



Low-frequency vibrations of polyamide-6 as a function of temperature and thermal history investigated by terahertz absorption spectroscopy

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ABSTRACT

The α and γ crystals of polyamide-6 were examined by terahertz absorption spectroscopy from -90 to 230 °C. For the α crystals, the absorption band at 6.5 THz, assigned as a lattice vibration perpendicular to the molecular chain, decreased in intensity with increasing temperature, ending near the Brill transition temperature ($T_{\text{Brill}} \approx 160$ °C). The band at 8.7 THz, assigned as the skeletal vibration along the molecular chain, shifted to higher frequency with increasing temperature. The rate of shift changed at the glass transition temperature ($T_g \approx 50$ °C), indicating coupling of the molecular vibration in the crystal with freezing/relaxing phenomena in the surrounding amorphous phase. A significant annealing effect was observed. On heating polyamide-6 films that had been annealed at a temperature (T_{ann}) ≥ 80 °C, an increase in spectral intensity above 9 THz occurred at $\sim T_{\text{ann}}$, due to the melting of semi-crystals formed by recrystallization during annealing.

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1. Introduction

The physical properties of crystalline polymers are difficult to investigate in detail because of their inhomogeneous, non-equilibrium natures. To achieve a complete understanding of these materials, comprehensive studies that consider the crystal structure, crystallinity, crystal size, and their dependence on temperature and thermal history are needed. Recently several works have been published, discussing the relation between structure and dynamics in crystalline polymers by combining techniques of neutron and X-ray scattering, and dielectric spectroscopy [1–3]. The interplay between inter- and intramolecular dynamics in amorphous polymer has also been revealed by dielectric spectroscopy, nuclear magnetic resonance, infrared spectroscopy, and differential scanning calorimetry [4]. In this work, we investigated the low-

frequency vibrations of crystalline polyamide-6 (PA6) to elucidate the intermolecular vibrations and molecular conformations changing as functions of temperature and thermal history.

PA6, also known as nylon-6, is a crystalline polymer used in various industrial products. Consisting of repeating $[-\text{NH}-\text{CO}-(\text{CH}_2)_5-]$ units, the polymer chains are connected intermolecularly by hydrogen bonds ($\text{N}-\text{H}\cdots\text{O}=\text{C}$). PA6 shows crystalline polymorphism, and two crystalline phases (α and γ) are well known (Fig. 1) [5–12]. In the α crystals, neighboring extended chains are connected by hydrogen bonds to form a sheet structure. The distance between neighboring sheets is shorter than that between hydrogen-bonded chains, which results in an asymmetric lattice structure, $a \neq c$. The γ crystals, on the other hand, consist of twisted molecular chains, and the lattice constants a and c are close in value. Thermodynamically, the α crystal is more stable than the γ crystal [9]. Upon rapid cooling from the melt, PA6 prefers to crystallize first into the metastable γ crystal, which can then transform into

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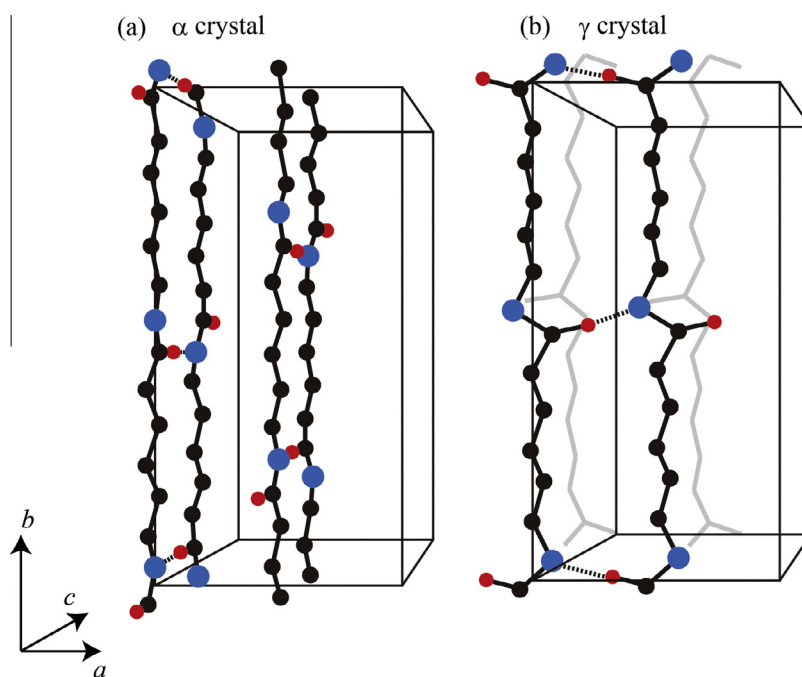


