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Nonlinear properties and optical limiting effect of phloxine B dye

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Dye-doped polymers are excellent substitutes for liquid dyes. This paper presents a study of the nonlinear optical properties of phloxine B dye in ethanol and dye-doped polymer film by the Z-scan technique using pulsed Nd: YAG laser of wavelength 532 nm. At 1 mM concentration, the dye sample exhibited a nonlinear refractive coefficient (n_2) of -2.50×10^{-8} and -3.6×10^{-8} cm^2/W, a nonlinear absorption coefficient (β) of -4.6×10^{-4} and -5.46×10^{-6} and susceptibility (χ^3) of 4.74×10^{-4} and 5.67×10^{-6} esu in ethanol and polymer, respectively. According to the results, the phloxine B dye in a solvent and a dye-doped polymer film exhibited negative nonlinearity. It is hence concluded that the phloxine B dye has excellent potential of use as nonlinear optical material.

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Keywords: Z-scan, Phloxine B, NLO properties

1. Introduction

Nonlinear optical materials are widely used in optical limiting and optical switching applications. Optical limiting is a nonlinear optical phenomenon in which the transmission intensity of a material decreases with increased intensity of incident light. This phenomenon is of high interest in the protection of eyes and sensors from an intense beam of light, such as the laser. Several organic polymers are commonly used as nonlinear optical materials in such applications as high speed telecommunication, optical limiters, and optical computers.

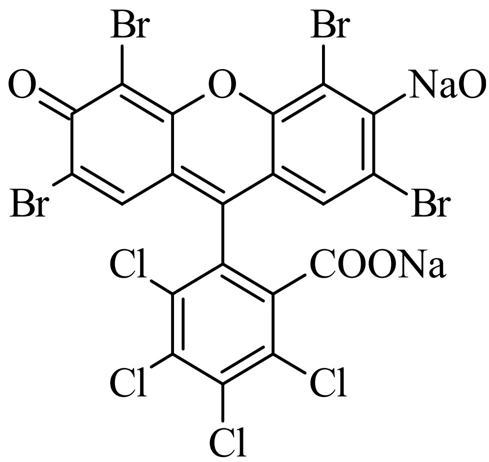
To assess the nonlinear optical properties of organic polymers, several techniques, such as nonlinear interferometry [1, 2] and degenerate four-wave mixing [3], have been proposed. Among others, the Z-scan method is simple and effective [4], because it can rapidly measure both nonlinear refraction and nonlinear absorption in solid and liquid samples, and uses the self-focusing or self-defocusing technique to assess nonlinear optical materials [5–7]. This method provides the magnitude of the real and imaginary parts of nonlinear susceptibility (χ^3) as well as the sign of the real part [8].

For this study, we chose phloxine B dye because its maximum absorption wavelength has an efficient value of 550 nm. We carried out experiments using the Z-scan technique to measure the sign and magnitude of optical nonlinearity of phloxine B dye in ethanol and dye-doped polymer film. The phloxine B dye showed saturable absorption in open aperture curve and negative nonlinearity in closed aperture curve. Overall, the dye exhibited a large third-order nonlinear susceptibility and negative optical nonlinearity. The optical limiting characteristics of phloxine B dye were also assessed.

2. Procedure

2.1 Materials and methods

The dye phloxine B was obtained from Sigma-Aldrich (India). Methyl methacrylate (MMA) was used as monomer and ethanol as solvent. The chemical structure of phloxine B dye is shown in Fig. 1.



$C_{20}H_2Br_4Cl_4Na_2$

Fig. 1 Chemical structure and molecular formula of Phloxine B

The spectral properties of the dye of concentration 0.01 mM in liquid medium were analyzed by recording the absorption spectra (Fig. 2). using a UV-VIS spectrophotometer (Varian, Mumbai). Spectral parameters such as peak absorption wavelength (λ_a), molar extinction coefficient ($\varepsilon(\lambda) = 5.7 \times 10^4$ L mol^{-1} cm^{-1}), oscillator strength (f = 2.84 × 10^{-24}) and bandwidth ($\Delta\gamma^{1/2}$ = 9.09 × 10^3 cm^{-1}) were measured at 550 nm [6].

