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Third order nonlinear properties of Rhodamine B dye doped PVA polymer determined by Eclipsing scan technique

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Abstract

Nonlinear (NL) optical properties were observed in Rhodamine B (RB) dyes doped in poly (vinyl alcohol) (PVA) polymer films. Eclipsing Z-scan (EZ-scan) with a continuous wavelength of 532 nm was used to investigate the effect of dye concentration on its NL properties.. The open aperture EZ-scan indicated a reverse saturable absorption behavior (positive type) of NL absorption (NLA) coefficient (β) in the RB+VA matrix, whereas the closed aperture EZ-scan exhibited transition from positive (focusing) to negative (defocusing) nonlinearity at increasing dye concentration. The NL refractive index n_2, NLA coefficient β, third-order susceptibility $\chi 3$, and second-order hyperpolarizability γ_h increased with the increase in dye concentrations. The magnitude of the n_2, β, χ^3, and γ_h were in the order of 10^{-12} (cm^2/W), 10^{-1} (cm/W), 10^{-8} (esu), and 10^{-12}, respectively.

Keywords: nonlinear absorption coefficient, nonlinear refractive index, Eclipsing scan technique, third order susceptibility

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1- Introduction

Dyes are one of the most commonly used organic materials because of their high third-order susceptibility ($\chi 3$), which is attributed to the fast nonlinear (NL) sensitivity of organic molecules. Xanthine dyes are used in optical switching, optical communications, optical power limiting, optoelectronics, and photonics devices [1-4]. The NL optics (NLO) Z-scan technique was proposed by Sheik-Bahae [5,7] for the evaluation of NL refractive (NLR) index (n_2) (Kerr effect) and the NL absorption (NLA) coefficient (β) via closed and open methods, respectively . Z-scan method is regarded as a standard technique because it has a simple alignment set-up [8]. The NLR is measured with a Z-scan setup in its closed aperture form. The NL material acts as a weak lens. Given that the NLR index governs the focusing power of nonlinear lens, restoring its value is possible.

The imaginary part of n_2 is evaluated through Z-scan in its open aperture form. In an open aperture measurement, the aperture is removed, and the total signal is collected by the detector. However, the original Z-scan theory is not completely accurate despite its simplicity.

In this paper, eclipsing z-scan (EZ-scan) was used, which is more sensitive compared with the Z-scan. In the EZ-scan technique, the secondary maximums are emphasized rather than the central part (airy disc) of a laser beam [9,10]. The EZ-scan, as its name implies, is accomplished by substituting an aperture in the Z-scan with an annular aperture, which obscures the central maximum of the laser beam in the same manner, making the beam to appear as an eclipse [11].

The Rhodamine B (RB) dye was doped in poly (vinyl alcohol) (PVA) polymer for the preparation of solid samples with thickness of 0.6 mm in various dye concentrations. The NL optical properties of the samples were studied with the EZ-scan technique. Organic RB (as shown in Fig. 1) With a molecular formula of $C_{28}H_{31}N_2O_3Cl$ and molar mass of 479.02 g/mol was supplied by the HiMedia Laboratories Pvt. Ltd. India.

