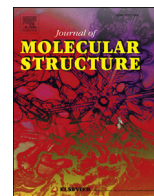




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Broadband terahertz dynamics of propylene glycol monomer and oligomers

Shota Koda^{*}, Tatsuya Mori, Seiji Kojima

Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

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ABSTRACT

We investigated the broadband terahertz spectra (0.1–5.0 THz) of glass-forming liquids, propylene glycol (PG), its oligomers poly(propylene glycol)s (PPGs), and poly(propylene glycol) diglycidyl ether (PPG-de) using broadband terahertz time-domain spectroscopy and low-frequency Raman scattering. The numerical value of the dielectric loss at around 1.5 THz, which is the peak position of broad peaks in all samples, decreased as the molecular weight increased. Furthermore, the peak at around 1.5 THz is insensitive to the molecular weight. For PPGs, the side chain effect of the oligomer was observed in the terahertz region. Based on the experimental and calculation results for the PPGs and PPG-de, whose end groups are epoxy groups, the beginnings of the increases in the observed dielectric loss above 3.5 THz of the PPGs are assigned to the OH bending vibration. The higher value of the dielectric loss in the terahertz region for the PPG-de can be the tail of a broad peak located in the MHz region. The difference between the Raman susceptibility and dielectric loss reflects the difference in the observable molecular dynamics between the infrared and Raman spectroscopies.

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1. Introduction

The relaxation processes and the inter- and intra-molecular vibrations of glass-forming materials have been studied for a long time. The relaxation processes of a super-cooled liquid state exist in a broad frequency range (mHz to THz) such as the α -, Johari-Goldstein, fast processes, etc. Using thermal [1], elastic and dielectric relaxation measurements [2], these processes have been extensively studied. Furthermore, the vibrational states of these materials were observed using inelastic neutron scattering [3], inelastic light scattering [4], and infrared spectroscopy [5]. These measurements enable to obtain higher frequency than a terahertz region. In the THz region spectrum of glass-forming liquids, the vibrational density of state (VDOS) peak can be observed at about 1 THz in addition to the fast relaxation process.

Infrared and Raman scattering spectroscopies provide molecular dynamics information through the change in the dipole moment and polarizability, respectively. The dielectric loss ϵ'' and the imaginary part of the Raman susceptibility χ'' have been often compared and discussed [6]. For molecules and crystals, the

selection rule holds for the infrared (IR) active and Raman active modes according to their point groups. In contrast, for liquids, there is little difference in the frequency shift of the vibrational state, while dipolar aprotic liquids were reported to have a relaxation mode of ϵ'' that deviates from that of χ'' [6]. Furthermore, Madden et al. reported that the relaxation process observed by ϵ'' and χ'' differs in the longitudinal and transverse modes during relaxation [7]. It is significant to investigate both measurements for the same sample. Unfortunately, the investigation of liquid samples in the THz region reached at most 2.5 THz even in recent research studies [8–10], thus those of the higher frequency THz region remain unsolved.

Propylene glycol (PG) is a typical intermediate glass-forming molecular liquid and commonly used for studies of glass transitions which are related to the dynamics of super-cooled liquids [11–13]. The dynamics of PG have been studied not only by the dielectric and infrared measurements, but also by nuclear magnetic resonance (NMR), triplet solvation dynamics, etc., and the slow β -process of PG, which is located in the kHz to MHz region, has been mainly revealed [14,15]. Furthermore, the propylene glycol esters with no hydroxyl group, which are modifications of PG, have recently been used for pharmaceutical application [16]. Therefore, the investigation of the relaxation process in the unsolved THz region for the simple glass-forming PG is important.

The oligomers of PG, called poly(propylene glycol)s (PPGs), are

^{*} Corresponding author.

E-mail addresses: s1420412@u.tsukuba.ac.jp (S. Koda), mori@ims.tsukuba.ac.jp (T. Mori), kojima@bk.tsukuba.ac.jp (S. Kojima).

investigated in this study. The relaxation processes of PPG have also been observed in a number of decades and revealed under the THz region [17–22]. PPG is used as the component of an amphiphilic block copolymer which has been reported to be a good lyotropic liquid crystalline [23,24]. The side chain effect of PPG has been reported in many ways [25–28]. Almost all of the reports suggested that the end hydroxyl groups in PPG influence the thermal and dielectric properties of PPG, and thus significant changes appeared when the hydroxyl groups are replaced for the other groups such as ethers and epoxy groups.

This work is aimed at the investigation of the broad THz dynamics using two types of terahertz time-domain spectroscopy (THz-TDS) systems, and the accurate analysis of the THz dynamics with the computational calculation using the Gaussian. Furthermore, the combined results of THz-TDS with those of Raman scattering enable us to discuss the discrepancy between ϵ'' and χ'' .

2. Experimental and calculation methods

PG, PPGs with molecular weights of 725 and 2000 g/mol (PPG725 and PPG2000), respectively, and poly(propylene glycol) diglycidyl ether (PPG-de) with the molecular weight of 640 g/mol were purchased from Sigma–Aldrich, and used without further purification. PPG725 and PPG2000 correspond to the polymerization degrees of $n \approx 12$ and 34, respectively.