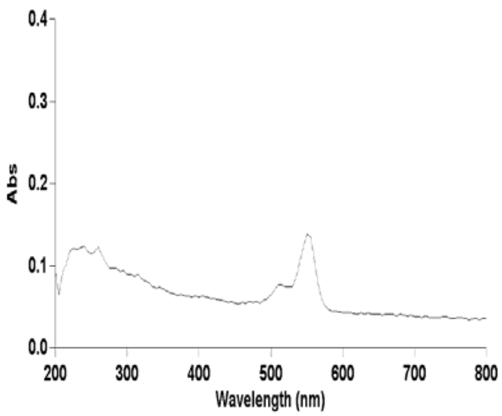


Fig.2 UV – VIS absorption spectra of dye Phloxine B dye in Ethanol

2.2. Synthesis of Dye-Doped Polymer Film

The dye-doped polymer film of concentration 1 mM was synthesized by thermal bulk-free radical polymerization [7]. MMA and ethanol were taken in a ratio of 4:1. Dye samples of predetermined weight were dissolved in this mixture. Benzyl peroxide (3 g) was added per liter of MMA. Benzyl peroxide was used as an initiator for polymerization. The solution was taken in polymerizing tubes [2] and kept in nitrogen atmosphere. Bulk polymerization was carried out in a temperature-controlled water bath. The viscous dye solution with initiator mixture was poured into a Petri dish placed in a glass enclosure and kept in the water bath. A film of thickness 0.5 mm was obtained.

2.3. Nonlinear Studies

For the Z-scan technique, a pulsed Nd: YAG laser (Quanta-Ray Model Lab-170-10, USA) of wavelength 532 nm was used as the excitation source. A laser of Gaussian beam was focused on a convex lens of focal length 20 cm to produce a beam waist (ω_0) of 523 μm. The peak intensity (I_0) of the incident laser beam was 4.77 kWcm^{-2} and the Rayleigh length was 1.6 mm. The schematic of the experimental arrangement is shown in Fig. 3.

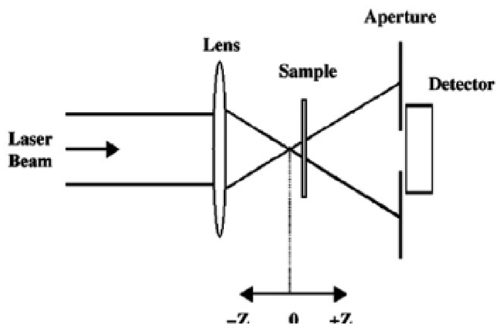


Fig. 3 Experimental setup for Z-scan Instrument

A 1-mm-wide optical cell containing the dye in ethanol was translated across the focal region along the axial direction (the direction of the propagation of laser beam). The transmission of the beam through an aperture placed in the far field was measured using a detector, and the output power was recorded by a digital power meter (EPM 2000; Coherent Molectron, USA). For open-aperture Z-scan, a lens was used to collect the entire laser beam transmitted through the dye. The same procedure was repeated using the polymer film [8].

2.4. Optical Limiting Effect

The optical limiting effect of phloxine B dye was studied using an Nd: YAG laser at 532 nm. A quartz cuvette (1 mm) containing the dye solution was kept at the position where the transmitted intensity showed a valley in closed aperture in Z-scan curve. An aperture of variable diameter was used to control the cross-section of the beam emerging out of the sample cuvette. The beam was then made incident on the photo detector. The input intensity values were varied systematically and the corresponding output intensity values were measured with a photo detector [9].

