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Third – Order Nonlinear Optical Properties and Optical Limiting Effect of Leishman Dye in Solution and Solid Polymer Film

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Abstract: We have investigated the third-order nonlinear optical properties of Leishman dye dissolved in Chloroform at different concentrations as a solution and dye doped in Poly(methylmethacrylate) (PMMA) as a solid polymer film. We have employed the z – scan technique with continuous wave (CW) solid – state laser (SSL) operating at wavelength 532 nm to measure the sign and magnitude of nonlinear refractive index (n_2) and the nonlinear absorption coefficient (β). The Leishman dye is found to exhibit negative nonlinearity (self – defocusing) and saturable absorption. Optical power limiting behavior was studied and the limiting threshold values were estimated for the dye solution at different concentrations and dye – doped polymer film at concentration 0.09 mM. Our study clearly shows that the Leishman dye is an excellent nonlinear material with large nonlinear response may provide the basis material for devices in optical applications.

Key words: Leishman dye; Third – order optical nonlinearity; Z – scan technique; Optical power limiting.

I. Introduction

Nonlinear optical (NLO) characterizations of various materials exhibiting nonlinear optical effects have attracted much attention because of their various potential applications, such as all - optical switching, optical data storage, optical power limiting and, optoelectronic and photonic devices [1 - 10]. Organic dyes are of great interest due to their large third – order nonlinearity, fast response time, applicability over a wide range of visible spectral region, photochemical stability, high damage thresholds, low cost, and easy to fabricate and integrate into optical devices. Nonlinear optical properties of organic dyes in various solvents have been investigated by many researchers [11-14] and there has been increasing interest in the nonlinear optical properties studies for these dyes. The present study focuses on the properties of Leishman dye in solution and solid polymer film (dye doped in poly(methylmethacrylate) (PMMA)). The chosen Leishman dye can be a promising candidate material for optical power limiting and other optical devices due to its large third – order optical susceptibility and strong nonlinear response at visible region wavelengths, as our present studies showed. Our studies are done using the standard single – beam z – scan technique. This technique has been used as an effective and convenient method for exploring the optical nonlinearity of many organic materials. It is a simple and sensitive method introduced in 1989 [15] to measure the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) of optical materials [15, 16]. Nonlinear properties of different materials can be characterized by z – scan technique because it allows the determination of both the value and sign of nonlinear refractive index (n_2) [16]. There are two types of the z – scan: closed – aperture z – scan and open – aperture z – scan. The closed – aperture z – scan is used to measure the nonlinear refraction, while the open – aperture z – scan is used to measure the nonlinear absorption. Z – scan experiment is done while sample (nonlinear medium) is moved through the focal point of the focused Gaussian laser beam, the transmittance is measured through a finite aperture placed in far field, and the sign and magnitude of the nonlinear refractive index (n_2) are determined from the resulting transmittance curve. The values of n_2 is positive if the laser beam tends to converge when passing the nonlinear medium and is negative when tends to diverge. In this paper, we report the third – order nonlinear optical properties of Leishman dye measured by z – scan technique.

II. Experimental

The Leishman dye solution was prepared by dissolving the Leishman dye powder in chloroform as a solvent. Four dye concentrations were prepared, these are: 0.03 mM, 0.05 mM, 0.07 mM, and 0.09 mM. The polymer solid films were prepared by dissolving appropriate amount of poly (methylmethacrylate) (PMMA) polymer in chloroform under continuous stirring until the solution becomes homogeneous. Leishman dye solution in desired concentration was then added to the polymer solution. After mixing the solutions using the magnetic stirrer, the polymer films were fabricated on thin microscope glass slides using casting method. Polymer films of thickness 0.80 – 0.85 μm at concentration 0.09 Mm were obtained. Examination the optical quality of these films by passing laser beam from He – Ne laser of output power 2 mW at 632.8 nm showed that they have good optical transparency in the visible spectral region. The UV – Vis absorption spectra of the Leishman dye in chloroform solvent at different concentrations and polymer film at concentration 0.09 mM were obtained

