

Low-loss polymers for terahertz applications

Alexander Podzorov and Guilhem Gallot*

Laboratoire d'Optique et Biosciences, École Polytechnique, CNRS, 91128 Palaiseau,
France and INSERM U696, 91128 Palaiseau, France

*Corresponding author: guilhem.gallot@polytechnique.edu

Received 25 March 2008; revised 21 May 2008; accepted 23 May 2008;
posted 23 May 2008 (Doc. ID 94159); published 12 June 2008

We have performed high-precision terahertz time-domain spectroscopy measurements on polymers (cross-linked polystyrene, TPX, Zeonor) from 0.2 to 4.2 THz. They show very interesting terahertz and visible transparency. We also investigated the terahertz characteristics of PDMS, a polymer extensively used in microfluidics, which showed absorption compatible with terahertz experiments. The thermoplastic properties of these polymers make them suitable for use as lens, window, waveguide, or support materials in such applications as biological imaging or microfluidics necessitating a constant visual control not provided by conventional silicon- or teflon-based devices. © 2008 Optical Society of America

OCIS codes: 300.6495, 300.6250, 320.7150.

1. Introduction

Nowadays, terahertz time-domain spectroscopy (TDS) has become the most popular technique in the still challenging frequency domain between 0.1 and 10 THz [1–8]. Terahertz TDS is based on the generation and detection by means of photoconductive antenna or nonlinear materials of a broadband terahertz electromagnetic pulse propagating in free space. Applications of TDS are numerous in spectroscopy, imaging, and waveguiding [9–13]. Increasing applications would benefit from materials transparent in both the terahertz and the visible domains, in particular imaging applications. Using transparent terahertz and visible materials would allow easy alignment and control of terahertz TDS experiments. The most transparent terahertz material is high-resistivity (HR) silicon [14], but it is totally opaque in the visible. Furthermore, HR silicon has a refractive index of approximately 3.4, generating a power loss at each air–silicon interface of about 30%. Classical visible materials such as silicate glass exhibit strong terahertz absorption [15], and crystals such as sapphire and quartz are anisotropic [1]. An ideal terahertz material should be transparent in the

terahertz and visible range. Its refractive index should be low to minimize reflection loss and geometric aberrations in lens design and should match its visible refractive index to allow alignment and control in the visible of the terahertz experiment. Thermoplastic properties would also be of great help in modeling lenses and waveguides.

Here, we investigated several materials that satisfy these requests. We precisely measured their terahertz power absorption and refractive index from 0.2 to 4.2 THz. We also measured their optical properties and refractive index matching. Some of them [polymethylpentene (TPX), cross-linked polystyrene] are well known far-infrared polymers [16–18] and required a better characterization in the terahertz domain. Zeonor is a polyolefin polymer as is TPX, showing improved visible and thermoplastic performances. We also studied PDMS, a polymer increasingly used in molding microfluidic circuits [19]. Even though its terahertz transparency is less efficient than the other tested polymers, PDMS is compatible with terahertz experiments and would prove to be very valuable in this frequency domain.

2. Terahertz Characteristics

The experimental setup is based on the classical terahertz TDS setup [1,3]. Broadband linearly polarized subpicosecond single cycle pulses of terahertz

0003-6935/08/183254-04\$15.00/0
© 2008 Optical Society of America

radiation are generated and coherently detected by illuminating photoconductive antennas with two synchronized femtosecond laser pulses from an 800 nm, 12 fs Femtolasers Ti:sapphire oscillator. The samples are positioned in the linearly polarized, frequency-independent, 4.8 mm waist ($1/e$ in amplitude) Gaussian THz beam. The dynamics of the terahertz pulse after propagation through the sample is recorded until a reflected pulse is observed and corresponds to a duration of typically 50 ps, yielding a 20 GHz frequency precision after numerical Fourier transform. A reference scan is taken without the sample. The average of 20 sample and reference scans has been used to increase the signal-to-noise ratio. The sample is enclosed in a box that is purged with dry nitrogen to remove absorption from atmospheric water (relative humidity remains below 1%), and the experiment temperature was 294 K. Numerical Fourier transform of the time-domain signal gives access to the characteristic transmission spectrum of the sample. The terahertz power absorption coefficient $\alpha(\nu)$ and refractive index $n(\nu)$ are 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 samples are thick enough so that no reflection echoes are observed in the measurement scan window. Therefore Fabry–Perot effects are absent, and the complex transmission $S(\nu)$ is simply given by

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

where L is the thickness of the sample and $\bar{n} = n + i\frac{c\alpha}{4\pi\nu}$ is the complex refractive index. Equation (1) cannot be analytically solved, and a classical iterative method has been used with no approximation [3,20]. Therefore large absorption materials can also be precisely treated.

