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Non-linear optical properties of epoxy-based polymers with covalently attached chromophores and metallic complexes[*]

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Non-linearl refraction and absorption in polymer structures based upon diglicidylether of bisphenol A has been studied. The polymers contain organo-metallic complex of nickel(II) NiL(ClO_4) 2- or 4-amino-azobenzene as non-linear optically active side groups covalently attached at each monomer unit. The studies have been carried out by polarization technique together with a real time pump and probe technique, dynamic holography and *Z*-scan. The materials were shown to exhibit fast non-linear response (relaxation time is about 20 ns) together with slow one (relaxation time of the order of tens of hours). This makes it possible to record fast- and long-lived (quasi-stationary) phase holograms. The analysis of possible mechanisms for the polymer refractive index non-linear response in the time range from 10^{-8} to 10^5 is presented. In particular, the role of electron polarizability, thermal excitation of the polymer, orientation of the chromophore molecules, and *trans-cis* isomerization processes are discussed.

Key words: *non-linear refraction; non-linear optical susceptibility; dynamic holography; azobenzene; isomerization*

1. Introduction

Molecular design is a new field in the materials science. This direction of scientific activity based upon practically unlimited opportunities in organic material synthesis has opened wide perspectives for development of new materials for the non-linear optics (NLO) [1]. By the end of XX century, sufficient progress has been made in the field of quadratic optical non-linear materials based on organic polymers [2]. In these materials, NLO active chromophores with large dipole moments have been as a rule covalently

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attached to polymer chains as side groups. Polymer matrices used for those purposes have to be thermally stable. This property made it possible to freeze the orientation of π-conjugated side groups so that the medium in question could be non-centrosymmetric. Thermally stable polyamide materials turned out to be the most suitable for those purposes. Regarding third order optical non-linear materials, the progress in their syntheses is not essential. Though it is clear that the perspectives of their practical application are very high.

To obtain effective cubic non-linear optical (NLO) polymer systems, it is necessary to use molecules with large effective length of π–π^* conjugation, which guarantee prompt electron excitation transfer over polymer chain and effective electron movement along the macrochains. The highest values of the third order optical non-linearity have been obtained in polymers (polyacetylene, polydiacetylene) with large effective π–π^*-conjugation length [3, 4], especially in the case of molecules with large dipole moments. However, the achieved values of optical non-linearity were too small to be used for the purposes of optical communication, information technology, transient holography and so on. Besides, it is well known that the increase of the π–π^* -conjugation length leads to an increase of absorption which, in turn, may cause overheating and thermal damage of the material under laser excitation. Also one has to take into account that the conjugated polymers are as a rule non-soluble. This limits their performance as well.

To obtain effective organic third order NLO materials we used non-conjugated polymer chain based upon epoxide (diglycidyl ether of bisphenol A) instead of a material with the strong π-conjugation along the polymer chain. To make the material optically and thermally stable and NLO sensitive, the following optically stable chromophores have been covalently attached to the polymer chain as side groups during polymerization:

- weakly conjugated organo-metallic complex of nickel(II) $NiL(ClO_4)_2$;
- photochromes capable of photoinduced isomerisation (*trans-cis* transition).

Polymers based on the monomers are transparent in the visible and IR spectral range as well as optically stable.

2. Third-order NLO response of epoxy polymer with nickel(II) complex, $NiL(ClO_4)_2$

One of the most promising approaches to increase thermal and radiation resistance is the modification of organic systems by organo-metallic or metal-complex compounds [1, 5]. In such a case we can expect that the role of the metal ion will be manifested in several ways: 1) manifestation of intrinsic hyperpolarizability through electronic transitions between molecular orbitals of the metal-containing compound (charge transfer from a metal to a ligand or from a ligand to a metal) and related possibilities of additive or synergistic effects in the metal-modified organic matrix; 2) strengthening of NLO characteristics of the organic matrix itself as a result of the polarizing donor-acceptor and/or electrostatic influence of the metal ion; 3) heat and light stabilization of polymers by the metal ion through deactivation of the triplet states of the macromolecules themselves and also singlet oxygen present in the polymers.

For the studies we have synthesized a new material consisting of a linear polymer based on an organic α-oxide with a covalently attached amine complex of nickel(II), $NiL(ClO_4)_2$. This particular compound was selected for the following reasons: 1) it contains a primary amino group that is sterically accessible and reactive in relation to the monomer, and this amino group can be incorporated into the polymer chain; 2) the macrocyclic complexes have high thermodynamic stability so that dissociation of the metal ion in the process of thermal polymerization and or under intense laser radiation can be avoided.

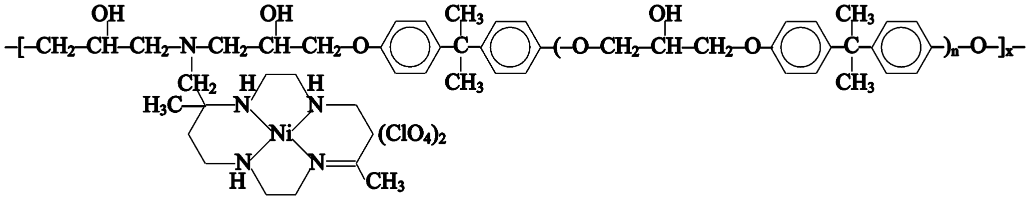

Fig. 1. Molecular structure of a linear polymer with metallocomplex of Ni(II) covalently attached at each unit of diglycidyl ether of bisphenol A, $n = 0; 1; 2$

The nickel(II) complex (Fig. 1) was synthesized and purified by procedures described in [6]. The complex was characterized by elemental analysis and by IR and electronic spectroscopy. As the epoxide monomer we used the diglycidyl ether of bisphenol A, which contained approximately 21% of epoxy groups. The metallopolymer was obtained by thermally initiated polymerization of a mixture of the epoxide monomer and the nickel complex in a ratio 3:1, with the reaction time of 7 h at 120 °C.

A comparison of IR spectra of the original α-oxide and the final polymer demonstrates that the polymerization is accompanied by spectral changes that are typical of epoxide systems, i.e., a decrease of intensity of the 917 cm^{-1} band corresponding to asymmetric stretching vibrations of the epoxide ring [7, 8]. Grafting of the nickel(II) complex, with the formation of a covalent bond, is evidenced by the fact that the spectrum of the polymer does not contain any bands of stretching vibrations of primary amino groups ($\nu = 3174$ cm^{-1}). Moreover, in the IR spectrum of the polymeric material, in comparison with that of the monomer, we observe a redistribution of intensities for the series of absorption bands in the 1000–1200 cm^{-1} region, possibly related to the appearance of intense bands of stretching vibrations of perchlorate ions in this region.

