International Journal of Applied and Advanced Scientific Research (IJAASR)
Impact Factor: 5.255, ISSN (Online): 2456 - 3080
(www.dvpublication.com) Volume I, Issue I, 2016

TYPE 1 & TYPE 2 OPTICAL LIMITING STUDIES IN DISPERSE ORANGE-25 DYE-DOPED PMMA-MA POLYMER FILMS USING CW LASER

Shubrajyotsna Aithal*, P. S. Aithal & G. K. Bhat*****

* Research Scholar, Department of Chemistry, Rayalaseema University, Kurnool, Andhra Pradesh

** Srinivas Institute of Management Studies, Pandeshwar, Mangalore, Karnataka

*** Department of Chemistry, Srinivas Institute of Technology, Valachil, Mangalore, Karnataka

Cite This Article: Shubrajyotsna Aithal, P. S. Aithal & G. K. Bhat, "Type 1 & Type 2 Optical Limiting Studies in Disperse Orange-25 Dye-Doped PMMA-MA Polymer Films Using CW Laser", International Journal of Applied and Advanced Scientific Research, Volume 1, Issue 1, Page Number 196-208, 2016.

Abstract:

Materials with exceptional third order nonlinear optical properties are critical to the continuing development of photonics and electro-optical devices such as those used in optical communications, networking, optical computation for signal processing, and data storage devices. The nonlinear optical material research is generally focussed on improving the efficiency of optical wavelength conversion, optical amplification, nonlinear absorption, refractive index changes etc. which are input light intensity dependent. During last few years, the organic dye-doped polymer films are getting more attention due to their advantages in fabricatingoptimum photonics devices. In this paper, we have studied the nonlinear optical properties like nonlinear absorption and nonlinear refraction of an azo dye Disperse Orange-25 (DO-25) doped in Polymethyl methacrylate-methacrylic acid (PMMA-MA) polymer matrix using open aperture and closed aperture Z-scan experimental methods for continuous wave (CW) laser input. The optical limiting properties of these films are also studied using Type 1 and Type 2 configurations at different input power using continuous wave (CW) laser beams of 532 nm wavelength.The nonlinear absorption coefficient, nonlinear refractive index, and saturated output power for type 1 and type 2 optical limiting are determined.

Index Terms: Organic Nonlinear Material, Dye-Doped Polymer Films, Optical Limiting & Open and Closed Aperture Z Scan

1. Introduction:

Nonlinear optical Materials with optimum properties are critical to the continuing development of photonics and electro-optical devices, such as those used in optical communications, networking, optical computation for signal processing, and data storage equipment. During last few years, the organic dye-doped polymer films are getting more attention due to their advantages to fabricate photonics devices [1-3]. Many organic dyes have shown considerable third order nonlinearity for intense laser light like Phthalocynamines [4-5], Porphyrins[6-7], and Rhodamine 6G [8]. Castillo et al. (1994) [9]) observed the thermal lensing effect resulting from one and two-photon absorption. Nonlinear characterization of Mercurochrome dye is studied for potential application in optical limiting by Krishnamurthy et al. (2010) [10]. Rekha et al. (2009) studied nonlinear characteristic and optical limiting effect of oil red O azo dye in liquid and solid media [11]. Muto et al.(1998) [12] shown that the nonlinear response of disperse red1 (DR1) dye with PMMA at 532 nm increases with increasing concentration up to 1 wt% of DR1 in PMMA and decreases for larger concentration. Zidan, et al. (2011) [13] have studied the optical limiting behaviour of disperse red 1 dye-doped polymer. Brzozowski et al. (2001) [14] reported the non-linear response of pseudo-stilbene type azobenzene dye embedded in a polymer (PMMA, poly (1,4-phenylene vinylene)) matrix by Z- scan technique. Third order optical nonlinearity and optical limiting studies of propane hydrazides is reported by Naseema, K et al. (2012) [15].

VenugopalRao et al. (2002) [16] reported the non-linearity of Rhodamine B dye in methanol. UmakantaTripathy et al. (2002) [17] published a few parameters of IR 140 dye in dimethyl sulphoxide (DMSO) using Z-scan techniques. Third order optical nonlinearities and spectral characteristics of a dye methylene blue are studied by Sukumaran et al. (2011) [18]. Chen et al. (2003) [19] reported the third-order optical nonlinearity of fullerene-containing polyurethane films at telecommunication wavelengths. Zidan et al. (2011) investigated the optical limiting properties of acid blue-29 in various solvents [20]. Dharmadhikari et al. (2004) observed the higher-order optical nonlinearities in 4-dimethylamino-N-methyl-4-stilbazoliumtosylate [21] and Ganeev et al. (2004) reported the fifth order optical nonlinearity of pseudoisocyanine solution [22]. Del Nero et al. (2005) determined the non-linear refractive index of methyl orange in acetone under different PH condition by using Z-scan technique [23]. Hassan et al. 2015 [24] studied optical limiting properties of Sudan red B in solution and solid film. R. P. Singh et al. (2003) studied two photon absorption cross section and nonlinear absorption properties of DASPB [25], DO-25, and DY-7 [26] at picoseconds regime in solution form. Jamshidi G. K. et al. (2007) have studied nonlinear responses and optical limiting behavior of fast green FCF dye under a low power CW He–Ne laser irradiation [27]. Many other studies have been reported on use of dye-doped polymer films for optical phase conjugation through degenerate four waves mixing (DFWM) using low power CW lasers [28-35]. The optical third harmonic nonlinearity in organic materials generally originated by two photon and multiphoton absorption, two photon florescence, excited state absorption, reverse saturation absorption, thermal lensing effect etc. Reports show that there have been less work carried on the study of nonlinearities of dyes in solid medium. It is expected that by studying nonlinear properties of dyes in solid medium and identifying active and efficient nonlinear dyes for low power CW laser beams, one can fabricate new elements/components, which have potential applications in optical limiting and optical switching.

2. Concept of Ideal Optical Limiter:

Ideal properties of a device or a system can be used to upgrade or improve its properties towards reaching 100% efficiency [36]. By comparing the properties/characteristics of a practical device/system with its ideal counterpart, one can find out the possible modifications in that device /system towards reaching the objective of achieving such an ideal system. An ideal limiter is a device which shows linear transmission characteristics below a threshold level and fixes the output to a constant level above it, thus providing safety protection to sensors or human eyes. An ideal optical limiter is a photonic device or component which has ideal optical limiting characteristics. It can take any intensity input laser beam both continuous wave (CW) or pulsed wave of any time duration. It has to process such incident light beam internally using nonlinear properties of the medium and provide output laser beam of constant intensity or fluency. The ideal optical limiter has the characteristics shown in Fig. 1. It has a high linear transmission for low input (e.g. energy E or power P), a variable limiting input E or P, and a large dynamic range defined as the ratio of the E or P at which the device damages (irreversibly) to the limiting input. Such devices can also be used as power or energy regulators. However, since the primary application of the optical limiter is for sensor protection, and damage to detectors is almost always determined by fluence or irradiance, these are usually the quantities of interest for the output of the limiter. Getting the response of ideal limiter at least above certain minimum input energy turns out to be possible using a wide variety of materials, however, it is very difficult to get the limiting threshold as low as is often required and at the same time have a large dynamic range. Because high transmission for low inputs is desired, the limiter material must have low linear absorption. Some of the characteristics predicted for ideal limiter are:

- ✓ An ideal limiter device should capable of taking input light beam of any intensity without any material damage.
- ✓ An ideal limiter device should capable of accepting input light beam without any reflection or scattering from incident surface.
- ✓ Any variation in the input intensity or power between zero to infinity should maintain constant output intensity irrespective of input intensity variations.
- ✓ An ideal optical limiter shows linear transmission characteristics below a threshold level and fixes the output to a constant level above it.
- ✓ The transmission characteristics of an ideal limiter vary depending upon the incident intensity due to nonlinear properties of the limiter material.
- ✓ The output intensity/fluency of ideal optical limiter is independent on the wavelength and pulse duration of the laser beam.
- ✓ An ideal optical limiter should limit the input light of wavelength throughout the electro-magnetic spectrum. i.e., it should have infinite bandwidth.
- ✓ The nonlinear material medium used for fabrication of ideal limiter should have very high nonlinearity for entire bandwidth.
- ✓ The nonlinear material medium used for fabrication of ideal limiter should limit any laser beam of any power of both CW and pulsed.
- ✓ An ideal limiter should provide constant output in any environmental conditions like changes in temperature, pressure, and aging of the material.
- ✓ The construction of ideal limiter should be easy and of low cost.