A. Cross-Linked Polystyrene

Cross-linked polystyrene (PSX) is a rigid, transparent, and colorless copolymer. The sample is provided by Goodfellow SARL, France. It can be easily machined and optically polished. Compared to normal polystyrene, it is harder, more temperature resistant, and most importantly in the terahertz domain, almost insensitive to water adsorption (more than 10 times less [21]). A 9.62 mm thick, 10 mm by 10 mm plate was cut parallel and optically polished. The terahertz absorption and refractive index can be found in Figs. 1 and 2 (triangles). The refractive index is low and nearly constant, and the absorption is very low for a polymer. No birefringence has been observed. These data are in good agreement with previous results on normal polystyrene [17,22] in the overlapping zone but contradict a recent work on materials in the terahertz domain [23].

B. Polymethylpentene

Poly 4-methyl pentene-1 (TPX) is a linear polyolefin polymer widely used in the microwave domain. It is semi-crystalline and thermoplastic. The sample was a 4.93 mm thick, 50 mm diameter plate cut from a rod obtained from Goodfellow SARL, France. It was optically polished in a parallel plate and showed a slightly yellow coloration. It can readily be molded into windows, lenses, or waveguides (molding point between 220 and 240 °C [21]). The terahertz absorption and refractive index can be found in Figs. 1 and 2 (open circles). The refractive index is nearly constant, lower than for PSX. The power absorption is much lower than for PSX. No birefringence has been observed. These data are compatible with results found in [17] in the overlapping zone but not in [18].

C. Zeonor

Zeonor, is a cyclo olefin polymer from Zeon Chemicals LP (ref. 1020R). It is three times less water absorbent than TPX and has excellent oxygen barrier properties. Zeonor is therefore a very good candidate for support material in biological imaging and microfluidic applications [24]. Its molding point is lower than TPX (100 to 105 °C) and can easily be molded into waveguides. The sample was made of three pieces of 2 mm thick optically polished plates stacked together in optical contact. The total thickness was 6.01 mm. The terahertz absorption and refractive index can be found in Figs. 1 and 2 (dots). Zeonor shows terahertz properties close to TPX, with power absorption slightly lower than for TPX.

D. PDMS

Polydimethylsiloxane (PDMS) is the most widely used silicon-based polymer in the design of microfluidic networks. PDMS has also been found to be useful as a matrix for plasmonic composites [19]. Far-infrared characterization has been done down to 1 THz [19]. We extended the measurements from 0.1 to 1.1 THz. We used the Sylgard 184 silicone elastomer

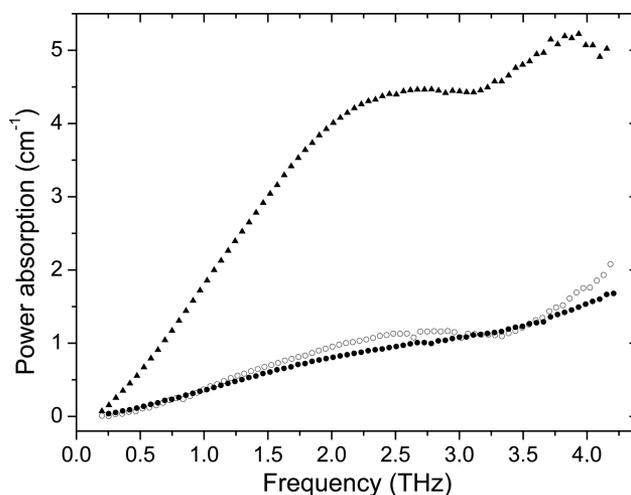


Fig. 1. Measured power absorption coefficient of PSX (triangles), TPX, (open circles), and Zeonor (dots) from 0.2 to 4.2 THz.