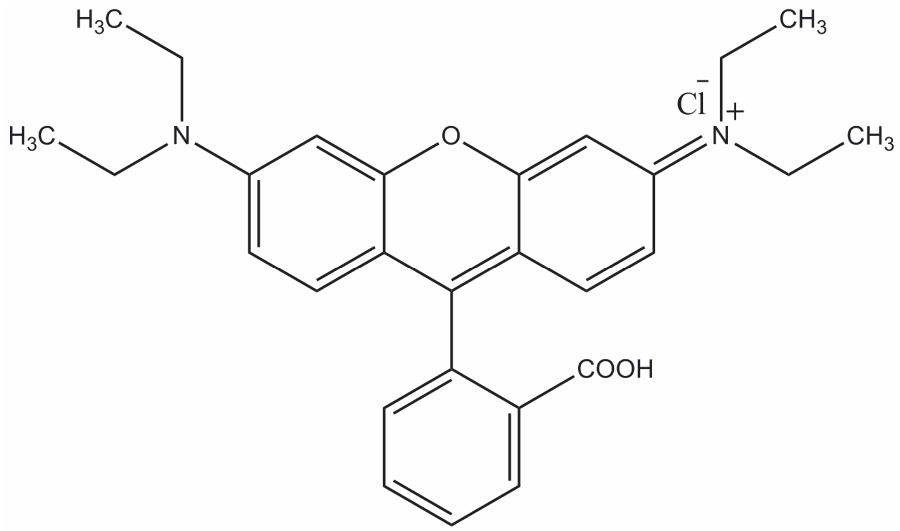


Fig. 1. Molecular structure of an RB dye molecule.

2-Expermental work

A UV-visible spectrophotometer (Instruments Co. T60) was used for the acquisition of the linear optical properties required for the evaluation of the EZ-scan data of the samples. The NLR behavior of the RB dye was investigated with single beam EZ-scan technique. The standard EZ-scan setup in closed form is shown in Fig. 2.

In - EZ-scan setup, an annular aperture (L2) was used, and with 0.6 mm-thick NL RB–PVA samples were scanned along the Z-axis. When the sample had a self-focusing nonlinearity (n_2) of >0, it behaved as a positive lens near the focus. When the sample was in front of the L1 focus, the laser beam divergence was increased, thereby allowing more light to pass through the annular aperture and reach the detector. The beam was collimated by the sample when the RB–

PVA sample passed behind the focal plane, and more laser beams are blocked by the annular aperture. The transmittance was increased as a result of self-focusing. Meanwhile, when the sample was transferred to the back of the L1 focus in the EZ-scan, the transmittance decreased and a valley was formed. For self-defocusing media, the positions of the valley and peak were reversed. Notably, these behaviors are the exact opposite of those of Z-scan in a closed aperture form.

The measurements of the NLO coefficients (n_2, β, and $\chi^{(3)}$) were performed by the arrangement shown in Fig. 2. The set-up consisted of a fixed low input (10 mW) laser (532 nm wavelength model; MHHL-532-100 mW). The Gaussian laser beam profile focussed by a biconvex lens (L1) with a focal length of 30 cm for the generation of 85 µm laser beam waist and 42 mm Rayleigh length. The sample thickness was 0.6 mm. The sample was considered thin because the Rayleigh length Z_R was larger the thickness of the sample. The EZ-scan setup also contains an annular aperture L2 with obscuration ratio (S) of 0.99 and a detector (D1).

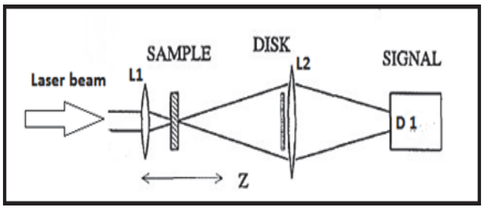


Fig. 2. EZ-scan setup [12].

The NLA coefficient was evaluated with an EZ-scan setup in open form. The RB-PVA matrix samples were scanned from (−Ve to +Ve Rayleigh range Z_R that passes through the lens focal point Z = 0).

3-Results and Discussion:

The linear absorption (LA) spectra of the RB-PVA for various dye concentrations are shown in Fig. 3. The standard value of the absorption maxima for RB dye was 548 nm. The observed absorption maximum values of the samples for different concentrations were all 545 NM. The absorption peaks increased with the increase in concentration, and this result is in agreement with the Beer–Lambert law.