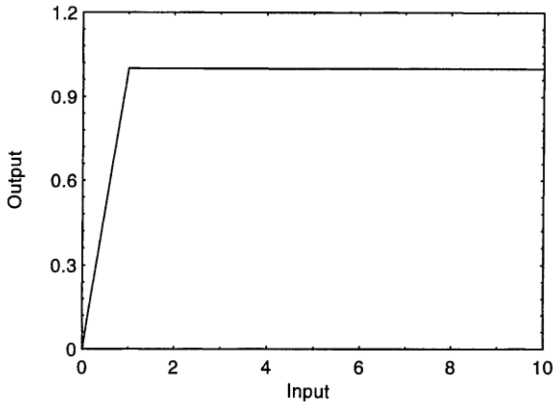
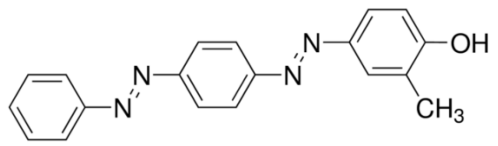


Figure 1: The ideal optical limiter input-output response characteristics [37].

The ultimate objective of any optical nonlinear materials research is to find a suitable material which can show optical limiter characteristics close to ideal optical limiter characteristics.

3. Preparation &Linear Optical Properties of DO-25 Doped Polymer Films:

Commercially available Disperse Orange-25 (DO-25) (Aldrich Chemical Co.) is purified by recrystallization twice with spectrograde ethanol and by vacuum sublimation. The purity is determined spectroscopically. Purified chloroform is used as the solvent. To prepare the film, Polymethyl methacrylate – metacrylic acid is used as a polymer matrix. The thin films of DO-25 doped in PMMA-MA are prepared using hot press technique [38]. Thin films of thickness (10 µm) with 1 mM, 2 mM, and 5 mM dye concentrations are prepared between two glass slides and are used as samples for optical nonlinearity study and optical limiting experiments.



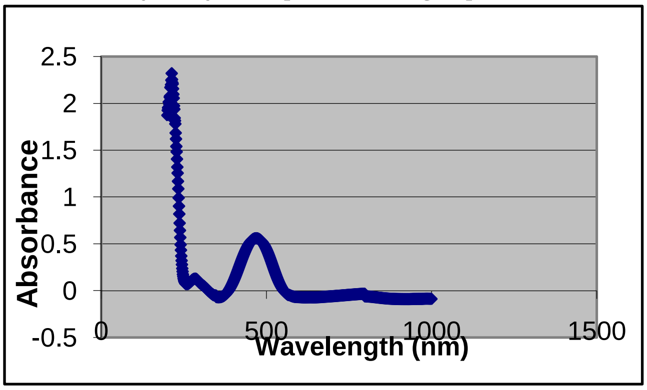


Figure 2: (a) Molecular structure of DO-25. (b) Linear absorption spectrum of DO-25.

The linear absorption spectrum of DO-25 doped in PMMA-MA is measured on a VARIAN Cary UV-vis-IR recording Spectrophotometer. The figure 2(b) shows the linear absorption spectrum of the film. The spectral curve has shown that there is a strong absorption band with peak absorption located at 468 nm with a bandwidth of 100 nm, a medium absorption peaked at 270 nm with a bandwidth of 60 nm and no linear absorption is observed in the entire spectral range of 530 to 1200 nm [39-40]. The Z-scan technique is used to study the nonlinear optical properties of the sample [41-42]. The linear absorption coefficient α_0 is determined for the chosen wavelength 532 nm by using formula $\alpha_0 = -\frac{1}{t}\ln\left[\frac{1}{T}\right]$ ---------- (1)

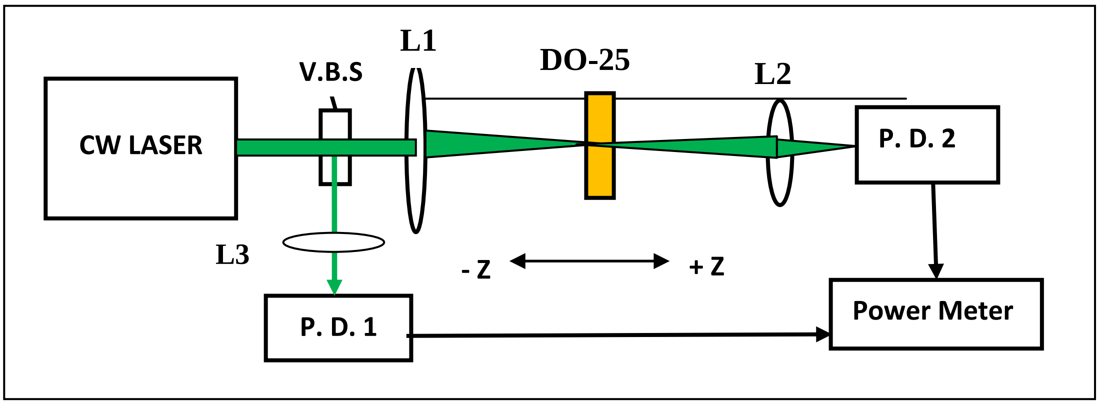
Where (t) is the thickness of sample and T is the transmittance. The refractive index n_0 can be found from transmittance spectrum of the film according to the following equation

$$n_0 = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)\right]^{1/2} \qquad \text{--------} \quad (2)$$

The linear absorption coefficient and refractive index of DO-25 are shown in table 1.

4. Nonlinear Absorption Using Open Aperture Z-Scan:

The block diagram of the experimental setup used for the open aperture Z-scan study of DO-25 doped in PMMA-MA film is shown in figure 3. A CW semiconductor diode laser of wavelength 532nm is used as the light source (BeamQ 30 mW Green Light Line). The Gaussian profiled laser beam is focused by a lens (L1) of focal length f = 3.5 cm to produce a beam waist ω_0 of 15 µm. The Rayleigh condition, diffraction length $Z_R = \pi\omega_0^2/\lambda > L$ is satisfied in this case so that the sample can be considered as a thin medium, where L is the thickness of the sample and λ is the free space wavelength of the laser beam. The diffraction length for the experimental setup is found to be 2.5 mm. The input power adjusted and noted by means of a convex lens (L3), Photo detector (P.D.1) and digital power meter assembly. The DO-25 dye-doped polymer sample is translated across the focal region of lens L1 along the axial direction that is the direction of the propagation of the laser beam.



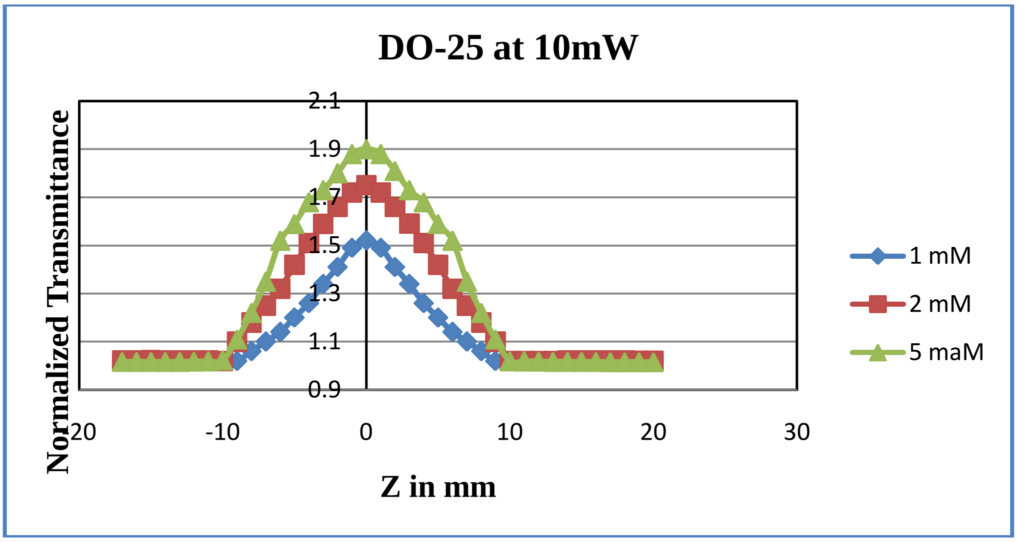


Figure 4: CW Open aperture Z-scan plot of DO-25 at different dye concentrations using 532 nm, 10 mW laser beam

The transmitted beam is collected by means of a convex lens (L2) and the output intensity is measured using photo detector (P.D.2) fed to the digital power meter. In open aperture (S=1) configuration, the system is insensitive to nonlinear refraction and can be used to measure the nonlinear absorption cross section. Such Z-scan trace with no aperture is expected to be symmetric with respect to the focus (Z = 0), where the minimum transmittance (e.g., multi-photon absorption) or a maximum transmittance (e.g., saturation of absorption) occurs. The nonlinear coefficient can be easily calculated from Z-scan transmittance curve.