In Figure 2, we show electronic absorption spectra of acetone solutions of the original nickel complex (curve 2) and the synthesized polymer material (curve 1). The vertical line corresponds to the light wavelength λ = 532 nm used to investigate NLO properties of the material.

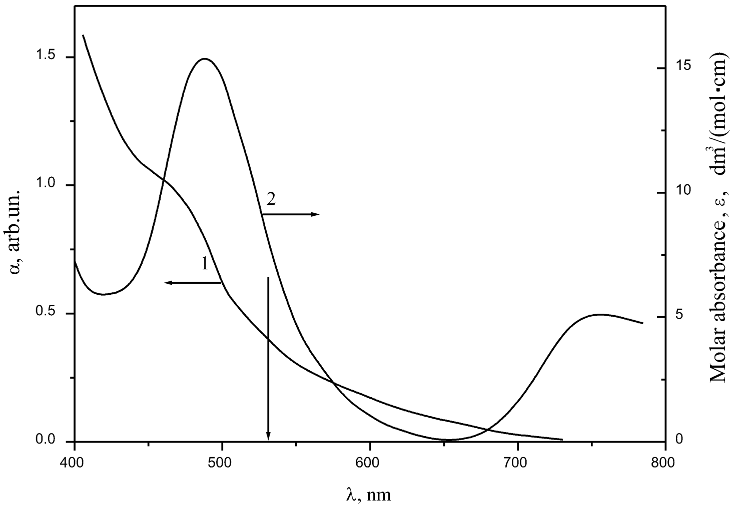

Fig. 2. Electronic absorption spectra: 1) acetone solution of the synthesized NLO polymeric material; 2) acetone solution of nickel(II) complex $NiL(ClO_4)_2$. The vertical arrow indicates the position of the Nd^{3+}:YAG second harmonic wavelength 532 nm

The spectrum of the $NiL(ClO_4)_2$ complex solution has a form that is typical of a six-coordinated nickel(II) ion [9] indicating that the primary amino group interacts with the metal ion. At the same time, in the spectrum of the polymer, against a background of organic matrix intense absorption (apparently produced by superposition of several bands of different types), we observe a shoulder at approximately 460 nm. Since this is the exact region in which we should observe a relatively intense band of the d–d transition of a square-planar complex of nickel(II) [9], such a feature of the spectrum can be regarded as indirect evidence of covalent insertion of the complex into the polymer matrix. As a consequence of the polymer formation, which proceeds through alkylation of the primary amino group, decoordination of the amino group should take place with a transition of nickel(II) from a six- to four-coordinated state.

For our study of the NLO properties of the synthesized polymer material, we prepared samples in the form of a polymer layer with a thickness of 100 μm between two glass plates. As the characteristic feature to be studied, we selected the non-linearity of refraction, which is the most promising NLO phenomenon from the standpoint of practical application in devices for controlling the parameters of laser radiation, and which is described by the tensor of third-order optical non-linear susceptibility $\chi_{\omega}^{(3)}(\omega; \omega, -\omega, \omega)$ [1].

The non-linear refraction of the medium in question have been studied by dynamic gratings recording using a scheme of the degenerate two-wave mixing. As a source of radiation we used a pulsed single mode frequency doubled YAG:Nd^{3+} laser (τ = 10 ns, λ = 532 nm, TEM$_{00}$).

In the course of the investigation, we measured an exposure characteristic of the samples, i.e., the dependence of the first-order diffraction pulse energy on the recording pulse energy. The experimental dependence shown in Fig. 3 is well described by the cubic equation $E_1 = aE_0^3$. This indicates that the phase dynamic gratings were recorded on the third-order optical non-linearity. The relaxation time of the non-linearity was estimated to be < 2 s. The positive sign of the non-linear refractive index was determined by the *Z*-scan method.

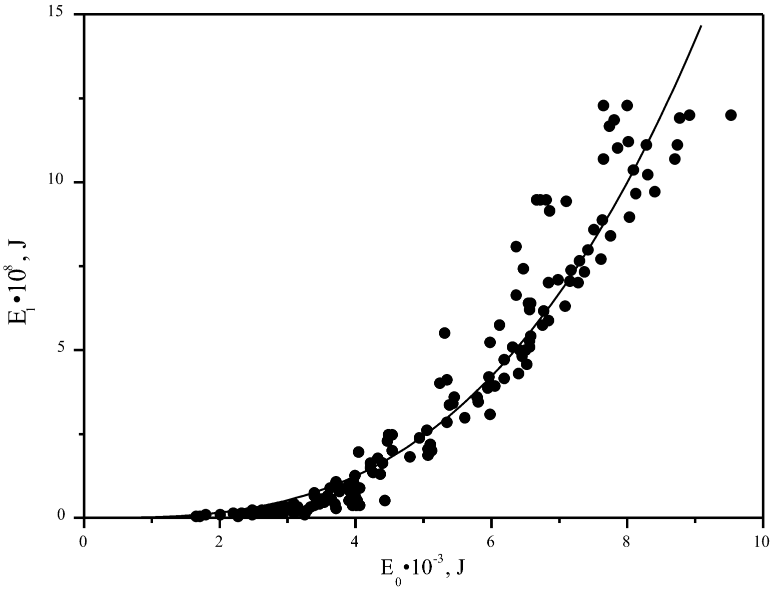

Fig. 3. First-order diffraction energy E_1 as a function of recording energy E_0

The value of $\chi_\omega^{(3)}$ was estimated using data obtained from the measurements of the diffraction efficiency by means of the following relationship [10]:

$$\left|\chi_\omega^{(3)}\right| = 3\left(\frac{n_0}{4\pi}\right)^2 \lambda \frac{\sqrt{\eta}}{\pi l I_0} \tag{1}$$

where n_0 = 1.67 is the refractive index of the sample; l = 100 μm is the thickness of the polymer layer; $\eta = 1.25\cdot10^{-4}$ is the diffraction efficiency; λ = 532 nm and I_0 = 5 MW/cm^2 are the wavelength and the intensity of the recording radiation. The value of $\chi_\omega^{(3)}$ was found to be $(2.6\pm1.3)\cdot10^{-10}$ esu.

It is known that with an increase of the intensity of irradiation (I > 1 GW/cm^2) of organic systems with conjugated bonds, the diffraction efficiency is gradually decreased as a result of damage of the conjugation system. Many tests on our material have shown that there is no such a decrease. However, with an irradiation power greater than 7 GW/cm^2, we observed a sharp disappearance of self-diffraction of the recording beams as a result of the polymer damage. Because of such a behavior the potential practical applications of the polymer material in question are restricted to a range of laser radiation power up to 7 GW/cm^2.

