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The concentrations and thicknesses effects of R6G dye on the nonlinear optical properties at lowintensity

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Abstract : As technology advances, optics will play an enormous role in a broad range of commercially available devices and medical instrumentation. Learning about the optical effects of R6G dye will provide further insight to some of the challenges the optical industry will face in the future. This study of nonlinear optical (NLO) properties of Rhodamine 6G dye doped epoxy resin polymer is analyzed at 532 nm using a continuous wave laser. Evaluating the sign and magnitude of the nonlinear refractive indexfrom the closed aperture Eclipsing Z-scan technology (EZ) while the nonlinear absorption coefficients were assessed using the open aperture EZ-scan. We observed that the NLO properties of the dyes doped in epoxy resin are affected by the dye concentration and the sample thickness. The sample shows ReverseSaturable Absorption (RSA) behaviour in case open EZ-scan, while in case close Z-scan both Self-focusing and self-defocusing were observed.
Keyword : Nonlinear properties, Eclipsing Z-scan, Rhodamine dye, Epoxy resin.

1. Introduction:

Nonlinear optical materials are critical owing to their potential applications in several devices: 3-D optical memory devices, all-optical switching, optical modulation, human eyes & optical sensor protection, telecommunications, and significant applications in biological and medical sciences [1]. The various nonlinear material andorganic dyes that are inexpensive and commercially available can be characterized by a vast nonlinear optical susceptibility; resulting from the fast nonlinear response of organic molecules, which has attracted much attention [2]. The study of nonlinear optical properties is usually done by the Z-scan technique; which is suggested by Sheikh Bahaei and et al. It was a simple method to measure both the sign and value the nonlinear refractive index n_2 and the nonlinear absorption coefficient β [3,4]. In this experiment, a polarized Gaussian laser beam was focused to a narrow waist (Ariy disk) [5]. The focus of the outer edges of the laser beamimproves the sensitivity of the measurement. This can be achieved using the disc instead of the aperture as in the Z-scan, to block the central part of the laser beam.The light of the laser around the edges of the disc appears as an eclipse just like the method called EZ-scan or Eclipsing Z-scan [6,7]. The enhanced sensitivity of the EZ-scan can be attributed to the larger fractional change in the intensity that exists in the wings of the laser beam as detected in an EZ-scan compared at the centre, as detected in a Z-scan [8].

There are some problems with the organic dye system in the liquid state case such as: static, flowing fluid systems and perishables. Therefore, the polymer used as a host for the dyes. Which leads to giving several significant advantages such as ease of handling, the safety of operation, toxicity removal, and lack flammability [9,10,11].

For the first time, the experimental measurements of third-order nonlinear susceptibility χ^3 of Rhodamine 6G (R6G) doped epoxy polymer using the EZ-scan technique with continuous wave Nd: YAG laser onemW, irradiation at 532 nm wavelength. The study has been evaluated with the concentration of the dye and thickness of sample effect using nonlinear properties.

2. Experimental work:

a- Material:

The dyeRhodamine 6G (R6G) supplied byHiMedia Laboratories Pvtcompany in India, is usedand the structure isshown in Fig.1[12].

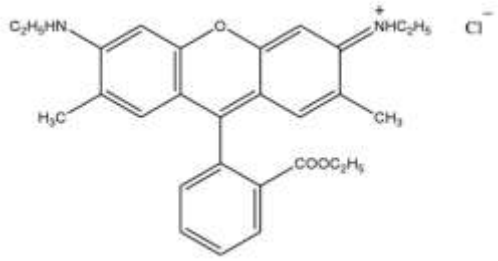

Fig. 1: The structure of Rhodamine 6G.

The acetone solvent was used in this study wassupplied by Central Drug House Ltd company, Indian.An epoxy resin polymer utilizedwas supplied by the Swiss chemical industry company, Egyptian. Epoxy consists of two materials, the first called epoxy resin and denoted by the variable (A), and the second material Sclerosing(hardener) denoted by the variable (B),with a matrix ratio is (3:1) (A:B).

