



## Density of states and vibrational modes of PDMS studied by terahertz time-domain spectroscopy

Alexander Podzorov, Guilhem Gallot \*

Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, 91128 Palaiseau, France  
INSERM U 696, 91128 Palaiseau, France

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### ABSTRACT

Using time-domain spectroscopy (TDS), we performed high-precision spectroscopic measurements of polydimethylsiloxane (PDMS) in the terahertz domain. We investigated the influence of crosslinking on the terahertz absorption and refractive index, and modeled the data with vibrational density of states and coupling between photons and vibrational modes of the polymer molecules. We also investigated the influence of the temperature on PDMS, and observed the glass transition temperature, as well as the cold crystallization peak and the melting zone.

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Amorphous polymers are characterized by glass transition and melting point [1], that induce modifications in their mechanical and dielectric properties and lead to their physical aging. Below the glass transition temperature, most polymers exhibit a drastic increase of their response time that grows up beyond experimentally accessible limits. The exact glass transition temperature also depends on the cooling rate and approaches an ideal transition point in the limit of an adiabatically slow cooling (see the review in [1]). One of the most challenging question in glassy state is related to the molecular motions which take place at the picosecond and sub-picosecond time scale. In particular, vibrational dynamics can exhibit a 'boson peak', that is an excess of low-energy density of states (DOS) compared to the Debye model. Very recently, terahertz spectroscopy was found to be a non destructive and contact-free method to study the glass transition of polyoxymethylene (POM) semi-crystalline polymer [2]. Here, we studied the terahertz properties of the PDMS polymer. We extracted relevant information on DOS, vibrational modes and boson peak. We also identified the glass transition, as well as melting zones and crystallization.

Nowadays, terahertz time-domain spectroscopy (THz-TDS) has become the most popular method to explore the frequency domain between 0.1 and 10 THz. This technique is based on the generation and detection by means of photoconductive antenna or non-linear materials of a broadband terahertz electromagnetic pulse propagating in free space [3,4]. Applications of terahertz spectroscopy are numerous in physics and chemistry, as well as in biology [5–10]. Microfluidics is also playing an increasing role in the terahertz domain [11,12] and polydimethylsiloxane (PDMS) is the most

widely used polymer to design microfluidic circuits [13]. PDMS was found to be applicable for terahertz applications, despite a relatively high absorption [14,15] and would allow quick and precise mixture of small quantities of liquids, as well as highly sensitive terahertz spectroscopic measurements.

The experimental setup is based on the classical scheme of THz-TDS (see Fig. 1) [3]. Broadband linearly polarized sub-picosecond single-cycle pulses of terahertz radiation are generated and coherently detected by illuminating photoconductive antennas with two synchronized 10 fs–780 nm laser pulses from a Femtolaser Ti:sapphire oscillator. The samples are positioned in a cryostat in the linearly polarized, 4.8 mm waist ( $1/e$  in amplitude) Gaussian THz beam. The cryostat is cooled by liquid nitrogen then heated at the desired temperature by a heating resistor. The dynamics of the terahertz pulse is recorded for 47 ps, yielding a 21 GHz frequency precision after numerical fast Fourier transform. A reference scan is also taken without the sample. Numerical Fourier transform of the time-domain signal gives access to the characteristic transmission spectrum of the sample in function of frequency  $\nu$ . The terahertz power absorption coefficient  $\alpha(\nu)$  and refractive index  $n(\nu)$  are directly calculated from the complex transmission  $S(\nu)$  given by the ratio of the complex field spectra of the sample  $E(\nu)$  and reference  $E_0(\nu)$  scans. The sample are chosen thick enough to avoid multiple reflections. The complex transmission is then given by