3. Third-order NLO response of epoxy polymer with chromophores*

For the synthesis of non-linear polymer with chromophores we used the epoxy monomer (diglycidylether of bisphenol A), which contained about 21% of epoxy groups. For the thermal polymerization of the monomer we used chromophore-4 -aminoazobenzene (AA). The amino group of every AA molecule combined two epoxy groups so that aminoazobenzene was covalently attached to the polymer chain. The information about the polymerization process and the structure of the resulting polymer can be obtained from the analysis of the changes in IR spectra [7, 12]. Actually, the polymerization leads to a rise of new OH groups in macromolecules and to an increase of the hydrogen bond amount. The presence of a large number of OH groups in macromolecules may lead to additional transverse bonds between polymer chains resulting in formation of a three-dimensional structure involving hydrogen bonds [7, 12]. The polymer obtained by us remained linear because it was soluble in polar solvents. When the polymer is heated over T_g, the hydrogen bonds break and the polymer turns into liquid state.

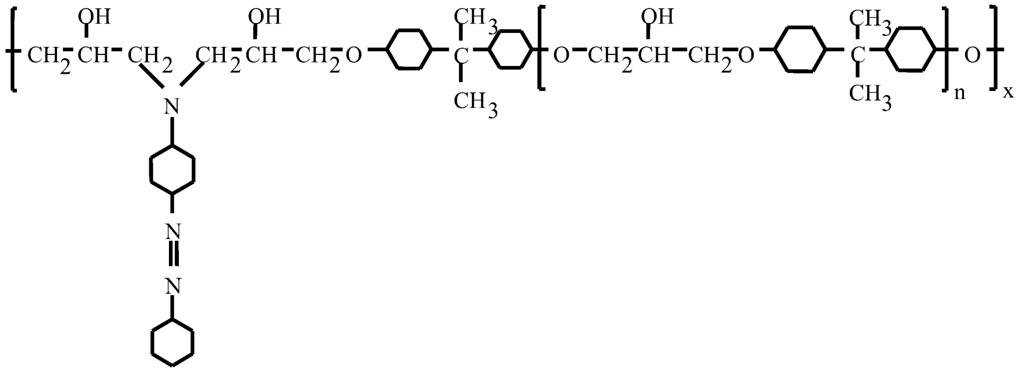

Fig. 4. Molecular structure of a linear polymer with 4-aminoazobenzene chromophore (AA), $n = 0; 1; 2$

The molecular structure of the synthesized linear polymer is shown in Fig. 4. The AA molecule can be viewed as a side group with respect to the polymer chain. In such a

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[*] Data presented in the chapter are mainly based on previously published results [11].

configuration, the azobenzene is capable of *trans-cis* isomerization upon light excitation. The absorption spectrum of the polymer in the visible spectrum range is shown in Fig. 5. The strong long-wave absorption band of the *trans* isomer of azobenzene (430–460 nm) is associated with the $n \to \pi^*$ transitions [13, 14], while a weak $\pi \to \pi^*$ absorption band is shifted towards short-wave spectral range and for the *trans* isomer of AA it is positioned at about 300 nm [15]. In Figure 5, the band $\pi \to \pi^*$ is not seen since it coincides with the absorption band of the sample glass substrate.

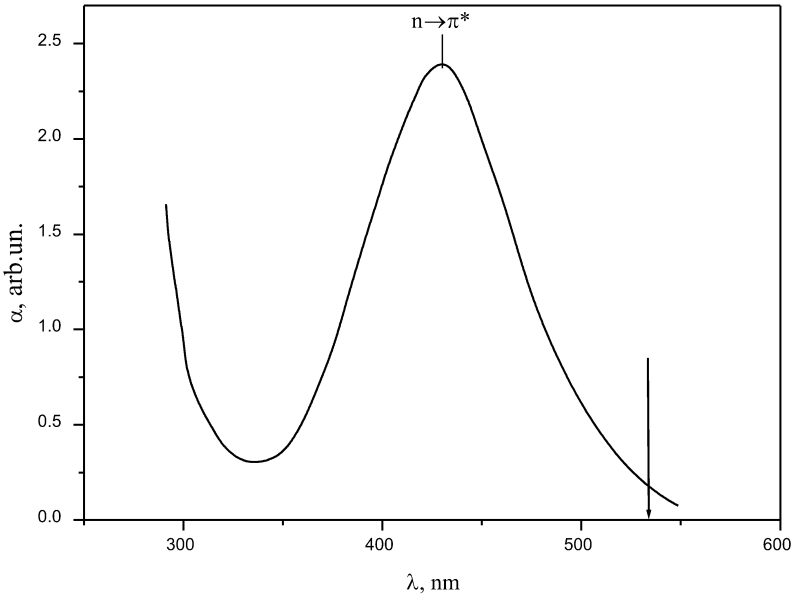

Fig. 5. Absorption spectrum of the structure shown in Fig. 4 in the visible spectrum range for AA (4-aminoazobenzene). The vertical line indicates the position of the Nd^{3+}:YAG second harmonic wavelength 532 nm

It is known that the *trans-cis* isomerization takes place for the excitation of both $n \to \pi^*$ and $\pi \to \pi^*$ transitions. However, the excitation of $n \to \pi^*$ transition is more preferable because the quantum yield of the isomerization in this case is two times higher [16]. The vertical line in Fig. 5 indicates the position of the wavelength 532 nm used for the sample excitation. It is seen that it coincides with the long-wavelength side of the absorption band so that the excitation of the $n \to \pi^*$ transition of AA is not resonant.

The samples studied were in the form of a thin polymer layers with the thickness of 140 μm placed between two glass plates. Two AA samples with the glass transition temperature T_g = 100 °C and T_g = 35 °C were prepared by thermal initialization.

The non-linear refraction was studied in the samples in question by means of recording transient phase gratings in the scheme of the degenerate two-wave mixing. The experimental set-up is shown in Fig. 6. A frequency doubled single-mode Nd^{3+}:YAG laser (λ = 532 nm) was used as a source of radiation. The laser delivered light pulses with the energy of 3 mJ and the pulse length of 10 ns. The laser pulse energy was changed by means of a polarizer attenuator A (a $\lambda/2$-plate together with a polarizer) and measured by a photodiode.

