Studying of dielectric properties of polymers in the terahertz frequency range

E.V. Fedulova[a], M. M. Nazarov[a], A.A. Angeluts[a], M.S. Kitai[b], V.I. Sokolov[b] and A.P.Shkurinov[a]

[a] Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia,
[b] Institute on Laser and Information Technologies of the Russian Academy of Sciences, Shatura, Moscow region, Russia
fedulova@physics.msu.ru

ABSTRACT

Absorption spectra of sixteen polymers have been examined using terahertz (THz) time-domain spectroscopy system in THz frequency range (0.1 – 3 THz). All the experimental data showed a characteristic wide absorption peak at the frequencies around 2.5 THz accompanied by smoothly decreasing of refraction (except "transparent" polymers). Such behavior could be described by a modified Debye model. We also tried to clarify the impact of flexibility, polymerization, crystalline degree and number of monomer end groups on polymer dielectric properties. We suggest that the absorption mechanism in spectral range lower than 3 THz is related with relaxation and amorphous state of polymers.

Keywords: terahertz, transparent, polymer, absorption and refraction spectra, the modified Debye model.

1. INTRODUCTION

Science and technology of THz waves have started being in progress since 60-70 years of the XX century when the first sources and detectors of this radiation became available in continuous wave (CW) mode[1,2]. As a result of developing research, the modern THz short pulses radiation with wavelengths from 30 to 3000 microns[3,4] has a widespread potential for such applications as biomedical sensing, noninvasive imaging, substance identification and many other. THz imaging and sensing techniques are presently used at major medical centers for cancer and burn diagnosis[5-7]. In recent years, many timely investigations have been performed to investigate the possible biological effects associated with THz radiation[8-11]. Biological effects studies are a valuable type of basic science research because they serve to enhance our fundamental understanding of the mechanisms that govern THz interactions with biological systems.

The "THz-region", also known as the sub millimetre region, spans the gap between the microwave and the infrared frequency ranges of the spectrum and extends from 0.1 up to 10 THz (3–300 cm^{-1}). The vibrations of molecular crystal space lattice and bending vibrations of long molecules, including polymers, are found in THz region[3,4].

Currently the efficient delivery of THz radiation (using wave guiding structures for example) is one of the major challenges because of two serious problems: the dispersion and the residual absorption even in the so called "THz-transparent" materials[4] (high-density polyethylene HDPE, low-density polyethylene LDPE, polytetrafluoroethylene PTFE or Teflon, polymethylpentene TPX and other). Nowadays some researches already made THz polymer waveguides[12]. For creating integrated polymer waveguides we should understand the nature of dielectric properties of these materials in the low frequency region. Literature data analysis[4,13,14] shows that absorption coefficient reduces as the degree of crystallinity grows, but it is not the only factor. When we will find a transparent and manufacturable polymer, we will try to make 2D integrated structures using different technology. We are going to use not drill – and – draw technology, but photopolymerization of wave guiding structures, since it is a well developed technique for the IR frequency range[15].

A polymer is a large molecule (macromolecule) composed of repeating structural units. There is a great variety of polymers. Crystalline polymers are usually quite transparent, but amorphous polymers are technological in the most of the cases. Technological for us means firm, steady photopolymers: those polymers that can be made by photopolymerization. Thus, the aim of this work is to find a transparent, dispersion-less and technological polymer

material for the broadband THz waveguide. We have started with the investigation of absorption and refraction physical mechanisms of polymers in THz frequency range.

2. LITERATURE REVIEW

The nature of far infrared (IR) absorption of glasses, similar to polymers by their structure, has been firstly discussed[16] in 1971. Author suggest that a characteristic high absorption of glasses in the millimeter and submillimeter ranges is caused by transitions between the low-frequency vibrational states of energy that are forbidden by selection rules in a crystalline material. The weakening of the selection rules is due to the lack of long-range order in the vitreous structure. The mechanism of absorption in the vitreous material is called "disorder-induced absorption" that is similar but not identical to the "defect-induced absorption" in disturbed crystals.