The Spectrophotometeris the device used to measure the absorption spectra of the samples; UV/Vis T60 supplied from the English company (Instruments). The thickness of the samples wasmeasured by using the Sonacoat III, supplied Sonatestcompany, UK.With the error about 9 µm.

b- Preparation of the samples:

The samples were prepared by using the casting method [13]. The appropriate weight of R6G was dissolved in 10 ml of acetone, then the epoxy (B) is added to the solution and then it is mixed for about (5) min. After that, add the epoxy (A) and mix until the mixture becomes homogeneous at room temperature. The samples are placed in the mold, which is shown in Fig. 2, where the samples are left to dry about three days in the mold.

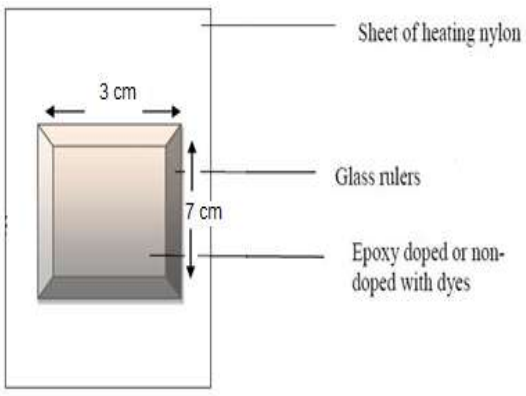

Fig. 2: Illustrate the mold with its parts.

c- Eclipsing Z-scan technique

EZ-scan which wasdeveloped by T. Xia et al.[12], was used for evaluating the nonlinear absorption coefficient β, the nonlinear refractive index n_2 and the magnitude and sign of the real and imaginary parts of third-order nonlinear optical susceptibility $\chi^{(3)}$ of the samples. The EZ-scan experiments for the samples were performed using CW Nd:YAG laser at 532 nm wavelength as an excitation source. The laser beam was focused to 85 μm and a Rayleigh length Z_R of 42 mm using a 30 cm focal length lens with one mW input power, and a diameter of the disk about 1.5 cm. The schematicsetup of EZ-scan is shown in the Fig. 3 [14].

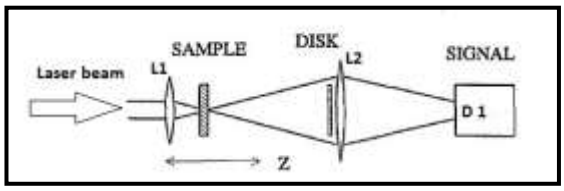

Fig. 3: Experimental arrangement for the EZ-scan.

The absorption coefficient(β) was determined by fitting the normalized transmittanceT(z) [15]:

$$T(z) = \sum_{m=0}^{\infty} \left[\frac{[-q_0(z)]^m}{(m+1)^{3/2}}\right] \qquad (1)$$

Where**:** $q_o(z) = I_o L e_{ff} \beta / [1+\left(\frac{z}{z_0}\right)^2]$, and $L_{eff} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$, the effective length of sample, L the thickness of the polymer sample, α is a linear absorption coefficient, and I_0 is the intensity of the laser at the focal point (z = 0).

While the nonlinear refractionn$_2$was calculated using simple expression [16]:

$$n_2 = \Delta\Phi_0 / I_0 L_{eff} k \qquad (2)$$

$$\Delta T_{pv} = 0.68(1-S)^{-0.44}|\Delta\Phi_0| \qquad (3)$$

Where: ΔT_{PV} is the difference between the peak and valley of the transmittance experimentally, $\Delta\Phi_o$ is nonlinear phase shift (red), and, k is the angular wave number, equal to $2\pi/\lambda$.

The fraction of light in front of the disk is simply the variable S, the aperture transmittance in a Z-scan, which is $S = 1- \exp(-2a^2/\omega_a^2)$, where ω_a is the beam radius on the disk plane in the linear region [17]. In practice, this limits the max sensitivity enhancement as the energy reaching the detector arrives too littlefor detection. In our system S = 0.99, this is used in the inset in Fig. 3. This quantity gavegreat enhancement while still giving sufficient energy for easy detection. In the EZ-scan method, the sensitivity increase compared Z-scan method, and the signal is inverted for EZ-scan [18], as shown in Fig. 4, in which both curves represent self-focusing nonlinearity.