using a Cecil spectrophotometer (double – beam Cecil spectrophotometer model CE – 7500). The schematic of the experimental setup used for the z – scan experiment is shown in Fig. 1. A continuous wave (CW) solid – state laser (SSL) of Gaussian beam profile at wavelength 532 nm was used as the excitation source. The laser provides by an adjustable knob to control the laser output over the range 0 – 100 mW. The Gaussian laser beam was focused into the sample using convex lens of focal length 50 mm. The beam waist (ω_0) at the focal plane was stimulated to be $\approx 24 \mu\text{m}$, producing a peak value of the on – z axis intensity at focus $I_0 = 1.11 \text{ kW} / \text{cm}^2$. The Rayleigh range (z_0) of the focused beam was calculated to be 3.4 mm. The sample is either a 1- mm quartz cell containing the dye solution or a solid polymer film of thickness $0.80 \mu\text{m}$. The sample thickness is therefore smaller than the Rayleigh range and satisfies the thin medium condition in the z – scan method, that is $L < n_0 z_0$, where L is the sample thickness and n_0 is the linear refractive index of the sample material. An aperture of variable diameter placed in the far field is used to control the cross – section of the laser beam coming out of the sample. In our present work, we fixed the diameter of the aperture so that 50 % of transmission is passed through the aperture (i.e., $S = 0.5$). The sample was scanned across the focal plane of the lens along the propagation of the laser beam (the z – axis direction) using translation stage. The power of the transmitted laser beam through the aperture was measured by the photo-detector PD_2 , coupled with digital power meter. The laser input power was measured by the photo-detector PD_1 , coupled with another digital power meter. The beam splitter (BS) was used to reflect part of the incident laser beam on the photo-detector PD_1 .

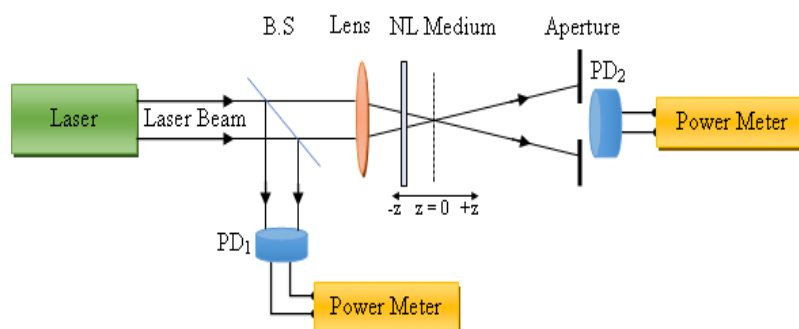


Figure 1: Z – scan experimental setup. BS, is a beam splitter; PD_1 and PD_2 are Photo - detectors.

III. Results and Discussion

The linear absorption spectra of the Leishman dye solution at different concentrations and solid polymer film at concentration 0.09 mM are shown in Fig. 2 (a) and (b), respectively. The spectra of the Leishman dye exhibit a wide absorption band with two distinct peaks, which are located at wavelengths 533 nm and 650 nm for the dye solution and a single peak at wavelength 653 nm for the dye – doped polymer solid film. We can also see from Fig. 2 (a) that the value the peak increases with increasing the Leishman dye concentration.

