

LASER NONLINEAR INTERACTION WITH MATTER

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**LOW POWER LASER INDUCED OPTICAL NONLINEARITIES
IN ORGANIC MOLECULES**

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Abstract. Experimental demonstration of low power laser induced optical nonlinearities in two different types of specially designed materials: dye doped liquid crystals and copolymers with new pendant azobenzene moieties, is presented. Saturation of the nonlinear refractive index change is observed for some of the samples. The origin of the huge nonlinearity and its saturation in the continuous wave laser regime and at low power levels are analyzed.

Key words: optical nonlinearity, nonlinear refractive index, I-Scan, quantum dots, liquid crystals, chromophores, polymers, azobenzene.

1. INTRODUCTION

Optical nonlinearities have become an interesting research field due to the development of the lasers as sources of high intensity electromagnetic field, comparable to the interatomic electric fields, necessary to induced anharmonic oscillation of atoms or molecules and therefore an anharmonic interaction of light with mater. The first observed nonlinear effect was the second harmonic generation from a quartz crystal pumped by a ruby laser, in 1961. From that moment the research in the field of nonlinear optics contains the explanation and discovery of different types of optical nonlinearities and the important development of materials

with high nonlinearity using intensities as low as possible. These researches are strongly motivated by applications in lasers, spectroscopy, microscopy, imaging, data processing and data transmission.

The development of synthetic materials with controllable optical properties from absorption to emission, by controlling the electronic structures of the materials is a huge step forward for the scientific community and for the optics market. The development of materials with tuneable nonlinear optical properties is the natural next step in the development process of these materials.

As the humanity is using the optical materials at their edges, the characterization of their optical nonlinearities is very important and different tools have been developed to deal with this demand.

In this paper, we have investigated nonlinear optical properties, more precisely nonlinear refractive index change, of some of the most novel materials at this time: liquid crystals and azobenzene containing polymers. To tailor their nonlinear optical properties, we have used different methods depending on the class of materials. Liquid crystals are known to have large nonlinear refractive indices. By doping them with special dyes [1], we can tune their response to the wavelength that is needed for an application and obtain huge optical nonlinearities. The same is true for the azobenzene containing polymers. Such polymers bearing suitable azobenzene moieties are well known for their induced nonlinear optical properties [2-4], due to their *cis-trans* clean photochemistry. Most azobenzenes can be optically isomerized from *trans* to *cis* with light, anywhere within the broad absorption band; and the molecule will subsequently thermally relax back into the *trans* state on a timescale dictated by the substitution pattern. These materials benefit from the inherent stability, rigidity, and processability of polymers, in addition to the unusual photo-sensitivity of the azo moieties.

We shall illustrate these phenomena experimentally in the next sections.

Same huge and tuneable nonlinear optical properties were recently observed in semiconductor quantum dots [5, 6].

2. I-SCAN METHOD FOR INVESTIGATION OF THE NONLINEAR REFRACTIVE INDEX

To measure the nonlinear refractive index change with the incident intensity and, to deduce from this, the nonlinear refractive index we have used the I-Scan method [7]. This method is a derivation of the Z-Scan method [8]. In this type of experiments a gaussian profile beam is propagating through a nonlinear medium. The total refractive index of the medium is:

$$n = n_0 + \Delta n, \quad (1)$$

where, n_0 is the linear refractive index and Δn is the nonlinear refractive index change – proportional to the intensity. In the simplest case of the single beam interaction, the third-order nonlinearity is proportional to the light intensity:

$$\Delta n = n_2 I. \quad (2)$$

In the case of higher-order nonlinearities involved in the beam propagation process, the nonlinear refractive index change can be written as:

$$\Delta n = n_2 \cdot I + n_4 \cdot I^2 + \dots \quad (3)$$

Saturation of nonlinearity is also possible and very interesting in our case, in which the nonlinear refractive index change is equal to:

$$\Delta n = \frac{n_2 I}{1 + I/I_{sat}}, \quad (4)$$

where I_{sat} is the intensity at which the saturation of the refractive nonlinear process occurs. For $I \ll I_{sat}$, equation (4) can be expanded in the form:

$$\Delta n(I) = n_2 I - \frac{n_2}{I_{sat}} I^2 + \frac{n_2}{(I_{sat})^2} I^3 - \dots \equiv n_2 I + n_4 I^2 + n_6 I^3 + \dots \quad (5)$$

Thus, equations (4) and (3) are similar, and can describe the refractive saturation process. For further calculations and measurements, we shall use the equation (4) as it directly relates to saturation through the I_{sat} .