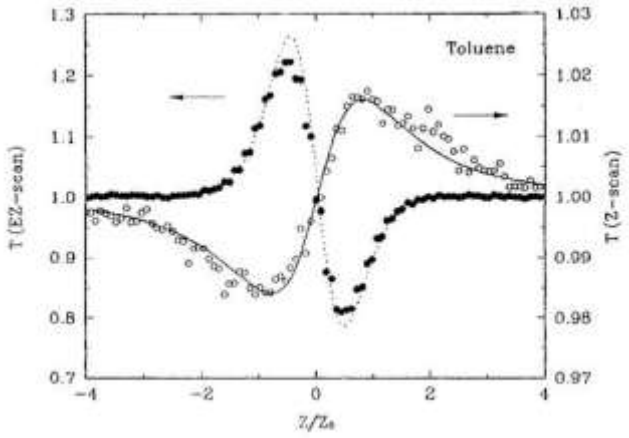

Fig. 4:Experimental comparison of an EZ-scan (filled circles) and a Z-scan (open circles) of toluene under identical conditions [12].

3. Results and discussion:

a- Absorption spectrum:

The absorption spectrum of the dye-epoxy resin is shown inFig. 5,atdifferentconcentrations: (a) with constant thickness 0.5 mm, and different thickness, (b) with the concentration $5x10^{-6}$mol/l. It may be seen that the absorption spectrum characterized bythe broad rangeand peak,whichis in the visible regionat 540 nm wavelength. The peak shifting to short wavelength (blue shift) as the concentration and thickness increasedby about 5 nm.The broad spectral range of the samples is due to them having many modes of oscillation because they aremassive [19].

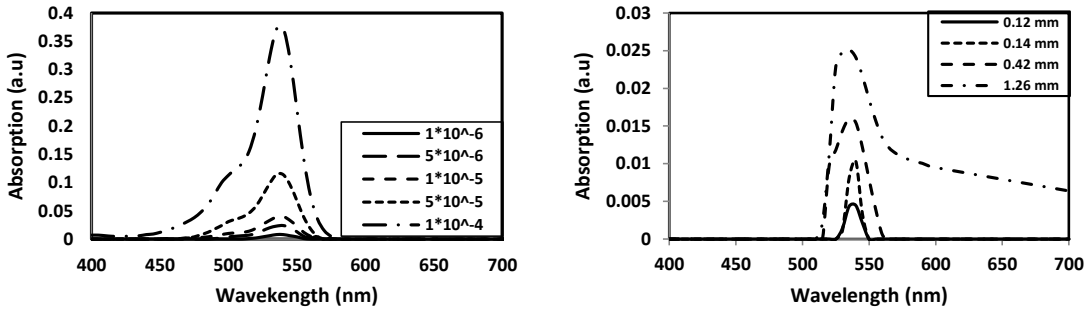

Fig. 5: Absorption spectrum of R6G-epoxy resin (a) different concentration(b) different thickness.

b- The nonlinear properties:

Fig. 6 shows the transmittance of the laser beam in open EZ-scan of dye for various concentrations (a)$1x10^{-6}$, $5x10^{-6}$, $1x10^{-5}$, $5x10^{-5}$ and $1x10^{-4}$mol/l, with thicknesses (b) 0.12, 0.14, 0.42 and 1.26 mm, as a function of the sample's position (z).Where the theoretical fit represented by solid lines and the circular points represents the experiment data. It is notedthat the transmission is symmetrical about the focus of the lens (z=0),and it decreases with an increase in thefocus to form a valley at (z=0) indicating a Reverse Saturable Absorption(RSA) behavior or positive type of nonlinear absorption coefficient β [20]. The RSA process can be due to any of the nonlinear mechanisms such as Excited State Absorption (ESA), Free Carrier Absorption (FCA), Nonlinear Scattering, and Two-Photon Absorption (TPA), or all of the aforementioned processes [21].

