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Broadband terahertz time-domain spectroscopic study on form II polyvinylidene fluoride

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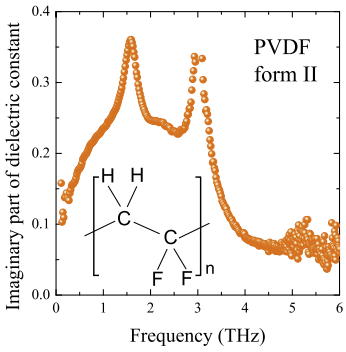
HIGHLIGHTS

- The THz complex dielectric constant of form II PVDF was determined by broadband THz-TDS.
- Four phonon modes and a broad relaxation mode were clearly observed.
- The glass transition temperature of form II PVDF was determined by THz-TDS.

GRAPHICAL ABSTRACT



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ABSTRACT

The complex dielectric constant of semicrystalline form II polyvinylidene fluoride (PVDF (II)) in the frequency range from 0.2 to 6.0 THz has been determined by broadband terahertz time-domain spectroscopy (THz-TDS). The obtained dielectric constant consists of superposition of four vibration modes at 1.60, 2.36, 3.04 and 5.31 THz of crystalline part and a broad relaxation mode with center frequency of 0.68 THz which will be attributed to boson peak of amorphous fraction. In addition, the temperature dependence of the dielectric constant has also been measured, and we have determined the glass transition temperature of amorphous fraction of PVDF (II) as about 192 K by analysis of the temperature variation of peak frequency of the lattice vibration mode.

Introduction

PVDF is a semicrystalline polymer which exhibits a polymorph of crystalline forms, and form I PVDF with TT conformation chain is known as one of the ferroelectric polymers [1,2]. PVDF (II) is non-polar and the most stable crystalline form having TGTG' conformation with point group of C_{2h} [2]. These semicrystalline polymers are known to consist of crystalline lamella regions and amorphous fractions, and glass transition of amorphous fraction of PVDF occurs and this transition influences to the thermal behavior of those lattice vibration mode in the crystalline lamella at THz frequency region [3]. The optical vibration modes of PVDF have been extensively investigated and assigned by infrared [4–6] and Raman [6,7] spectroscopy studies. In a THz region, several intermolecular and intramolecular vibration modes of PVDF (II) have been reported [3,5]. In addition, a broad and temperature independent

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relaxation-type absorption along *c*-axis, which along polymer chain, has been reported at around 0.5 THz by far-infrared spectroscopy [8], but an accurate entire structure of this mode has been unclear.

Development of THz-TDS in recent decades enables an accurate determination of both real and imaginary parts of complex dielectric constants of materials in a far-infrared region [9–11]. By obtaining the amplitude and phase of THz pulse simultaneously, we can directly determine the dielectric property without any assumption or Kramers–Kronig analysis. However, one of disadvantage of THz-TDS is a long measurement time due to the mechanical delay stage. The measurement time of the THz time-domain *E*-field waveform by conventional THz-TDS is about several minutes and this long measurement time causes inaccuracy and less number of trials in experiment. Recently, ultrafast THz-TDS measurement technique has been established utilizing high-speed asynchronous optical sampling (AOS) technique [12]. This technique uses two femtosecond lasers in substitution for mechanical delay stage. The AOS technique drastically decreases measurement time down to about 10 ms for one shot of THz pulse. In addition to the ultra-fast scan of THz-TDS, we can use widely tunable monochromatic Cherenkov phase-matched THz wave generator, which was developed using nonlinear optic crystals of ferroelectric MgO doped $LiNbO_3$ (LN) [13,14].

In this paper, we have performed broadband THz-TDS measurements with transmission configuration to investigate the far-infrared dielectric properties of PVDF (II).

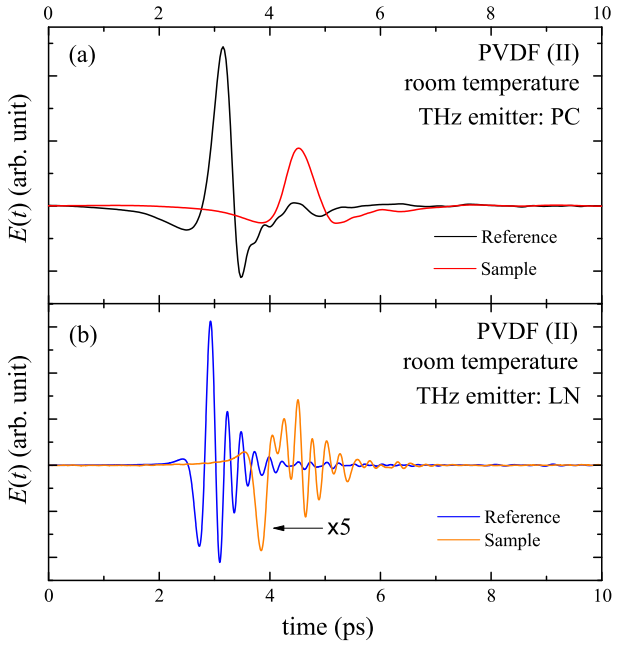

Fig. 1. The time-domain *E*-field waveforms of the reference (solid blue line) and PVDF (II) (solid orange line) measured by (a) RT-10,000 and (b) TAS7500SU. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Experimental