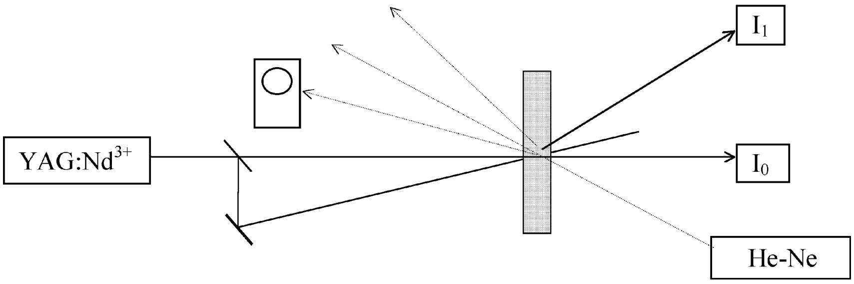

Fig. 6. Experimental set-up. Dynamic grating recording. YAG:Nd^{3+} – frequency-doubled single-mode pulsed laser (τ = 10 ns, λ = 532 nm, TEM_{00}). He-Ne – cw laser for reading out the recorded dynamic gratings

The laser beam was split into two beams of equal intensity. The beams intersect each other at an angle of $2\theta = 3°$. Our sample was placed where the beams were totally overlapped. The sample was excited by the interference pattern of the two beams so that a refractive index transient grating causing self-diffraction of the writing beams was induced in the sample. The first diffraction order pulse energy was measured by a photodiode. For our samples with AA molecules covalently attached to the polymer chain the self-diffraction pattern contains up to eight diffraction orders at recording energy of 0.4 mJ. In this case, the diffraction efficiency, $\eta = I_1/I_0$, (where I_0 is the recording beam intensity, I_1 is the first diffraction order beam intensity) of 20% can be achieved.

The exposition characteristic of the transient grating recorded in the sample with the glass transition temperature T_g = 100 °C is presented in Fig. 7. Actually it is the dependence of the first diffraction order intensity upon the recording one. The dependence is described by the cubic equation of a type $I_1 \sim aI_0^3$ fairly well. One can conclude that the transient gratings are recorded incorporating the non-linearity of the third order in the electric field, which is described by the non-linear susceptibility $\chi_{\omega}^{(3)}(\omega, \omega, -\omega, \omega)$. The value of $\chi_{\omega}^{(3)}$ can be estimated using the measured value of the diffraction efficiency and Eq. (1). For the following experimental data: η = 10%, E_0 = 0.3 mJ, l = 140 μm, $n_0(0.53) = 1.8$, [17] the laser beam diameter d = 2 mm and the laser pulse duration τ = 10 ns the value of $\chi_{\omega}^{(3)}$ was shown to be of $(4.7–2.4)\cdot 10^{-8}$ esu.

By means of Z-scan method we have found that the non-linear changes of the refractive index in our samples are negative that is the refractive index decreased in the field of the laser light.

To understand the mechanism of the medium non-linear response, it is important to determine the response time of the system that is the time of the refractive index changes. The kinetics of the refractive index non-linear variation was measured by means of pulsed recording (λ = 532 nm) and cw reading out the dynamic grating. A cw He-Ne laser (λ = 633 nm) was used for the grating reading out.

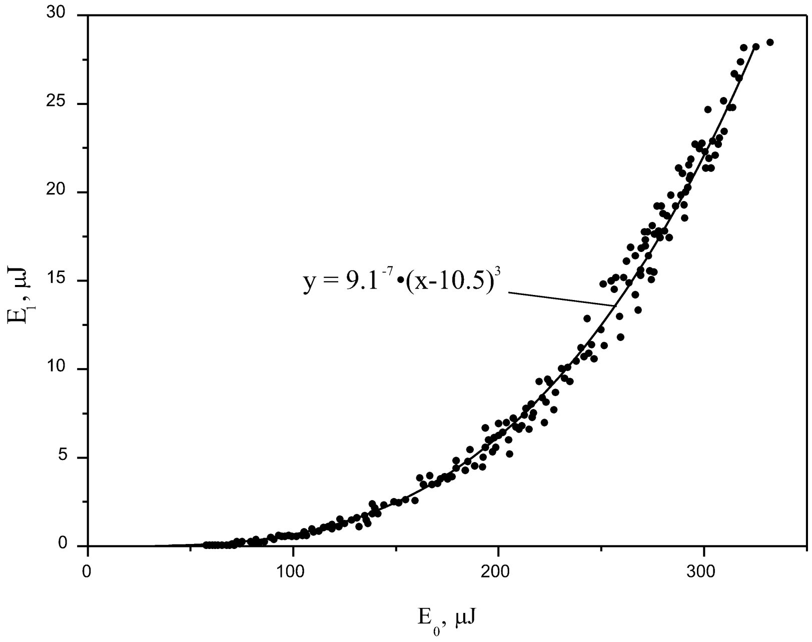

Fig. 7. The first order diffraction pulse energy versus writing pulse energy. Polymerized state. Experimental data (dots) and the solid line which presents an approximation by the equation shown in the figure

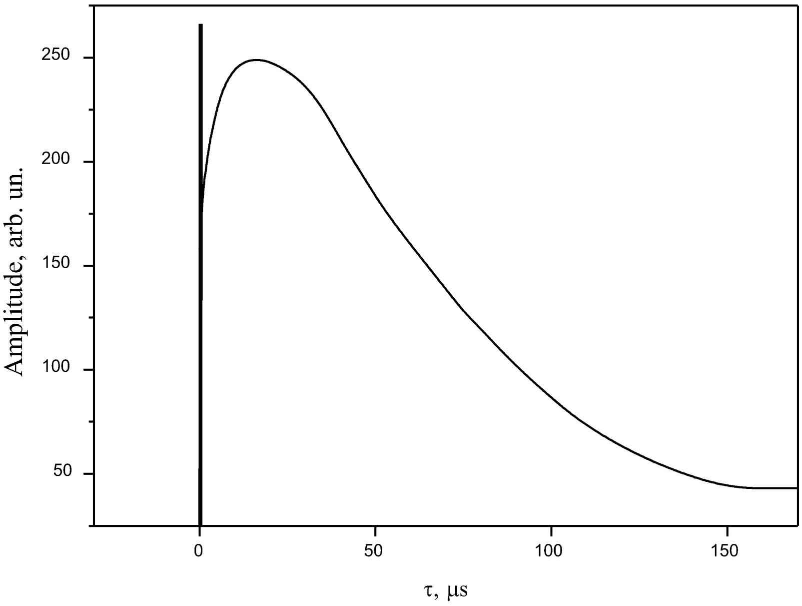

Fig. 8. Fast relaxation of the dynamic grating. Oscilloscope trace of a light pulse diffracted into the first order at reading out the grating by cw laser beam (He-Ne laser, λ = 0.63 μm)

The oscilloscope trace of the signal is shown in Fig. 8. Both grating writing and erasing occur with two different times: one in ns-, the other – in μs time scale. The μs component maximum is reached when the recording pulse is already absent. So that the measured $\chi_{\omega}^{(3)}$ value corresponds to ns component. Therefore it can be concluded that two different mechanisms participate in a fast non-linear process. It should also be mentioned that the samples with T_g = 100 °C and T_g = 35 °C have the same value of the diffraction efficiency in the μs time region.