3. Results and discussion

The third-order nonlinear refractive coefficient (n_2) and nonlinear absorption coefficient (β) of phloxine B dye in ethanol at various concentrations and incident intensity (I_0) of 4.77 kW/cm^{-2} were evaluated using the Z-scan technique. The saturation absorption of the dye in solvent is shown by the open Z-scan curve (S = 1), where S is the aperture linear transmittance and given by S = 1–exp ($2r_a^2\omega_a^2$), and r_a and ω_a indicate the aperture radius and radius of the laser spot before the aperture, respectively. The open-aperture Z-scan curves for the phloxine B dye are shown in Fig. 4.

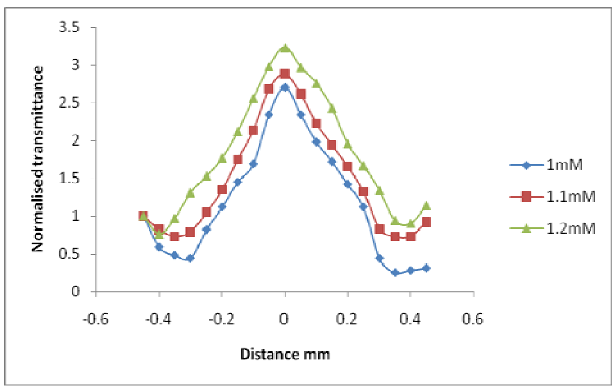


Fig. 4 Open aperture z- scan curve for dye in solvent at various concentrations

The open-aperture transmittance curve is symmetric with respect to the focus, and transmittance is calculated at the focal point indicating intensity dependence on absorption effect. The Z-scan curves for closed aperture are shown in Fig. 5.

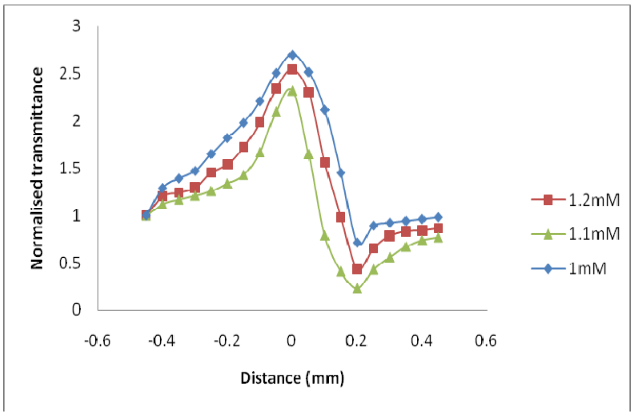


Fig. 5 Closed aperture z- scan cure for dye in solvent at various concentrations

The peak-to-valley configuration of the curve suggests that the refractive index is negative, exhibiting a self-defocusing effect. The curve also reveals a self-defocusing effect with a large negative nonlinear refraction [10]. The quantity $\Delta T_{(p-v)}$ can be defined as the difference between the normalized peak and valley transmittances, i.e., $T_p - T_v$. The variation of this quantity [11] as a function of $|\Delta\Phi_o|$ is given by:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\Phi_o| \tag{1}$$

where $\Delta\Phi_o$ is the on-axis phase shift at the focus. The on-axis phase shift is related to n_2 given by:

$$|\Delta\Phi_o| = kn_2 L_{\text{eff}} I_o \tag{2}$$

where I_0 is the intensity of laser beam at focus $Z = 0$; k is the wave number ($k = 2\pi/\lambda$), λ is the wavelength of the light used; $L_{\text{eff}} = (1-e^{-\alpha L})$ is the effective thickness of the sample; L is the sample length, and α is the linear absorption coefficient. If we could collect all the energy transmitted by the sample (open-aperture Z-scan), the measurement is sensitive to nonlinear absorption only. When an aperture was placed in front of the detector (closed-aperture Z-scan; Fig. 5), the measurement is sensitive to both nonlinear absorption and nonlinear refraction [12].