A comprehensive review of polymer studies using spectroscopy in the low-frequency infrared region was published by Bernshtein and Ryzhov[13]. It was shown that the molecular dynamics and intermolecular interactions in polymers determine to a considerable extent their physical properties. The FIR spectra appeared to be fruitful in revealing the molecular nature of β, γ and δ-relaxations in glassy polymers. Raman and IR absorption spectra of glassy polymethylmethacrylate (PMMA) in the frequency range 10-150 cm^{-1} were obtained and discussed in the following papers[17,18]. Authors emphasized weakly visualized Boson peak (a characteristic band in the range $10 - 50$ cm^{-1} caused by the low-frequency vibrational excitations in the flexible chain polymers, pronounced in Raman spectra) and referred it to libration at the basic chain section comparable to its random segment. Boson peak is not a dominant absorption reason, a wide asymmetric absorption band with maximum at $\sim$ 90-95 cm^{-1} is prevalent. This band is assigned to absorption provided by libration of monomer sections in PMMA macromolecules i.e. by Poley absorption[19] (a broad peak in disordered media whose frequency decreases with increase in temperature and amplitude increases). We suppose that the mentioned processes are prevailing for the most investigated polymers in THz frequency range.

Dielectric properties of polymers such as polypropylene (PP), Teflon, HDPE, polycarbonate (PC) and other were recently examined by THz time-domain spectroscopy[14] (THz-TDS). The absorption coefficients at the frequency of 1 THz of the nine polymer samples varied from 2 to 40 cm^{-1}, the characteristic value of refractive indices at this frequency was found to be 1.6.

Thus there are either only experimental spectra without discussion of the nature of polymer dielectric properties or a reference to Poley absorption and Boson peak in the found publications related to THz frequency range. However no detailed interpretation of the experimental data by those approaches has been found. So it is very important to clarify the nature of dielectric response of polymers in THz frequency range.

A few words about already made THz polymer waveguides should be said. The paper[12] reports on a new class of polymer photonic crystal fibers for low-loss guidance of THz radiation. The use of the cyclic olefin copolymer Topas in combination with the drill-and-draw fabrication technology results in bendable THz fibers with unprecedented low loss and low material dispersion in THz frequency range. Near-field, frequency-resolved characterization with high spatial resolution of the amplitude and phase of the modal structure proves that the fiber is single-moded over a wide frequency range, and there is the onset of higher-order modes at high frequencies as well as indication of microporous guiding at low frequencies and high porosity of the fiber. Transmission spectroscopy demonstrates low-loss propagation (< 0.1 dB/cm loss at 0.6 THz) over a wide frequency range.

3. THE EXPERIMENTAL METHOD AND SAMPLES

The so called method of THz-TDS[3] has been turned an established technique already, in which both the amplitude and the phase of a broadband coherent THz pulse are measured. This fact allows obtaining direct absorption and refraction spectra at once. Employed THz-TDS system and methods of data processing were described in detail previously[20]. The operation principle of THz-TDS in brief is the following (Fig.1): a laser provides continuous sequence of visible femtosecond pulses; the laser radiation is splitted into two parts. The first part, contains 80% of initial beam power, illuminates GaAs crystal which is used for THz generation. The second part of the beam serves as the probe for electro-optic detection using ZnTe crystal. After measuring instant THz field in time domain we make the ratio of Fourier transforms of the temporal profiles with the sample and without it and as a result we obtain a complex transmission

spectrum. Then we recalculate absorption coefficient and refractive index from transmission spectrum of a parallel plate of material with known thickness. Below we will analyze absorption and refraction spectra.
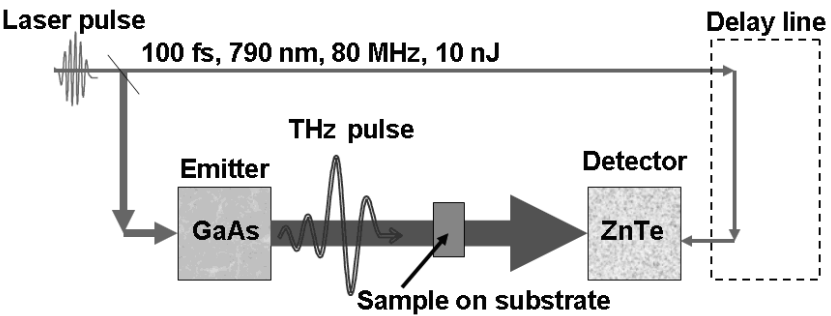

Figure 1.The experimental THz-TDS setup.