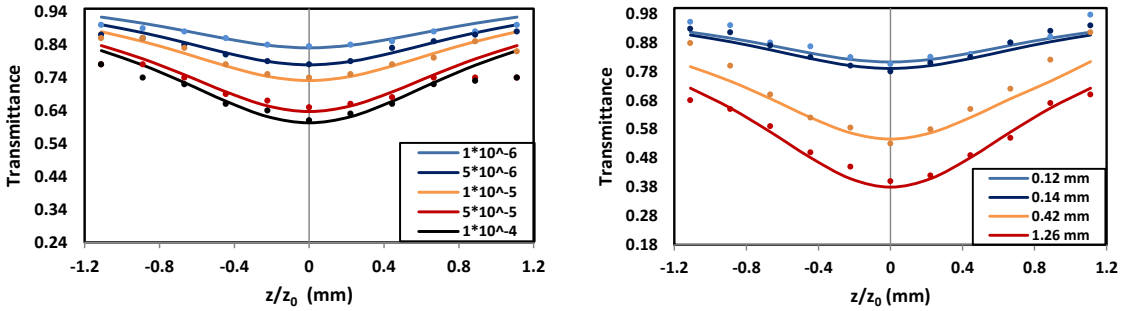

Fig. 6. Open EZ-scan of R6G-epoxy resin solid samples (a) different concentration (b)different thickness.

The nonlinear absorption process of the dye molecule can be explained by using 5 level model as shown in Fig. 7: (i) Excite electron from ground state S_0 to the first excited state S_1 and then to T_1, through an Inter-System Crossing (ISC). (ii) An electron can be transmitted directly from S_0 to the higher excited states S_n, and this is TPA process. (iii) From state S_1 to excited states S_n, are calledthe ESA process. (iv) From T_1 state to T_n states, which is called ESA. In the absorption case the cross section of excited state σ_{exc} is larger than that of ground state σ_g, then it is called as an RSA process [22].

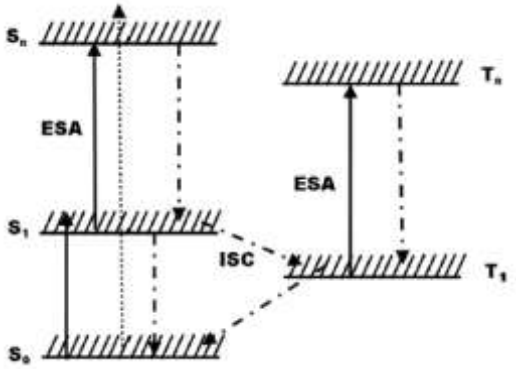

Fig. 7. Five level energy diagram of a typical dye molecule [22].

Fig. 8shows the variation of the transmittance curve of thelaser beam with theposition of samples (z) by using the closed EZ-scan method for different concentrations. It is observed that the nonlinear refraction in change concentration case is negative, i.e. self-defocusing for all concentrations except the concentration $5x10^{-6}$ mole/l, which showed positive (self-focusing) [17].

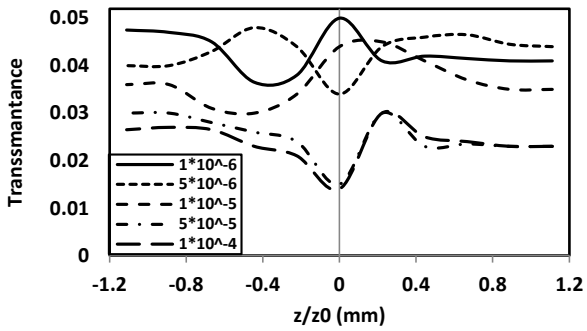

Fig. 8. Close EZ-scan of R6G-epoxy solid sample different concentration.

Fig.9 indicates the effect of sample thicknesson transmitted data. It is shown that $n_2$has a positive valuefor allsample thicknesseswhile the transitionhasa negative value and they increased as the sample thickness increased. The change in the refractive index sign can be due to a single charge carrier as a result of photoexcitation, which isdue to the Kerr nonlinearities of bound electrons [23].

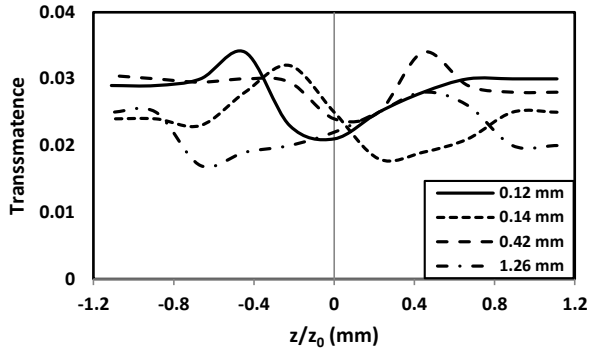

Fig. 9. Close EZ-scan of R6G-epoxysolid samples different thickness.