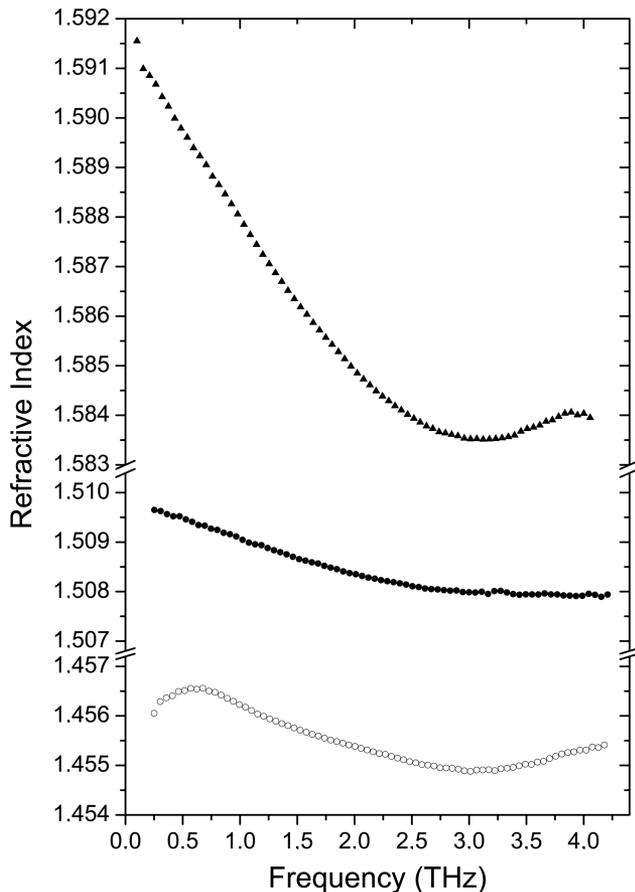


Fig. 2. Measured indices of refraction of PSX (triangles), TPX (open circles), and Zeonor (dots) from 0.2 to 4.2 THz.

kit, from Dow Corning. In a plastic box, we mixed 9 parts of Sylgard 184 prepolymer and 1 part of curing agent. The box was placed for 20 min in a dessicator to degas, then the mixture was poured into a large Petri dish. The Petri dish was placed horizontally in an oven and cured at 70 °C for 60 min. A 10 mm by 10 mm piece was then cut from the center of the PDMS to obtain a parallel plate. Since PMDS is elastic, the thickness has been measured with an optical microscope. The PDMS plate was placed on a reference plane, then both the reference plane and the upper surface were focused by the microscope. The PDMS plate had a thickness of 5.42 ± 0.02 mm. The terahertz power absorption and refractive index are presented in Fig. 3.

3. Visible characteristics of the polymers and comparison with terahertz

The visible optical properties of the polymers have been determined using an Abbe refractometer that provides the optical refractive index n_d as well as the dispersion given by Abbe number $\nu_d = (n_d - 1)/(n_f - n_c)$. Here, n_d , n_f , and n_c refer to the refractive index at 588, 486, and 656 nm, respectively. Table 1 summarizes the optical data of the different polymers, together with the mean terahertz refractive index n_{THz} . As a comparison with HR silicon, L_{ref} is the thickness of polymer plate exhibiting the same loss as HR silicon (interface loss), as

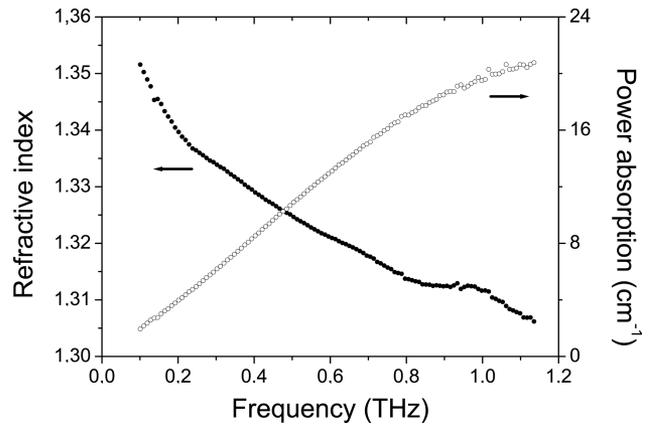


Fig. 3. Measured power absorption coefficient (open circles) and refractive index (dots) of PDMS from 0.1 to 1.1 THz.