In the present study 16 polymers such as PMMA, PC, polystyrene (PS), polyethyleneterephthalate (PET), Teflon and some specific samples were examined. The specific polymers were produced in the Institute on Laser and Information Technologies of the RAS. The abbreviations, chemical structures and legend numbers of the examined materials are shown in the Table 1.

We have also investigated polyacrylates – the representatives of homologous set (№ 6-№ 8). These substances consist of two parts: changing part (AC-1, 75 %) where number of end groups varied (m=2, 6, 8) and constant part (AC-2, 25 %).

Table 1. The examined polymers, their abbreviations, and chemical structures.

№	Full Name	Abbreviation	Chemical structure
1	Polymethlmethacrylate	PMMA, Plexiglas	
2	Oligocarbonatemethacrylate +17% photoinitiator	OCM-2	
3	Phenoxy ethylmethacrylate + 0,6 % photoinitiator	PEM	
4	Benzylacrylate + 0,6 % photoinitiator	benzyl AC	

Table 1. The examined polymers, their abbreviations, and chemical structures.

№	Full Name	Abbreviation	Chemical structure
5	Polycarbonate	PC	(chemical structure)
6	Homologous set	AC-1 + AC-2, m=2	(chemical structure)
7		AC-1 + AC-2, m=6	
8		AC-1 + AC-2, m=8	
9	Polystyrene	PS	(chemical structure)
10	Polyethyleneterephthalate	PET	(chemical structure)
11	Polytetrafluoroethylene	PTFE, Teflon	(chemical structure)
12	Tsurupica	Picarin	not available
13	Polyethylene	PE	(chemical structure)
14	Polymethylpentene	TPX	(chemical structure)
15	Cyclic olefin copolymer	COC	(chemical structure)
16	Polypropylene	PP	(chemical structure)

The samples №1-№8 were created by photo polymerization (photo initiator - irgacur), PS (№9) was made by the method of thermal radical polymerization (initiator - benzoyl peroxide). The samples №10-№14, №16 are commercially

available. Cyclic olefin copolymer (analogue of TOPAS) was obtained from A.V.Topchiev Institute of Petrochemical Synthesis, RAS.

The received polymers were formed as cylinders of 4 cm height, with the diameter 5 or 20 mm. The samples were prepared by cutting off from these cylinders thin disks (from 0.4 to 2 mm), which were further polished to make their surfaces plane-parallel and smooth enough not to scatter THz radiation. The Teflon cuvette of 3 mm thickness was used for the measurements of liquid polystyrene monomer (styrene).

4. RESULTS AND DISCUSSION

At first stage the technological photopolymers (№1-№8) were examined, but they showed quite high absorption values (Fig.2). Despite different structures, all these photopolymers demonstrate similar behavior in THz frequency range - a characteristic broad peak or absorption curve band at the frequencies 2.5-3 THz accompanied by noticeable negative dispersion (dn/df = − 0.01 THz^{-1} at the average) in lower frequencies. There is the right slope of this peak at higher frequencies for sure, this fact is confirmed by published data from FTIR measurements[14,17] of similar substances. Unfortunately the center of this peak is at the limiting frequency for our spectrometer in the most of cases.
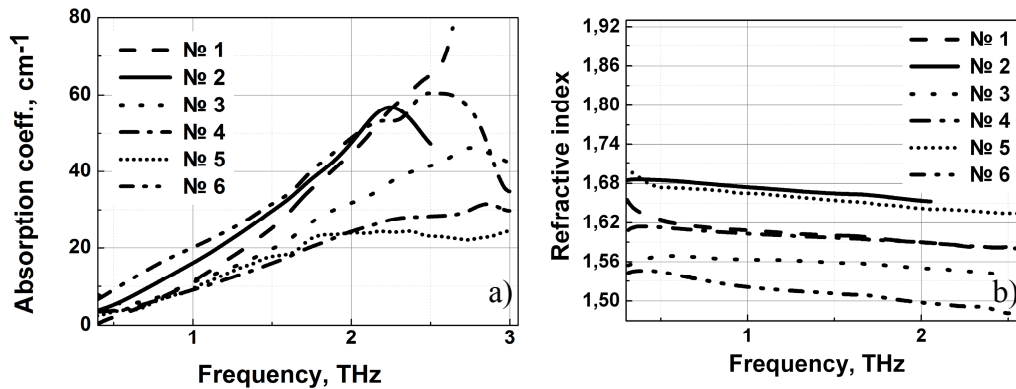