In this way, the beam induces inside the sample a gaussian shape refractive index change, which is following the incident intensity profile. This induced refractive index profile is acting like a lens and the changes in the propagation of the laser light through this lens can be easily monitored by the transmission through an aperture placed in the far field.

The experimental setup that we are using in our experiments is shown in the Fig. 1. In this setup, we have used a continuous wave laser at $\lambda = 532$ nm, a controlled motorized variable optical attenuator to modify the value of the intensity incident to the sample, a $f = 5$ cm focal length lens to focus the laser beam on the sample and a detection system formed by a detector placed behind an aperture and connected to a computer with an oscilloscope and an analogic/digital converter. The sample is positioned at 0.85 of Rayleigh distance before the focus. This position is determined by the position of the maximum in a Z-Scan curve acquired before the I-Scan experiments.

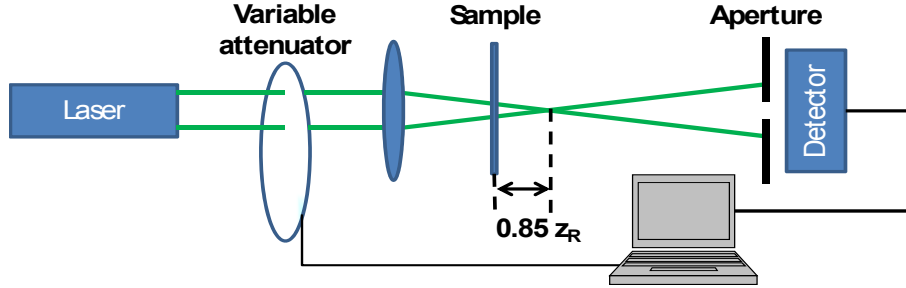


Fig. 1 – I-Scan experimental setup.

For fitting the experimental data, we have derived an I-Scan formula starting from the formula for Z-Scan one [8]:

$$T_{closed}(z, \Delta\phi) \cong 1 - \frac{4\Delta\phi \cdot z/z_0}{\left((z/z_0)^2 + 1\right)\left((z/z_0)^2 + 9\right)}, \quad (6)$$

where $\Delta\phi = k \Delta n L_{eff}$, z_0 – the Rayleigh distance, $L_{eff} = (1 - e^{-\alpha L})/\alpha$ – the effective length of the medium, α – the linear absorption and L – the thickness of the medium. For fitting the I-Scan signal, we have considered a fixed position of the sample at $z = -0.85z_0$ and a simplified formula for the transmission versus incident intensity [9]:

$$T_{closed}(z = -0.85z_0, I) \cong 1 + 0.2k \frac{n_2 I}{1 + I/I_{sat}}. \quad (7)$$

In the case when saturation is not achieved, the equation (7) reduces to a linear function with the intercept to one and the slope proportional to the nonlinear refractive index:

$$T_{closed}(z = -0.85z_0, I_{sat} \rightarrow \infty, I) \cong 1 - 0.2k \cdot n_2 \cdot I. \quad (8)$$

3. SAMPLES PREPARATION AND CHARACTERIZATION

3.1. DYE DOPED LIQUID CRYSTALS

For experiments using liquid crystals we have chosen the 4-cyano-4'-pentylbiphenyl which is a commonly used nematic liquid crystal with the chemical formula $C_{18}H_{19}N$ and chemical structure presented in Fig. 2a.