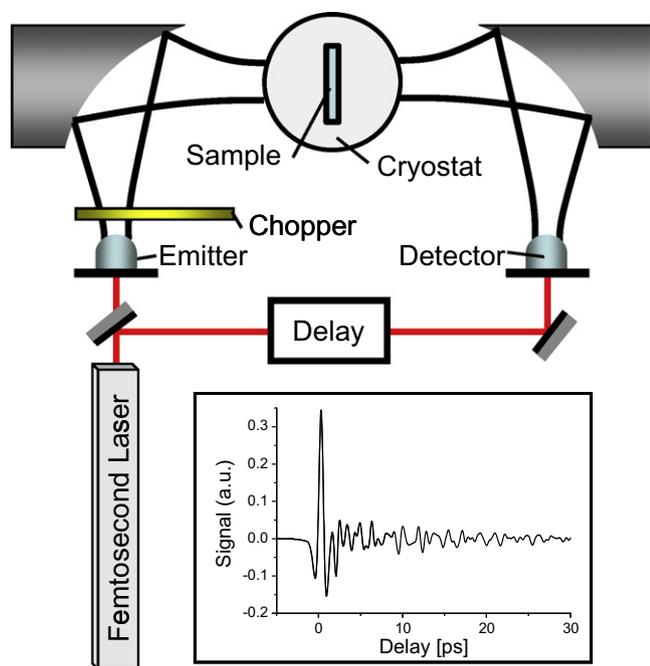
$$S(\nu) = \frac{E(\nu)}{E_0(\nu)} \frac{4\bar{n}}{\bar{n} + 1} \exp\left[-\frac{1}{2}\alpha(\nu)L\right] \exp\left\{i\frac{2\pi\nu}{c}[n(\nu) - 1]L\right\}, \quad (1)$$

where  $L$  is the sample thickness and  $\bar{n} = n(\nu) + i\frac{\alpha(\nu)}{4\pi\nu}$ .

PDMS (polydimethylsiloxane) is a semi-crystalline thermoplastic polymer. It exhibits a glass transition between elastomeric and vitreous phases, as well as a melting temperature since amorphous

\* Corresponding author at: Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, 91128 Palaiseau, France. Fax: +33 1 69 33 50 84.

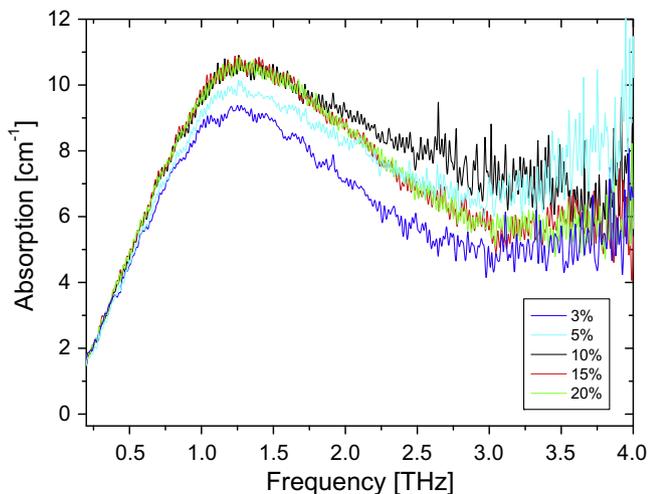
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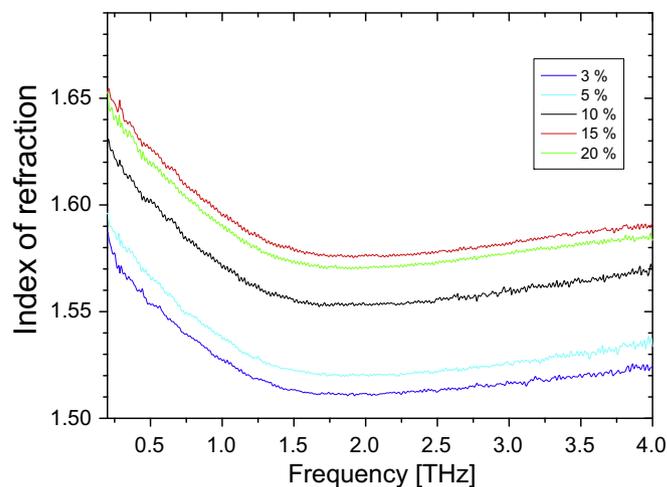
**Fig. 1.** Setup for terahertz time-domain spectroscopy. A femtosecond laser generates terahertz pulses, which propagate through free space. A chopper and lock-in device allow one to record the amplitude of the electric field. Terahertz radiation is focused through a nitrogen-cooled cryostat with quartz windows where the PDMS sample is positioned.

and crystalline phases can coexist. To study the dielectric properties of PDMS, we used a Sylgard 184 fabrication kit from Dow Corning. A mixture of pre-polymer and curing agent was poured in a 5 cm diameter Petri dish and placed in an oven at 70 °C for 60 min. Cutting a 10 mm by 10 mm piece from the center we obtain a PDMS sample with two parallel faces of optical quality for the terahertz range.