Fig. 1. Schematic representation of crystal structures for (a) α and (b) γ crystals.[12].

the α crystal by annealing above 120 °C [13]. The α phase undergoes a structural transition, known as the Brill transition, at $T_{\text{Brill}} \approx 160$ °C. As the temperature rises from room temperature, the values of the a and c lattice constants gradually converge, and coincide at T_{Brill} . The higher temperature phase is called the α' crystal or pseudo-hexagonal (PH) phase, in which the lattice parameters a and c are nearly equal and librational motion of the molecular chain is possible [14–16].

The crystallites are surrounded by an amorphous phase which has a glass transition at ~ 54 °C (T_g) [6,10]. The degree of crystallinity depends on the cooling rate from the melt, i.e., the amorphous portion increases with increasing cooling rate. Since the boundary between the crystalline and amorphous phases is not clear, various intermediate states have been proposed, such as imperfect crystals [17] or rigid amorphous phases [18]. Such intermediate states continuously reorganize to more ordered states with time and temperature [13].

THz absorption spectroscopy detects low-frequency vibrational modes between 0.1 and 10 THz. As techniques for the generation and detection of THz waves have been developed in recent years [19], THz spectroscopy has recaptured interest in various research fields [20–23]. For polymers, rich spectral features are observed in this frequency range, such as skeletal vibrations and the libration of side groups [24–32]. As these motions are strongly coupled with intermolecular motions, assignment is usually not a straightforward task. In crystalline polymers, lattice phonon modes can also be detected, which depend sensitively on the crystal structure. Therefore, THz spectroscopy provides information not only about the local conformations in the polymer chains but also about the packing structures of the chains.

In this work, we measured the THz absorption spectra of PA6 in different condensed forms under various thermal conditions. By comparing those results with differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements, the conformational changes due to temperature variations and thermal history were investigated in detail.

2. Experimental

PA6 pellets ($M_w \approx 10,000$; $\rho \approx 1.08$ g cm $^{-3}$) were purchased from Sigma Aldrich and used without further purification. The pellets were first heated above the fusion temperature and then pressed into a film with a thickness of 100–200 μ m. α and γ crystals were obtained by annealing the supercooled liquid at 190 °C (15 h) and 100 °C (5 h), respectively. Since crystallinity depends sensitively on thermal history, one piece of the sample film was divided into several pieces for analysis by THz spectrometry, XRD measurement, and DSC.

The THz spectra (1–11 THz) were obtained by Fourier-transform far-infrared (FT-FIR) spectroscopy with a frequency resolution of 0.06 THz. The measurements were conducted using a JASCO FARIS instrument equipped with a high-pressure mercury lamp, Mylar beam splitter, and a Si bolometer. The sample chamber was purged with dry nitrogen gas to reduce the absorption of water vapor. The film sample was placed on a highly resistive Si plate that was horizontally attached on a temperature-controlled heating stage (Linkam 19113L). A transmission-type optical geometry was adopted. The sample temperature was changed from -90 to 230 °C, which was indirectly measured using a platinum resistor sensor attached on the heating stage. The temperature difference between the

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