Figure 2. The experimental THz absorption (a) and refraction spectra (b).

At second stage the known low absorbing polymers (№11-№16) were examined. Unfortunately they are not photopolymers, but they should help us to analyze specific features of "transparent" polymers.
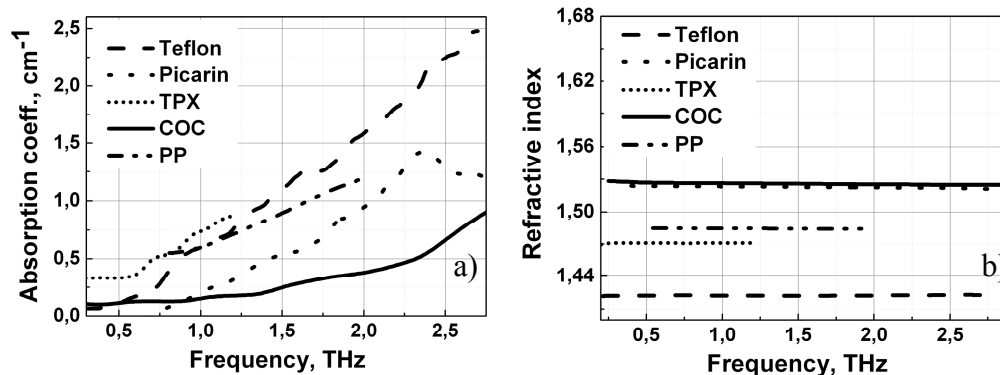

Figure 3. The experimental THz absorption (a) and refraction spectra (b).

The "transparent" polymers (Fig. 3) reveal following common features: almost linear increase of absorption, absence of absorption broad peak, negligible dispersion (dn/df = − 0.0003 THz^{-1} at the average) in the 0.1-3 THz frequency range.

4.1 Model of dielectric response

Dielectric relaxation, also called Debye relaxation, refers to the delayed response of a dielectric medium to applied electric fields. The momentary delay of the response is accounted for by random thermal fluctuations which slow down the reorientations of the dipole moments in the material. The simplest model to describe the relaxation process is expressed as the Debye model[4]:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D} ,$$

(1)

where the frequency-dependent electric permittivity is determined by the static permittivity ε_s, the high-frequency permittivity ε_∞, and the Debye relaxation time τ_D. The Debye relaxation time varies widely depending on the material system. Typical time scales range from microseconds to nanoseconds at room temperature.

The simplest model appropriate for THz polymers spectra is the relaxation process that can be expressed as the Debye expression, which predicts the decrease of refractive index, but it does not explain wide absorption decrease at the frequencies higher 2.5 THz.

Let us consider an example of PET (№10 in Table 1), as far as its absorption decrease at the frequencies lower than 3 THz is the most reliable experimental data from our measurements.