$$\beta = 2\sqrt{2}\Delta T / I_o L_{\text{eff}} \tag{3}$$

The imaginary parts of χ^3 is estimated using the value of the β obtained from open-aperture Z-scan data (Fig. 4), where ΔT is the normalized transmittance of the sample at position Z. Experimentally determined n_2 and β can be used to find the real and imaginary parts of χ^3 [13] according to the following relations:

$$\operatorname{Re}\chi^3 = 10^{-4}\frac{\varepsilon_o c^2 n^2}{\pi} n_2 \tag{4}$$

$$I_m \chi^3 = 10^{-2}\frac{\varepsilon_o c^2 n^2 \lambda}{4\pi^2}\beta \tag{5}$$

where ε_0 is vacuum permittivity and c is light velocity in vacuum. The absolute value of χ^3 is given by the relation:

$$\chi^3 = \left\{[\operatorname{Re}\chi^3]^2 + [\operatorname{Im}\chi^3]^2\right\}^{1/2} \tag{6}$$

The experiment was repeated for various concentrations of the dye phloxine B to obtain the nonlinear parameters. The experimentally determined values of $\Delta T_{(p-v)}$, n_2, β, Δn and χ^3 are given in Table 1.

The value of $\Delta T_{(p-v)}$ was found to have increased for the dye-doped polymer film in contrast to the dye in ethanol, which difference could be due to that heat dissipation (S) is quicker in liquid than in a solid medium (Figs. 6 and 7). The values of n_2 in dye-doped polymer film were found to be higher than in the case of dye in solvent, which could be due to the Anderson localization of photons [14].

Table.1.Nonlinear parameters of phloxine B dye in solvent and polymer film

Concentration	$\Delta T_{(p-v)}$	$n_2\times10^{-8}$ (cm²/W)	$\beta\times10^{-4}$ (cm/W)	$\Delta n\times10^{-4}$	$\chi^3\times10^{-6}$ (esu)
Ethanol					
1 mM	1.99	-2.50	-4.6	-1.15	4.74
1.1 mM	2.09	-2.63	-4.9	-1.20	5.13
1.2 mM	2.11	-2.65	-5.5	-1.21	5.73
Polymer film					
1 mM	2.93	-3.6	-5.46	-1.65	5.67
1.1 mM	3.0	-3.78	-5.89	-1.73	6.19
1.2 mM	3.16	-3.98	-6.40	-1.83	6.72

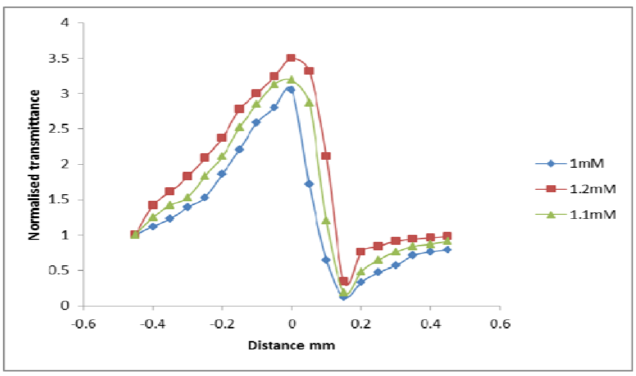


Fig. 6 Closed aperture z- scan curve for dye in polymer film at various concentrations

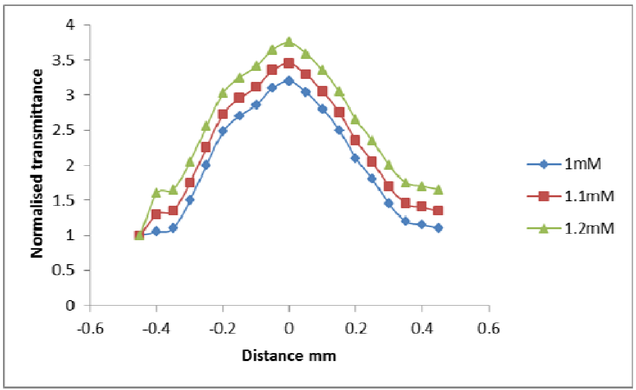


Fig. 7 Open aperture z –scan curve for dye in polymer film at various concentrations

3.1. Experimental

3.1.1. For phloxine B dye in ethanol (1 mM):

Using Fig. 5. and the formula $\Delta n = n_2 I_0$, we calculated $\Delta T_{(p-v)} = 1.99$ and $n_2 = -2.50\times10^{-8}$ cm^2/W. Correspondingly, the refractive index changes to $\Delta n = -1.15\times10^{-4}$ for $I_0 = 4.77$ kW/cm^{-2}. Now, β can be calculated from open-aperture normalized transmittance as in Fig. 4. The obtained β was -4.6×10^{-4} cm/W. According to equations [4–6], the absolute value of χ^3 was found to be 4.74×10^{-6} esu.

