

テラヘルツ周波数領域における高分子の振動分光

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Vibrational spectroscopy of polymer in terahertz frequency region

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Introduction

Absorption spectra of organic molecules in THz frequency region (0.1-10 THz) show vibrational peaks which reflect their molecular structure. In particular, intermolecular interactions such as the hydrogen bond are key to understanding THz spectra, because THz spectral features dramatically change with the intermolecular conformations. THz spectroscopy may become a powerful tool to investigate polymers because their physical properties highly depend on their intermolecular conformation.

In this paper, THz absorption spectra of polymers containing hydrogen bonds were studied. The hydrogen bond is one of the tightest intermolecular interactions which make firm crystal structures in polymers. The spectra show absorption peaks due to the vibration of the hydrogen bonds.

Experiments

THz absorption spectra of two kinds of polymers, PHB and Nylon, were measured. The samples were first melted and then slowly cooled down to room temperature to form a film shape. A THz time-domain spectrometer (AISPEC pulse IRS 2300) and a Fourier transform far infrared spectrometer (ABB Bomem Inc.: DA8, JASCO FARIS) were used for the measurement. For the polarization spectroscopy, the samples were heated to 165 °C and stretched to align the direction of the crystal axis. Temperature dependent spectra were measured by controlling the sample temperature with a liquid-helium-cooled cryostat and a heating stage.

Results and Discussions

Figure 1 shows the absorption spectra of PHB measured at 10 K, 300 K, and 440 K. The peak positions shift with the temperature due to the anharmonicity of the vibrational potential (shown by the dashed lines). The polarization dependence of

the peaks is shown on the top of each peak, and was obtained by changing the angle between the THz electric field and the *c* axis of the crystal. Polarization dependence helps us to understand the direction of vibrational dipole moments. We have also measured low-frequency Raman scattering in this frequency region. THz and Raman spectra were compared with the DFT calculations with Cartesian coordinate tensor transfer method, and vibrational modes of the peaks are assigned. For example, the peak at 2.82 THz has a vibrational dipole moment perpendicular to the *c* axis, and is observed in both THz and Raman spectra. This mode was assigned as the combination band of C=O and CH₃ bending motion, which changes the distance of C=O...H-C hydrogen bond.

We applied those assignments for the study of polymer-crystallization process.

PHB was isothermally crystallized at 90 °C and spectral change was observed as a function of time. By using two-dimensional correlation spectroscopy, spectra clearly show the sequential change of the peak intensities, which clearly suggests that vibration of hydrogen bond grows faster than the other modes during crystallization.

Conclusion

THz spectra of PHB were measured and successfully assigned. The results of the assignment provide information about higher order conformation and the role of hydrogen bonds in the crystallization of PHB. We also measured Nylon polymers that have N-H...O=C hydrogen bonds. Detail of those results will be discussed.

Reference

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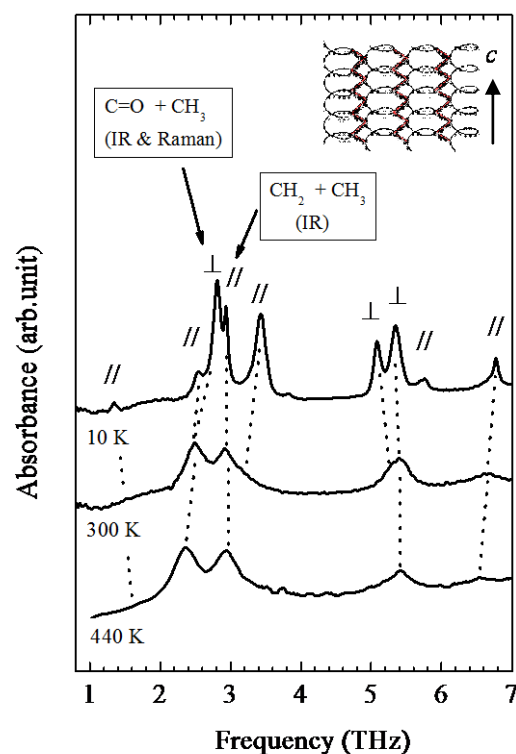


Fig. 1: THz absorption spectra of PHB measured at 10 K, 300 K and 440 K. Polarization and assignments are shown.