We have prepared a pellet of PVDF (II) with a thickness of 0.75 mm and diameter of 15 mm by compressing commercial PVDF (II) powder purchased from Sigma Aldrich Co. Ltd. with an average molecular weight of 534,000. The sample was annealed at 473 K for 2 h and quenched by liquid nitrogen after annealing.

Terahertz spectra at room temperature were measured utilizing two different THz-TDS systems to cover the broad frequency range from 0.2 to 7.0 THz. Lower frequency THz transmission spectra in the frequency range from 0.2 to 4.0 THz were measured by conventional transmission THz-TDS system (RT-10,000, Tochigi Nikon Corp.), where low temperature-grown (LT) GaAs photoconductive (PC) antennas are used for both the emitter and detector. These antennas were triggered by a mode-locked Ti: sapphire laser with a wavelength of 780 nm, a pulse width of less than 100 fs, and a repetition rate of 80 MHz. On the other hand, higher frequency broadband THz transmission spectra were measured covering the frequency range from 0.5 to 7.0 THz using another THz-TDS system (TAS7500SU, Advantest Corp.) which takes a high-speed AOS technique where two femtosecond lasers were used instead of mechanical delay stage. To generate broadband THz source, a Cherenkov-type MgO doped LN was used as the emitter and a PC antenna was used as the detector. These emitter and detector were triggered by a femtosecond laser with a wavelength of 1560 nm and a pulse width of about 45 fs. The repetition rate of the femtosecond laser for the emitter was 50 MHz, and for the detector it was slightly modulated from 50 MHz [17]. Fig. 1(a) and (b) shows the time-domain THz *E*-field waveforms measured by RT-10,000 with PC antenna emitter and TAS7500SU with MgO doped LN emitter, respectively. The THz waveform generated by a PC antenna has a monocycle shape. On the other hand, THz pulse from LN emitter shows the shape that vibrates several times. The power spectra converted from those waveforms are shown in Fig. 2(a) and (b), respectively. The THz spectra of PC antenna has one maximum at around 0.5 THz caused by the monocycle time-domain waveform, on the other hand, the spectra of LN emitter show a plateau in the

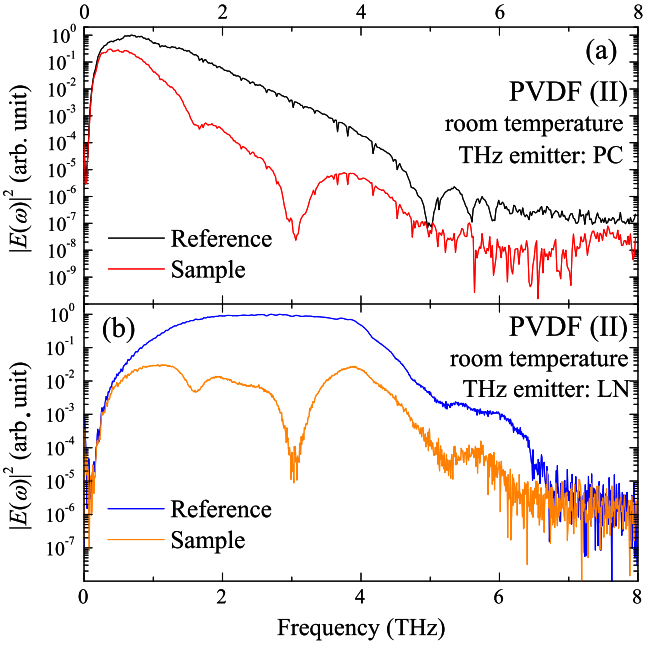

Fig. 2. The power spectra converted from time-domain waveforms of the reference (solid blue line) and PVDF (II) (solid orange line) measured by (a) RT-10,000 and (b) TAS7500SU. For convenience, 1 THz ≈ 33.3 cm^{-1} ≈ 4.14 meV ≈ 48 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

frequency range from 2 to 4 THz reflecting the optical properties of THz region of LN. The total available frequency range of the combined system at room temperature is from 0.2 to 6.0 THz. In the analysis of the room temperature data obtained by the two spectrometers, we connected the absolute value of the complex dielectric constants at about 4 THz based on the lower frequency data.