The Z- scan experiment is performed for DO-25 dye-doped PMMA-MA polymer films of the dye concentration 1mM, 2mM, and 5 mM using 532 nm laser beam at 10mW, 20 mW and 30 mW input power. The results are depicted in Fig. 4, to Fig. 6 respectively. In open aperture Z-scan, DO-25 has shown a decrease in transmittance with an increase in irradiance/input intensity due to reverse saturation absorption [43-44].

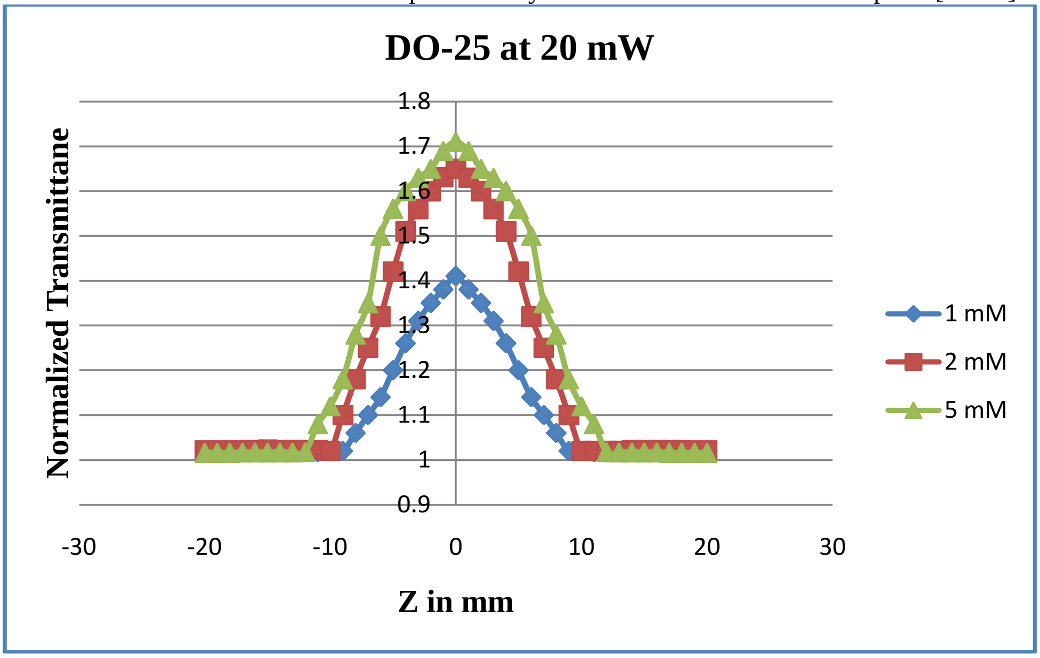


Figure 5: CW Open aperture Z-scan plot of DO-25 at different dye concentrations using 532 nm, 20 mW laser beam.

It is seen from the Z-scan plot that the DO-25 shows strong saturable absorption at low input intensity of laser beam. Even if the linear transmittance of the sample is low (transmittance T = 0.6), it is observed that due to nonlinear absorption, the transmittance of the sample is increased initially with the increase in intensity. But it is interesting to note that, the saturation absorption (SA) is overtaken by reverse saturation absorption (RSA) effect at higher input intensity (figure 6). The transformation from SA to RSA with the increase in intensity level of the laser is observed in some organic dyes including DO-25 and this behavior can be used for optical limiting as well as optical switching.

Based on open aperture Z-scan plots of DO-25 for different concentrations and at different input power, it is observed that:

- ✓ At low input power, saturation absorption (SA) increased with increase in the concentration of dye in the sample.
- ✓ At the higher intensity of input light, DO-25 has shown reverse saturation absorption (RSA) so that saturation absorption (SA) of the sample is decreased.

Reverse saturable absorption is observed in the open aperture Z-scan trace for DO-25 dye in PMMA-MA matrix as it shows minimum transmittance. The nonlinear absorption coefficient β can be estimated from the open aperture Z-scan data, where $\beta = (2\sqrt{2}\,\Delta T)/\,(I_0 L_{eff})$ ----- (3)

I_0 is the intensity at the focal spot given by $I_0 = 2P_{peak}\,/\pi\omega_0^2$ --------- (4)

The effective length of the sample, can be determined from the formula $L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0$ ------- (5)

At low input intensity, the transmittance increases with the increasing excitation intensity and has a maximum value at the focus, which is the signature of saturation absorption according to Sheik-Bahae's theory. In eq. (3), ΔT is maximum transmittance at the focus (at Z =0).When saturation absorption occurs, the absorption coefficient α is no longer a constant. Instead, it becomes a function of the excitation intensity as in the relation,

$\alpha = \alpha_0 + I\beta$ ------- (6), where α_0 is the linear absorption coefficient, α is the total absorption coefficient, β is the nonlinear absorption coefficient, and I is the incident intensity of the laser beam.

In the simplest case, when only third-order nonlinearities are considered in the sample, the resultant change in refractive index becomes: $n = n_0 + n_2 I$. -------- (7)

Where n is the total refractive index of the sample, n_0 is the linear refractive index of the sample, n_2 is the third order nonlinear refractive index of the sample, and I is the excitation intensity.

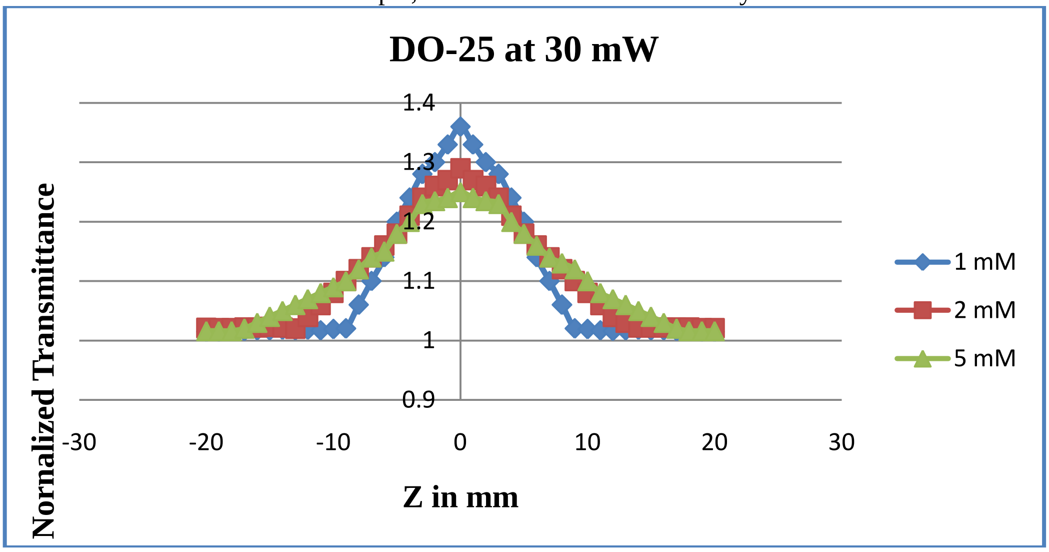


Figure 6: CW Open aperture Z-scan plot of DO-25 at different dye concentrations using 532 nm, 30 mW laser beam

