NONLINEAR OPTICAL PHENOMENA

Measurement of cubic nonlinear-optical susceptibility of new metalloorganic polymer films and solutions

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Abstract. The cubic nonlinear-optical susceptibility of solutions and films of new metalloorganic polymers is studied by the z-scan method using 1064-nm, 40-ps laser pulses. The contribution of the electronic susceptibility is measured with the help of probe beams with circular and linear polarisations. The greatest electronic susceptibility amounting to -9.5×10^{-11} and -1.7×10^{-10} CGSE units is found in films of poly[(arylene)(ethynylene)silylene] and chromium-doped bis(aren)polyacrylonitrile, respectively.

1. Introduction

The development of laser methods and their applications stimulate a search for new nonlinear optical materials. In this connection, conjugated organic polymers have attracted considerable recent attention of researchers [1, 2]. Recent studies of these materials revealed their high electronic nonlinearity. The high optical nonlinearity of conjugated polymers of some types is caused by the specific features of their molecular structure such as the presence of strongly conjugated and polarisable π- and σ-electron systems, the possibility of intramolecular charge transfer, etc. [2].

At the same time, the optical nonlinearity of conjugated electronic systems remains virtually inertialess, the characteristic time of its establishment being a few femtoseconds. The high and quick-response electronic nonlinearity of polymers, along with the convenience of their manufacturing and processing in the form of films and fibres, makes these materials quite promising for the development of a number of devices such as fast optical switches, which can be used in optical communications, integrated optics, optical computers, etc. [3].

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A great interest in the study of nonlinear optical properties of conjugated polymers is also explained by their prospect for using as active laser media with optical or electric pump, which can produce lasing in a broad spectral range from the near-IR to the UV region [4].

Despite a certain success achieved in the study of nonlinear optical properties of conjugated polymers, the number of organic and metalloorganic materials possessing the high nonlinearity that have been studied so far is very small compared to the number of relevant substances that can be synthesised. Our paper is devoted to the study of the electronic nonlinearity of two classes of new conjugated organic polymers doped with silicon atoms or transition-metal ions. The polymers were synthesised at the Institute of Metalloorganic Chemistry (Nizhnii Novgorod, Russia) and the Université Montpellier (France). The earlier nanosecond laser studies of solutions of polymers of this class revealed polymers that had the highest cubic susceptibility [5–7].

The aim of this paper is to continue studying the nonlinear-optical susceptibility of films and solutions of these polymers using picosecond 1064-nm pulses from a Nd : YAG laser. Such a study is required for confirming the electronic mechanism of nonlinearity of polymer films. This is explained by the fact that upon excitation by short (picosecond) laser pulses, the contributions from other nonresonance mechanisms (thermal, striction, or orientation) to the total cubic nonlinear susceptibility prove to be negligible compared to that from the electronic mechanism because the characteristic times of the development of nonresonance mechanisms greatly exceed the laser pulse duration.

2. Metalloorganic compounds studied

We studied new metalloorganic polymers of two classes: polyarylenethynylenes and polyacrylnitriles, which exhibited high nonlinear susceptibilities in earlier experiments with nanosecond pulses [5–7].

Silicon-doped polymer poly[(arylene)(ethynylene)silylene] (PAES) was synthesised at the Université Montpellier [6]. Films of this polymer of thickness 40 μm (the mass content of PAES was 5%) were deposited from the solution of phenyltrimetoxysilan (75%) and tetraethoxysilan (20%) in tetrahydrofurane (THF). Some films of this polymer that were used in experiments were prepared by the sol–gel method. A great length of the electronic conjugation chain of the PAES molecule suggests that this molecule should possess a considerable nonlinear polarisability (Fig. 1a).

Conjugated polymers of another class under study were represented by chromium-doped bis(aren)polyacrylonitrile
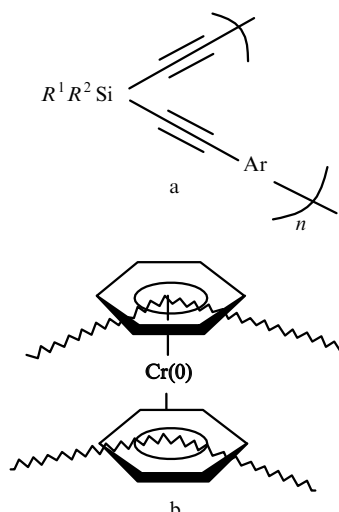
Figure 1. Structural unit of the chain of the PAES molecule (a) and the CPAN molecule (b).