We fabricated and spectroscopically characterized PDMS samples with a weight ratio of curing agent to pre-polymer ranging from 3% to 20%. At room temperature, the amplitude absorption coefficient and the refractive index are shown in Figs. 2 and 3, respectively. We observe that absorption coefficients for the different curing agent ratio have approximately the same shape, but in-



**Fig. 2.** Intensity absorption coefficient of PDMS for curing agent/pre-polymer ratio of 3%, 5%, 10%, 15% and 20%.



**Fig. 3.** Refractive index of PDMS for curing agent/pre-polymer ratio of 3%, 5%, 10%, 15% and 20%.

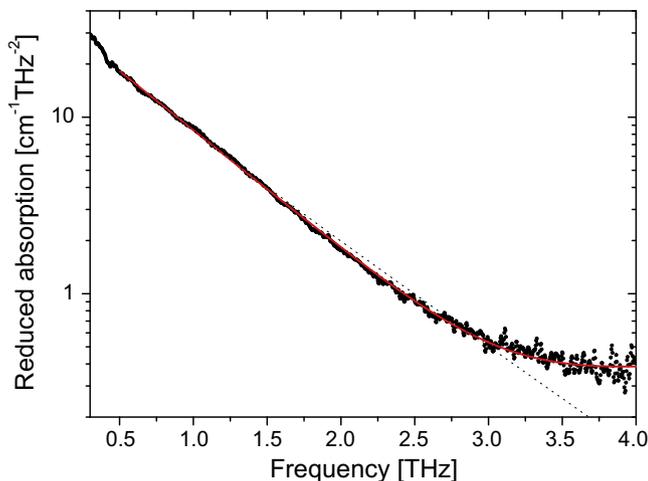
crease with the ratio for the lower part, and then remain approximately constant. More precisely, both 15% and 20% curves show lower absorption than for the 5% and 10% curves at higher terahertz frequencies. Absorption exhibits a maximum around 1.25 THz. The refractive index monotonely increases with the curing agent ratio until reaching a saturation or even a small decrease for the higher concentration of 20%. The refractive index has also a local minimum around 1.7 THz.

In order to investigate the origin of absorption spectra of PDMS at terahertz frequencies, we followed the theoretical framework of Taraskin et al. on the universal features of terahertz absorption in disordered materials [16], and used a simple representation of the absorption coefficients  $\alpha(\nu)$  as the product of the vibrational density of states  $g(\nu)$  and of the coupling coefficient  $C(\nu)$  describing the interaction of photons with the vibrational modes of the polymer molecules, as

$$\alpha(\nu) = g(\nu) \cdot C(\nu). \quad (2)$$

In the Debye model, a solid is considered as a set of independent harmonic oscillators whose characteristic frequencies are those of normal modes. As their number is very large, the spectrum of characteristic frequencies is quasi-continuous and their density is then proportional to  $\nu^2$  [17]. The quantity  $g(\nu)/\nu^2$  is called the reduced density of states, and can show important deviations from Debye model, like boson peaks for instance in the case of polyethylene [18]. It has recently been shown that in the polymeric phase the reduced density of states follows, excepting boson peaks, an exponential behavior, that is  $g(\nu)/\nu^2 \sim \exp(-\nu/\nu_0)$ , where  $\nu_0$  is the decay frequency, which is correlated to that of the boson peak frequency and does not depend on temperature [19]. In Fig. 4 (dots) we show the reduced amplitude absorption coefficient  $\alpha(\nu)/\nu^2$  for a curing agent/pre-polymer ratio of 3%, which exhibit a clear exponential behavior between 0.5 and 2 THz.