5. Nonlinear Refraction Using Closed Aperture Z-Scan:

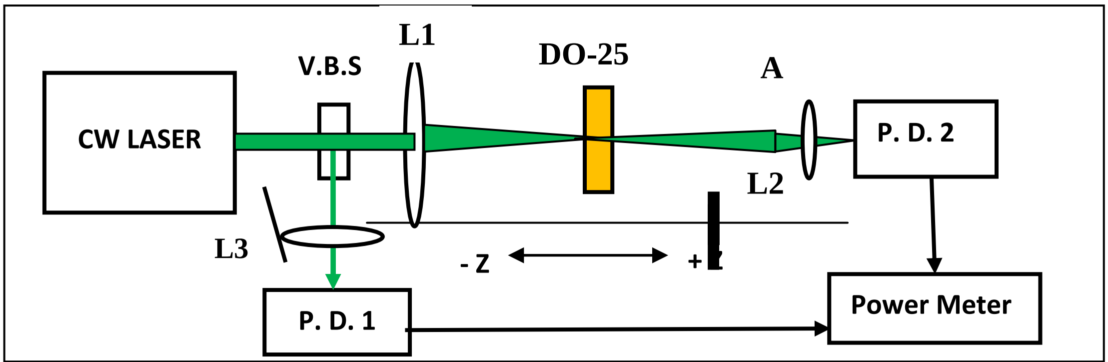


Figure 7: Experimental setup for closed aperture Z scan for DO-25 sample.

The experimental setup used for the closed aperture *Z*-scan technique is same as the setup used for open aperture Z-scan except for the output beam from the dye sample is collected through an aperture of a fixed hole size instead of collecting entire output beam through collecting lens L2. The diode laser of wavelength 532 nm (BeamQ 30 mW Green Light Line) is used as the excitation source and the Gaussian beam profile was focused by a convex lens (L1), of focal length, *f* = 3:5 cm to produce a beam waist ω_0 of 15 µm. The peak intensity of the incident laser beam is I_0 = 3:5 kW/cm^2. The diffraction length, Z_R was found to be 2.5 mm. The schematic of the experimental setup used is shown in figure 7. The dye sample is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The transmission of the beam through an aperture placed in the far field is measured using photo detector fed to the digital power meter. The closed aperture Z-scan plot between Z in mm and normalized transmittance for different dye concentrations is shown in figure 8.

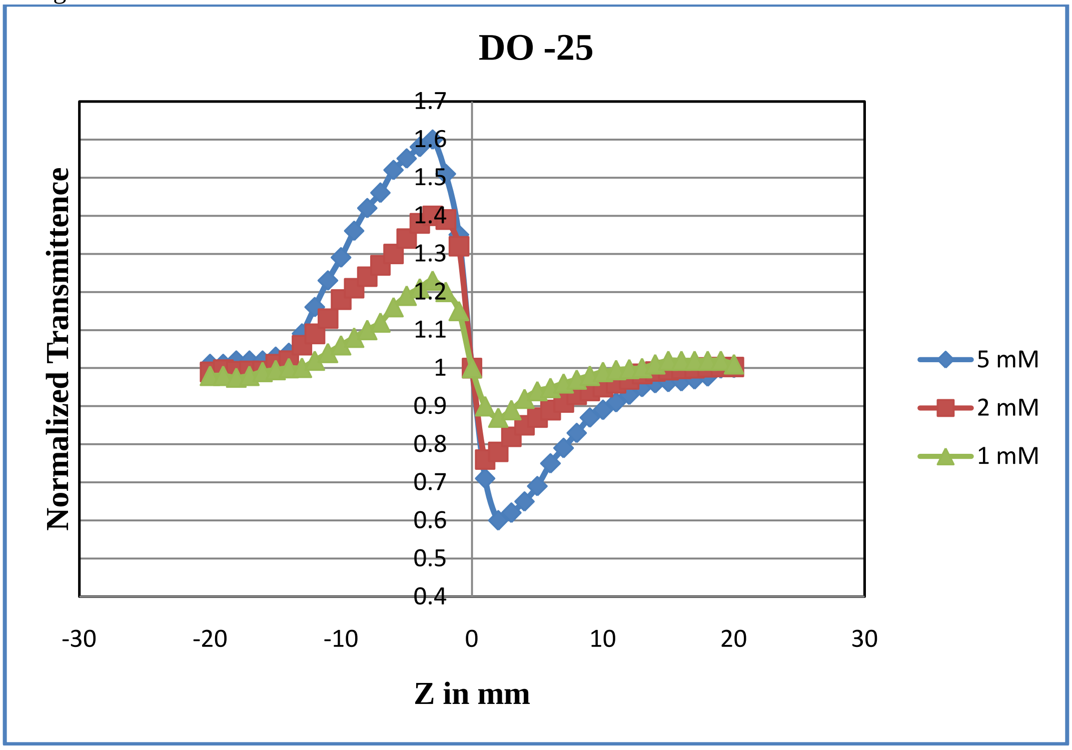


Figure 8: Nonlinear refraction of DO-25 using CW 532 nm 20 mW laser beam.

The normalized transmittance curve obtained from the closed aperture *Z*-scan data contains a positive peak followed by a negative valley, which indicates that the sign of the refraction nonlinearity is negative, i.e. the dye sample shows self-defocusing nonlinearity. This self-defocusing effect is mainly due to the local variation of the refractive index with temperature. It can be argued that the defocusing effect for the dye in polymer film shown in figure 8 is attributed to a thermal nonlinearity resulting from the absorption of radiation at 532 nm. From the normalized nonlinear refraction graph, the measurable quantity $\Delta T_{p\text{–}v}$ can be defined as the difference between the normalized peak and valley transmittances. Since the closed aperture transmittance is affected by the nonlinear refraction and nonlinear absorption, to determinenonlinear refractive coefficient, it is necessary to separate the nonlinear refraction effect from nonlinear absorption effect. As per Sheik-Bahae [42], an effective method to obtain purely nonlinear refractive index $n_2$is to divide the closed aperture transmittance data by the corresponding open aperture scan data. The *Z*-scan curve for pure nonlinear refractionfor 5 mM concentration DO-25 dye doped sample is shown in figure 9 at the input laser beam intensity of 20 mW. Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient βcan be used in finding the absolute value of the third-order nonlinear optical susceptibility [43-44]. In order to know the contribution from pure PMMA-MA polymer film to the observed nonlinear response, the *Z*-scan is performed on pure film without doping DO-25 dye. Neither nonlinear absorption nor nonlinear refraction is observed. The nonlinear refractive index n_2 can be calculated using the formula $n_2 = \frac{\Delta\emptyset\,\lambda}{2\pi I_0 L_{eff}}$ ------ (8)

and $|\Delta\emptyset| = \Delta T_{(p\text{-}v)}\ /[0.406\,(1\text{-}s)^{0.25}]$ --------- (9)

where $\Delta T_{p\text{-}v}$ is the peak-valley transmittance difference from the closed aperture plot, $|\Delta\emptyset_0|$ is the on axis nonlinear phase–shift and (s) is the linear aperture transmittance given by s = $[1\text{-}\exp(-2r_a^2/w_a^2)]$ where r_a is the aperture radius and w_a is the beam radius at the aperture. S=1 for open aperture configuration and S is in between 0.1 to 0.5 for closed aperture configurations. In eq. (8), I_0 is the intensity at the focal spot as per eq.(4) and L_{eff} is the effective length of the sample and is given by eq. (5).

The change in refractive indexΔncan be calculated using the formula,

$\Delta n = n_2 I_0$------- (10).