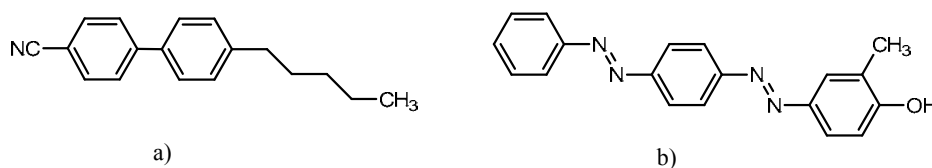


Fig. 2 –Chemical structure of: a) 5CB liquid crystal; b) chemical structure of DY7 dye.

To sensitize the liquid crystal to the laser wavelength used in the nonlinear optical experiments, we have used the dispersed yellow 7 dye (DY7), from Aldrich, with the chemical structure presented in Fig. 2b.

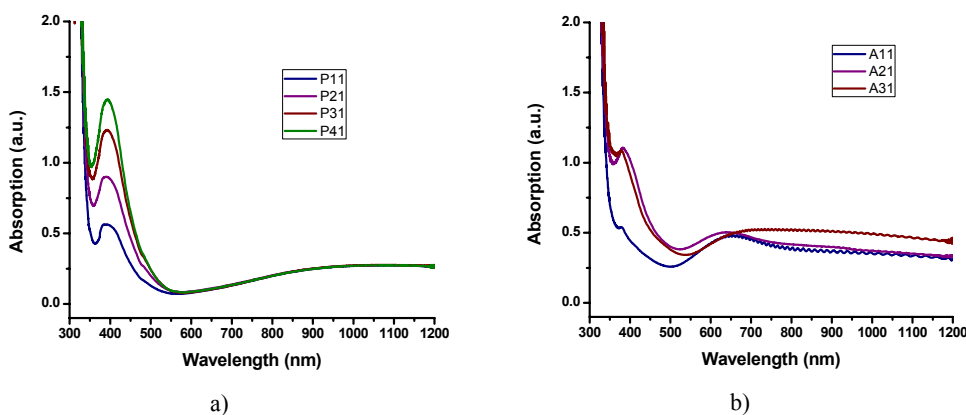


Fig. 3 – Linear optical absorption of nematic liquid crystals doped with DY7 dye oriented perpendicular (a) and parallel (b) to the optical axis.

For the orientation of the liquid crystals, we have used two geometries: first, in which the liquid crystal molecules are parallel to the cell windows (perpendicular to the optical axes – perpendicular geometry) and second one, in which the liquid crystal molecules are oriented perpendicular to the cell windows (parallel to the optical axes – parallel geometry). To obtain these types of orientations, we used as alignment layers on the cell windows unidirectionally rubbed polyvinyl alcohol layers and sputtered gold layers respectively.

Different concentrations of dye in the liquid crystals were used to observe the colorant influence over the nonlinear optical response of the solution. We have obtained eight samples: four using the perpendicular geometry with four different concentrations of dye (P11 - 0.25%, P21 - 0.5%, P31 - 0.75% and P41 - 1%) and four with parallel geometry (A11 - 0.25%, A21 - 0.5%, A31 - 0.75%, A41 - 1%). The linear absorption spectra of these Pxx samples are presented in Fig. 3, showing that the wavelength used in our experiments is situated near the minimum of

absorption. The absorption peak at $\lambda \sim 400$ nm is given by the DY7 dye. It can be observed that this absorption peak of the sample is increasing with the DY7 dye concentration.

3.2. AZOBENZENE CONTAINING POLYMERS

The polymers used in our experiments (see Fig. 4) are some poly(methacrylate)s bearing pendant azo moieties (P1, P2 and P3), which were prepared by free radical copolymerization (starting from methyl methacrylate and some original azo-monomers), while the other class of side-chain maleimide-styrene polymers (P4 and P5) have been synthesized from a maleimide-*alt*-styrene copolymer and some azo-moieties using the polymer analogous reaction. Full synthesis and characterization of both classes of polymers were previously reported by us [10, 11].