(CPAN), which was synthesised at the Institute of Metalloorganic Chemistry [8]. The presence of a transition-metal Cr ion in the CPAN molecule and extended electronic conjugation chains of side groups of this molecule indicate to the possibility of a strong charge separation and large nonlinear-optical polarisability (Fig. 1b).

We also investigated the films that were prepared from solutions of these polymers (the mass content $\sim 50\,\%$) in acetonitrile. Along with CPAN, the films contained a plasticizer — malonodinitrile. Polyethylcyanoacrylate (PECA) prepared from the solution in acetonitrile CH_3CN was used as a matrix. We also studied a film containing the charge-transfer polymer complex of CPAN with tetracyanoethylene (TCE).

We studied polymers PAES and CPAN in films and solutions. PAES was dissolved in chloroform and toluene, and CPAN was dissolved in acetonitrile.

3. Schematic of experimental studies

Fig. 2 shows the schematic of a picosecond laser setup that we have built for our experimental studies. As a master oscillator, a passively Q-switched pulsed Nd:YAG laser 1 was used, which operated near the lasing threshold at 1064 nm. A polymer switch based on a polyurethane matrix doped with polymethine dyes deposited on one of the cavity mirrors was used as a passive modulator [9]. The laser emitted trains of ~ 40-ps pulses (20 – 30 pulses) with repetition period of 18 ns. The pulse energy was $\sim 10^{-6}$ J and polarisation of the output radiation was linear.

We used only one picosecond pulse from each train for nonlinear-optical measurements. It was separated with the help of a Pockels cell 2 placed between two crossed polarisers (Glan prisms). The separated picosecond light pulse was directed to a two-pass Nd:YAG amplifier 3 with a polarisation decoupling, which amplified the pulse energy to $10 - 50$ μJ. After the amplifier, the pulse was incident on a glass wedge, where a part of its energy (about of 4 %) was directed on a photodetector 4, which controlled the probe-beam energy.

Then, the light beam was focused by a lens with the focal length 12 cm on a polymer sample (film or a thin cell with solution), which was mounted on a micrometer table, which provided a precision displacement of the sample along the focal waist of the laser beam. The intensity of the beam propagated through a nonlinear layer was measured near the axis in the far-field zone with a photodetector 6. The total power of the transmitted beam was also measured using a wide-aperture photodetector 5.

4. Experimental method

The study was performed by the so-called z-scan method [10]. This method is based on the measurement of a nonlinear refractive index n_2 from the dependence of the intensity of a beam propagated through a thin nonlinear layer on the position of the latter with respect to the lens focus (Fig. 2).
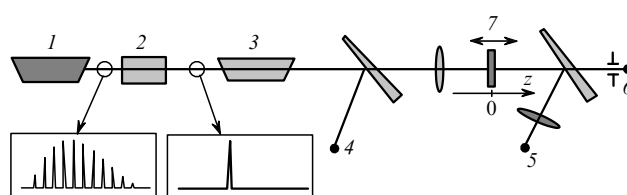
Figure 2. Schematic of z-scan measurements of nonlinear optical susceptibility of polymers: (1) master oscillator; (2) polarisation switch; (3) amplifier; (4–6) photodetectors; (7) polymer sample.

The z-scan method is described by the theory of self-focusing. In the approximation of a small nonlinear inertialess variation in the refractive index, the following expression can be obtained [10, 11]:

$$\Delta T \simeq 0.4\Phi_{NL} = 0.4kn_2Il,$$

where ΔT is the difference of the transmittances (the ratio of the power of a beam propagated through a small aperture on the axis to the total beam power behind a nonlinear layer) at the extreme points of the z-scan curve; Φ_{NL} is the nonlinear phase incursion at the beam axis; n_2 is the nonlinear refractive index caused by the cubic nonlinearity of the crystal; I is the light-beam intensity at its axis; k is the wave number; and l is the nonlinear layer thickness. Knowing the beam intensity at the axis and measuring ΔT, we can determine the nonlinear refractive index n_2.

The theoretical dependence of the transmittance T on the position of a nonlinear layer with respect to focus ($z = 0$) is described by the expression [10, 11]

$$T = 1 - \frac{2(z/z_d)\Phi_{NL}(0)}{\left[1 + (z/z_d)^2\right]^2}, \tag{1}$$

where z is the coordinate of the position of a sample along the focal waist axis and z_d is the diffraction length. Expression (1) shows that the dependence $T(z)$ has the form of the 'dispersion curve' with the centre of symmetry at the focal point (see Figs 3 – 5). Depending on the sign of nonlinearity, the positions of the maximum and minimum of the curve are interchanged: In the case of focusing nonlinearity, the location of a sample between the lens and the focal point corresponds to the minimum of the curve,

whereas for defocusing nonlinearity, the maximum of the curve is observed.