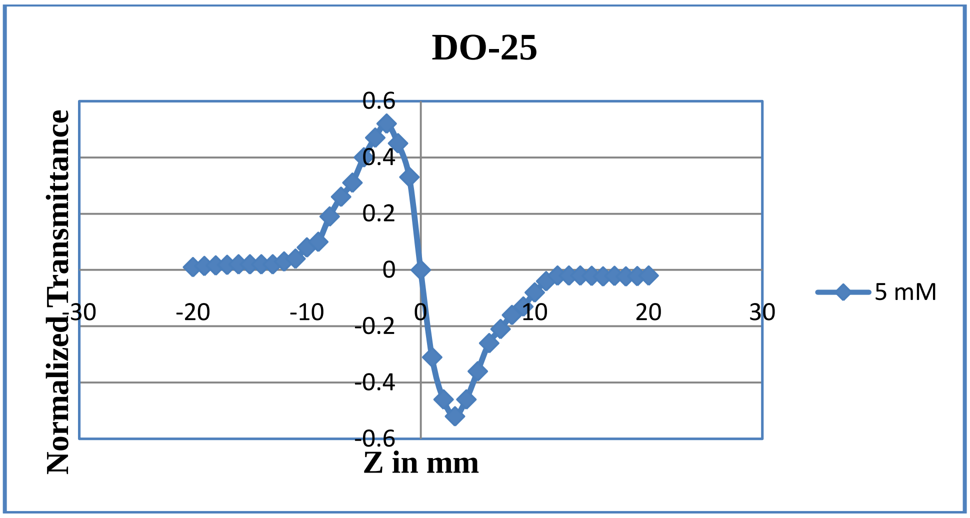


Figure 9: Pure nonlinear refraction plot of DO-25 using CW 532 nm 20 mW laser beam.

6. Experimental Configuration for Optical Limiting:

The optical limiting effect of the DO-25 dye-doped polymer film is studied by using a 30 mW CW semiconductor laser at 532 nm (BeamQ 30 mW Green Light Line). Two experimental setups are used for the demonstration of optical limiting. In the first experimental setup, the dye sample is placed in the focus of the focusing lens L1 of Z-scan setup. The emergent beam from the dye sample is collected to a photodetector by means of a collecting lens L2 to measure the output power. By fixing the sample position at the focus, the input power is varied and output power is noted. Such experimental setup is named as *Optical limiting without an aperture* or ***Type 1 optical limiting***. This type of optical limiting study will take care of nonlinear absorption property of the dye sample. In the second experimental setup, an aperture of fixed hole size is used between the dye sample and the collecting lens & photo detector. The dye sample film is kept at the position where the transmitted intensity shows a valley in closed aperture *Z*-scan curve [42]. The input laser intensity is varied systematically and the corresponding output intensity values are measured by the photo detector. At very high peak intensities (closer to the focus) we could observe diffraction type pattern with concentric ring structures probably due to self-phase modulation. However, in limiting experiments, we have ensured that there is no ring pattern formation by placing the sample away from focus. Such experimental setup is named as *Optical limiting with an aperture* or ***Type 2 optical limiting***. This type of optical limiting study will take care of nonlinear refraction property of the dye sample.

Case (1) Optical Limiting without Aperture (Type 1):

The pure nonlinear absorption property of the dye sample is measured using this method of optical limiting without aperture at the output side (Type-1 optical limiting). The entire light beam transmitted through the sample is focused by a collecting lens to the photo detector-power meter assembly. The optical limiting effects of the DO-25 dye-doped PMMA-MA films are studied by using a CW laser source (BeamQ 30 mW Green Light Line). The experimental set-up for the demonstration of type-1 optical limiting is shown in figure 10. The dye sample is kept fixed at the focal point of the lens L1 of aperture Z-scan setup. A variable beam splitter (VBS) is used to vary the input power. By means of a convex lens, the output light beam is made to fall on the photo detector (PD). The input light intensity is increased systematically and the corresponding output intensity is measured by a photo detector. The output power is measured using a power meter. The experiment is performed at different input power and the corresponding output power of transmitted beam is noted and a graph is drawn between input power and output power for different dye concentrations and is shown in figure 11.

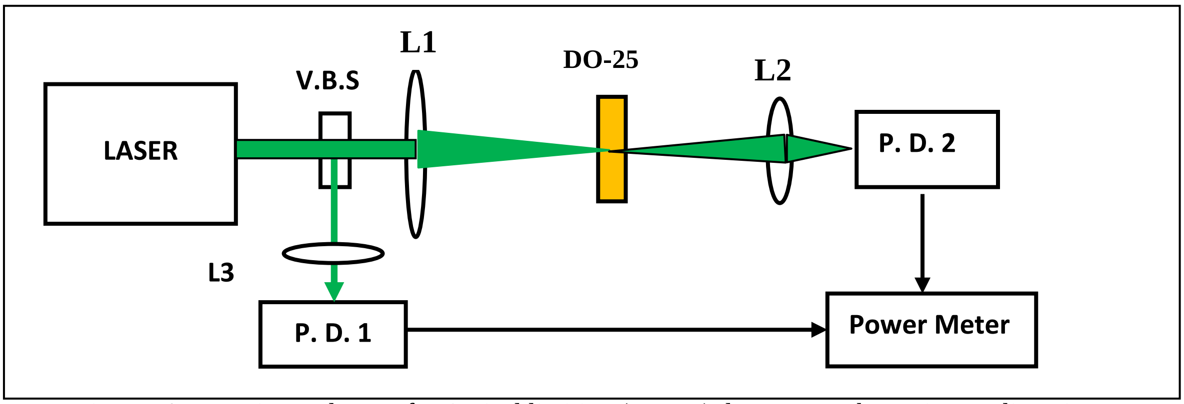


Figure 10: Experimental setup for Optical limiting (Type 1) due to pure absorptive nonlinearity.

In this case, the intensity of the transmitted output beam is found to vary linearly with the incident input intensity for low values of input but starts to saturate at high incident intensities due to nonlinear two-photon absorption. Hence, after a certain threshold value of the input intensity, the nonlinear absorption of the dye sample becomes dominant, resulting in a limiting of the intensity of output beam. Thus the transmittance recorded by the photo detector remained reasonably constant showing a plateau region.

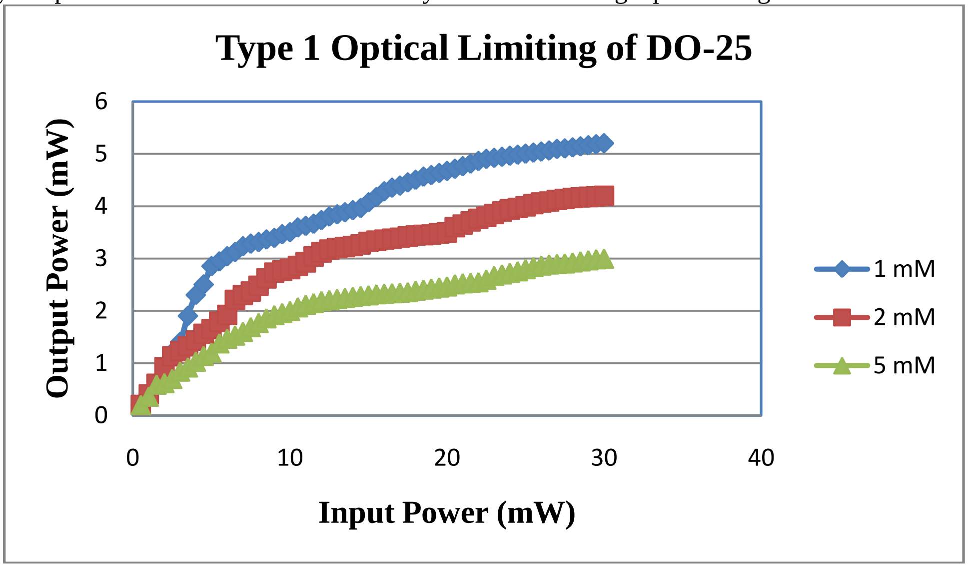


Figure 11: Open aperture (Type 1) Optical limiting behavior of DO-25 dye-doped PMMA-MA film at CW 532 nm.

Case (2) Optical Limiting with Aperture (Type 2):

The pure nonlinear refraction property of the dye sample is measured using this method of optical limiting with an aperture at the output side (Type-2 optical limiting). The light beam transmitted through the sample is passed through an aperture A of fixed diameter and then passed through a collecting lens L2 to the photo detector-power meter assembly. The optical limiting effects of the DO-25 dye-doped PMMA-MA films are studied by using a CW laser source. The experimental set-up for the demonstration of type-2 optical limiting is shown in figure 12. The dye sample is kept at the position where the transmitted intensity shows a valley in the closed aperture Z-scan curve. The experiment is performed at different input power and the corresponding output power of transmitted beam is noted and a graph is drawn between input power and output power for different dye concentrations and is shown in figure 13.