The Debye expression cannot fit the experimental THz absorption and refraction spectra, so we used the phenomenological Havriliak – Negami model[21] (the modified Debye model):

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (i\omega\tau_{HN})^\beta)^\gamma} , \text{ where } 0 < \gamma < 1.$$

(2)

The most successful agreement between the model and the experimental data (Fig.4) was obtained in cases when the power index γ was out of its applicable range: $\gamma=2.9$ (!), $\tau_{HN}=0.05$ ps, $\beta=0.9$, $\varepsilon_s-\varepsilon_\infty=0.46$, $\varepsilon_\infty=2.54$. It is important to notice: first, that the obtained γ value $=2.9$ is quite large that could mean the distributed relaxation time; and second, γ significantly differs from 1 that means large deviation of dielectric response of polymers from the Debye model.
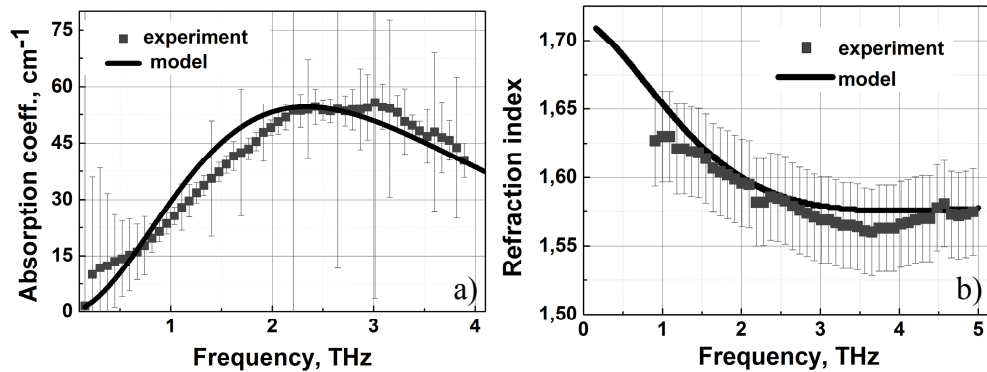

Figure 4. The experimental and theoretical THz absorption (a) and refraction spectra (b) of PET.

4.2 Impact of the monomer structure

Especially because of "strong" absorption of samples №1-№8, we should understand its reasons to avoid it. We tried to investigate the influence of different parameters on the absorption and refraction spectra of polymers.

We started with the clarifying the impact of number of monomer end groups on polymer dielectric properties with the homologous set of polyacrylates (№ 6 - № 8). The experimental THz absorption and refraction spectra of №6 is shown at Fig.1 (spectra of other representatives are similar).

For clear presentation of proceeding changes we graphed absorption coefficient and refractive index at frequency of 1 THz as a function of monomer end group number. These graphs demonstrate (Fig.5) that both absorption and refraction of the polymers reduce as monomer chain length increases.
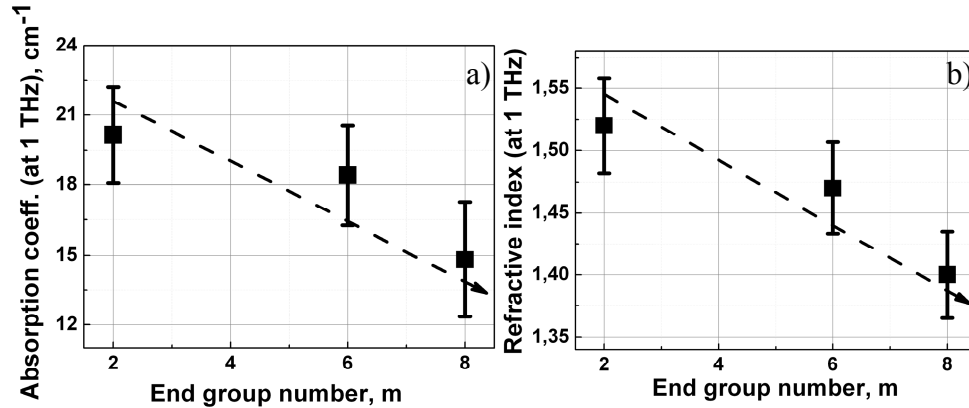

Figure 5. Absorption coefficient (a) and refractive index (b) at frequency of 1 THz as a function of monomer end group number.

