

Research Article

Study of Third Order Optical Nonlinearity in DASP B Dye-doped Polymer Films using CW Laser

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Abstract: The optimum self-focussing materials with an intensity-dependent refractive index and the realization of the ability of these materials to produce intensity dependent phase shift in all-optical photonic devices have become a topic of continuous investigation. Many organic materials including dye-doped polymer films are creating interest due to their advantages in terms of enhanced efficiency, and optimum mechanical properties to fabricate reliable devices. In this paper, we have studied the nonlinear optical properties like nonlinear absorption and nonlinear refraction of a two-photon fluorescent dye DASP B doped in Polymethyl methacrylate-methacrylic acid (PMMA-MA) polymer matrix using open aperture and closed aperture Z-scan experimental methods by means of low power continuous wave (CW) laser beam. The optical limiting properties of these films are also studied using Type 1 and Type 2 configurations at different input powers using continuous wave (CW) laser beams of 532 nm wavelength. The nonlinear refractive index n_2 , nonlinear absorption coefficient β , changes in refractive index with input intensity, and the magnitude of third-order optical nonlinearity of the dye-doped film are experimentally determined. The saturated output power for type 1 and type 2 optical limiting are determined. The input limiting threshold and saturated output power level for both type 1 and type 2 optical limiting configurations are recorded. DASP B dye-doped in PMMA-MA polymer film has shown saturation absorption at lower input irradiance and reverse saturation absorption along with two-photon absorption at higher input irradiance and hence found to be a potential candidate for the third harmonic property based photonic devices.

Keywords: Organic nonlinear material, Dye-doped polymer films, Optical limiting, Open and closed aperture Z scan, DASP B doped PMMA-MA films.

INTRODUCTION

The field of nonlinear optics has been rigorously studied for over fifty years to identify suitable effective optimum materials to realize nonlinear optical phenomenon like the third harmonic generation, stimulated scattering, multi-photon absorption, and nonlinear refraction to be used in optical limiting, optical switching, and all optical devices. Further, the optimum self-focusing materials with an intensity-dependent refractive index and the realization of the ability of these materials to produce intensity dependent phase shift in all-optical devices have become a topic of continuous investigation. Many organic materials including dye-doped polymer films are finding potential attraction in this regard due to their advantages in terms of enhanced efficiency, optimum material, and mechanical properties to fabricate reliable

devices. Both nonlinear absorption and nonlinear refraction property of a material for an input light beam decide its third harmonic generation efficiency. For improving the third-order NLO-effects of organic materials, it is found that there is a relationship between electronic structure and molecular geometry, especially the length of the π -system. Whenever an excitation of an electron takes place, there will be a relaxation of the molecular geometry which can lead to the formation of nonlinear excitations. It is found that the relaxation of the molecular geometry is much slower than the change in π -electron distribution and it is this instantaneous shift in π -electron density that is responsible for the large and fast polarizabilities of π -electron networks [1]. Thus by tailoring the molecular geometry, one can modify the polarizability of the molecules and hence third order optical nonlinearity of the material.