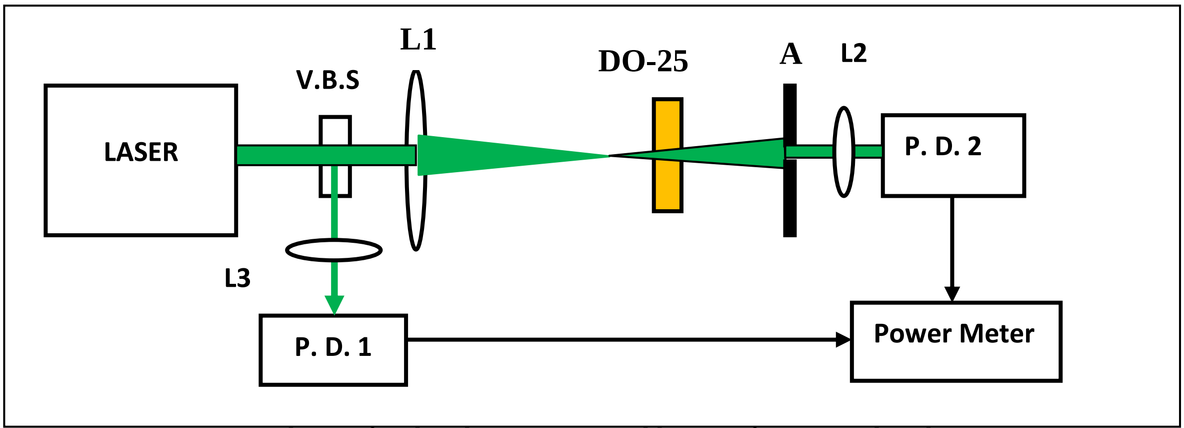


Figure 12: Experimental setup for closed aperture Optical limiting for DO-25 doped PMMA-MA using nonlinear refraction.

In this case of DO-25 dye sample with defocusing nonlinearity (negative nonlinearity), the intensity of transmitted output beam is found to vary linearly with the incident input intensity for low values of input, but starts to saturate after a certain threshold value due to the fact that the samples starts defocusing the beam, resulting in a greater part of the beam cross-section being cut off by the aperture A placed in between the sample and the collecting lens before the photo-detector. Thus the transmittance recorded by the photo detector remained reasonably constant showing a plateau region as shown in figure 13.

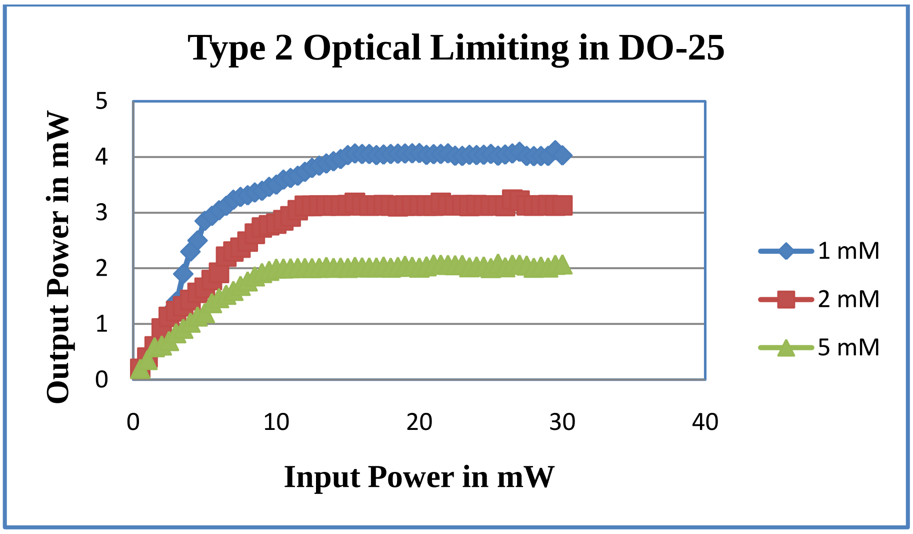


Figure 13: Closed aperture (Type 2) Optical limiting behavior of DO-25 dye-doped PMMA-MA film at CW 532 nm.

7. Results & Discussion:

The optical nonlinearity of DO-25 doped PMMA-MA polymer film is studied using open aperture and closed aperture Z-scan techniques using low power CW laser ar different dye concentrations. The open aperture Z-scan study shows that the sample dye shows a considerable amount of saturable absorption property. But at higher input intensity, the reverse saturation absorption property of the dye in polymer film becomes prominent as shown in Z-scan graph figure 6. It is seen that the transmission at the focus decreases with increasing sample concentration. At higher concentration, the sample gives better nonlinear optical properties. Absorption saturation in the sample enhances the peak and decreases the valley in the closed aperture *Z*-scan and results in distortions in the symmetry of the *Z*-scan about $Z = 0$. The closed aperture Z-scan study shows that the dye sample shows a considerable amount of negative nonlinear refraction and hence defocuses the laser beam passes through it [45- 50]. Table 1 shows the experimentally calculated Nonlinear optical parameters of DO-25 dye-doped PMMA-MA film at 532 nm.

Table 1: Nonlinear parameters for DO-25 dye-doped PMMA-MA film at 532 nm

S.No	Parameter	Dye Concentration	DO-25
1	α_0(Linear absorption coefficient) (Using equation 1)	2 mM	0.051
2	n_0 (Linear refractive index) (Using equation 2)	2 mM	2.99
3	ΔT_{p-v} (The difference between the normalized peak and valley transmittance)	1 mM	0.37
		2 mM	0.65
		5 mM	1.02
4	$n_2 \times 10^{-7}$ (cm^2/W) (Pure nonlinear refractive index n_2 is obtained by dividing the closed aperture data by the open aperture data)	1 mM	-0.35
		2 mM	-0.63
		5 mM	-1.0
5	$\beta \times 10^{-3}$ (cm/W) (Using equation 3)	1 mM	- 0.32
		2 mM	- 0.38
		5 mM	- 0.41
6	$\Delta n = n_2 I_0$ ($\times 10^{-4}$)	1 mM	- 1.22
		2 mM	- 2.205
		5 mM	- 3.50
7	$\alpha = \alpha_0 + I_0\beta$ (Using equation 6)	1 mM	1.17
		2 mM	1.38
		5 mM	1.49
8	$n = n_0 + \Delta n$ (Using equation 7)	1 nM	1.77
		2 mM	0.785
		5 mM	0.51

The optical limiting behaviour of Disperse Orange -25 dye-doped PMMA-MA polymer filmsfor type 1 and type 2 configurations under low power CW laser irradiation for different dye concentrations are studied. The mechanism responsible for optical limiting is mainly attributed to the reverse saturation absorption of dye molecules which further increased with thermally induced nonlinear refraction. The defocusing effect observed in the DO-25 dye-doped sample under CW irradiationdue to nonlinear absorption and nonlinear refraction is utilized to demonstrate their optical limiting action. Based on the comparatively high nonlinear refractive index, the DO-25 dye in PMMA-MA matrix behaves as good optical limiter even at low power and broad power range. These results are quite encouraging for possible applications in nonlinear optical devices [51-52].

Table 2: Optical limiting Regions in Dye-doped Polymer film at 532 nm CW laser beam.

