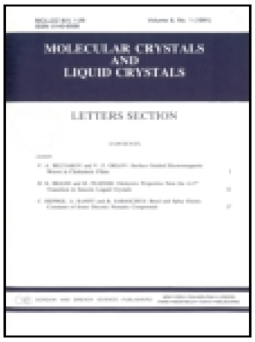

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Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Yusuke Hashimoto, Tatsuya Mori & Seiji Kojima (2016) Broadband terahertz time-domain spectroscopy and low-frequency Raman scattering of glassy polymers: Boson peak of PMMA, Molecular Crystals and Liquid Crystals, 629:1, 258-263, DOI: 10.1080/15421406.2015.1105042

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1105042

Published online: 16 Jun 2016.

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MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 629, 258–263
http://dx.doi.org/10.1080/15421406.2015.1105042

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Broadband terahertz time-domain spectroscopy and low-frequency Raman scattering of glassy polymers: Boson peak of PMMA

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ABSTRACT
The low-energy vibrational properties of polymethyl methacrylate (PMMA) were studied by terahertz time-domain spectroscopy and Raman scattering. The real and imaginary parts of a complex dielectric constant were accurately determined in the frequency range from 0.2 to 5.0 THz. The imaginary part of the dielectric constant shows a line-shape similar to the imaginary part of the Raman susceptibility measured by Raman scattering. These two spectra show broad peaks at about 2.3 THz. We also separately determined the Raman and far-infrared light-vibration coupling constants of the PMMA using the vibrational density of states determined by cold neutron inelastic scattering in the literature.

KEYWORDS
THz dynamics experiments; polymethyl methacrylate; THz time-domain spectroscopy; Raman scattering; PMMA; boson peak

Introduction

Polymethyl methacrylate (PMMA) is one of the technologically important glassy polymers. As the common nature of glassy materials with no translational symmetry, the inelastic scattering spectra show broad and asymmetric peaks called the ‘Boson peak’ (BP) [1-3]. The correlation lengths of the glassy structures estimated from the BP in the Raman spectra were comparable to those from the width of the first sharp diffraction peak reflecting the medium range order [2]. To determine more information regarding the BP of PMMA, neutron inelastic scattering, Raman scattering and far-infrared (FIR) spectroscopy were extensively utilized [4-6].

Both the FIR and Raman spectra reflect the vibrational density of state (VDOS) determined by cold neutron scattering and were influenced by the light-vibration coupling constant such as the Raman coupling constant. A Raman coupling constant contains information regarding the characteristics of the vibration in the glassy state, and may give insight about the origin of the BP. The FIR absorption coefficient and the imaginary part of a dielectric constant can also be related to the VDOS through the FIR coupling constant. However, a complex dielectric constant in the FIR region cannot be easily measured due to the generally weak intensity of the FIR light sources. Thus a reliable value for the FIR coupling constant of PMMA has not yet been reported.

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This paper was originally submitted to *Molecular Crystals and Liquid Crystals*, Volumes 620–622, Proceedings of the KJF International Conference on Organic Materials for Electronics and Photonics 2014.

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The development of terahertz time-domain spectroscopy (THz-TDS) in recent decades has enabled the accurate determination of both the real and imaginary parts of the complex dielectric constants of materials in the FIR region [7, 8]. By simultaneously obtaining the amplitude and phase of a THz pulse, we can directly determine the complex optical constants without the Kramers-Kronig analysis.

The purpose of the present study is to compare the imaginary part of a dielectric constant measured by THz-TDS and Raman susceptibility in the THz range. We also determined the FIR and Raman coupling constants, and discuss their frequency dependences.

Experimental

PMMA was purchased from the RADIA Industry Co., Ltd. The thicknesses of the samples prepared for the THz-TDS measurement were 0.584 and 1.522 mm, which allowed us to obtain transmission spectra with a moderate intensity.

The present THz-TDS measurements were performed using the conventional transmission configuration (RT-10000, Tochigi Nikon Corp.). Low-temperature grown GaAs photoconductive (PC) antennas were utilized for the THz pulse emitter and detector. The PC antennas were triggered by a mode-locked Ti:sapphire pulsed laser at a wavelength of 780 nm, a pulse width of less than 100 fs, and a repetition rate of 80 MHz.