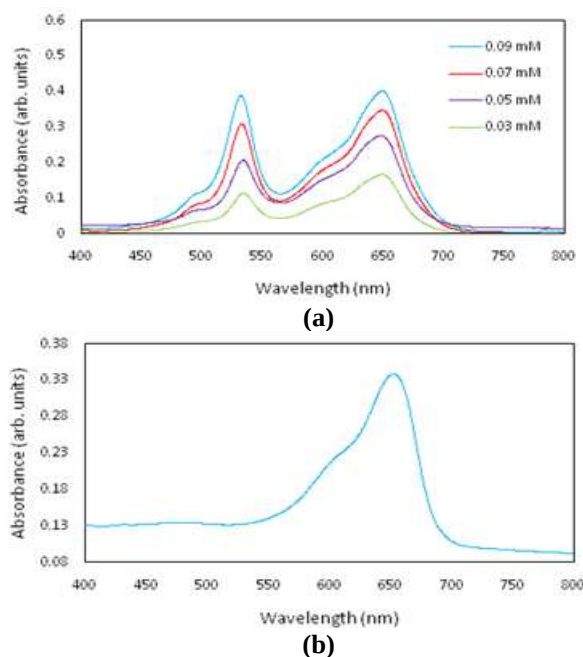


Figure 2: Linear absorption spectra of Leishman dye. (a) Dye solution at different concentrations. (b) Dye – doped polymer film of concentration 0.09 mM.

The closed – aperture and the open – aperture z – scan transmittance curves of the Leishman dye solution at different concentrations are shown in Fig. 3 (a) and (b), respectively. The normalized transmittance curve in the closed – aperture z – scan is characterized by a peak followed by a valley (peak-valley transmittance). This behavior indicates that the sign of the nonlinear refractive index of the Leishman dye is negative ($n_2 < 0$), i.e., self – defocusing resulting from the rate change of the refractive index (n) with temperature (T), dn / dT . The behavior of the open – aperture z – scan transmittance curve in Fig. 3(b) indicates that Leishman dye solution exhibits nonlinear saturable absorption process.

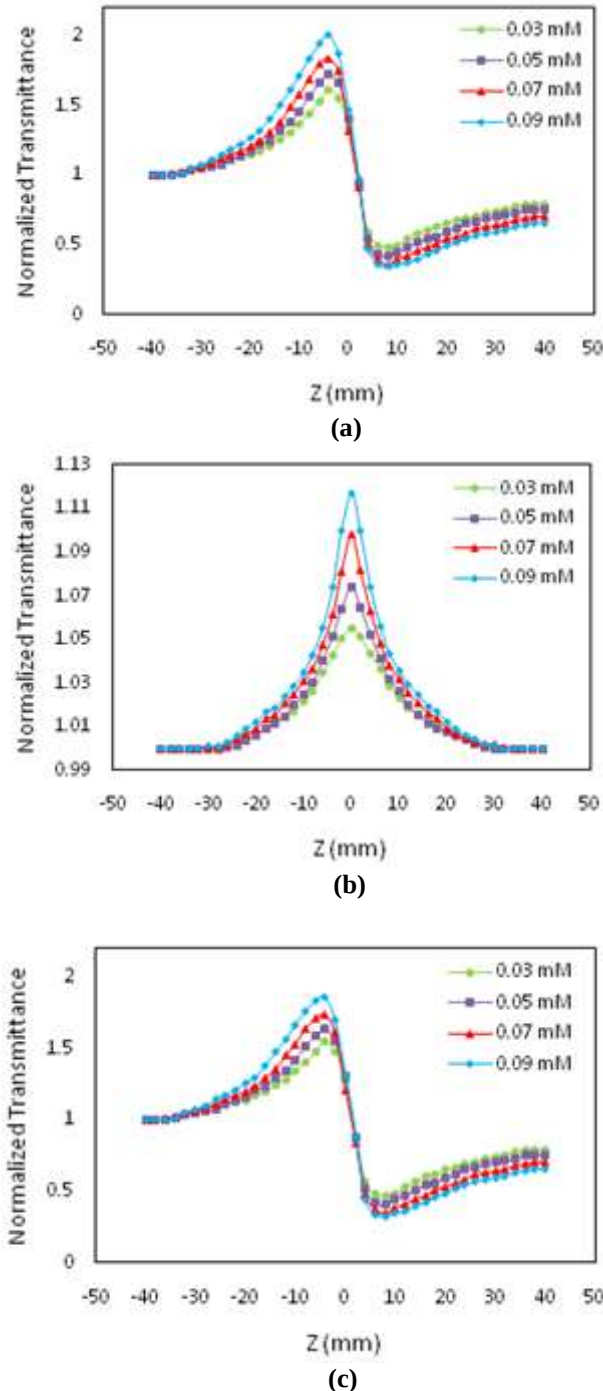
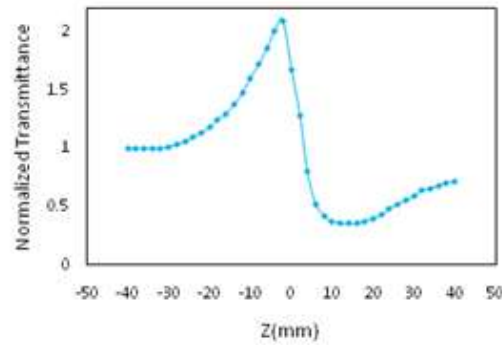