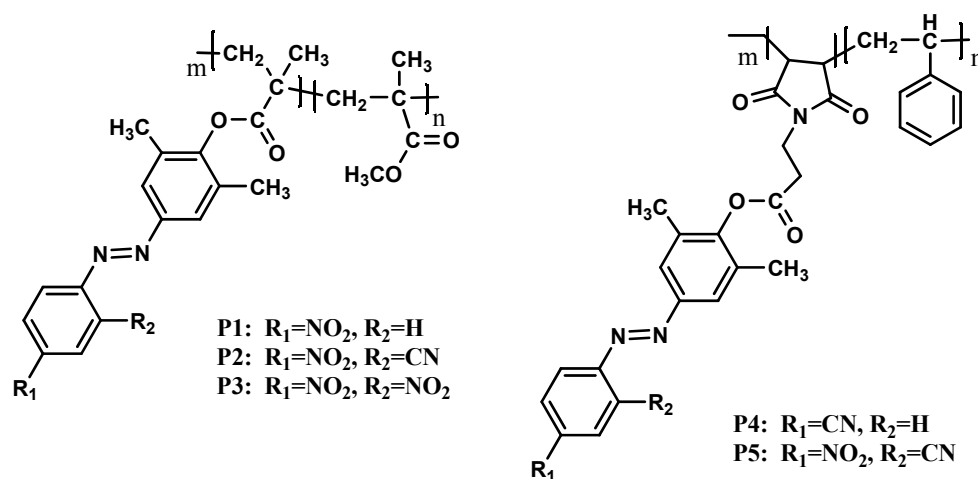


Fig. 4 – Chemical structure of the polymers used in our experiments.

The poly(methacrylate)s have a $\sim 25\%$ chromophore load, while the poly(maleimide-styrene)s have a $\sim 40\%$ load. The linear absorption spectra of the polymers are presented in Fig. 5. One can observe the two absorption peaks at $\lambda \sim 455$ nm and $\lambda \sim 620$ nm, which are present in all spectra. The different absorption intensities are due to both azo-content and the substitution pattern of each azo-moiety (R_1 and R_2).

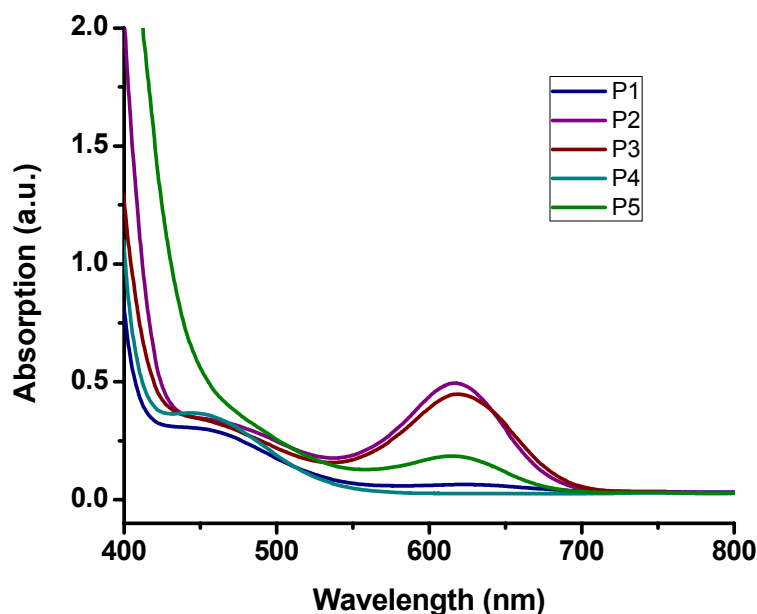


Fig. 5 – Linear absorption of the polymers used in our experiments.

4. NONLINEAR OPTICAL PROPERTIES OF THE INVESTIGATED ORGANIC MATERIALS. MEASUREMENTS AND DISCUSSIONS

4.1. LIQUID CRYSTALS

We measured the nonlinear optical properties using the I-Scan method. The data obtained for the liquid crystals are presented in Fig. 6. In the first column, we show the data for the liquid crystals oriented perpendicular to the optical axes and the light polarization parallel to the liquid crystal molecules, at different dye concentration. In the case when the polarization is perpendicular to the orientation of the molecule, we did not observe any nonlinear optical response.