As for the contribution of the coupling  $C(\nu)$ , it has been proposed a universal behavior  $C(\nu) = A_2 + B_2\nu^2$ , where  $A_2$  and  $B_2$  only depend on the material, from spectroscopic measurement of  $\text{SiO}_2$  and  $\text{As}_2\text{S}_3$  in the glass phase [16]. The first term is due to static charge fluctuations caused by medium- and long-range structural irregularities at long distances, whereas the second one originates in structural disorder at interatomic scale leading to correlated charge fluctuations. However, this universal equation could not properly fit our terahertz data on PDMS in particular for higher terahertz frequencies (see Fig. 4, black dotted line). Much better results (see Fig. 4, red solid line) were found using a dependence



**Fig. 4.** Reduced amplitude absorption coefficient  $\alpha/v^2$  of PDMS versus terahertz frequency (curing agent/pre-polymer ratio is 3%). The dots are experimental data, the red solid line is the fit using Eq. (3) and parameters of Table 1 and the black thin dotted line is a fit using a square power instead of the 8th power as in Eq. (3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

Characteristic frequency  $\nu_0$  and coupling parameters  $A_8$  and  $B_8$  in function of the curing agent/pre-polymer ratio.

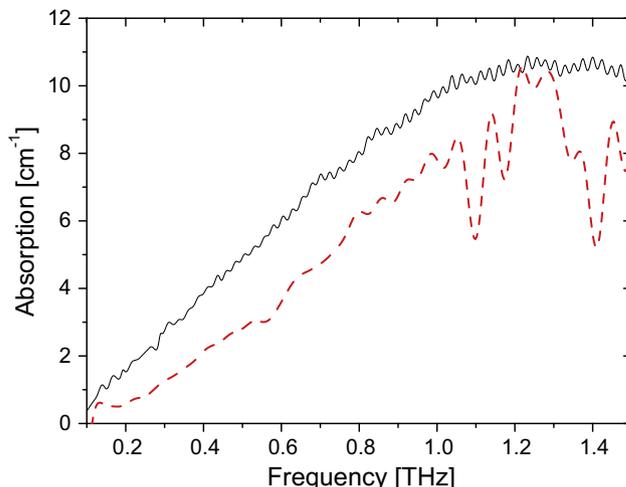
Curing agent/ pre-polymer ratio %	$\nu_0$ THz	$A_8$ $\text{cm}^{-1} \text{THz}^{-2}$	$B_8$ $\text{cm}^{-1} \text{THz}^{-8}$	$R^2$
3	$0.65 \pm 0.01$	$39 \pm 1$	$2.4 \pm 0.2 \times 10^{-3}$	0.9987
5	$0.69 \pm 0.01$	$38 \pm 1$	$2.2 \pm 0.2 \times 10^{-3}$	0.9986
10	$0.72 \pm 0.01$	$38 \pm 1$	$1.6 \pm 0.2 \times 10^{-3}$	0.9976
15	$0.69 \pm 0.01$	$40 \pm 1$	$1.4 \pm 0.2 \times 10^{-3}$	0.9987
20	$0.69 \pm 0.01$	$40 \pm 1$	$1.4 \pm 0.2 \times 10^{-3}$	0.9990

with the 8th power of the frequency, as  $C(\nu) = A_8 + B_8\nu^8$ . As a result, the terahertz absorption was modeled by

$$\alpha(\nu) = (A_8 + B_8\nu^8)\nu^2 \exp(-\nu/\nu_0). \quad (3)$$

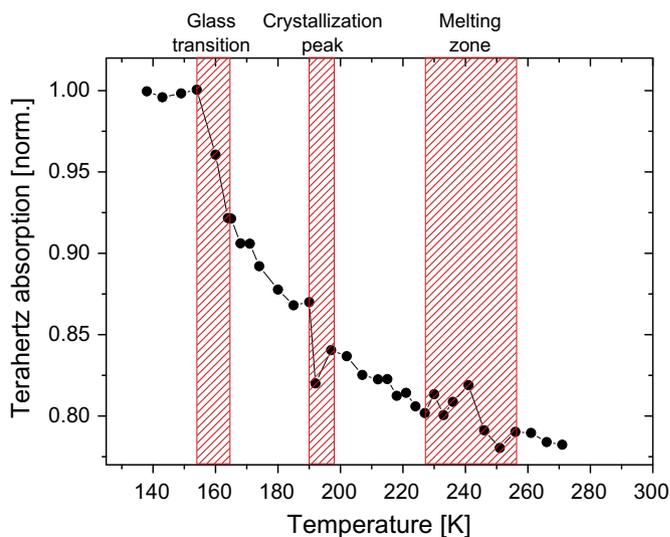
The values of  $\nu_0$ ,  $A_8$  and  $B_8$ , obtained by a least-square fitting procedure [20], are found in Table 1 for various curing agent/pre-polymer ratio, as well as the statistical error  $R^2$ . Comparing the fitting quality for the 8th and 2nd power, values of  $R^2$  are 0.9987 and 0.989, respectively, for a curing agent/pre-polymer ratio of 3%. The need to use higher power law to fit our data indicates stronger short-scale correlations in the case of elastomeric PDMS, compared to silica in the glass phase. These results show that the terahertz absorption of PDMS originates from its partially disordered, glass-like structure. A characteristic frequency  $\nu_0$  close to 0.65 THz (2.7 meV) but different for different curing agent/pre-polymer ratios (see Table 1) corresponds approximately to the half of the resonant frequency (Fig. 2). We can notice that the behavior of the absorption (Fig. 2) and refractive index (Fig. 3), for the higher concentrations of 15% and 20% is also related to the evolution of the parameters, and shows a correlation with a small decrease of the low-energy DOS, as well as an increase of medium- and long-range structural fluctuations for higher concentrations.

