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Generation of ultra-short THz pulses in new optical nonlinear materials based on organic polymers

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Abstract. **Using the method of optical rectification of femtosecond laser pulses, we report the generation of short (a few field cycles) terahertz pulses in the samples of films based on polyimides with covalently bound chromophore molecules of DR type. The spectral width of the produced pulses is limited by the pump pulse duration. The quadratic nonlinear optical properties are imparted to the films in the process of their fabrication by orienting the chromophore molecules in the external electric field of the applied electrodes having an original configuration. The samples are compared with the ZnTe crystal. Using the methods of coherent spectroscopy, their transmission and refractive index dispersion spectra are investigated in the frequency range 0.5–2.6 THz. The studied polymer composition is promising for the application in coherent spectrometers both for increasing the working spectral range without dips and for improving the spatial resolution in the near-field terahertz spectroscopy.**

Keywords: *coherent terahertz spectroscopy, electro-optic polymers, polyimides.*

1. Introduction

The use of organic polymers with acquired nonlinear optical properties (electro-optic polymers [1]) for generating and detecting terahertz (THz) pulses and for time-domain spectrometers [2] allows the possibilities of THz spectroscopy to be significantly expanded. The electro-optic polymers are a composition of a polymer matrix and chromophore molecules oriented in one direction in the process of fabrication [3]. The purpose-oriented synthesis of chromophores with a large dipole moment, high hyperpolarisability of the first order, and the resonance band matched with the pump wavelength allow one to obtain nonlinear coefficients higher by orders of magnitude than those of crystalline materials, which provides advantages in the width and continuity of the spectral working range.

In electro-optic polymers the chromophore molecules can be mechanically mixed with the molecules of the polymer matrix (the guest–host system [4, 5]), or covalently bound to the side chains of the polymer [3, 6]. In the process of sample preparation, the dipole moments of the chromophore molecules are oriented in one direction by the external electric field (poling) near the temperature of the matrix vitrifaction, maintained during the subsequent complete cooling of the sample. As a result, the composition becomes non-centrosymmetric, acquiring nonlinear optical properties, and it becomes possible, in particular, to observe the second harmonic generation, optical rectification and electro-optic effect. The closeness of the absorption band of the chromophore molecules to the pump radiation wavelength essentially enhances the nonlinear response of the composition. As the matrix, the amorphous polycarbonate and polymethylmethacrylate [4, 6] are often used. Of great interest are the polymers of the polyimide class, characterised by a higher temperature of vitrifaction than other polymers (180–300 °C for different compounds), which allows the improvement of the stability and heat resistance of the ordered state. They also offer a wide choice for purpose-oriented synthesis [7].

Previously, using the method of second harmonic generation, the quadratic optical nonlinearity and its stability were studied for the compositions of different polyimides and chromophores in the guest–host system [8] and the system with covalent bonds [3, 7, 9]. In the present paper we report the optical properties (in the terahertz range) of the polyimide films [3, 7, 10] based on the 3,3'-dihydroxy-4,4'-diaminodiphenylmethane diamine and 1,3-bis-(3,4-dicarboxyphenoxy) benzene dianhydride with the covalently bound groups of the DR-13 dye, as well as the generation of THz pulses in them using the method of optical rectification.

2. Experiment

The electro-optic polymer film (Fig. 1) is spin-coated on glass substrates and then dried and baked [7]. The thickness of the films did not exceed 1 μm. Some samples were poled along the normal to the film using the traditional method of the corona discharge [3]. The rest samples were poled along the film surface using the applied electrodes having the original design developed by the authors. The samples poled in the corona discharge were used as control ones for the comparison of the nonlinear response by means of the second harmonic generation implemented in the setup described in Ref. [3].

We performed the numerical simulation of the electric field strength distribution in the gap between the applied electrodes of different configurations using the finite element method (EStat_Edu 7.0 Field Precision programme). The model allowed for the appearance of conductivity in the polymer and in the substrate under heating. We also performed

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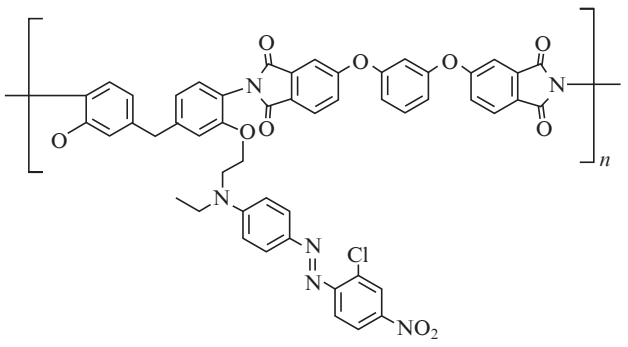

Figure 1. Structural formula of the polymer composition.

the control modelling for the conditions, described in Ref. [11] (two electrodes 3 μm thick with the gap of 100 μm on the silica substrate) and obtained good agreement of the results. For the poling of samples, we used the configuration of electrodes that demonstrated the minimal nonuniformity and asymmetry of the field distribution in the calculations. In fact, it was a planar capacitor with a transverse cut, where the sample was inserted. The electrodes were firmly pressed the to sample through an isolating, 15-μm-thick, polyethylene terephthalate film, which reduced the current in the circuit and protected the polyimide film from damage. For the interelectrode gap of 3 mm and the voltage between the electrodes 1610 V, the calculated field strength in the sample was from 0.2 V μm^{-1} (in the middle) to 1.5 V μm^{-1} (near the electrodes). The current in the circuit did not exceed 10 μA at the heating temperature 180°C. The field remained applied to the samples during up to 3 h (including the time of cooling).