The depolarized Raman scattering spectra were measured in the frequency range from 0.2 to 6.0 THz under the scattering angle of 180° using a single-frequency green YAG laser at the wavelength of 532 nm. The spectrometer is a double-grating monochromator (U-1000, Horiba Corp.) and the spectral resolution of the Raman spectrometer was 0.04 THz. The Raman spectra were measured at room temperature.

Results and discussion

Figure 1 shows the complex dielectric constant of PMMA determined by the THz-TDS at room temperature. For the data analysis, we smoothly connected the absolute value of

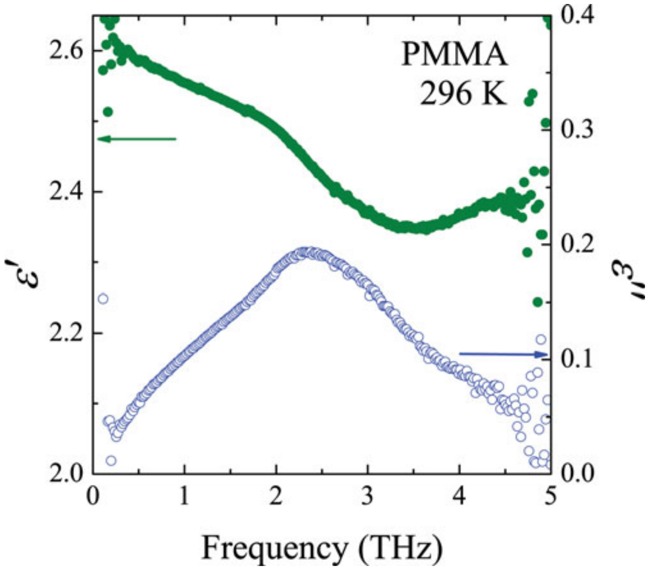

Figure 1. The complex dielectric constants, $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$, of PMMA at room temperature determined by THz-TDS.

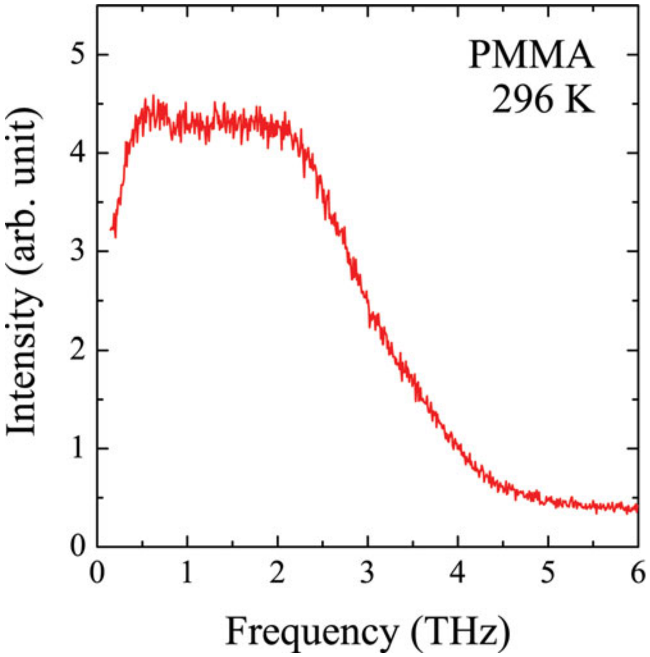

Figure 2. The depolarized Raman spectrum of PMMA at room temperature.

the complex dielectric constants of the different thickness samples on the basis of the low-frequency data of the thick samples. The real part of the dielectric constant, $\varepsilon'(\nu)$, shows step-wise decrease from 0.2 to 3.5 THz, while the imaginary part of dielectric constant, $\varepsilon''(\nu)$, showed a broad peak at about 2.3 THz.