In the second column of Fig. 6, we show the data for the liquid crystals molecules oriented parallel to the optical axis, when we not observe a light polarization dependence of the nonlinear optical response, which is plausible.

From Fig. 6, one can observe that the nonlinear refractive indices of the two alignments of liquid crystals have different signs, due to different interactions of the optical field with the liquid crystal structures.

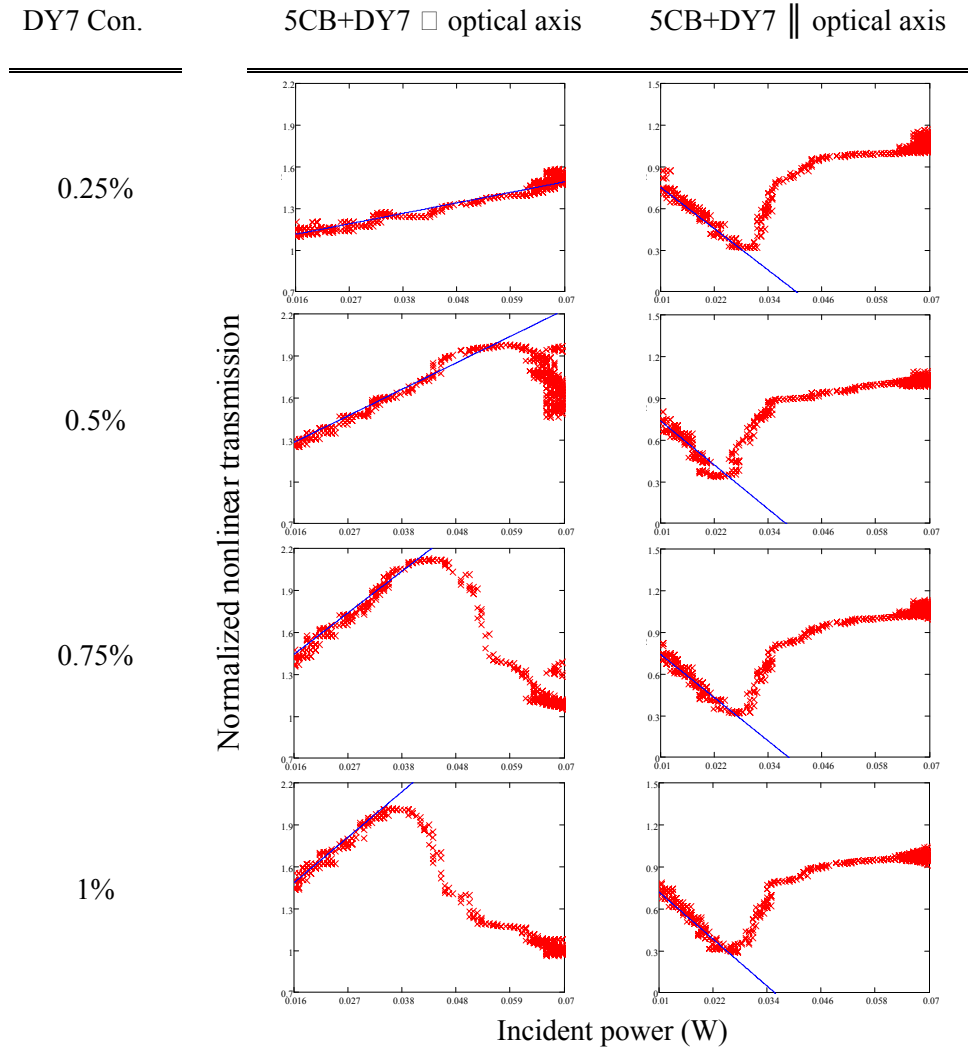


Fig. 6 – I-Scan experimental data (x) and theoretical fitting (line) for the liquid crystal samples.