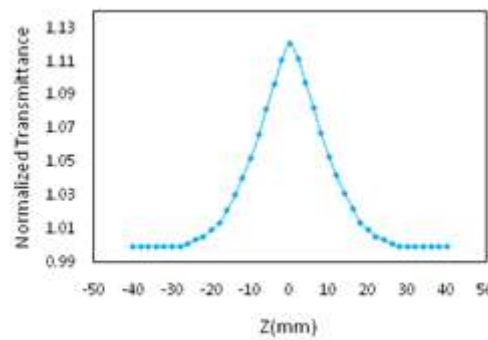
Figure 3: Normalized transmittance curves for Leishman dye solution at different concentrations. (a) Closed – aperture z – scan. (b) Open – aperture z – scan. (c) Pure nonlinear refraction.

The closed – aperture z – scan contains contribution from both the nonlinear absorption and nonlinear refractive index. The pure nonlinear refractive index (n_2) was obtained by dividing the closed – aperture z – scan data by the open – aperture z – scan data [16]. The obtained normalized transmittance curves for different Leishman dye concentrations are shown in Fig. 3(c). It is seen from Fig. 3 that Leishman dye exhibiting comparatively

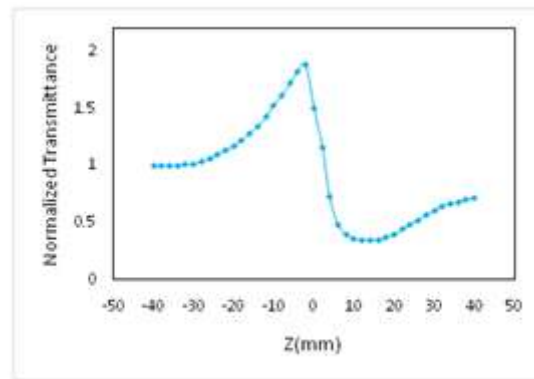
lower transmittance when the concentration increases, this due to the increase in the number density of molecules. Similar normalized transmitted curves for the dye – doped polymer film at concentration 0.09 mM were obtained as shown in Fig. 4 (a) and (b).



(a)



(b)



(c)

Figure 4: Normalized transmittance curves for Leishman dye - doped polymer film at concentration 0.09 mM. (a) Closed – aperture z – scan. (b) Open – aperture z – scan. (c) Pure nonlinear refraction.

The difference between normalized peak and valley transmittance ΔT_{p-v} is given by [15,16]:

$$\Delta T_{p-v} = 0.406 (1 - S)^{0.25} |\Delta \phi_0| \quad (1)$$

where $|\Delta \phi_0|$ is the on – axis nonlinear phase shift at the focus and S is the linear transmittance of the aperture and given by:

$$S = 1 - \exp(-2 r_a^2 / \omega_a^2) \quad (2)$$

where r_a is the radius of the aperture and ω_a is the radius of the laser beam at the entrance of the aperture.