For analysis of THz–TDS spectra, the observed spectra of two THz–TDS systems are combined to cover a broad THz region [29–33]. The high frequency sides of the THz transmission spectra were measured in the frequency range from 1.0 to 5.0 THz using THz–TDS equipment (TAS7500SU, Advantest Co.) with a Cherenkov type THz generator and high speed asynchronous optical sampling technique [30–32,34]. The low frequency sides of the THz transmission spectra were measured in the frequency range from 0.1 to 3.0 THz using another THz–TDS instrument (RT-10000, Tochihi Nikon Co.) with low temperature-grown GaAs photoconductive antennas for both the emitter and detector [31,32]. Since the difference in the spectra observed by these systems was at most 5%, we smoothly connected the absolute value of the complex dielectric constants of the samples multiplied by a constant in the data analysis.

Depolarized Raman scattering spectra were measured in the frequency range from 0.3 to 5.0 THz in the *VH* geometry under the scattering angle $\theta = 180^\circ$ using a single frequency green-YAG laser at the wavelength of 532 nm. The Raman spectrometer was a double-grating monochromator (U 1000, Horiba Co.). χ'' is determined by the following equation,

$$\chi''(\nu) = \frac{I(\nu)}{n(\nu) + 1}, \quad (1)$$

where $I(\nu)$ is the Raman intensity and $n(\nu)$ is the Bose–Einstein factor ($n(\nu) = (\exp(h\nu/kT) - 1)^{-1}$).

Geometry optimizations and the frequency calculations of PPG and PPG-de were performed using the density functional theory (DFT) at the Gaussian09 B3LYP/6-31G + (d, p) level of the theory [35,36]. The polymerization degrees of PPG and PPG-de for the calculations were $n = 8$ ($M_n = 482$ g/mol for PPG and $M_n = 594$ g/mol for PPG-de).

3. Results and discussion

Fig. 1 shows the complex dielectric constants $\epsilon^*(\nu) = \epsilon'(\nu) + i\epsilon''(\nu)$ in the broad THz region of PG, PPG725, PPG2000, and PPG-de. The dielectric spectrum of PG consists of a broad peak at 1.5 THz and a small shoulder at 3.6 THz. The peaks at

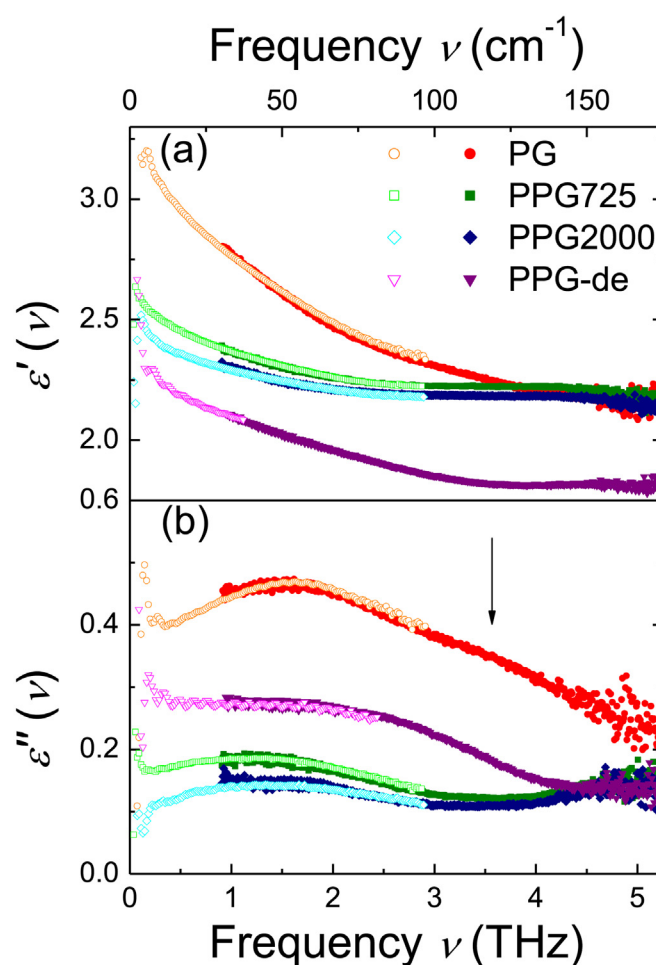


Fig. 1. Complex dielectric constants of PG (red and orange dots), PPG725 (green and yellow green squares), PPG2000 (blue and sky blue diamonds), and PPG-de (pink and purple triangles) which are obtained by the two THz–TDS systems. The arrow in Fig. 1(b) indicates the broad peak observed in PG (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

1.5 THz of the alcohols have been discussed for some vibrational modes. Yomogida et al. observed the peak at 1.5 THz for pentanol isomers and suggested it to be a vibrational mode which originated by the location of the OH groups and the carbon chain structure [37–39]. They fitted the peak at 1.5 THz using the damped harmonic oscillator (DHO) model, which is commonly used for fitting the vibrational mode. The calculated VDOS values of PG and PPG were reported to be below 6.0 THz by the molecular dynamics simulation [40], and the result showed a broad peak at around 1.5 THz.

The shoulder at 3.6 THz observed in the dielectric spectrum of PG has never been reported. The Gaussian calculation for the PG monomer shows no vibrational mode below 4.5 THz. The molecular dynamics simulation showed the CH_2 peak at 3.6 THz in addition to the peak around 1.5 THz. The prior researches of glycerol reported two kinds of vibrational modes at around 3.0 THz for the cyclic glycerol trimers. One is the collective motions of the OH groups and the other is the translational motions of the CH_2 and CH groups [17,41]. These experimental and calculation results indicate that the observed small shoulder at 3.6 THz can be attributed not to the intra- but the inter-molecular vibrations.

The broad peaks at 1.5 THz are also seen in ϵ'' of the PPGs as shown in Fig. 1(b). The value of ϵ'' at 1.5 THz decreases as the

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