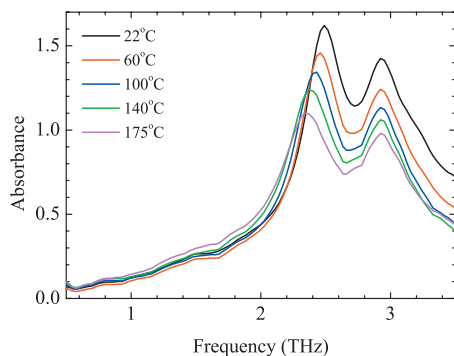


FIG. 4. (Color) THz absorption spectra of stretched PHB measured at different temperatures.

linity of PHB increases. This result can be explained by the increase in the hydrogen bonding interaction in the sample.

The temperature dependence of the spectra supports the above assignments. Figure 4 depicts the absorption spectra of semicrystalline PHB [sample (a)] measured at different temperatures. As the temperature increases, the peak at 2.49 THz shifts toward lower frequency and reaches to 2.35 THz at 175 °C. On the other hand, the frequency shift of the peak at 2.92 THz is negligibly small. From the result of wide angle x-ray diffraction,⁹ coefficients of thermal expansion along the *a*- and *b*-axis were determined, respectively, as 1.6×10^{-4} and 3.6×10^{-5} . The large frequency shift of the peak at 2.47 THz may be due to a change in the thermal expansion along *a*-axis, which changes the distance of C—H···O=C hydrogen bonding. As the temperature increases, the intensities of peaks at 2.47 and 2.92 THz decrease, and the baseline of the spectrum arises. This change reflects the change in molecular conformation from lamellar crystal to amorphous phase, which has already been observed in IR spectra of PHB and P(HB-*co*-HHx).¹⁰

In the present study, three different types of vibrational modes of different types of molecular conformation of PHA were observed in the THz spectra as follows: the libration of polymer chain in amorphous phase, vibration of crystal

lamellae along to the *c*-axis, and the vibration due to the hydrogen bonding interaction between helical structures. In the previous studies,^{8–10,13} the hydrogen bonding in PHA has been studied by IR spectroscopy as shifts of C—H and C=O fundamental modes. The difference between amorphous and crystalline structure has also been observed. However, the detail of the conformational information was difficult to obtain because the fundamental modes are the local vibrations and the global motions of molecular chain are hard to be coupled with. In contrast, vibrational modes in THz region are global and provide detailed information about the higher order conformation of large molecules.

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