The nonlinear refractive index (n_2) is given by the relation:

$$n_2 = \frac{\Delta \phi_0 \lambda}{2 \pi I_0 L_{eff}} \quad (3)$$

where λ is the laser wavelength and I_0 is the intensity of the laser beam at focus $z = 0$, and given by:

$$I_0 = \frac{2 P_0}{\pi \omega_0^2} \quad (4)$$

where P_0 is the laser input power. The L_{eff} is the effective length of the sample and given by:

$$L_{\text{eff}} = (1 - \exp(-\alpha_0 L)) / \alpha_0 \quad (5)$$

where L is the true sample length and α_0 is the linear absorption coefficient.

The nonlinear absorption coefficient (β) can be calculated from the open – aperture z – scan data and using the following relation:

$$\beta = \frac{2 \sqrt{2}}{I_0 L_{\text{eff}}} \Delta T \quad (6)$$

where ΔT is the normalized transmittance difference between peak at the focal point ($z = 0$) in the open – aperture z – scan normalized transmittance curve and the baseline.

The real part ($\text{Re}(\chi^{(3)})$) and the imaginary part ($\text{Im}(\chi^{(3)})$) of the third – order nonlinear optical susceptibility ($\chi^{(3)}$) for the Leishman dye were calculated using the following relations, respectively [17]:

$$\text{Re}[\chi^{(3)}] (\text{esu}) = 10^{-4} \frac{\epsilon_0 c^2 n_0^2 n_2}{\pi} \quad (\text{cm}^2 / \text{W}) \quad (7)$$

$$\text{Im}[\chi^{(3)}] (\text{esu}) = 10^{-2} \frac{\epsilon_0 c^2 n_0^2 \lambda \beta}{4 \pi^2} \quad (\text{cm} / \text{W}) \quad (8)$$

where ϵ_0 is the vacuum permittivity, c is the velocity of light in vacuum, and n_0 is the linear refractive index of the medium.

The absolute value of the third – order nonlinear optical susceptibility was calculated from the following relation:

$$|\chi^{(3)}| = [(\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2]^{1/2} \quad (9)$$

The various calculated values of the nonlinear parameters for the Leishman dye solution at different concentrations and the dye doped – polymer film at 0.09 mM are given in Table 1. We can see clearly from this table that the values of the nonlinear refractive index (n_2), nonlinear absorption coefficient (β), and the third – order nonlinear optical susceptibility ($|\chi^{(3)}|$) are increased with increasing the concentration of the Leishman dye. This may be attributed to the fact that the number of dye molecules increases as concentration increases, more number of particles are thermally heated resulting an increase in the third – order optical nonlinearity of the dye medium.

Table 1: Summary of the various calculated nonlinear parameters for Leishman dye solution and dye – doped polymer film.

Sample	Concentration (mM)	ΔT_{p-v}	n_2 (cm^2 / W) $\times 10^{-7}$	β (cm / W) $\times 10^{-3}$	$ \chi^{(3)} $ (esu) $\times 10^{-5}$
Solution	0.03	1.077	- 2.454	- 1.433	1.314
	0.05	1.226	- 2.818	- 1.934	1.588
	0.07	1.377	- 3.196	- 2.599	1.901
	0.09	1.534	- 3.588	- 3.108	2.260
Polymer film	0.09	1.546	- 4.178	- 3.726	3.156