Except the fast non-linear mechanism which is observed over a wide range of the writing intensities, a slow non-linearity with the characteristic relaxation time about 24 h appears starting from the recording intensity I = 300 kW/cm^2 (see Fig. 9). The slow grating mechanism has the maximum diffraction efficiency of about 15%. The self-diffraction pattern contains up to ten diffraction orders in this case. Thus the non-linear refractive index relaxation time range for the polymer with AA is from 10^{-8} to 10^5 s.

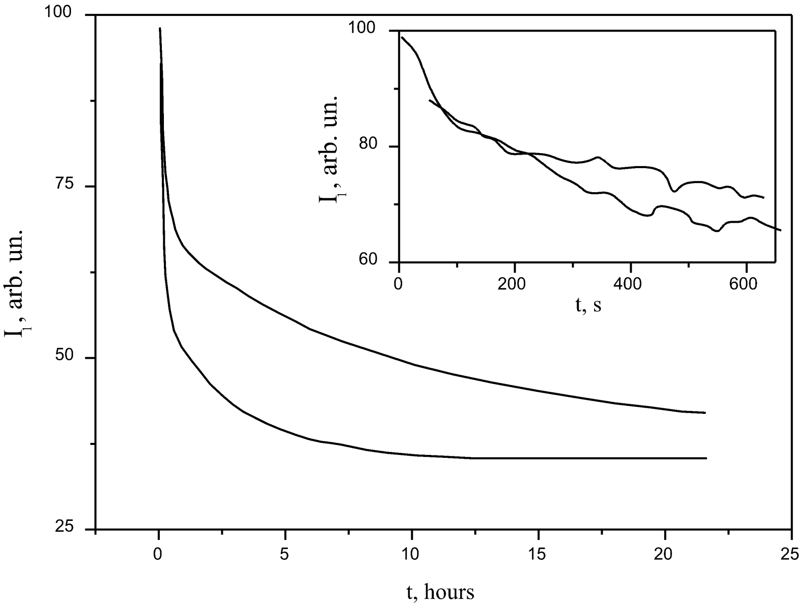

Fig. 9. Slow relaxation of the dynamic grating recorded by a single pulse taken as in Fig. 8. The insert shows in more detail the beginning of the dependence

The same experimental scheme was used for the studying the kinetics of the grating relaxation in this case. The grating was written by a single laser pulse with the intensity I = 0.8 MW/cm^2 and λ = 0.53 μm. Then it was read by cw He-Ne laser. The data on the diffraction efficiency were being taken every 10 s. The results are shown in Fig. 9. The insert shows the beginning of the dependence in more detail. Curve 1 has been obtained for the sample with T_g = 100 °C, curve 2 – for the sample with T_g = 35 °C. From the figure one can see that both curves are coincided in the time region from 0 to 200 s. Then the curves show sufficiently different character of relaxation. It is clear from the curves that the decreasing the T_g value of the polymer material leads to the faster decreasing of the diffraction efficiency of the long lived grating.

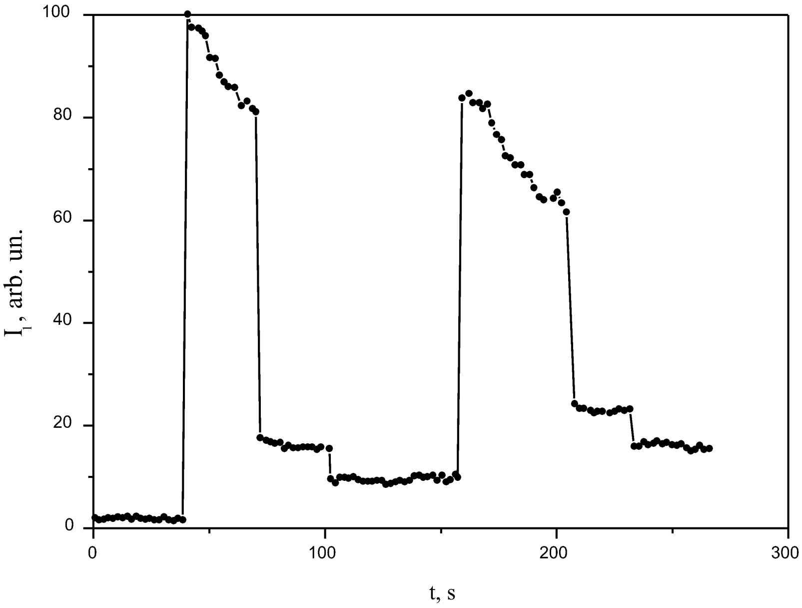

Fig. 10. Reversible writing and erasing a quasi-stationary grating

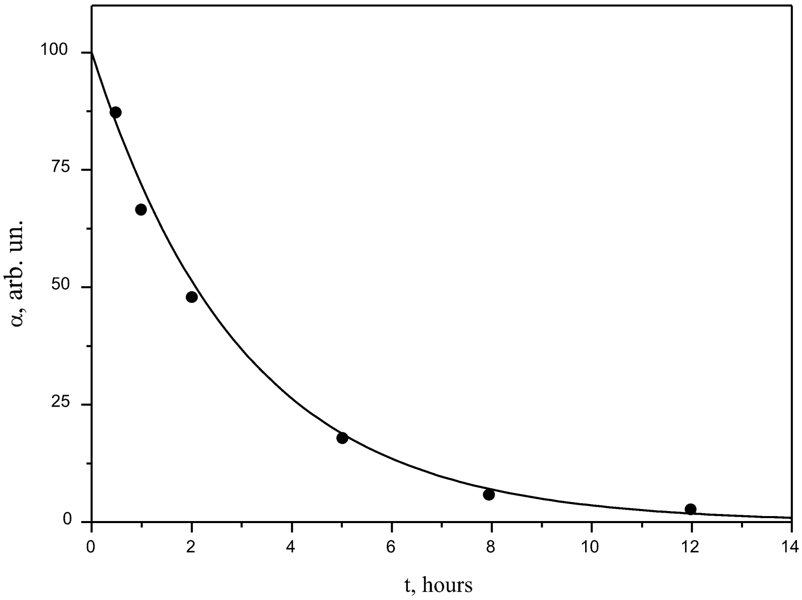

Fig. 11. *Cis* → *trans* relaxation curve for the T_g = 100 °C
obtained by means of UV spectrometry

Writing the dynamic gratings with the relaxation time higher than 10 h makes it possible to use the polymer in question as a memory medium for information storage. We have carried out studies on the possibility of reversible writing of the phase gratings in a polymer with 4-aminoazobenzene (T_g = 100 °C). We have chosen the sample because its damage threshold intensity is much higher than that of the sample with T_g = 35 °C. The dynamic grating has been written by a single laser pulse (λ = 0.53 μm) with the intensity I = 0.8 MW/cm^2. Then the grating was erased by one of the writing beams with the intensity I = 2 MW/cm^2. The writing and erasing cycles were then repeated several times. The reading out the recorded grating was carried out by the cw radiation of a He-Ne laser. Results of the studies are shown in Fig. 11. The results vividly manifest that the polymer with AA can be used as a recording medium for holographic reversible writing and storage of information.