The maximum nonlinear refractive index, i.e. $n_2 \approx 10^{-5} \text{ cm}^2/\text{W}$, was measured for dye concentrations of 1%, in both geometries. We have to mention that this large nonlinearity was observed in the composite material only; for separated components, the measured optical nonlinearity was negligible (Fig 7). We should also mention that the gold aligning substrate is strongly influencing the composite nonlinear response: in the case when the electric field component of the optical field is perpendicular to the LC molecule, we have nonlinear response only for cells with a gold substrate.

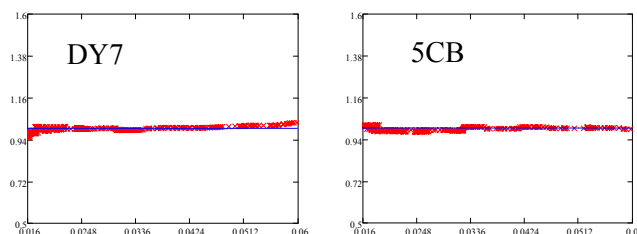


Fig. 7 – I-Scan traces for unmixed DY7 dye and 5CB liquid crystal, each showing negligible nonlinear refraction.

It can also be observed, that increasing the incident light power (and intensity), at one particular power level, the nonlinear response starts to decrease rapidly, going to zero. This power level is dependent on the concentration of the dye in the liquid crystal. As the transition point from crystalline to isotropic phase for 5CB is at rather low temperatures, about 35°C, we consider that this is the cause for the vanishing of the nonlinear response. As the incident power is increasing, the local temperature is increasing. Consequently, the 5CB goes from its liquid crystal phase to isotropic one, gradually, but quite rapidly, until all the material in the interaction area is transformed and the nonlinear optical response vanishes.

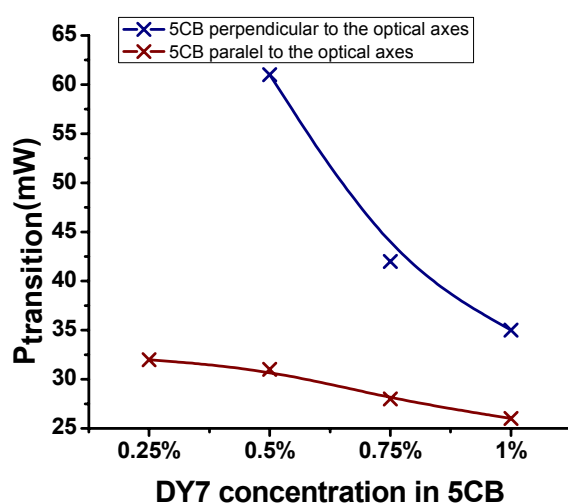


Fig. 8 – Dependence of the light power for the liquid crystal transition on the concentration of DY7.

In support to this hypothesis, we bring the dependence of the light power for the liquid crystal transition on the concentration of the DY7 dye, shown in Fig. 8. As one can see in Fig. 3, the increase of dye concentration in the liquid crystal leads to increase of the composite absorption, at the wavelength used in the

nonlinear experiments ($\lambda=532\text{nm}$). This absorption increase leads to a higher thermal effect. Consequently, the samples with a higher DY7 dye concentration reach the transition temperature at lower incident optical powers.

Table 1

Nonlinear refractive index and the incident transition power for the 5CB doped with DY7 liquid crystals obtained by I-Scan method

| DY7 Con. | 5CB+DY7 \perp optical axes | | | 5CB+DY7 \parallel optical axes | | |
|----------|---|---------------------------------|------------------|---|---------------------------------|------------------|
| | n_2 ($\times 10^{-6} \text{ cm}^2/\text{W}$) | $P_{\text{transition}}$ (mW) | W_{max} | n_2 ($\times 10^{-6} \text{ cm}^2/\text{W}$) | $P_{\text{transition}}$ (mW) | W_{max} |
| 0.25% | -3.3 | - | 0.84 | 9 | 27 | 0.36 |
| 0.5% | -8 | 50 | 1.16 | 9 | 22 | 0.25 |
| 0.75% | -12 | 40 | 1.1 | 9 | 28 | 0.33 |
| 1% | -13.5 | 35 | 1.23 | 10 | 25 | 0.36 |