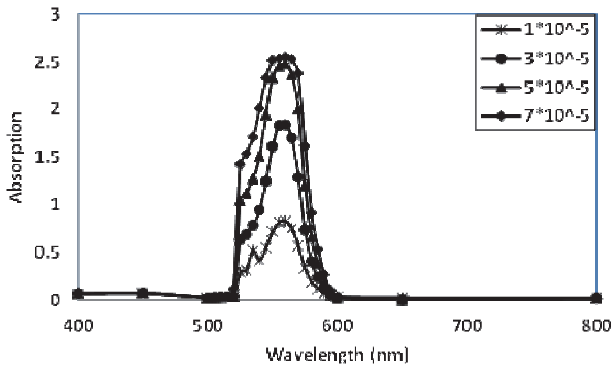


Fig. 3. Absorption spectrum of the RB dye-doped PVA polymer at different concentrations.

NLA coefficient β was evaluated by using Equations (1) and (2) [13]:

$$T(z) = 1 - \frac{q_0}{2\sqrt{2}} \qquad \ldots(1)$$

$$q_o(z) = I_o\, \beta\, L_{eff}\ \left[1+\left(\frac{z}{z_0}\right)^2\right] \qquad (2)$$

where $L_{eff} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$ is the sample effective length, d is the sample thickness, α_o is a linear absorption coefficient, and I_0 is the laser intensity at L1 focal point (z=0).

The NLR index n_2 can be calculated using the following expression [14,15]:

$$n_2 = \Delta\Phi_0 / I_0\, L_{eff}\, k \qquad \ldots(3)$$

$$\Delta T_{pv} = 0.68(1-S)^{-0.44}\ |\Delta\Phi_0| \qquad (4)$$

where ΔT_{PV} is the difference between the peak and the valley of the transmittance, $\Delta\Phi_o$ is a nonlinear phase shift, and k is the angular wave number $2\pi/\lambda$.

Meanwhile, $\chi^{(3)}$ is a sum of real and imaginary parts, as shown below [16,17]:

$$\chi^{(3)} = \chi_R^{(3)} + \chi_I^{(3)} i \quad \text{...(5)}$$

The imaginary part is related to the NLA coefficient β through

$$\chi_I^{(3)} = \frac{n_0^2 \varepsilon_0 c \lambda}{2\pi} \beta \quad (\frac{m^2}{V^2}) \quad (6)$$

The real part is;

$$\chi_R^{(3)} = 2n_o^2 \varepsilon_o c n_2 \quad (\frac{m^2}{V^2}) \quad (7)$$

The absolute value of $\chi^{(3)}$ is:

$$|\chi^{(3)}| = \sqrt{(\chi_I^{(3)})^2 + (\chi_R^{(3)})^2} \quad (\frac{m^2}{V^2}) \quad (8)$$

where n_o is the LR index of the sample and ε_{o}, λ and c is the vacuum permittivity and the velocity of light in vacuum and laser wavelength (cm), respectively.

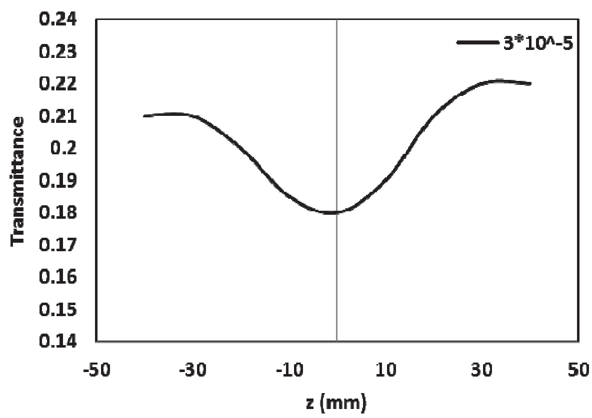
Second-order hyperpolarizability (γ_h), which describes the nonlinear induced polarization per molecule, is related to the third-order bulk susceptibility as follows [18]:

$$\gamma_h = \frac{\chi^{(3)}}{L^4 N} \quad \text{....(9)}$$

where N is the molecular density, and L is the local field factor in which the Lorentz approximation is given by $L = (n_0^2 + 2)/3$.