The comparison of the nonlinear response, evaluated using the second harmonic generation, with that of the control sample having the nonlinear coefficient $d_{33} \approx 5$ pm V^{-1} at the wavelength 750 nm [3], has shown that the nonlinearity of longitudinally poled samples is comparable with that of the control samples.

To generate and record the THz pulses, we used the radiation from a femtosecond Ti:sapphire laser (760 nm, ~70 fs, 110 MHz, the mean power of 200 mW) as pumping for the excitation and as probing for the registration of THz pulses [12]. The focused pump beam was incident on the sample from the substrate side in the direction close to the normal; the polarisation plane was parallel to the poling direction in the film. It is important to note that the polymer film was not destroyed under the action of pump radiation with the maximal density of the mean power (in the focal spot) ~1.5 $kWcm^{-2}$, which was facilitated by the low absorption of the DR13 dye at the pump frequency [3]. Note that Ree et al. [13] reported the destruction of the samples based on the amorphous polycarbonate with the DDHF-6-V dye at the mean power density ~2 $W\,cm^{-2}$. The electric field of THz pulses was detected using the method of electro-optic sampling in the <110> ZnTe crystal having the thickness 0.5 mm.

Figure 2 presents the THz pulse and the spectrum of its power, averaged over three realisations. Although the thickness of the film sample and ZnTe crystal differ by two orders of magnitude, the amplitude of the THz pulse generated in the film is only by 2–2.5 times smaller (for comparison the inset of Fig. 2a shows the pulse, obtained from the <110> ZnTe crystal with the thickness 0.5 mm). The generated pulse has the duration less than 1 ps and consists of a few field oscil-

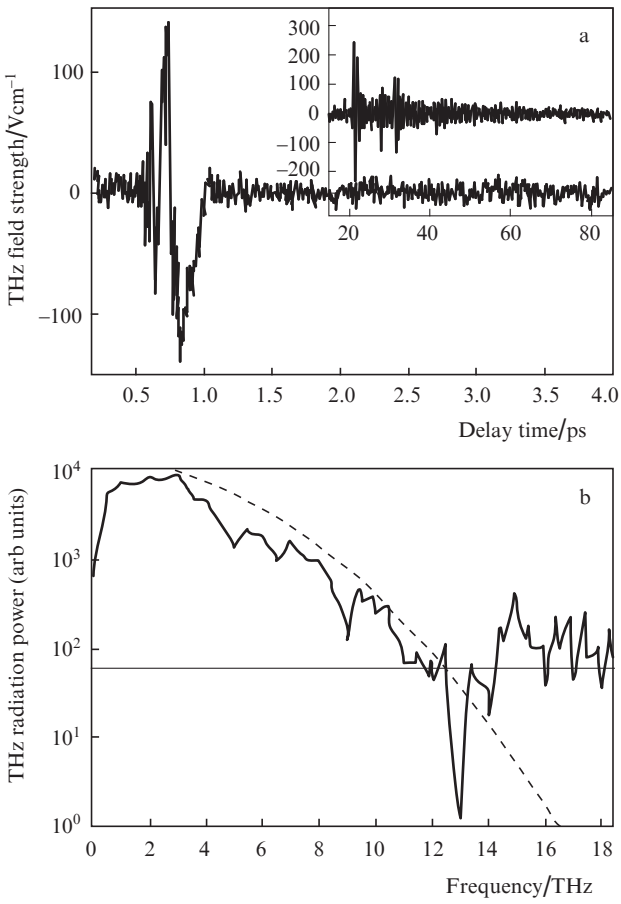

Figure 2. (a) THz pulse and (b) its power spectrum.

lations. In Fig. 2b the horizontal line shows the level of noise, which is determined as a mean square of the amplitude in the spectrum of the noise signal, recorded with the blocked THz beam under the same conditions. The dips present in the spectrum of the THz pulse in the frequency range 3–12 THz, correspond to the absorption bands in the atmosphere water vapours and in the ZnTe crystal of the registration system.

To characterise the optical properties of the electro-optic polymer in the terahertz range, we measured the spectra of the refractive index and the absorption coefficient (Fig. 3) using the methods of coherent spectroscopy [14]. Due to the considerable absorption of terahertz pulses in the glass, we used a fragment of a non-poled polymer film separated from the substrate.