Optical power limiting has received considerable attention due to its functional applications [10, 13, 18 – 20]. It can be used for the protection of human eyes and sensitive equipments such as sensors from intense laser beams by controlling the intensity of incident laser beam. In this nonlinear optical process, the transmitted laser intensity (or power) of a material increases linearly with increased input laser intensity at low input intensities, but above certain input intensity (threshold intensity), the transmitted intensity becomes relatively constant. The optical power limiting behavior was observed for the Leishman dye in solution at different concentrations and in polymer film at concentration 0.09 mM, as shown in Fig. 5. This nonlinear behavior arises from the nonlinear

absorption as well as self – defocusing effects. Values of the optical power limiting threshold, which is defined as the minimum input power at which the transmittance drops to half its initial transmittance, were estimated from Fig. 5, for the dye solution and the dye – doped polymer film. Fig. 6 illustrates the relation between the value of the power limiting threshold and the Leishman dye concentration. It is clearly evident that the power limiting threshold linearly decreases with increasing the dye concentration. This is due to the fact that the number of absorbing molecules increases with increasing the dye concentration which in turn lowers the limiting threshold. It was found that the value of the power limiting threshold for the dye – doped polymer film at concentration 0.09 mM about 10.4 mW, which is less than the value of limiting threshold of the dye solution (13.7 mW) at the same concentration, and this is due to the sample thickness effect.

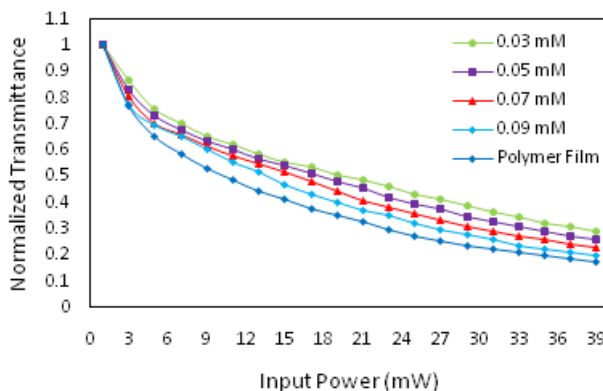


Figure 5: Optical power limiting behavior (normalized transmittance versus laser input power) of Leishman dye solution for different concentrations and dye – doped polymer film at concentration 0.09 mM.

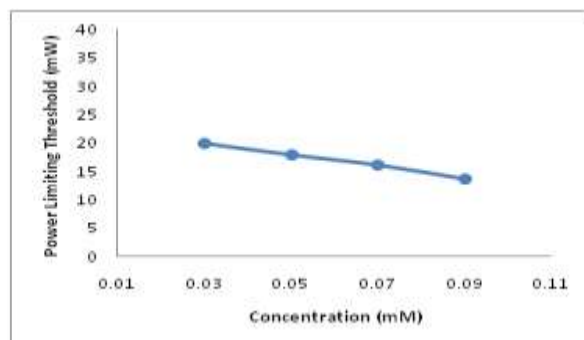


Figure 6: Power limiting threshold of Leishman dye solution as a function of concentration.

IV. Conclusion

We have investigated the third – order optical nonlinearities of Leishman dye in chloroform at different concentrations and in dye – doped polymer film (Leishman dye with PMMA polymer) at concentration 0.09 mM. We have used the z – scan technique with continuous wave (CW) solid – state laser (SSL) at wavelength 532 nm for measuring the nonlinear optical parameters of the Leishman dye, such as nonlinear refractive index (n_2), the nonlinear absorption coefficient (β), and the third – order optical susceptibility ($|\chi^{(3)}|$). It is found that the Leishman dye shows nonlinear saturation absorption and a negative nonlinear refractive index ($n_2 < 0$), leads to self – defocusing refraction effect. Our results show that the values of the optical parameters (n_2 , β , and $|\chi^{(3)}|$) of the Leishman dye are linearly increased with the dye concentration. We have also investigated the optical power limiting behavior of Leishman dye and estimated the limiting threshold for the dye solution at different concentrations and the dye – doped polymer film at 0.09 mM. Good optical limiting action with relatively low limiting threshold was obtained. Our results show that the Leishman dye is promising material for applications in optical devices, such as all – optical switching, optical limiter, and photonic devices.

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