depicted in Fig. 4. PSX, TPX, and Zeonor show excellent matching of visible and terahertz refractive index. The refractive index is close to 1.5, providing optimal focusing properties in lens design. TPX and Zeonor show comparable terahertz absorption, Zeonor being slightly more transparent. PSX is more absorbent, by about a factor of 4. Dealing with a thickness of less than 15 mm of TPX or Zeonor (see Table 1) provides better transmission than HR silicon at 1 THz. On the other hand, PDMS shows much higher absorption, even though the refractive index is low. Thickness below the millimeter range is necessary to overcome absorption. It is however compatible with typical microfluidic devices.

4. Conclusion

We performed high-precision terahertz TDS from 0.2 to 4.2 THz on and compared the visible properties of cross-linked polystyrene, TPX, and Zeonor. All these polymers are transparent in the visible. TPX and Zeonor show the lowest terahertz absorption. Compared to TPX, Zeonor shows improved visible, water sensitivity, and thermoplastic characteristics. We

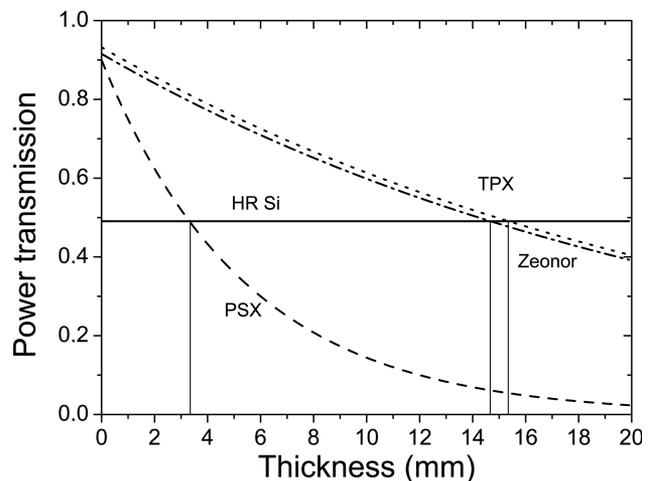


Fig. 4. Evolution of the transmission at 1 THz through a parallel plate versus thickness for HR silicon, PSX, TPX, and Zeonor. The crossing with the HR silicon curve corresponds to L_{ref} .

Table 1. Visible and Terahertz Optical Properties of PSX, TPX, Zeonor, and PDMS^a

Material	n	ν_D	n_{THz}	L_{ref} (mm)
PSX	1.589(4)	30(1)	1.587(3)	3.3
TPX	1.462(4)	58(1)	1.456(1)	15.3
Zeonor	1.531(4)	48(1)	1.525(1)	14.8
PDMS	1.414(4)	57(2)	1.33(2)	0.3

^a n_D is the visible refractive index at 588 nm. ν_D is the Abbe number, n_{THz} is the mean terahertz refractive index, and L_{ref} is the sample thickness matching the absorption of a HR silicon plate at 1 THz. The numbers in parentheses refer to the absolute precision of the last digit.

also showed that PDMS can easily be used as a microfluidic medium in both terahertz and visible experiments. This work also improved and clarified the measurements of terahertz absorption and refractive index for some polymers.

We thank Daniel R. Grischkowsky and R. Alan Cheville for the generous donation of terahertz antennas used for this work and Charles Baroud for providing PDMS samples.