In our z-scan experiments, photodetector *6* was located at a distance of 50 cm from the sample and collected a part of the laser beam of diameter 1 mm near its axis. The total diameter of the beam in the detection cross section was ~ 10 mm. The corresponding ratio of diameters of the detected beam and of the entire beam provided the stable detection of the beam power near its axis. An additional detection of the entire power of the beam propagated through a nonlinear layer (with the help of a broad-aperture detector *5*) allowed us to measure the linear and nonlinear absorption in the sample.

To calibrate the z-scan scheme and verify the reliability of the method, we used a cell filled with chloroform (the layer thickness was 2 mm) with the well-known linear refractive index $n_2 = 5 \times 10^{-15}$ cm^2 W^{-1} [2], whose sign corresponds to focusing nonlinearity. The nonlinearity of the chloroform layer determines its dominating contribution into a complete nonlinear phase incursion of the wave propagated through the cell compared to the contribution from glass walls (the typical nonlinear refractive indices of glasses are $(4 - 14) \times 10^{-16}$ cm^2 W^{-1} [12]). Our measurements with the use of 20-μJ laser pulses demonstrated focusing nonlinearity in chloroform. Within the experimental error (about 10 %), the calibrated value of n_2 for chloroform was 5×10^{-15} cm^2 W^{-1}, coinciding with the known value from Ref. [2].

To determine the applicability of the approximation of weak nonlinear perturbation, which was used to derive expression (1) for z-scan, we performed a series of experiments with different energies of probe pulses (10 – 50 μJ). To determine the type of nonlinearity (electronic or orientation), the linear polarisation of the probe beam was changed to the circular one by placing a $\lambda/4$ plate in front of the lens at an angle of 45° to the direction of the initial polarisation of the beam.

## 5. Discussion of the results

Measurements of the dependence of the sample transmission to the full aperture by using $\sim 10 - 20$-μJ laser pulses showed that absorption of polymer films of PAES and CPAN was $10 - 30$ cm^{-1}. This corresponds by the order of magnitude to the linear absorption of polymers in the absence of a resonance transition in this region. This result is also confirmed by the measurements of absorption spectra of these polymers, which absorb beginning from the wavelengths $400 - 450$ nm.

Measurements of the dependence of the sample transmission to the full aperture on the sample position along the focal waist showed the absence of two-photon absorption at 1064 nm at the laser beam intensities used. This result also is consistent with the absorption spectra of polymers studied.

The z-scan measurements (the detection of the laser beam power by detector *6* at different positions of a cell in the focal region) gave the nonlinear refractive indices of polymer films under study. The experimental dependences of the detected power on the coordinate obtained by us are in good agreement with theoretical curves, which were described by expression (1) with different nonlinear refractive indices n_2 (Fig. 3). We calculated the cubic optical susceptibility of polymers from experiments with linearly polarised probe beams (Table 1). The largest values of $\chi^{(3)}$

amounting to -9.5×10^{-11} and -1.7×10^{-10} CGSE units were obtained in films of PAES and CPAN, respectively.
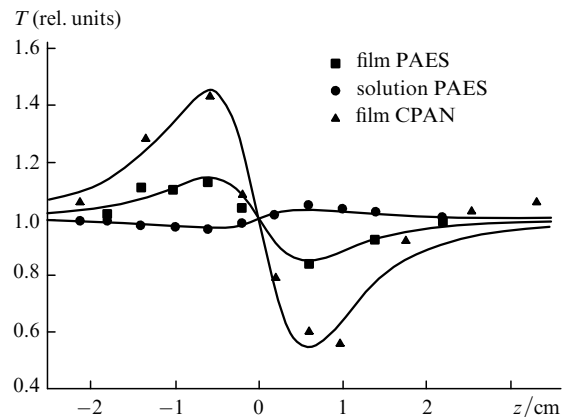
Figure 3. Experimental data (dots) for z-scan measuring cubic optical susceptibility of PAES and CPAN polymer films and PAES solution in toluene and theoretical curves corresponding to the obtained values of $\chi^{(3)}$.