4. Analysis of non-linearity mechanisms of epoxy polymers with chromophores

The phase dynamic diffraction gratings are usually the result of periodic modulation of the refractive index caused by contribution of population of electronic or vibration states (phonons) or medium density modulation caused by heat or electrostriction. However in the case of polymer optical non-linear materials isomerization and reorientation of azo dye molecules make sufficient contribution into the writing and erasing the dynamic gratings. Therefore in this chapter we dwell upon these non-linear mechanisms.

4.1. Isomerization

The long-wave shift of the absorption band accompanied by the absorption increase was observed during the dynamic grating recording in our samples. The complete restoration of the initial spectrum took about 11 h. The kinetics of the absorption spectrum restoration is shown in Fig. 11. These variations of the absorption spectrum are caused by the *trans-cis* isomerization of the aromatic azo compounds (AA) induced by rotation of one part of the AA molecule around the double bond N=N [15, 18–20].

Trans and *cis* forms of the azobenzene molecules are shown in Fig. 12a. Among possible mechanisms of the isomerization associated with the N=N and C=N bonds, it is necessary to distinguish a rotational mechanism that is rotation around X=Y bond and an inversion mechanism as the movement of a part of a molecule in plane without rotation as for instance in azo compounds with AA [15, 20].

The scheme of the inversion mechanism is shown in Fig. 12b [15]. The linear configuration along X=Y–a bond corresponds to a transition state. The inversion isomerization is possible only in the case when one of the atoms forming double bond possesses not only a substituent but also not shared electron pair or unpaired electron. For the azo compounds with AA such as unsubstituted azobenzene, the inversion mechanism takes place for both the *trans-cis* photoisomerization and the thermal *cis*

-*trans* isomerization [15, 20]. Figure 12c shows simplified energy diagram where the route of the thermal *cis-trans* isomerization is shown separately (γ).

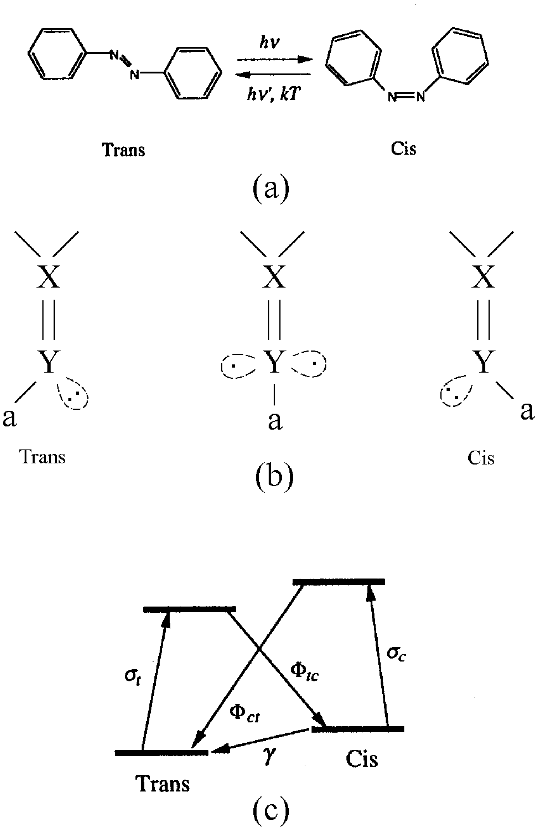

Fig. 12. Isomerization of AA (4-aminoazobenene): (a) azobenzene molecule change under the *trans-cis* isomerization, (b) the inversion isomerization mechanism scheme, (c) a simplified model of the molecular states. σ_t and σ_s are the cross sections for absorption of the one photon by a molecule in the *trans* and *cis* forms, respectively; γ is the thermal relaxation rate; and Φ_{ct} and Φ_{tc} are the quantum yields of photoisomerization

Such an isomerization can be viewed as a possible way of non-radiative relaxation of the molecular excitation [15, 18, 20]. That is why the fluorescence is not observed in many *trans* and *cis* isomers of azo compounds. The luminescence is not observed in our samples under laser excitation. The response time of the *trans-cis* photoisomerization of the azo compounds in solvents with different viscosity is from 10 to 100 ps [21]. Any triplet or other short-lived states in *trans-cis* transitions of the azobenzene have not been found by means of picosecond photolysis although the triplet nature of the isomerization is assumed [15, 20]. By means of the measurements of time-resolved absorption spectra it was shown [22] that in azo compounds dissolved in liquid crystals, the *trans-cis* transition time is about 10 ns under pulsed excitation (τ_p = 10 ns) at the wavelength of 355 nm. So the *trans-cis* isomerization is a fast process the response time of which could be comparable with the laser pulse duration (20 ns in our experiments).

It is known that the *cis-trans* thermoisomerization time is dependent upon the medium used as a solvent for chromophore molecules and may be of the order of minutes or even hours for the azobenzene without luminescence [15, 19]. The kinetics of the absorption spectrum restoration (reflects the *cis-trans* transition) measured in our samples after the pulsed laser excitation is fairly well approximated by the exponential relation of the form $y = y_0 e^{(-t/\tau)}$ (where time constant $\tau = 3$ h) in the time range from several minutes to 12 h when the spectrum is restored completely (see Fig. 11). Such a long transition time could be connected with the thermally activated rotational mobility of side or end polymer chain branches (β-relaxation at a temperature lower than T_g) [15, 23, 24].

4.2. Orientation

It is known [25–27] that the light polarized linearly orients azobenzene molecules in the plane perpendicular to the plane of oscillation of the electric field light wave. The orientation of the azobenzene molecules can be established during a very short time period. Thus, it was shown [28] that the azobenzene molecules in the polymer are oriented during 1 ps under excitation by the linearly polarized light pulse with the duration of 100 fs.