One can see from Fig. 3a that in the range 0.8–2.6 THz the refractive index is $n_{THz} \approx 1.45$ and declines from this value by approximately 0.02. The weak dispersion is typical also for some other types of polyimides [15] and is considered as a positive characteristic from the point of view of stable phase relations between the pump and terahertz radiation within a broad spectral band. The absorption spectrum of the studied polymer (Fig. 3b) does not exhibit strong absorption and broad expressed bands in the range 0.8–2.6 THz. The use of this polymer in coherent spectrometers allows one to obtain the maximal possible dynamic range within the entire working spectral interval.

According to the data of Ref. [3], in the wavelength region near 760 nm the polymer possesses the refractive index $n = 1.71$ and the dispersion $\Delta n/\Delta\lambda \approx -2.5 \times 10^{-4}$ nm^{-1}. Therefore, the

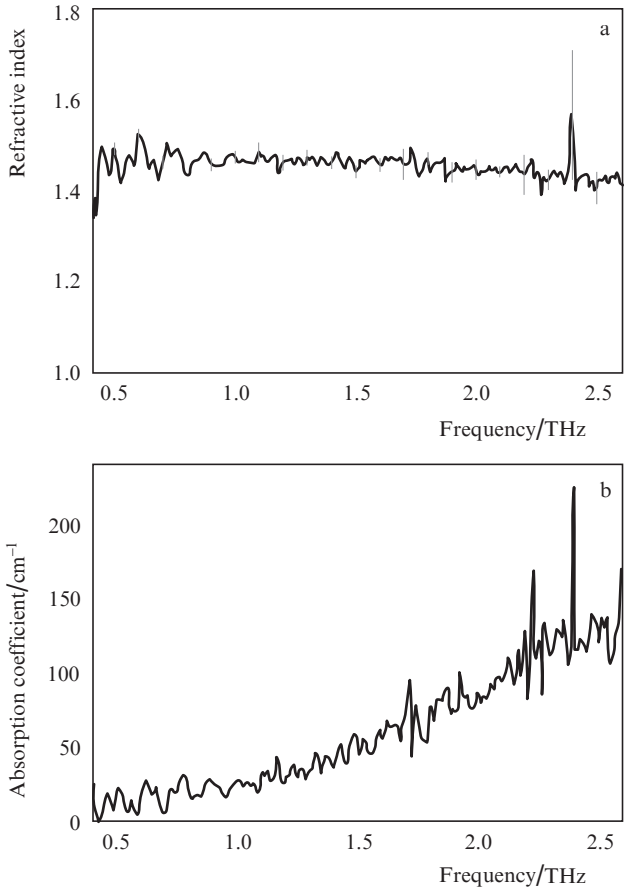

Figure 3. (a) Refractive index and (b) absorption dispersion coefficients of the electro-optic polymer in the THz spectral region.

group refractive index for the pump pulse $n_{gr} = n(\lambda) - \lambda\Delta n/\Delta\lambda \approx 1.86 > n_{THz}$. This fact means that the THz radiation overtakes the parent pump pulse. The source, exciting THz oscillations, which is a spike of the envelope electric field, produced by rectifying the optical oscillations of the pump pulse, propagates in the medium with the velocity c/n_{gr}, and at $n_{gr} = n_{THz}$ the accumulation of the THz wave power following the Cherenkov mechanism occurs. As follows from the obtained data, the frequency, at which this is possible, lies above 2.6 THz. However, the accumulation effects have no time to manifest themselves at such a small thickness of the polymer, which is much smaller not only than the length of interaction between the pump pulse and the THz wave, $L_{int} = c/(2f|n_{gr} - n_{THz}|) \approx 180$ μm, but also than the typical radiated wavelength $\lambda_{THz} = c/f$. It follows that the generation of THz radiation should occur in the maximally broad frequency band, corresponding to the rectified optical oscillations appearing when the pump pulse crosses the entrance boundary of the film. This conclusion agrees well with the experimental data: in whole, the spectrum of the THz pulse is well approximated by the spectral curve of the intensity envelope of the pump pulse having the duration 70 fs, shown by the dashed line in Fig. 2b.

3. Conclusions

In the present paper the generation of THz pulses in the electro-optic polymer based on the 3,3'-dihydroxy-4,4'-diaminodiphenylmethane diamine and 1,3-bis-(3,4-dicarboxyphenoxy)benzene dianhydride with the covalently bound groups of the DR-13 dye is reported for the first time. Under pumping by femtosecond laser pulses having the wavelength 760 nm, the electric field strength of the THz pulse, obtained from the film having the thickness smaller than 1 μm, is by 2.5 times smaller than that in the <110> ZnTe crystal having the thickness 500 μm. The resulting THz pulses (a few field oscillations) have sub-picosecond duration. We also studied the frequency dependences of the energy and optical properties of the polymer in the frequency range 0.5–2.6 THz. The results show that the studied composition is promising for the design of efficient broadband radiation-resistant devices intended for the generation and detection of THz radiation.

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