4.3 Polymerization

Then we tried to answer the question: what will happen as a result of polymerization? We investigated the solid polystyrene (№9) and its monomer - styrene that is liquid and obtained unexpected result for THz-TDS. Absorption spectra of solid and liquid were found to be identical although the changes proceeded – the refractive index modified (Fig.6). This could mean that polystyrene does not have crystal lattice and intermolecular interactions are not crucial for polymer THz absorption.
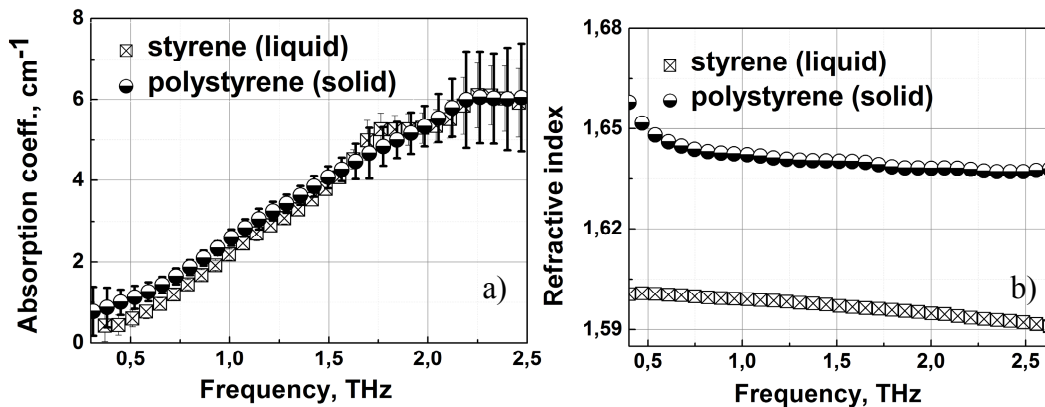

Figure 6. Absorption coefficient (a) and refractive index (b) of styrene and polystyrene.

5. CONCLUSION

Absorption coefficients and refractive indices at the frequency of 1 THz of investigated polymers (Table 2) are compared with the values compiled from different sources as indicated. It should be mentioned that dielectric data vary in different publications and our experimental data lie within the range of published values.

Table 2. Absorption coefficients and refractive indices at the frequency of 1 THz of investigated polymers.

Submission of the measured in the present work and published data.

Abbreviation	PMMA	PET	PC	PS	PP	Teflon	TPX	HDPE	Picarin	COC
α, cm^{-1} (measured)	11.3	15.2	9.6	2.2	0.58	0.6	0.74	1.66	0.2	0.15
α, cm^{-1} (published)	60[13] 21[14] 12.5[17]	20[14]	10[14] 11[22]	2.4[13] 2.0[22]	0.6[4] 1.9[14]	0.6[4] 2[14]	0.4[4]	0.3[4] 0.5[22] 2.2[14]	0.15[23]	0.15[23]
n (measured)	1.61	1.63	1.665	1.64	1.50	1.42	1.47	1.36	1.52	1.53
n (published)	1.596[14]	1.712[14]	1.651[14] 1.66[22]	1.59[22]	1.50[4] 1.51[14]	1.43[4] 1.445[14]	1.46[4]	1.53[4] 1.534[14] 1.53[22]	1.52[23]	1.52[23]

So, for creating integrated polymer waveguides in the THz region we need to obtain amorphous polymers (they are the most suitable for photopolymerization technology) with small absorption, for this – long chain of monomer molecule, and we need to decrease or shift broad absorption peak out of THz region. We suggest that the absorption mechanism (in spectral range lower than 3 THz) is related with relaxation and amorphous state of polymers. In conclusion, it was found that the modified Debye model (the Havriliak – Negami model at $\gamma > 1$) can describe both absorption and refraction spectra of amorphous polymers in the frequency range from 0.1 up to 3 THz.

We still should understand the nature of low frequency absorption peak in most of the polymers in details.