References

1. D. Grischkowsky, S. R. Keiding, M. van Exter, and C. Fattinger, "Far-infrared time-domain spectroscopy with terahertz beams of dielectrics and semiconductors," *J. Opt. Soc. Am. B* **7**, 2006–2015 (1990).
2. Q. Chen, M. Tani, Z. Jiang, and X. C. Zhang, "Electro-optic transceiver for terahertz-wave applications," *J. Opt. Soc. Am. B* **18**, 823–831 (2001).
3. L. Duvillaret, F. Garet, and J.-L. Coutaz, "A reliable method for extraction of material parameters in terahertz time-domain spectroscopy," *IEEE J. Sel. Top. Quantum Electron.* **2**, 739–746 (1996).
4. G. Gallot, J. Zhang, R. W. McGowan, T.-I. Jeon, and D. Grischkowsky, "Measurements of the THz absorption and dispersion of ZnTe and their relevance to the electro-optic detection of THz radiation," *Appl. Phys. Lett.* **74**, 3450–3452 (1999).
5. J. Han, W. Zhang, W. Chen, L. Thamizhmani, A. K. Azad, and Z. Zhu, "Far-Infrared characteristics of ZnS nanoparticles measured by terahertz time-domain spectroscopy," *J. Phys. Chem. B* **110**, 1989–1993 (2006).
6. K. Wang and D. M. Mittleman, "Metal wires for terahertz wave guiding," *Nature* **432**, 376–379 (2004).
7. W. J. Padilla, A. J. Taylor, C. Highstrete, M. Lee, and R. D. Averitt, "Dynamical electric and magnetic metamaterial response at terahertz frequencies," *Phys. Rev. Lett.* **96**, 107401 (2006).

8. H. Cao, T. F. Heinz, and A. Nahata, "Electro-optic detection of femtosecond electromagnetic pulses by use of poled polymers," *Opt. Lett.* **27**, 775–777 (2002).
9. C. Baker, I. S. Gregory, W. R. Tribe, I. V. Bradley, M. J. Evans, M. Withers, P. F. Taday, V. P. Wallace, E. H. Linfield, A. G. Davies, and M. Missous, "Terahertz pulsed imaging with 1.06 mm laser excitation," *Appl. Phys. Lett.* **83**, 4113–4115 (2003).
10. N. C. J. van der Valk and P. C. M. Planken, "Electro-optic detection of subwavelength terahertz spot sizes in the near field of a metal tip," *Appl. Phys. Lett.* **81**, 1558–1560 (2002).
11. J. Kitagawa, T. Ohkubo, M. Onuma, and Y. Kadoya, "THz spectroscopic characterization of biomolecule/water systems by compact sensor chips," *Appl. Phys. Lett.* **89**, 041114 (2006).
12. A. J. Fitzgerald, E. Berry, N. N. Zinovev, G. C. Walker, M. A. Smith, and J. M. Chamberlain, "An introduction to medical imaging with coherent terahertz frequency radiation," *Phys. Med. Biol.* **47**, R67–R84 (2002).
13. R. Mendis, "Nature of subpicosecond terahertz pulse propagation in practical dielectric-filled parallel-plate waveguides," *Opt. Lett.* **31**, 2643–2645 (2006).
14. J. Dai, J. Zhang, W. Zhang, and D. Grischkowsky, "Terahertz time-domain spectroscopy characterization of the far-infrared absorption and index of refraction of high-resistivity, float-zone silicon," *J. Opt. Soc. Am. B* **21**, 1379–1386 (2004).
15. M. Naftalya and R. E. Miles, "Terahertz time-domain spectroscopy of silicate glasses and the relationship to material properties," *J. Appl. Phys.* **102**, 043517 (2007).
16. D. R. Smith and E. V. Loewenstein, "Optical constants of far infrared materials. 3: plastics," *App. Opt.* **14**, 1335–1341 (1975).
17. J. R. Birch, "The far-infrared optical constants of polypropylene, PTFE and polystyrene," *Infrared Phys.* **33**, 33–38 (1992).
18. G. W. Chantry, J. W. Fleming, and P. M. Smith, "Far-infrared and millimetre-wave absorption spectra of some low-loss polymers," *Chem. Phys. Lett.* **10**, 473–476 (1971).
19. S. C. Nemat-Nasser, A. V. Amirkhizi, W. J. Padilla, D. N. Basov, S. Nemat-Nasser, D. Bruzewicz, and G. Whitesides, "Terahertz plasmonic composites," *Phys. Rev. E* **75**, 036614 (2007).
20. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C* (Cambridge U. Press, 1992).
21. www.Goodfellow.com.
22. R. Piesiewicz, C. Jansen, S. Wietzke, D. Mittleman, M. Koch, and T. Krner, "Properties of building and plastic materials in the THz range," *Int. J. Infrared Millim. Waves* **28**, 363–371 (2007).
23. M. Naftaly and R. E. Miles, "Terahertz time-domain spectroscopy for material characterization," *Proc. IEEE* **95**, 1658–1665 (2007).
24. www.zeonchemicals.com.