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Brill transition of nylon-6 characterized by low-frequency vibration through terahertz absorption spectroscopy

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ABSTRACT

With the aim of opening a route toward new applications of terahertz (THz) spectroscopy to studies of polymer science, the conformations and structural transitions of polycaprolactam (nylon-6) were investigated by THz spectroscopy in the α, γ, pseudo-hexagonal, and amorphous phases. A Brill transition from the α form to the pseudo-hexagonal form was detected at 160 °C from a temperature variation of the peak intensity at 6.6 THz in the second-derivative spectrum of nylon-6. In the amorphous phase, a glass transition was observed at 60 °C, and a new anomaly was found at 110 °C.

Recently, spectroscopic techniques in the terahertz (THz) range, such as THz time–domain spectroscopy (THz-TDS), have undergone rapid development, facilitating investigations of molecular vibrations in a lower frequency range[1,2]. One of the most promising applications of THz spectroscopy to material science is of investigating conformations of soft materials such as polymers. Conformations of soft materials are important indicators of their functionality; however, the detailed structures of soft materials have rarely been clarified thus far. The difficulty in analyzing those conformations by conventional X-ray or neutron crystallography comes from the disorder in their molecular arrangements. Conformational studies of such disordered systems have been conducted by nuclear magnetic resonance (NMR) [3] and vibrational spectroscopy [4]. NMR is advantageous in providing information about the local conformation, because magnetic dipoles interact with each other over a short distance. Mid-infrared (MIR) and Raman spectroscopy [5] are also good for investigating the local molecular structure [6], because they expose intramolecular vibrations. To investigate global conformation, low-frequency vibrational spectroscopies such as THz and far-infrared (FIR) spectroscopy [7–9], low-frequency Raman scattering [10,11], and inelastic neutron scattering (INS) [12,13] are more useful for observing intermolecular interactions. These methods are different in their selection rules and are complementary to each other. THz spectroscopy is suitable for investigating the dynamics of hydrogen bonds (H-bonds), since it directly measures the dipole transition [14]. It is also advantageous in that the time resolution of THz-TDS is on the order of picoseconds, which is expected to soon lead to ultra-fast investigations of molecular dynamics, such as THz pump–probe spectroscopy for exploring the vibrational relaxation or time evolution of conformational changes.

Despite the long history of investigations, the conformation of polymers in relation to the molecular dynamics has not been fully understood and is even now under intense research [15]. THz spectroscopy has recently received attention with the expectation that it will provide new insights into complex polymer conformations, and several relevant studies have been reported. For example, Koch et al. succeeded in observing the glass transition of several polymers in their amorphous phases by using THz-TDS [16,17]. Similarly, Fuse et al. succeeded in assigning a peak of polylactide at 1.5 THz to molecular vibrations parallel to the molecular helical axis in amorphous regions [18]. In our previous work, we revealed that the THz spectrum of poly(3-hydroxybutyrate) (PHB) depends significantly on the conformation and we succeeded in assigning the absorption peaks [19,20]. In addition, the temporal evolution of THz spectra showed that the crystallization of PHB at 90 °C is a two-step process in which the H-bonds are initially formed before well-defined crystal structures are established [21].

In the present work, we measured the THz spectra of polycaprolactam (nylon-6) in various solid states, and succeeded in detecting a phase transition (known as the ‘Brill transition’) and a glass transition, in addition to a new anomaly in the amorphous phase. Although the low-frequency molecular vibration of nylon-6 has been investigated by FIR [22,23], Raman [11], and INS [13], its Brill transition has not been a subject of research. To the best of our knowledge, this is the first observation of the Brill transition in

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the low-frequency vibrational mode, i.e., intermolecular vibration, by THz spectroscopy.

Nylon-6 is one of the well-known polyamide fibers (nylons) used in various industrial products. The molecular chain of nylon-6 is represented by a repeating unit of [–NH–CO–$(CH_2)_5$–], and the neighboring chains are connected by strong H-bonds (N–H···O═C) which contributes to its superior mechanical strength and toughness [24]. Nylon-6 shows rich crystalline polymorphism, in which different structures possess different H-bond configurations; hence, it is interesting how H-bonds contribute to polymer conformation and to THz spectra.

The phase behavior and crystal structures of nylon-6 have been studied by various methods [13,22,25–27], and two crystalline forms (α and γ) of nylon-6 are well known [28,29]. The α form is monoclinic, where H-bonds connect to neighboring antiparallel chains, forming a sheet structure. The distance between neighboring sheets is shorter than that between H-bonded chains which results in different lattice parameters, $a \neq c$ (a = 9.56 Å, and c = 8.01 Å [29]). The γ form of nylon-6, however, consists of molecular chains with H-bonds between parallel chains. The γ form is also monoclinic, but the lattice parameters a and c are similar (a = 9.56 Å, and c = 9.33 Å [30]), and the angle between them is close to 60°, which is close to the hexagonal structure. The α and γ forms are clearly distinguished by the position of their diffraction peaks of (200) and (002/202) reflections. Thermodynamically, the α form is more stable than the γ form [27]. Upon rapid cooling from the melt, nylon-6 prefers to crystallize first into the metastable γ form, which can then transform into the α form through annealing at a temperature slightly below the fusion point ($T_{fus} \approx 220$ °C). The α form has a Brill transition at ~160 °C [31], which has mainly been studied by X-ray crystallography [31,32] and IR spectroscopy [33]. The conformation above the transition is close to the hexagonal structure, which is often called the 'pseudo-hexagonal form'. The pseudo-hexagonal form has often been confused with the high temperature state of the γ form [28]. A sequence of IR bands in the α form is known to disappear in the pseudo-hexagonal form, but this phenomenon has not been explained in detail thus far. Similar to most crystalline polymers, the crystallites of nylon-6 are surrounded by an amorphous phase, which has a glass transition at $T_g \approx 54$ °C [25,28]. The degree of crystallinity depends on the cooling rate from the melt, and hence, a sample with a large proportion of the amorphous phase can be obtained by rapid cooling from the melt.