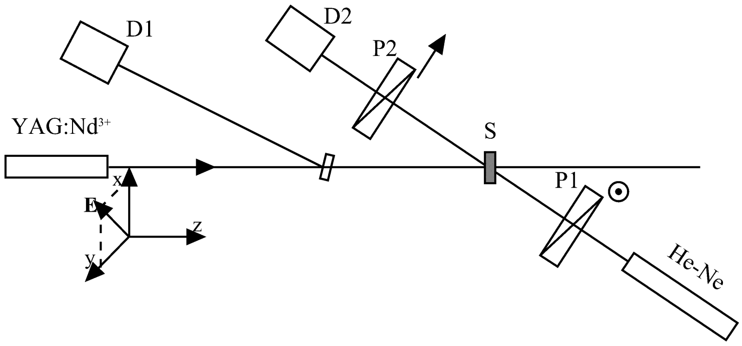

Fig. 13. Experimental set-up. Studies of the effect of induced birefringence due to azo dye molecules orientation in the field of linearly polarized YAG:Nd^{3+} laser light. P1, P2 – crossed polarizes, S – sample, D1, D2 – photodiodes

The contribution of the molecular reorientation into non-linear refraction of the polymers with 4-aminoazobenzene has been studied by means of the measuring the induced anisotropy. The experimental set-up is shown in Fig. 13. A frequency doubled single-mode pulsed Nd^{3+}:YAG laser (λ = 532 nm, τ_p = 10 ns, E_p = 0.3 μJ, TEM_{00}) was used as a source of radiation. The linearly polarized laser beam with the Gauss intensity profile was directed at the sample. The plane of the electric field oscillation is oriented at 45° to the vertical plane. The pulse energy was measured by a photodiode D_1. cw radiation of a He-Ne laser with a vertical polarization was directed at the sample at a small angle towards the pump beam. The He-Ne beam passed through two crossed polarizers and the pumped area of the sample placed between the polarizers. Initially our samples were isotropic so that the system "crossed polarizers–sample" was not transparent for the He-Ne radiation. However, in the case when the polarized pulsed radiation induced birefringence in the sample as a result of chromophore molecule orientation, the radiation of the Ne-He laser appeared at the output of the crossed polarizers. The radiation passed through the system "crossed polarizers–sample" is monitored by a photodetector D_2. The system makes it possible to study the dynamics of anisotropy induced in the sample in the time range from microseconds to hours.

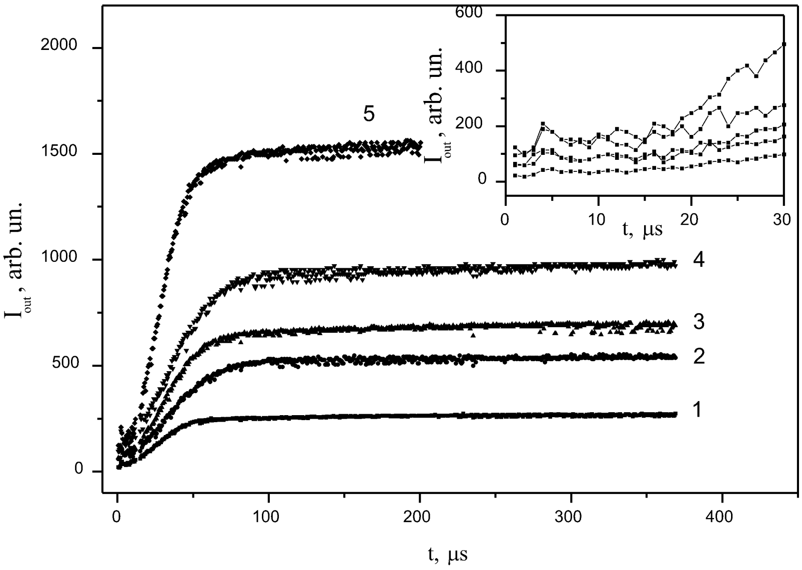

Fig. 14. Time dependence of induced anisotropy onset (He-Ne laser radiation amplitude at the output of the system "crossed polarizers-sample") for different pump pulse energy: 1 – 340 μJ; 2 – 560 μJ; 3 – 680 μJ; 4 – 1080 μJ; 5 – 1500 μJ

Figure 14 shows dependencies of the amplitude of the He-Ne laser radiation passed through the system versus time in the range from 0 to 400 μs for different values of the energy of the pump pulse. Each curve is a response of the sample at the single pulse action. The insert shows the beginning of the dependencies in detail. It is seen from the figure that the anisotropy appeares in spurts (see insert) under pulsed excitation and then after the pump pulse end the anisotropy continues to grow on during 50–70 μs until saturation. The level of the saturation linearly depends upon pump pulse energy.

The relaxation of the induced anisotropy is shown in Fig. 15. It was found that induced anisotropy relaxation has two time components: a fast one, τ_1~5–10 s and a slow one, τ_2 of the order of hours. It should be noted that the anisotropy does not decay completely. Some part of it remains for a long time. It could be removed by heating the sample above the glass transition temperature T_g.

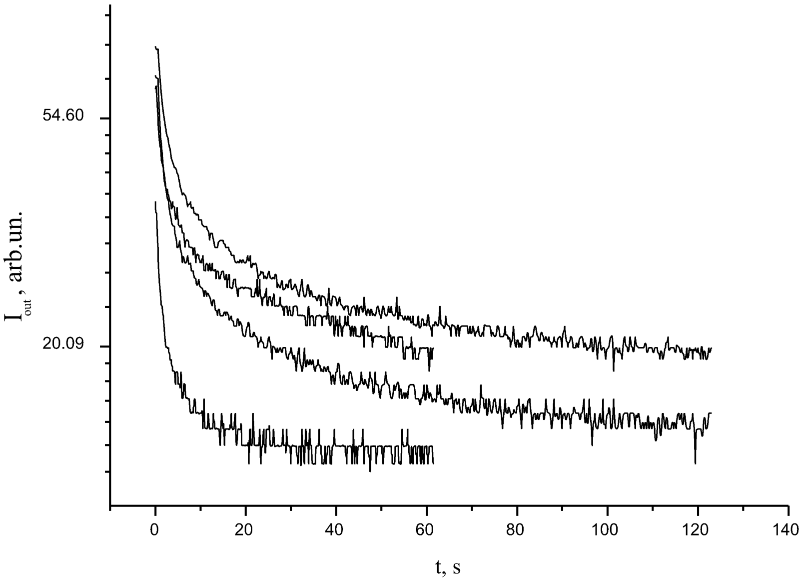

Fig. 15. Time dependence of the induced anisotropy decay (He-Ne laser radiation amplitude at the output of the system “crossed polarizers-sample”) for different pump pulse energy: 1 – 340 μJ; 2 – 560 μJ; 3 – 680 μJ; 4 – 1080 μJ

Photochromic, anisotropic molecules of azo dyes are characterized by double bond –N=N– between two phenyl rings and have a rod-like shape. Delocalization of π-electrons along the principal axis of the molecule leads to a strong anisotropy of polarisability and absorption dichroism ($\alpha_{\|}>>\alpha_{\perp}$). The dipole transition moment is oriented along the long axis of the molecule. Initially, all chomophore molecules are oriented randomly in the polymer so that the sample is isotropic. Linearly polarized light excites molecules selectively with the probability dependent on $\cos^2\theta$ where θ is the angle between the molecule axis and the electric field vector **E**. As the result of such a selective excitation some number of *trans* molecules transform into long-lived *cis* form. It leads to an anisotropic decrease of a number of *trans* molecules in some angle close to the light polarization plane. This effect is called “angular hole burning” [27]. It also could be viewed as a latent reorientation. *Trans-cis* isomerization of azo molecules takes place through excitation levels with very short lifetimes so that it takes 10 to 100 ps [21].