Table 1 shows that the values of the nonlinear refractive index for the liquid crystal oriented parallel to the optical axes are not depending on the dye concentration and that the transition power occurs at lower levels. The lower transition power could be attributed to a higher thermal effect in this geometry, due to the presence of the gold layer. Another reason for this may be the lower solubility of the DY7 in this geometry leading to a diffusion of the dye to the edges of the cell, which was also experimentally observed in the linear absorption spectra at the centre of the samples. The absorption peaks, due to the DY7 molecules in CB5 for the cells having gold layers as alignment layers are not so dependent on the dye concentration (Fig. 3b) as for the samples aligned with polyvinyl alcohol (Fig. 3a). This could lead to errors in the measurement of the concentration of the dye in the interaction area and to errors in the measured dependence of the nonlinear response on concentration.

A better characterization of the nonlinearity of these samples is obtained from Stegeman merit factors and conditions [12]. First of them imposes:

$$W = \frac{|\Delta n|}{\alpha_0 \lambda} > 1 \quad (9)$$

and states that the effect of linear absorption should be weak compared to the effect of nonlinearity. The second one asks for:

$$T = \frac{2\beta_2 \lambda}{n_2} < 1 \quad (10)$$

i.e. the effect of nonlinear absorption, β_2 , should be weak compared to nonlinear refractive index (at a fixed wavelength).

In Table 1, we present the maximum W values obtained for all the dye doped liquid crystal samples. These values are obtained for the maximum of refractive index change, Δn , at the transition power of the liquid crystal. As we could not observe nonlinear absorption at the intensity levels used in our experiments, in any

sample, we considered the T merit factor to be close to zero. Table 1 shows that only few samples have W larger than one, qualifying them for switching applications. This is primarily due to the low transition power that prohibits their use at higher incident intensity and limits the value of the refractive index change that can be obtained.

4.2. AZOBENZENE CONTAINING POLYMERS

The polymers presented in the previous chapter have nonlinear responses, which are presented in Fig. 9, while the corresponding nonlinear refractive indices are shown in Table 2. From these experiments, one can observe a dependence of the nonlinear response on the azo group, which led us to the supposition that the main mechanism for the nonlinearity, or at least a major part of it, is the *trans-cis* transition of the azo molecule.

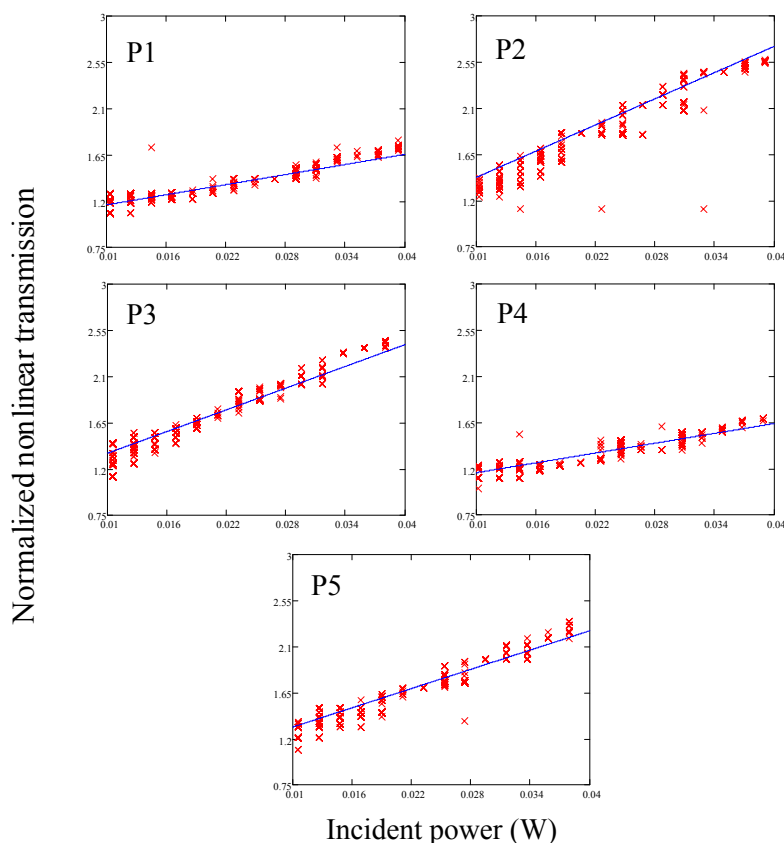


Fig. 9 – I-Scan experimental data (x) and the corresponding theoretical functions (line) for the copolymer samples.