S.No	Sample & Type of Limiting	DY-7 dye Concentration	Linear Region (mW)	Active Region (mW)	Saturation Region (mW)
1	DO-25 in PMMA-MA Type 1 Limiting configuration	1 mM	1 – 5 mW	5 – 22mW	22mW onwards
		2 mM	1 – 8 mW	8 – 25 mW	25 mW onwards
		5 mM	1 – 10 mW	10 – 27mW	27mW onwards
2	Type 2 Limiting configuration	1 mM	1 – 5mW	5 – 15mW	15mW onwards
		2 mM	1 – 9mW	9 – 12mW	12mW onwards
		5 mM	1 – 8 mW	8 – 10 mW	10 mW onwards

Table 3: Concentration dependence of limiting threshold of DO-25 dye-doped in PMMA-MA film

S.No	Dye Concentration (mM)	Type 1 Optical Limiting Threshold (mW)	Type 2 Optical Limiting Threshold (mW)
1	1 mM	5.10	15
2	2 mM	4.0	12
3	5 mM	2.92	10

Table 4: Concentration dependence of saturated output power in DO-25 dye-doped in PMMA-MA film

S.No	Dye Concentration (mM)	Type 1 Optical Limiting Saturated Output Power (mW)	Type 2 Optical Limiting Saturated Output Power (mW)
1	1 mM	22	4.0
2	2 mM	25	3.10
3	5 mM	27	1.99

Both type 1 and type 2 optical limiting effects show an increase in limiting action with increasing the concentration of the dye in the polymer film as shown in figure 11 & figure 13. The optical limiting responses of the low dye concentration films are generally much weaker than those of high dye concentrated films. This shows that the number density of dye molecules in the polymer matrix along the path of the laser beam is the deciding factor to fix output clamping level. From table 3, it can be seen that the optical power limiting threshold is inversely proportional to the dye concentration in the film. The limiting experiment shows that as the concentration increases, a reduction in linear transmittance as well as the output clamping level. The experimentally determined optical limiting saturated output power values at different dye concentrations are shown in Table 4. The results are comparable to some of the reports of low power optical limiting [53-54].

In the case of type 2 optical limiter with aperture, as observed in our experiment and in other published results, it is seen that at the valley positions, the limiter works at low input powers as the self-defocusing effect is increased by the thermal effect due to the absorptive properties of the dye used in polymer matrix. Thus it can be suggested that the best position for a dye sample, when used for optical limiting based on Type 2 self-defocusing position is at the valley point of the Z-scan curve.

8. Conclusion:

The nonlinear absorption, nonlinear refraction properties of prepared films of Disperse orange–25 dyes doped in Polymethyl methacrylate methacrylic acid (PMMA-MA) are studied using the Z-scan experimental method. The optical limiting properties of these films are also studied at different input fluency. Good films are grown without any crack using the hot-press technique. Linear absorption and nonlinear absorption using z-scan are studied. we have studied the nonlinear optical properties like nonlinear absorption and nonlinear refraction of an azo dye disperse orange-25 (DO-25) doped in Polymethyl methacrylate-methacrylic acid (PMMA-MA) polymer matrix using open aperture and closed aperture Z-scan experimental method. Finally, the optical limiting properties of these films are also studied at different input power using continuous wave (CW) laser beams of 532 nm wavelength. It is found that the type of nonlinear absorption depends on the intensity of input beam. Disperse orange-25 has shown saturation absorption at lower input irradiance and then reverse saturation absorption at higher irradiance. Optical limiting study using type 1 and type 2 configurations is carried out and is found that type 2 has shown better limiting characteristics for DO-25 doped PMMA-MA polymer films.

9. References:

1. Nalwa, H. S., & Miyata, S. (1996). Nonlinear optics of organic molecules and polymers.CRC press.
2. Bhawalkar, J. D., He, G. S., & Prasad, P. N. (1996). Nonlinear multiphoton processes in organic and polymeric materials. Reports on Progress in Physics, 59(9), 1041.

3. Almosawe, A. J., & Saadon, H. L. (2013). Nonlinear optical and optical limiting properties of new structures of organic nonlinear optical materials for photonic applications. Chinese Optics Letters, 11(4), 041902.
4. Perry, J.W., Mansour, K., Mander, S.R., Perry, K. J., Alverez, D. & Choong, I. (1994). Enhanced reverse saturable absorption and optical limiting in heavy-atom-substituted phthalocyanines, Opt. Lett., 19, 625-627.
5. Shirk, J. S., Pong, R. G., Flom, S. R., Heckmann, H., & Hanack, M. (2000). Effect of axial substitution on the optical limiting properties of indium phthalocyanines. The Journal of Physical Chemistry A, 104(7), 1438-1449.
6. Blau, W., Byrne, H., Dennis, W. M. and Kelly, J. M. (1985). Reverse Saturable absorption in tetraphenylporphyrines, Opt. Commun., 56, 25-29, 1985.
7. Sevian, A., Ravikanth, M. and Kumar, G.R. (1996). Optical limiting in short chain basket handleporphyrins, Chem. Phys. Lett., 263, 241-246, 1996.
8. Sharma, S., Mohan, D., & Ghoshal, S. K. (2008). Measurement of nonlinear properties and optical limiting ability of Rhodamine 6G doped silica and polymeric samples. Optics Communications, 281(10), 2923-2929.
9. Castillo, J., Kozich, V.P. and Marcano, A.O. (1994). Thermal lensing resulting from one and two-photon absorption studied with a two color time-resolved Z-scan. Opt. Lett., 19, 171-173.
10. Krishnamurthy, R. R., & Alkondan, R. (2010). Nonlinear characterization of Mercurochrome dye for potential application in optical limiting. Opt. Appl. XL, 187-196.
11. Rekha, R. K., & Ramalingam, A. (2009). Nonlinear characteristic and optical limiting effect of oil red O azo dye in liquid and solid media. Journal of Modern Optics, 56(9), 1096-1102.
12. Muto, S., Kubo, T., Kurokawa, Y. and Suzuki, K. (1998). Third-order nonlinear optical properties of Disperse Red 1 and Au nanometer-size particle-doped alumina films prepared by sol-gel method.Thin Solid Film, 322, 233-237.
13. Zidan, M. D., &Ajji, Z. (2011). Optical limiting behavior of disperse red 1 dye doped polymer. Optics & Laser Technology, 43(5), 934-937.
14. Brzozowski, L. & Sargent, E. H. (2001). Azobenzenes for photonic network applications: Third–order nonlinear optical properties. J. Material Science: Materials in Electronics, 12, 483-489.
15. Naseema, K., Manjunatha, K. B., Sujith, K. V., Umesh, G., Kalluraya, B., &Rao, V. (2012). Third order optical nonlinearity and optical limiting studies of propane hydrazides. Optical Materials, 34(11), 1751-1757.
16. Venugopal Rao, S., Naga Srinivas, N.K.M. and Narayana Rao, D. (2002). Nonlinear absorption and excited state dynamics in Rhodamine B studied using Z-scan and degenerate four wave mixing techniques, Chem. Phys. Lett., 361, 439-445.
17. Umakanta Tripathy, R., Justin Rajesh, R., Prem, B.B. & Subrahamanyam, (2002).Optical nonlinearity of organic dyes as studied by Z-scan and transient grating techniques.Procs. Indian Acad. Sci. (Chem. Sci.), 114(6), 557-564.
18. Sukumaran, V. S., & Ramalingam, A. (2011). Third order optical nonlinearities and spectral characteristics of methylene blue. Journal of Quantum Information Science, 1(02), 69.
19. Chen, Q., Kuang, L., Sargent, E.H. and Wang, Z.Y. (2003). Ultrafast nonresonant third-order optical nonlinearity of fullerene-containing polyurethane films at telecommunication wavelengths, Appl. Phys. Lett., 83, 2115-2117.
20. Zidan, M. D., Ajji, Z., Allaf, A. W., &Allahham, A. (2011). Investigation of the optical limiting properties of acid blue 29 in various solvents. Optics & Laser Technology, 43(7), 1347-1350.
21. Dharmadhikari, A.K., Roy, B., Roy, S., Dharmadhikari, J.A., Mishra, A. and Kumar, R.G. (2004). Higher-order optical nonlinearities in 4-dimethylamino-N-methyl-4-stilbazolium tosylate. Opt. Commun., 235, 195-200.
22. Ganeev, R.A., Baba, M., Morita, M., Ryasnyansky, A.I., Suzuki, M., Turu, M. and Kuroda, H. (2004). Fifth-order optical nonlinearity of pseudoisocyanine solution at 529 nm, J. Opt. A: Pure Appl. Opt., 6, 282-287.
23. Del Nero, J., de Araujo, R.E., Gomes, A.S.L. and de Melo, C.P. (2005).Theoretical and experimental investigation of the second hyperpolarizabilities of methyl orange, J. Chem. Phys., 122(104506), 1-6.
24. Hassan, Q. M. A., (2015). Optical limiting properties of sudan red B in solution and solid film Optical and Quantum Electronics, 47(2), 297-311.
25. Aithal, P. S., Singh, R. P. &Rao, D. N. (2003). Optical limiting due to frequency up-converted fluorescence in DASPB dye doped polymer matrix. Proceedings of SPIE, 4797, 229-239.
26. Singh, R. P., Aithal, P. S. &Rao, D. N. (2003). Optical limiting studies of Disperse Orange and Disperse Yellow in PMMA-MA matrix.Proc. of SPIE, 4797, 52-58.