3.1.2. For phloxine B dye in doped-polymer film (1 mM):

Using Fig. 6 and the formula $\Delta n = n_2 I_0$, we calculated $\Delta T_{(p-v)} = 2.93$, $n_2 = -3.6\times10^{-8}$cm^2/W. correspondingly, the refractive index changes to $\Delta n = -1.65\times10^{-4}$ for $I_0 = 4.77$ kW/cm^{-2}. β can be calculated from open-aperture normalized transmittance as in Fig. 7. The obtained β was -5.46×10^{-4} cm/W. According to equations [4–6], the absolute value of χ^3 was found to be 5.67×10^{-6} esu. The values of n_2, β and χ^3 increased as the molar concentration of the dye increased. As the number of dye molecules increased as concentration increased, more particles are thermally agitated resulting in an enhanced effect. A pulsed Nd: YAG laser beam when passed through an absorbing medium induces temperature and density gradient, leading to a change in the refractive index profile. This intensity-induced localized change in the refractive index would result in a lensing effect on the optical beam [6, 10]. The optical limiting curve obtained with an Nd: YAG laser of wavelength 532 nm for the dye at various concentrations in solution is shown in Fig.8.

The output power rose initially with an increase in input power, but on reaching the threshold values, the sample began to defocus the beam, resulting in a greater part of the beam's cross-section being cut off by the aperture. Thus, the transmittance recorded by the photo detector remained reasonably constant, shown as a plateau region. The UV-VIS absorption spectra of the sample before and after laser irradiation showed that no change in pattern and intensity, indicating that the sample possessed excellent photo stability [15].

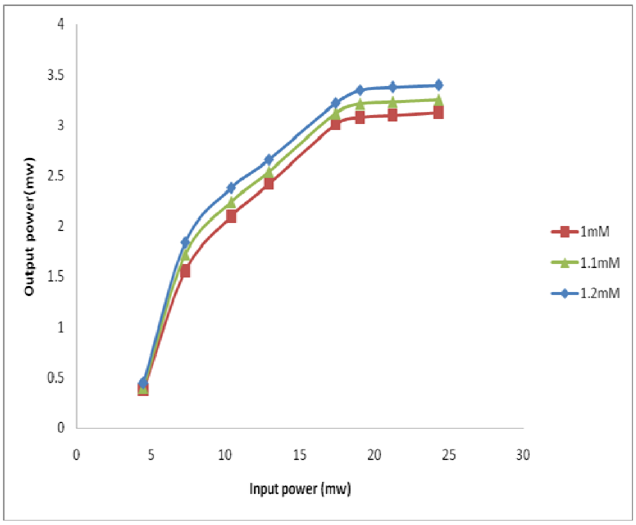


Fig.8 Optical limiting effect of the dye in solvent at various concentrations

4. Conclusion

This study evaluated n_2, β and χ^3 for phloxine B dye in ethanol and polymer film using Z-scan method with pulsed Nd: YAG laser of wavelength 532 nm. In all experiments, the phloxine B dye exhibited negative nonlinearity, saturation absorption was nonlinear, and nonlinear refraction exhibited a self-defocusing effect. The concentration dependent nonlinear refractive index was observed in this dye. The nonlinear refractive index and nonlinear absorption coefficient for various concentrations of the film were found. This shows that the sample has a large optical effect and susceptibility values of the dye were large, indicating that phloxine B dye could be an excellent nonlinear optical material.

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