Results from the open aperture EZ-scan of the RB dye matrix at various concentrations ($1*10^{-5}$, $3*10^{-5}$, $5*10^{-5}$ and $7*10^{-5}$) mol/l are shown in Fig. 4. The curve shape indicates the RSA behavior or positive type of NLA coefficient β process in the RB matrix [18]. The RSA process can be attributed to all or any of the following NL mechanisms: excited state absorption (ESA), free carrier absorption (FCA), NL scattering, and two-photon absorption [19]. The closed aperture EZ-scan data are shown in Fig. 5, which indicate that the NLR index is changed from negative to positive as the RB increased in the PVA matrix when the sample temperature increased with dye concentration. Change in the refractive index sign can be attributed to a single charge carrier as a result of photoexcitation, which is caused by the Kerr nonlinearities of bound electrons [20].

Table 1 shows the NLR indexes and NLA coefficients of the samples. Both values increased with concentration, possibly because of the increase in dye molecules when the concentration increases. At high concentrations, particles become thermally agitated and thus elicit an enhanced effect [21].



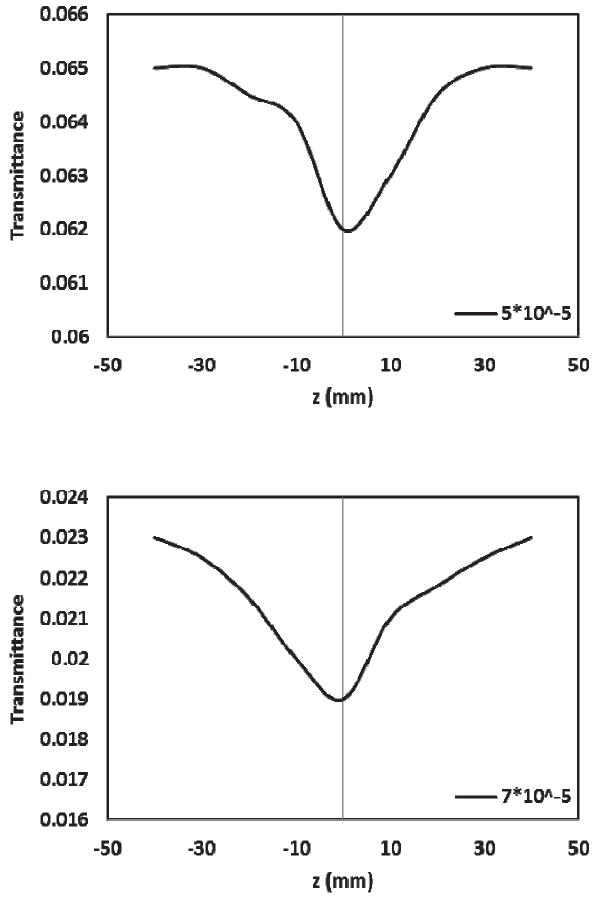
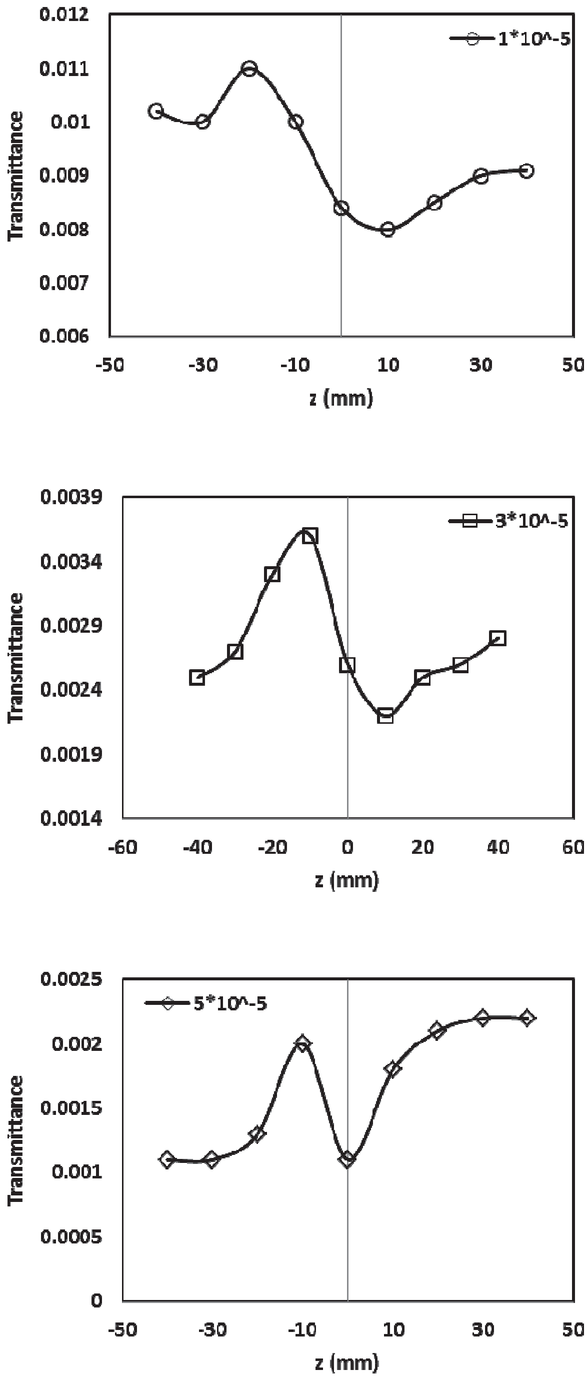