Table 1. Results of measurements of the nonlinear refractive index n_2 and cubic optical susceptibility Re $\chi^{(3)}$ using linearly polarised probe wave (except the cases indicated). The laser pulse energy is 40 μJ (except the case indicated)

Polymer	n_2/cm^2 W^{-1}	Re $\chi^{(3)}$/CGSE units
PAES (film, 14.4 %)	-1.9×10^{-12}	-9.5×10^{-11}
PAES (solution in toluene, 64 g l^{-1})	1.5×10^{-14}	7.5×10^{-13}
PAES* (solution in toluene, 64 g l^{-1})	8.3×10^{-15}	4.2×10^{-13}
CPAN + TCE + PECA + CH$_3$CN (film, 1:10)	-2.5×10^{-12}	-1.2×10^{-10}
CPAN + TCE + PECA + CH$_3$CN (film, 1:3)	-3.5×10^{-12}	-1.7×10^{-10}
CPAN + TCE + PECA + CH$_3$CN* (film, 1:3)	-2.2×10^{-12}	-1.1×10^{-10}
CPAN + TCE + PECA + CH$_3$CN** (film, 1:3)	-3.6×10^{-12}	-1.8×10^{-10}
Chloroform; (CHCl$_3$) [2]	5.0×10^{-15}	2.5×10^{-13}
Optical glasses [12]	$(4 - 14) \times 10^{-16}$	$(2 - 7) \times 10^{-14}$
Polymer PTS [10]	5.0×10^{-12}	2.5×10^{-10}

Notes: *Circularly polarised probe wave.
** Pulse energy is 10 μJ.

The duration of probe laser pulses in our experiments was 40 ps. On the other hand, the typical thermal relaxation time of excitations in polymers (vibronic relaxation time in films) is ~ 30 ps [13]. This means that the absorbed energy is converted to heat only at the laser pulse end. In addition, the travel time of sound in a polymer film of thickness 40 μm is even longer, about of 10 ns. As is known, it is this time that determines the instant of the development of strong thermal nonlinearity caused by thermal expansion of the medium at a constant pressure [14]. Taking the above two factors into account, we can state that the thermal nonlinearity has no time to appear during irradiation by the probe pulse.

Therefore, the nonlinear susceptibility measured by us is caused by fast electronic or orientation mechanisms. This conclusion is additionally supported by good agreement

between our results and the results of measurements of some polymers using 3-ps pulses from a neodymium–phosphate glass laser [15].

The sign of the nonlinear refractive index for most polymers studied here corresponds to the defocusing non-linearity. This means that nonlinearity of these polymer films cannot be explained by orientation effects that cause the self-focusing of a Gaussian beam. The only mechanism capable of explaining nonlinearity of our samples is the electronic nonlinearity. The nonlinear susceptibility corresponding to this nonlinearity can be both positive and negative [1, 2, 12].

To confirm the electronic mechanism of nonlinearity, we performed, along with experiments with linearly polarised waves, the experiment with a circularly polarised probe beam. The idea of this experiment is to separate the isotropic electronic nonlinear susceptibility $\chi^{(3)}$, which has the same nondiagonal tensor components $\chi^{(3)}_{xyyx} = \chi^{(3)}_{xxyy} = \chi^{(3)}_{xyxy}$, and the orientation nonlinear susceptibility, which has different nondiagonal tensor components [16]. This leads to the difference between nonlinear refractive indices n_2 for the waves with circular (n_2^{cir}) and linear (n_2^{lin}) polarisations in these media. In the medium with the electronic nonlinearity, the relation between these indices has the form $n_2^{lin-el} = (3/2)n_2^{cir-el}$, while in the media with the orientation nonlinearity, $n_2^{lin-or} = 4n_2^{cir-or}$ [16, 17].