We first investigated the THz spectra of nylon-6 in different solid conformations. Nylon-6 pellets were purchased from Sigma–Aldrich. The pellets were first heated above the fusion temperature and then pressed into a film with a thickness of ~100 μm. We prepared three types of samples using different thermal treatments. Sample (a) was obtained by dipping the melted film into liquid nitrogen. The cooling rate was about −400 °C s^{-1}. Sample (b) was obtained by rapidly cooling (−100 °C s^{-1}) the melted sample down to 110 °C and then maintaining it at this temperature for 16 h. Sample (c) was obtained by slowly cooling (−5 °C min^{-1}) the melted sample down to 160 °C and then maintaining it at this temperature for 16 h. The crystalline forms of the three samples were verified by X-ray diffraction (XRD) measurements, which were conducted at room temperature using an Ultima IV (Rigaku) diffractometer with CuKα (λ = 0.154056 nm) radiation. The results are shown in Figure 1A. The XRD pattern of Sample (a) shows a broad peak centered at 21°, which is typical for the amorphous phase. A tiny cap on the top of the broad peak indicates that a small portion of the γ form is present. For Sample (b), a sharp peak is clearly observed at 21.5° on top of the broad peak, indicating that the γ form has been achieved. The XRD pattern of Sample (c) shows two peaks at 20° and 24°, which are typical for the α form.

THz spectra (0.5–20 THz) for these three samples were obtained by Fourier transform far-infrared (FT-FIR) spectroscopy with a frequency resolution of 0.06 THz. It should be emphasized that the samples were identical to those used for the XRD measurements. The FT-FIR measurements were conducted at room temperature using FARIS (JASCO) equipped with a deuterated triglycine sulfate (DTGS) detector (8–20 THz) and a Si bolometer (0.5–8 THz). The film samples were horizontally oriented during the measurements and the sample space was purged with nitrogen gas to reduce water-vapor absorption. The spectrum of Sample (a) (amorphous phase) shows broad peaks at 3 and 9 THz. Sample (b) (containing the γ form) shows similar peaks, although these peaks are sharper than those of Sample (a). Sample (b) also shows sharp peaks at 13.5, 15.5, and 17.5 THz, indicating the formation of a crystalline phase. The spectrum of Sample (c) (containing the α form) is clearly different from the spectra of the other samples, in particular below 10 THz, where additional peaks are observed at 2.0 and 6.5 THz. Moreover, the large peak at 9 THz for Samples (a) and (b) shifts down to 8.8 THz for Sample (c). The results of Samples (a) and (c) are consistent with those of a previous study by Matsubara et al. [22] It is interesting that the result of Sample (b) (the γ

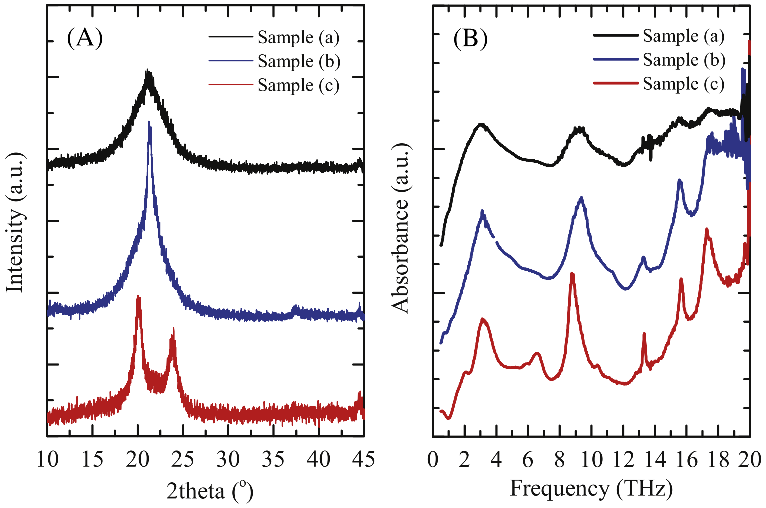

Figure 1. (A) XRD patterns and (B) THz absorption spectra of three kinds of nylon-6 samples: Sample (a), Sample (b), and Sample (c). Sample (a) is in the amorphous phase, and Sample (b) and Sample (c) contain the γ and α forms, respectively.