ACKNOWLEDGMENTS

REFERENCES

[1] Mirimanov R.G., [Millimeter and submillimeter waves], M.: Edition of foreign literature (1959) (in Russian).
[2] Valitov R.A., Djubko S.F, .Camishan V.V., [Technique of submillimeter waves], M.: Sov. Radio (1969) (in Russian).
[3] Zhang X.-C. and Xu J., [Introduction to THz Wave], Photonics© Springer Science+Business Media, LLC (2010).
[4] Lee Y.-S., "Principles of Terahertz Science and Technology", Springer Science+Business Media, LLC (2009).
[5] Taylor, Z.D., et al., "Reflective terahertz imaging of porcine skin burns", Opt. Lett. 33(11), 1258–1260 (2008).
[6] Brun M.-A. and et al., "Terahertz imaging applied to cancer diagnosis", Physics in Medicine and Biology, 55(16), 4615 (2010).
[7] Woodward R.M., et al., "Terahertz pulse imaging of ex vivo basal cell carcinoma", J Invest Dermatol, 120(1), 72–8 (2003).

[8]   Smye S.W., et al., "The interaction between terahertz radiation and biological tissue", Phys Med Biol, 46(9), R101-12 (2001).

[9]   Homenko A., et al., "Effects of 100 GHz radiation on alkaline phosphatase activity and antigenantibody interaction", Bioelectromagnetics, 30(3), 167–175 (2009).

[10] Scarfi M.R., et al., "THz Exposure of Whole Blood for the Study of Biological Effects on Human Lymphocytes", Journal of Biological Physics, 29(2), 171–176 (2003).

[11] Cherkasova O., et al., "Influence of terahertz laser radiation on the spectral characteristics and functional properties of albumin", Optics and Spectroscopy, 107(4), 534–537 (2009).

[12] Nielsen K., Rasmussen H., Adam A., Planken P., Bang O. and Jepsen P., "Bendable, low-loss Topas fibers for the terahertz frequency range", Opt. Exp. 17 (10), 8592-8601 (2009).

[13] Bershtein V.A., Ryzhov V.A., "Far Infrared Spectroscopy of Polymers, Advances in Polymer Science", Vol. 114, Springer-Verlag Berlin Heidelberg (1994).

[14] Jin Y.-S., Kim G.-J., and Jeon S.-G., "Terahertz Dielectric Properties of Polymers", J. Korean Phys. Soc., Vol. 49, No. 2, pp. 513-517 (2006).

[15] Sokolov V. I., Panchenko V. Ya., Seminogov V. N., "Narrowband 1.5-μm Bragg filter based on a polymer waveguide with a laser-written refractive-index grating", Quant. Electr., 40 (8), 739–742 (2010).

[16] Amrhein E.-M., "The vibrational spectrum of noncrystalline solids", Annals New York Academy of Sciences, p.179-195 (1971).

[17] Ryzhov V. A., "Low-energy libration excitations in glassy PMMA", Solid State Physics, 44 (12), 2229-2233 (2002).

[18] Ryzhov V.A., Bershtein V.A., "Low – frequency libration vibrations, Boson peak and interchain interactions in glassy polymer", Solid State Physics, 50 (10), 1901-1905 (2008).

[19] Poley J. Ph., "Microwave dispersion of some polar liquids", Appl. sci. Res. Section B, 4, 337-387 (1995).

[20] Nazarov M.M., Shkurinov A.P., Kuleshov E.A., Tuchin V.V., "Terahertz time-domain spectroscopy of biological tissues", Quant. Elect., 38 (7), 647-654 (2008).

[21] Havriliak S., Negami S., "A complex plane representation of dielectric and mechanical relaxation processes in some polymers", Polymer, 8, 161–210 (1967).

[22] Piesiewicz R., Jansen C., Wietzke S., Mittleman D., Koch M., and Kürner T., "Properties of building and plastic materials in the THz range", Int. Journal of Infrared and Millimeter Waves, 28 (5), 363-371 (2007).

[23] Sengupta A., Bandyopadhyay A., Boweden B. F., Harrington J., and Federici J. F., "Characterization of olefin copolymers using terahertz spectroscopy", IEE Electr. Lett., 42 (25), 1477-1479 (2006).