The *trans-cis* transition, schematically presented in Fig. 10, Fig. can be induced by light with frequencies near the absorption resonances. In this transition, the distance between the carbon atoms from the acceptor and donor groups decreases from 0.9 nm to 0.55 nm and produces a drastic reduction of the molecular dipole momentum. The result is the decrease of the material polarizability and very high and negative nonlinear refractive index.

From the absorption spectra in Fig. 5, one can observe that we are very well situated near the absorption maximum, in the *trans-cis* transition region, but at low absorption levels, resulting in a high nonlinearity and low losses in the sample.

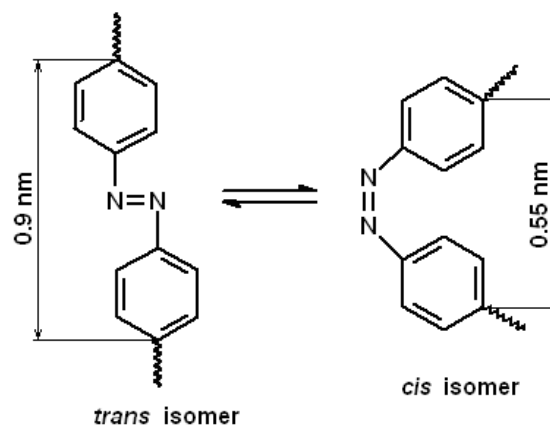


Fig. 10 – Schematic representation of the *trans-cis* transition of the azo group.

The calculated values of W factors for our azo-polymer samples are very large and are summarized in Table 2. At the intensities used in our measurements, no nonlinear absorption was observed ($\beta_2 \sim 0$), leading to $T \sim 0$. We mention here that the very large W of our copolymers is the result of the material excitation in a spectral region characterized by high third order nonlinearity (due to the *trans-cis* transition) and by minimum absorption (α_0). These large figures of merit are very important for application of these materials in nonlinear devices with low losses.

Table 2

The measured nonlinear refractive index, n_2 , and the calculated W merit factor, for the azo-polymer samples

| Sample | P1 | P2 | P3 | P4 | P5 |
|--|------|-----|------|-------|-----|
| $n_2 (\times 10^{-7} \text{ cm}^2/\text{W})$ | -1.5 | -4 | -3.2 | -1.45 | -3 |
| W | 4.1 | 8.3 | 6.2 | 3.3 | 7.5 |

5. CONCLUSIONS

In conclusion, we have obtained some molecular structures with large, controllable optical nonlinearities.

In this work, we prove that in the case of LC (CB5) doped with the dye (chromophore DY7), LC may be sensitized to have a huge nonlinear response in the wavelength region of interest. We show that, at a certain (low) threshold intensity (which depends on the dye concentration), the transition of LC from its mesomorphic phase to isotropic phase can occur leading to a progressive decrease of the nonlinear response with further increase of incident light intensity. We also show that the nonlinear response of this composite depends on the geometry between the electric field of the light and the orientation of the molecules, leading to the change of the sign for the nonlinear refractive index at low intensities. Further investigation related to the gold influence on the composite LC-chromophore optical nonlinearity is in progress.

For the azo-polymers we have demonstrated very good Stegeman factors due to a special approach: excitation of the high *trans-cis* induced optical nonlinearities at a minimum of their absorption and near the absorption resonance. We have also observed a dependence of the nonlinear response with the azo dye that was used, dependence that is related to the mobility and availability of the electrons that produce the *trans-cis* transition.

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