Fig. 4. Open EZ-scan curve of the RB-PVA with laser wavelength of 532 nm and intensity I_o of 88.18 W/cm^2 at different concentration.


0.012
0.011
0.01
0.009
0.008
0.007
0.006
Transmittance
1*10^-5
-50
-30
-10
10
30
50
z (mm)
0.0039
0.0034
0.0029
0.0024
0.0019
0.0014
Transmittance
3*10^-5
-60
-40
-20
0
20
40
60
z (mm)
0.0025
0.002
0.0015
0.001
0.0005
0
Transmittance
5*10^-5
-50
-30
-10
10
30
50
z (mm)

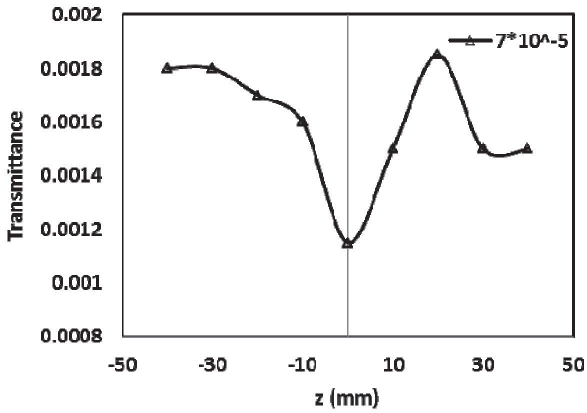


Fig. 5. Closed EZ-scan of RB-PVA with laser wavelength of 532 nm and intensity I_o of 88.18 W/cm^2 at different concentration.

Table (1): Nonlinear properties of the RB dye matrix at different concentrations.

Concentration Mol/l	Absorption At 532 nm	α_o cm^{-1}	n_2 10^{-12} cm^2/W	B 10^{-1} cm/W	$\|\chi^{(3)}\|$ 10^{-3} V^2/m^2	γ_h 10^{-12} esu
$1*10^{-5}$	0.312	11.97	3.59	4.6	9.3	1.07
$3*10^{-5}$	1.312	50.35	3.8	13.9	11	18.54
$5*10^{-5}$	2.312	88.74	4.12	26.8	35	15.39
$7*10^{-5}$	3.312	127.12	4.57	40	50	24.95

4-Conclusion:

EZ-scan method was employed for the study of the NLR index n_2 and NLA coefficient β of an RB dye-doped PVA polymer. The results show that both values vary with concentration. The EZ-scan measurements indicated that the dye exhibited positive and negative NLR index. In addition, the NLA of the samples can be attributed to a reverse saturable absorption. Thus, EZ-scan produces accurate results when low-energy laser is used.

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