The difference between nonlinear refractive indices in such media results in a substantial difference between the results of the z-scan for beams with circular and linear polarisations. The ratio of ΔT for the z-scan by a circularly polarised beam (ΔT_{cir}) and a linearly polarised beam (ΔT_{lin}) determined by the ratio of nonlinear refractive indices n_2 for each of the polarisations is different for media with the electronic and orientation nonlinearity mechanisms. For media with the electronic nonlinearity, $\Delta T_{lin}^{el}/\Delta T_{cir}^{el} = n_2^{lin-el}/n_2^{cir-el} = 3/2$, for media with the orientation nonlinearity, $\Delta T_{lin}^{or}/\Delta T_{cir}^{or} = n_2^{lin-or}/n_2^{cir-or} = 4$. By measuring ΔT for each polarisation of the probe beam and calculating their ratio with weight coefficients, we can calculate the contributions of electronic and orientation mechanisms to the total nonlinear susceptibility of the medium [5].
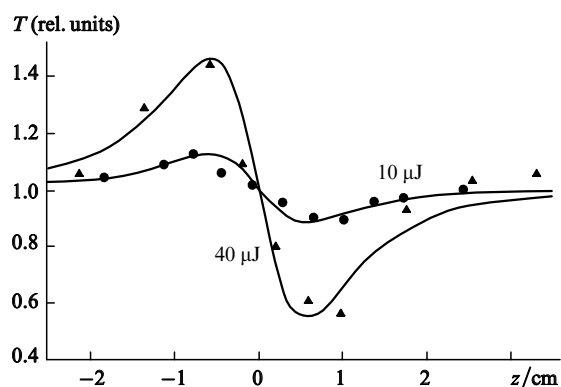
The comparative results of z-scan measurements of the CPAN film presented in Fig. 4 and Table 1 show that the ratio of differences ΔT for linearly and circularly polarised
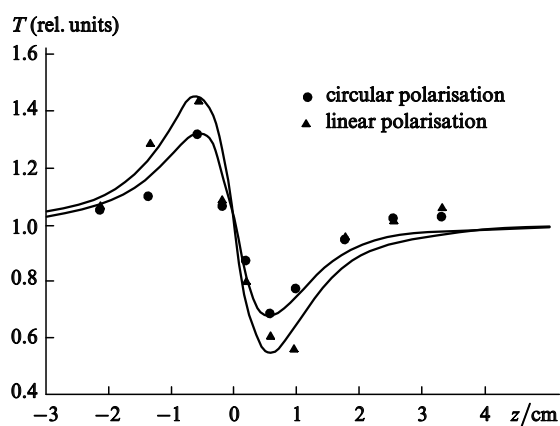
Figure 4. Results of z-scan measurements with circularly and linearly polarised probe beams for the determination of the type of nonlinearity in the CPAN film.

probe beams is approximately 3/2. Therefore, the electronic mechanism of nonlinearity dominates in the films. This fact is consistent with the physical concept about the smallness of the coefficient of orientation nonlinearity in films because of the strong interaction between their molecules (molecular elasticity), which prevents the reorientation of polymer molecules upon the interaction with the electroc field of a light wave [12].

To verify the validity of the z-scan formula, which was obtained assuming that nonlinear perturbations are weak, we performed experiments using probe beams of different intensities. These experiments showed that the values of n_2 measured at energies of the probe pulse equal to 10 and 40 μJ were in good agreement (Fig. 5).

Figure 5. Results of z-scan measurements of the CPAN film using 10- and 40-μJ probe pulses.

The unexpected results were obtained upon z-scan measurements of polymer solutions. Thus, measurements of the nonlinear-optical susceptibility in solutions of polymers PAES and CPAN in chloroform and acetonitril yielded (within the experimental error $\sim 10\%$) the same values of n_2, with the same sign, as in pure solvent. On the other hand, nonlinearity of the PAES solution in toluene was noticeably different from the nonlinearity of the solvent (see Fig. 3). Moreover, the sign of the nonlinear refractive index n_2 of the PAES solution in toluene (corresponding to the focusing nonlinearity) proved to be opposite to the sign of n_2 for this polymer in a film (see Table 1).

Measurements of the nonlinear refractive index of polymer solutions by the z-scan method using linearly or circularly polarised laser beams showed that the orientation contribution in solutions is also negligible compared to the electronic contribution (see Table 1). Similarly to films, this conclusion follows from the magnitude of the ratio of ΔT for circularly and linearly polarised probe beams, which was approximately 0.65. This value shows that the electronic mechanism of nonlinearity also dominates in solutions irradiated by picosecond pulses. Therefore, orientation effects cannot explain the change in the nonlinear refractive index of polymers in different solutions.

It seems that the interaction of solvent molecules with polymer molecules plays an important role and can change the nonlinear polarisability of the latter. This can explain the fact that the same polymer in different solutions has different nonlinear refractive indices, which strongly differ from (even by sign) from nonlinear refractive indices of films.

6. Conclusions

We have studied nonlinear-optical properties of solutions and films of new metalloorganic polymers by the z-scan method and measured their cubic optical susceptibility. By using linearly and circularly polarised probe beams, we have found that the electronic mechanism of nonlinearity dominates. The coefficients of cubic optical susceptibility equal to -9.5×10^{-11} and -1.7×10^{-10} CGSE units for polymers PAES and CPAN, respectively, according to our measurements, greatly exceed these coefficients for typical nonlinear optical materials (for example, they are greater than in glasses by 10^3 times [10]).

The nonlinear-optical properties of organic compounds studied in this paper compare well with those of compounds having the largest nonlinearity constants (for example, for the best polymer PTS known to us, $\chi^{(3)} = 2.5 \times 10^{-10}$ CGSE units at a wavelength of 1064 nm [10]. The important advantage of the polymers studied here is their weak linear and two-photon absorption in the near-IR region (near 1 μm), which makes them promising for the use in various systems (in particular, as nonlinear-optical splitters and summators in fibre-optic communication systems).

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