Then, we studied the absorption of PDMS with respect to temperature. We included a home-made cryogenic cell in the previously described terahertz setup. The thermostat is cooled with liquid nitrogen, and a heating resistance maintains constant a chosen temperature. The spectroscopic measurements of 15% cross-linked PDMS for the vitreous phase at  $122 \pm 5$  K and for the



**Fig. 5.** Amplitude absorption coefficient of PDMS (15% curing agent/pre-polymer ratio) in the elastomeric phase (294 K, black solid line) and vitreous phase (122 K, red dashed line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

elastomeric phase at 294 K are presented in Fig. 5. The signals are measured up to 1.5 THz due to the presence in the thermostat of quartz windows, which absorbs terahertz radiation. This explains also a smaller signal to noise ratio in the region from 1 to 1.5 THz. One can see that the spectra in elastomer and vitreous phases are qualitatively similar, due to the origin of the terahertz absorption of PDMS from its partially disordered, glass-like structure. However, there is still a quantitative difference, the absorption in the vitreous phase being lower by about  $2 \text{ cm}^{-1}$ . This gives the possibility to easily distinguish between both phases. We made the dynamical observation of a 15% crosslinked PDMS sample. In order to be comparable to classical techniques [21], we chose a cooling rate of 5 K/min, therefore only a small portion of the time-domain signal was recorded, and the evolution of its peak amplitude was followed in function of temperature (Fig. 6), contrary to previous terahertz studies where full scans were recorded [2]. Thus we can quickly measure the quantity  $\bar{\alpha}L$  where



**Fig. 6.** Normalized terahertz absorption ( $\bar{\alpha}L$ ) in function of temperature. Hatched zones correspond to glass transition ( $160 \pm 5$  K), cold crystallization peak ( $193 \pm 3$  K) and melting zone (between 227 and 255 K).

$\bar{\alpha}$  is the mean value of absorption and  $L$  is the thickness of the sample. We can identify a melting zone between 227 and 255 K, a cold crystallization peak at  $193 \pm 3$  K and a glass transition at  $160 \pm 5$  K. The results are close to those found with the differential scanning calorimetry [22]. The difficulty of getting more precise data is the same as in calorimetry: the main concern is the temperature distribution inside the thermostat. Moreover, one has to recall that the vitrification is not an exact phase transition as it depends on the sample used and on hysteresis effects. For these reasons, an exact characterization of polymers is still a difficult task depending on observation conditions. Nevertheless, we believe that the terahertz TDS can be a novel method to study vitreous phases and glass transitions. Comparing to the conventional method of DSC used to identify phase transitions [22], the terahertz time-domain spectroscopy has the great advantage of being a non-contact technique.

In conclusion, we studied the effects of crosslinking on the terahertz properties of PDMS, extracting the absorption coefficient and refractive index for PDMS with a curing agent/pre-polymer ratio ranging from 3% to 20%. We modeled the results and found a classical vibrational density of states and mainly exponential reduced absorption. Precise measurements at higher frequencies allowed to model the coupling between photons and vibrational modes of the polymer molecules, which exhibits very strong short-scale correlations. We also investigated the glass phase transition of PDMS, as well as crystallization peak and melting, with this non-contact spectroscopic technique.

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