The third-order nonlinear susceptibility $\chi^{(3)}$ is dependent on the nonlinear refractive index n_2 and nonlinear absorption coefficient β, which determined according to equations [24]:

$$\chi^{(3)} = \chi_R^{(3)} + \chi_I^{(3)} i \qquad (4)$$

The imaginary part of $\chi^{(3)}$ depends on the nonlinear absorption coefficient β through:

$$\chi_I^{(3)} = \frac{n_o^2 \varepsilon_o c \lambda}{2\pi} \beta \quad (\frac{\mathrm{m}^2}{\mathrm{V}^2}) \qquad (5)$$

The real part is:

$$\chi_R^{(3)} = 2 n_o^2 \varepsilon_o \, c \, n_2 (\frac{\mathrm{m}^2}{\mathrm{V}^2}) \qquad (6)$$

The absolute value of the nonlinear susceptibility is:

$$|\chi^{(3)}| = \sqrt{(\chi_I^{(3)})^2 + (\chi_R^{(3)})^2} (\frac{\mathrm{m}^2}{\mathrm{V}^2}) (7)$$

Where:n_o: Linear refractive index,ε_o: Vacuum permittivity ($8.85*10^{-14}$ F.cm^{-1}),c: Light speed in vacuum ($3*10^{10}$ cm/Sec), n_2: Nonlinear refractive index (cm^2/W), β: Nonlinear absorption coefficient (cm/W) and λ: The wavelength (nm).

The samples showed nonlinear optical properties very high,although the power of the laser is low, as shown in Tables (1) &(2).This is because material possessing electron donors to exhibit NLO properties, and the strong π-electrons delocalization of it causes a high molecular polarizability and thus lead to third-order nonlinear optical property [25,26]. The error in the measurement between theoretical fit and experimental datais about 6% in case concentration changes, and 16% of thickness change.

Table (1): Nonlinear properties of thesolid sample at adifferent concentrationwith 0.5mm constant thickness.

Concntration (mol/l)	Peak Absorption at (532) nm	α $(cm)^{-1}$	L_{eff} (cm)	n_2 (cm^2/W) 10^{-10}	β (cm/W)	$\lvert\chi^{(3)}\rvert$ (esu) 10^{-7}
$1*10^{-6}$	0.011	0.50	0.04900	-1.40	1.10	0.25
$5*10^{-6}$	0.020	0.92	0.04800	1.47	1.45	0.34
$1*10^{-5}$	0.038	1.75	0.04700	-1.60	1.50	0.36
$5*10^{-5}$	0.139	6.40	0.04278	-1.80	2.27	0.59
$1*10^{-4}$	0.140	6.44	0.04274	-1.92	2.98	0.77

Table (2): Nonlinear properties of solid samples at different thickness with $5x10^{-6}$mol/l constant concentration.

Sample thickness (mm)	Peak absorption at (532) nm	α $(cm)^{-1}$	L_{eff} (cm)	n_2 (cm^2/W) 10^{-10}	β (cm/W)	$\lvert\chi^{(3)}\rvert$ (esu) 10^{-7}
0.12	0.000448	0.0859	0.012	5.56	5	1.18
0.14	0.000517	0.0850	0.014	5.13	4.5	1.047
0.42	0.008	0.43	0.0416	-1.23	3.2	1.05
1.26	0.05	0.91	0.119	-0.47	1	0.6

The nonlinear absorption coefficient βand nonlinear refraction index n_2 and the absolute value of third order susceptibility$|\chi^{(3)}|$, increase with increasing the concentration of samples.Due to thatincrease, the particle number absorbslight at the same wavelength of the laser 532 nm which leads to anenhanced thermal effect andan increase in the nonlinear effects. The nonlinearity can be due to thermal impact under laser irradiation [27,28]. But the nonlinear properties decrease as the thickness increased, shown in tables (1) & (2). The nonlinear absorption, refraction index, and susceptibilityare all in agreement with the researchers' work [29,30].

Conclusion

The nonlinear optical properties of the R6G dye epoxy resin that is dopedareobtained using CW excitation at 523 nm, and their responsivity to the dye concentration and sample thickness were discussed. The observed nonlinearities behavior has a significant dependence on the concentration and thickness. The NLO properties of smaller thickness are very high. Based on nonlinear properties, these samples find potential applications in optical limiting and signal processing applications.

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