Earlier we have observed *trans*-*cis* isomerization in the samples in question under pulsed excitation (τ_p = 10 ps). Therefore the observed fast onset of the anisotropy (see insert in Fig. 14) could be attributed to angular hole burning in the angular distribution of the *trans* azo molecules.

Not all molecules are transformed into *cis* form due to steric hindrance [29] that is some molecules have not enough free volume for the transition into *cis* form. In this case the excitation energy transforms into heat. However, if the excitation energy is increased, the number of isomerized *trans* molecules may be increased due to additional molecules, which could overcome steric potential barriers. This effect is observed in the experiment. The level of the fast anisotropy onset is increased with the pulse energy (see insert in Fig. 14).

As we have already mentioned, in the field of the linearly polarized light azo molecules trend to reorient in a position perpendicular to the polarization plane of the light wave as a result of multiple acts of absorption-deactivation. This effect is called angular redistribution of azo molecules and contrary to latent orientation is direct reorientation that also gives its contribution to the induced anisotropy. As it was pointed out above, some molecules cannot transform into *cis* form due to conformational limiting. In that case absorbed energy is transformed into heat. Thermal oscillations of the surrounding of the azo molecule increase the rotational mobility of the azo molecules in the steric potential of the surrounding [29]. This effect causes direct reorientation of the molecule during laser pulse (10 ns) and dark reorientation of the molecules after laser pulse end. It is seen from the Fig. 14 that the process of the dark reorientation takes about 50–70 μs. The nature of such a strong reorientation is not clear at the moment. It needs to be studied additionally. It could be however supposed that azo dye molecules covalently attached to the polymer chains which occupy new position as a result of reorientation pull the polymer chain and cause reorientation of some its fragments [30]. Such a movement of the medium mass is an inertial process and it could not occur during short laser pulse because the conformational mobility of the matrix is much smaller than that of azo dye molecules.

Relaxation curves of the induced anisotropy decay are presented in Fig. 15. One can see that the relaxation has two characteristic times. Some part of induced anisotropy decays during 5–10 s and could be connected with the thermal diffusion of some oriented molecules. More slow decay (relaxation time about hours) is supposed to be connected with *cis-trans* isomerization that is the decay of the latent orientation. Such a relaxation time is in agreement with the *cis-trans* relaxation [11] (see Fig. 11).

Now we can distinguish different contributions into the non-linear refraction in the samples under study incorporated in dynamic grating recording [11]. Figure 16 shows the diffraction pulse of He-Ne laser radiation (curve 1) at dynamic grating recorded in the samples by two beams of a frequency doubled neodymium laser. Curve 2 obtained at the same pump pulse energy shows a contribution due to induced anisotropy. Curve 3 is a result of subtracting of curve 2 from curve 1. The curve manifests the contribution relaxing during 30 μs. This contribution could be attributed to the thermal effect. Actually this time is a time of erasing the thermal dynamic grating due to thermal diffusion. Taking into account that the period of the recorded grating Λ is equal to 6.5 μm, it is possible to calculate the coefficient of the thermal diffusion in the material under study:

$$D_T = \frac{\Lambda^2}{4\pi^2\tau} = 3\cdot10^{-7}\ \mathrm{m^2/s} \qquad (2)$$

Here $\tau = 30$ μs is the thermal grating relaxation time deduced from curve 3 in Fig. 16.

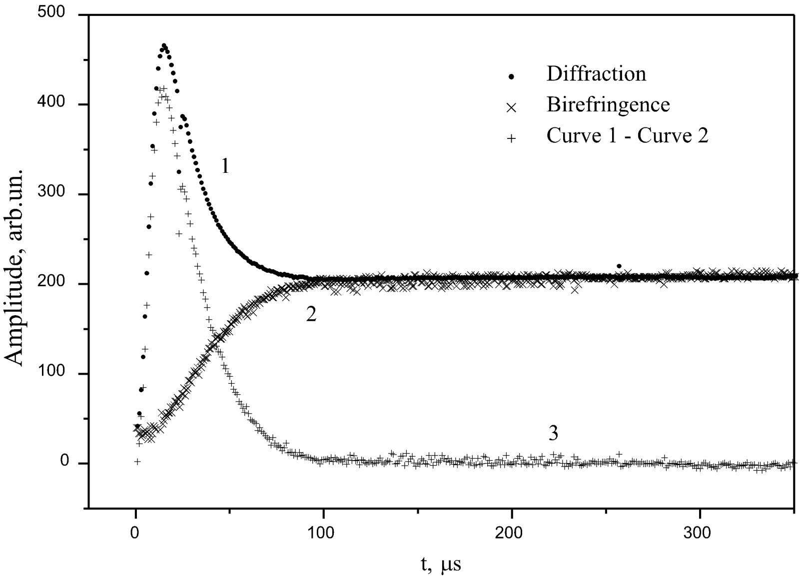

Fig. 16. He-Ne laser radiation diffraction at dynamic grating recorded in the sample by the frequency doubled neodymium laser pulse (1); anisotropy contribution (2); thermal grating contribution (as a result of subtracting curve 2 from curve 1) (3)

Conclusions

We have shown the possibility of creating new, effective, third-order non-linear polymer materials without strong π-conjugation along polymer chains but having π-conjugation in the side groups.

The results on non-linear refraction in epoxy-based polymer materials with covalently attached metal complex of nickel and NLO chromophores are presented. Third order optical non-linear susceptibility $\chi^{(3)}_{\omega}(\omega, \omega, -\omega, \omega)$ has been measured in the materials by means of degenerate two-wave mixing using frequency doubled pulsed YAG:Nd^{3+} laser. The kinetics of the dynamic grating recording and erasing in the materials in question have been studied in the time range of 10^{-8}–10^{5} s. The role of such mechanisms of non-linear refraction as electron, thermal isomerization and orientation has been discussed.

It should be finally pointed out that unlike second order polymer materials in which matrixes with high T_g are usually used to freeze molecular orientation in third order optical non-linear materials, it is recommended to use matrixes with not high T_g to guarantee free molecular reorientation and insomerization. Besides, using matrixes with different T_g makes it possible to control the relaxation time of the third order optical non-linear polymer materials.

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