27. Jamshidi-Ghaleh, K., Salmani, S., &Ara, M. H. M. (2007). Nonlinear responses and optical limiting behavior of fast green FCF dye under a low power CW He–Ne laser irradiation. Optics Communications, 271(2), 551-554.
28. Shubhrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2013).Study of Optical Limiting and Optical Phase Conjugation in DASPB dye-doped polymer films, GSTF Journal of Physics and Applications (JPA), 1(1), 15-24.DOI: 10.5176/2335-6901.1.1.3.
29. Shubhrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2012).Study of Degenerate Four-Wave Mixing in Disperse Orange Dye-doped Polymer Film, Advanced Materials Research Journal, 584, 526-530. doi:10.4028/www.scientific.net/AMR.584.526.
30. Shubhrajyotsna Aithal, Aithal, P. S. & Bhat, G. K.(2015),Comparative Study on Azo dye-doped Polymer Films for Optical Phase Conjugation.International Journal of Science and Research (IJSR), 4(4), 436-441. DOI: 10.5281/zenodo.61724.
31. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2013). Degenerate four-wave mixing in DASPB dye-doped polymer film,published in Part IV Quantum Optics, Chapter 12, Advances in Laser Physics and Technology**,** Edited by Man Mohan, Anil Kumar Maini, Aranya A. Bhattacherjee and Anil K. Razdan under the imprint of Foundation Books, Cambridge University Press India Pvt Ltd., pp. 179 - 195, ISBN: 978-93-844634-1-0.,DOI : 10.5281/zenodo.62048.
32. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2012). Phase Conjugation in Two Photon Absorbing Dye films by Degenerate Four-wave Mixing, 3rd International Conference on Photonics 2012, 1-3 October 2012, Penang, Malaysia. Published in IEEE Xplore ISBN: 978-1-4673-1463-3, pp.235-239.
33. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2012). Study of Degenerate Four-Wave Mixing in Disperse Orange Dye-doped Polymer Film, Advanced Materials Research Journal, 584, 526-530.
34. Shubrajyotsna Aithal, Aithal, P. S. (2012). Study of Phase Conjugated wave in DASPB dye-doped polymer films, Photonics Global Conference 2012, 13-16, December 2012, Nanyang Technical University, Singapore.In Photonics Global Conference (PGC), Singapore, pp.1-5.IEEE.ISBN : 978-1-4673-2513-4, DOI:10.1109/PGC.2012.6458057.
35. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2016). Study of Low Power Degenerate Four-Wave Mixing in Disperse Yellow Dye-doped Polymer Film.International Journal of Engineering Research and Modern Education (IJERME), 1(2), 200-209. DOI: http://dx.doi.org/10.5281/ZENODO.198716.
36. Aithal, P. S. (2016). Review on Various Ideal System Models Used to Improve the Characteristics of Practical Systems. International Journal of Applied and Advanced Scientific Research, 1(1), 47-56. DOI : http://doi.org/10.5281/zenodo.159749
37. Van Stryland, E. W., Wu, Y. Y., Hagan, D. J., Soileau, M.J. &Kamjou Mansour (1988). Optical Limiting with Semiconductors.JOSA B5, 1980-1989.
38. Yee, K. C. Tou, T.Y. & Ng, S. W. (1998). Hot-press molded PMMA matrix for solid-state dye lasers. Applied Optics, 37, 6381-6385.
39. Shubhrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2011). Nonlinear Absorption Studies of Disperse Orange Doped Polymer Film, Trends in Optics and Photonics II, Proceedings of International Conference on Trends in Optics and Photonics, December 7-9, 2011, Kolkata, India. Editors: Ajay Ghosh and Debesh Choudhury, ISBN 978-81-908188-1-0, P. 132-137, (2011), DOI : 10.5281/zenodo.62034.
40. Shubhrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2015). A Review on Sustainable Organic Materials for Optical Limiting Technology.International Journal of Management, IT and Engineering (IJMIE), 5(7), 527-544, DOI: 10.5281/zenodo.62032.
41. Sheik-Bahae, M., Said, A. A. & Van Strayland, E. W. (1989). High Sensitivity Single beam n2 Measurement. Opt. Lett., 14, 955-957.
42. Sheik-Bahae, M., Said, A. A., Wei, T., Hagan, D. J. and Van Strayland, E.W. (1990). Sensitivitive measurement of optical nonlinearities using a single beam. IEEE J. Quantum Electron. 26, 760-769.
43. Rekha, R. K. & Ramalingam, A. (2009). Non-linear characterization and optical limiting effect of carmine dye. Indian Journal of Science and Technology, 2(8), 27-31.
44. Cassano T, Tommasi R, Ferrara M, Babudri F, Farinola GM and Naso F (2001). Substituent dependence of the optical nonlinearities in poly (2, 5-dialkoxy-pphenylenevinylene) polymers investigated by the Z-scan technique. Chem. Phys. 272,111-118. DOI: 10.1016/S0301-0104(01)00453.
45. Rajashekar, B. Sagar Limbu, Kamarusu Aditya, Nageswara Rao, G. & Siva Sankara Sai, S. (2013). Azo doped polymer thin films for active and passive optical power limiting applications. Photochem. Photobiol. Sci., 12(10), 1780-1786.
46. Nagaraja, K. K., Pramodini, S., Santhosh Kumar, A. Nagaraja, H. S., Poornesh, P. & Dhananjaya Kekuda. (2013). Third-order nonlinear optical properties of Mn doped ZnO thin films under cw laser illumination. Optical Materials**.** 35 (3), 431–439.

47. Pradeep, C., Mathew, S., Nithyaja, B., Radhakrishnan, P. and Nampoori, V.P.N., (2014). Studies of nonlinear optical properties of PicoGreen dye using Z-scan technique, Applied Physics A, 115, 291-295.
48. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2011). Optical Nonlinearity of Dye-doped Polymer Film using Z-scan Technique. Proceedings of Second International Conference on Photonics 2011, Kota Kinabalu, Malaysia, IEEE Xplore, ISBN 978-1-61284-265-3, pp 62-66. DOI: 10.1109/ICP. 2011.6106884.
49. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2011). Study of nonlinear absorption in a dye doped polymer film due to frequency up-converted fluorescence. Proceedings of the International Conference on Laser, Material Science and Communication, Ed. Chatterjee, U. & Chakrabarti, P. K. ISBN : 978-93-80813-14-1, pp. 107-109, (2011), DOI : 10.5281/zenodo.62033.
50. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2012). Phase Conjugation in Two Photon Absorbing Dye films by Degenerate Four-wave Mixing, 3rd International Conference on Photonics 2012, Malaysia. IEEE Xplore ISBN: 978-1-4673-1463-3, pp - 235-239. DOI: 10.1109/ICP.2012.6379868.
51. Shubrajyotsna Aithal, Aithal, P. S. & Bhat, G. K. (2015). A Review on Sustainable Organic Materials for Optical Limiting Technology. International Journal of Management, IT and Engineering (IJMIE), 5(7), 527-544. DOI: 10.5281/zenodo.62032.
52. Shubhrajyotsna Aithal, & Aithal P. S., (2016). ABCD analysis of Dye doped Polymers for Photonic Applications, IRA-International Journal of Applied Sciences, 4(3), 358-378. DOI: http://dx.doi.org/ 10.21013/jas.v4.n3.p1.
53. Kaladevi, S. Vijayan, C. Kothiyal, M.P. (2004). Opt. Mater. 27, 1606.
54. Balaji, G. Rekha R. K. & Ramalingam, A. (2011). Nonlinear Characterization of Safranin O Dye for Application in Optical Limiting.ACTA PHYSICA POLONICA A, 119(3), 359-363.