Figure 2 shows the depolarized Raman scattering spectrum of PMMA at room temperature. This result is in good agreement within experimental accuracy to those reported in Refs. 4 and 5. As shown in Fig. 2, the Raman spectrum shows a plateau from 0.48 THz to 2.0 THz,

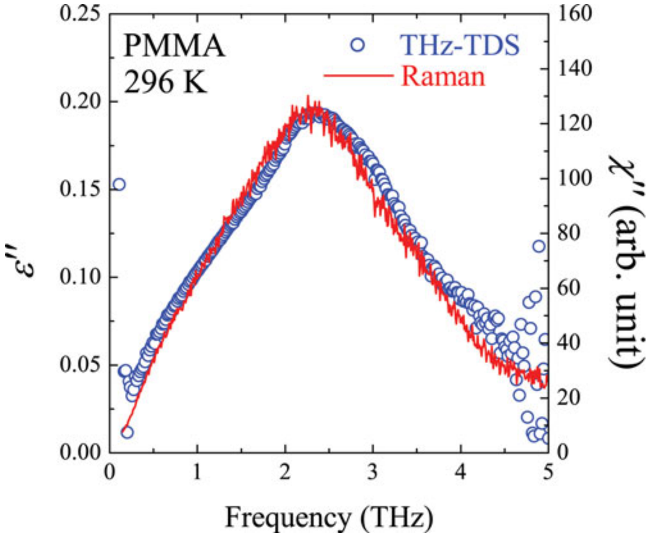

Figure 3. The comparison between the imaginary parts of the dielectric constant and Raman susceptibility of PMMA at room temperature.

and it was reported that the low frequency edge of the plateau was related to the BP, which was observed in some organic glass-forming materials [5].

In order to compare $\varepsilon''(\nu)$ to the Raman intensity, $I_{raw}(\nu)$, the imaginary part of the Raman susceptibility, $\chi''(\nu)$, is defined by the following equation,:

$$\chi''(\nu) \equiv \frac{I_{raw}(\nu)}{[n_B(\nu, T) + 1]}, \tag{1}$$

where $n_B(\nu, T)$ is the Bose distribution function. Figure 3 shows the comparison between $\varepsilon''(\nu)$ and $\chi''(\nu)$. In order to compare the shape of the two spectra, they were stacked at the maximum of the peak. It was found that $\varepsilon''(\nu)$ and $\chi''(\nu)$ have similar line-shapes in the frequency range from 0.2 to 5.0 THz, and both spectra show a broad peak at around 2.3 THz.

Figure 4(a) shows the VDOS of PMMA at 30 K which was extracted from Ref. 9. The vertical axis of Fig. 4(a) is the VDOS, $g(\nu)$, divided by the square of the energy, E (meV), while the horizontal axis was converted to the frequency ν. According to the reported results,

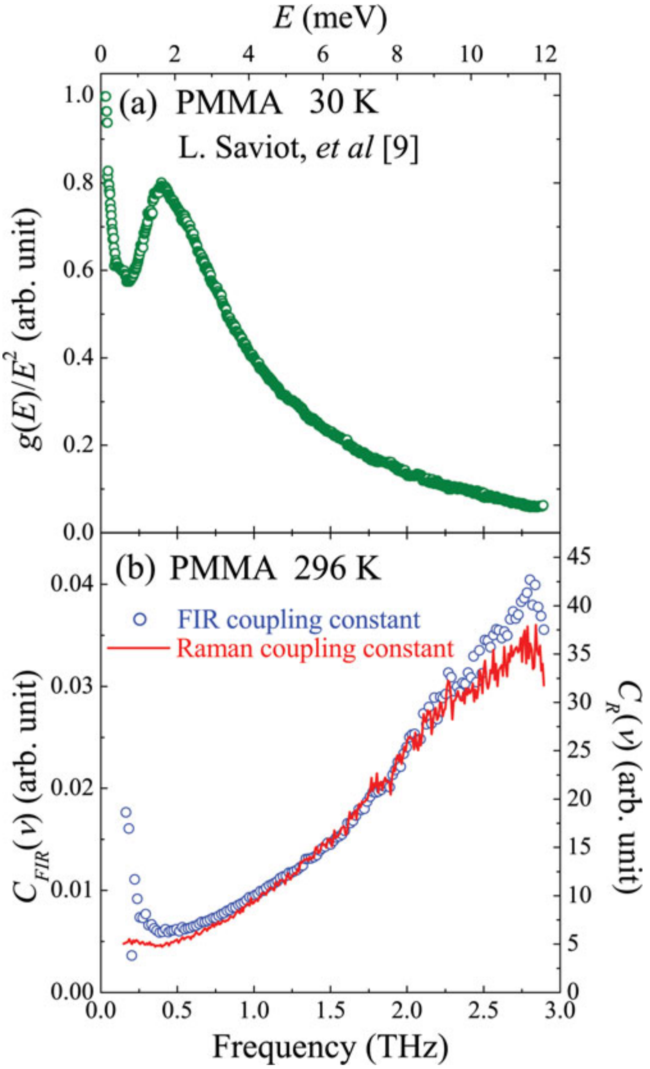

Figure 4. (a) The vibrational density of states of PMMA at 30 K extracted from the Ref. 9. (b) The FIR and Raman coupling constants of PMMA at room temperature.

the PMMA spectrum at 30 K reveals that the apparent BP frequency, ν_{BP}, is about 0.48 THz (2 meV) [9]. The observed $\varepsilon''(\nu)$ in a glass is closely related to the VDOS, $g(\nu)$, in a glass [10, 11].

$$\frac{2\pi \cdot \varepsilon''(\nu)}{c \cdot n'(\nu) \cdot \nu} = \frac{\alpha(\nu)}{\nu^2} = C_{FIR}(\nu) \cdot \frac{g(\nu)}{\nu^2}, \tag{2}$$

where $n'(\nu)$, $\alpha(\nu)$ and $C_{FIR}(\nu)$ are the real part of the complex refractive index, the absorption coefficient and FIR coupling constant, respectively. In the Raman scattering studies, the following relationships have been used in the studies of the BPs of glassy materials [12]:

$$\frac{\chi''(\nu)}{\nu} = \frac{I_{raw}(\nu)}{\nu \cdot [n(\nu) + 1]} = C_R(\nu) \cdot \frac{g(\nu)}{\nu^2}, \tag{3}$$

where $C_R(\nu)$ is the Raman coupling constant. Figure 4(b) shows the FIR and Raman coupling constants, $C_{FIR}(\nu)$ and $C_R(\nu)$, which were respectively calculated using the $\varepsilon''(\nu)$ and $\chi''(\nu)$ obtained in this study and the VDOS from a previous study by neutron inelastic scattering [9]. As shown in Fig. 4(b), the FIR and Raman coupling constants of PMMA show a similar line-shape in the frequency range from 0.2 to 1.2 THz and the frequency dependence of $C_R(\nu)$ is in good agreement with a previous report [13, 14]. The author of Ref. 13 suggested that $C_R(\nu)$ is proportional to the frequency around the ν_{BP}. This proportionality is related to the localized vibrations in the microstructure of the glass [13]. In our study, it was revealed that $C_{FIR}(\nu)$ is also proportional to the frequency. Above 2.0 THz, a slight difference between $C_{FIR}(\nu)$ and $C_R(\nu)$ is observed. At the present time, there are very limited reports for $C_{FIR}(\nu)$. Thus, it is still unclear why this difference appeared. Further investigations are now underway.

Conclusion

The THz dynamics of glassy PMMA were investigated by broadband THz-TDS and low-frequency Raman scattering spectroscopy in the frequency range from 0.2 to 5.0 THz. The imaginary part of the dielectric constant determined by THz-TDS showed a broad peak at 2.3 THz. The imaginary part of the Raman susceptibility also showed a broad peak related to the high-energy limit of a the Boson peak at about 2.3 THz. The depolarized Raman spectrum showed a plateau from 0.48 to 2.0 THz, which is related to the Boson peak. The Raman and FIR light-vibration coupling constants of PMMA were also determined using the reported values of the VDOS [9]. They show a similar line-shape and proportionality between 0.2 and 1.2 THz, but a slight difference in line-shape above 2.0 THz.

Acknowledgments

This work was partially supported by a Grants-in-Aid for Young Scientists (B) (24740194) from JSPS and the Sasakawa Scientific Research Grant from The Japan Science Society.

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