Organic molecules with enhanced Two photon absorption properties generally have long electron delocalization length and are experience intramolecular charge transfer from the centre to edges or vice versa. Hence, π -conjugated organic molecules of type D- π -D, D- π -A- π -D, and A- π -D- π -A, where A and D denote electron accepting and donating groups, have been studied [2-4]. By enhancing the conjugation length of a molecule can increase the distance of distribution of charge density with the polarizability of the molecule, which increases the TPA cross section, δ . Such effect has been observed in many symmetrical series of chromophores of the A- π -A and A- π - π -A types, showing large enhancements of the TPA cross section, δ [5-7]. It is possible to expect a similar effect in dipolar chromophores of the D- π - π - π -A and D- π - π - π -A type. Modification of such molecules systematically in a controlled manner is expected to modify the nonlinearity of the molecules and affects the strengths of electron-withdrawing end groups under one- and two-photon excitation. Many organic chromophores including commercial dyes, such as Rhodamine B, Rhodamine 6G, spiropyran, etc., have been reported for their two-photon absorption behavior but most of them have relatively small σ values and weak upconverted fluorescence emission. After 1990s, there have been further advances in design and synthesis of new organic molecules with enhanced two-photon cross-sections has opened up many new applications in optical technologies [5-14]. The strategy for the construction of molecules with large TPA cross sections has been studied both experimentally [15-16], and theoretically by many researchers [17-18], and some relationship between the structure and property has been found. For example, extended π -conjugated systems symmetrically substituted with electron-donating (D) and/or electron-accepting (A) functionalities have been revealed as efficient two-photon absorption (TPA) dyes. Based on this result, many affecting factors have been identified which have shown important role in increasing TPA, such as the conjugation length, the efficiency of intramolecular charge transfer (ICT), the molecular planarity, the vibronic coupling, the dimensionality of the charge-transfer network, and the donating and withdrawing abilities of the electron donor and acceptor [2].

Albota *et al.* [2] have proposed a design strategy recently by dealing with molecules based on benzene ring as π -center which is attached symmetrically by either electron-donor (D) part or electron-acceptor (A) part through various lengths of conjugated connectors, D- π -D or A- π -A. They found that the nonlinearity is increased by increasing the length of conjugation, and is changed with the Donor/Acceptor strength and the extent of symmetric intra

molecular charge-transfer (CT) from the Donor ends to the π -center or vice versa. This means that symmetric charge redistribution effectively occurs upon excitation of such symmetric molecules. A similar approach was made in designing molecules by Reinhardt and his coworkers [19], dealing with benzene ring as π -center which is symmetrically coupled with two electron acceptor (A- π -A) or asymmetrically with D and A (D- π -A), respectively. There is no clear effect of structural symmetry on σ values, although increasing conjugation length of π -center brings about a significant improvement of the value. This suggests that there must be more crucial molecular factors involved that affect the molecular asymmetry and third harmonic property other than structural symmetry involved. In this study, we have considered a D- π -A dye molecule 4-[4-(Dimethylamino)styryl]-1-docosyl pyridinium bromide (DASPB), with a π centre for studying third-order optical properties. The nonlinear optical properties DASPB are first invented by Aithal *et al.* during 2003 [20] using nano and picosecond pulsed laser. Shubrajyotsna *et al.* have studied nano and picosecond optical limiting study [21] and also studied optical phase conjugation property using Degenerate Four Wave Mixing setup [21-25]. In this paper, we have studied the nonlinear optical properties like nonlinear absorption and nonlinear refraction of this two-photon fluorescent dye DASPB, doped in Polymethyl methacrylate-methacrylic acid (PMMA-MA) polymer matrix using open aperture and closed aperture Z-scan experimental methods using low power 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 powers using continuous wave (CW) laser beams of 532 nm wavelength. The nonlinear refractive index n_2 , nonlinear absorption coefficient β , changes in refractive index with input intensity, and the magnitude of third-order optical nonlinearity of the dye-doped film are experimentally determined. The optical limiting properties are also studied.

Molecular Structure and Linear Optical Properties of DASPB

Even though DASPB can be prepared in the laboratory, to maintain high quality, DASPB is purchased from Aldrich Chemical Co. and is purified by repeated recrystallization with spectrograde ethanol and by vacuum sublimation. The purity of the sample is determined spectroscopically. Purified chloroform is used as the solvent. To prepare the thin film, Polymethyl methacrylate – methacrylic acid is used as the polymer matrix. The thin films of DASPB doped in PMMA-MA are prepared in a clean laboratory environment using hot press technique [26]. Thin films of variable thickness are prepared between two glass slides. The film thickness is determined to be about 10

μm for the dye concentration of 1 mM, 2 mM, & 5 mM. This is consequently verified by the cross-sectional studies of the film using Scanning Electron Microscope

by mounting the film vertically to measure the thickness directly [27].

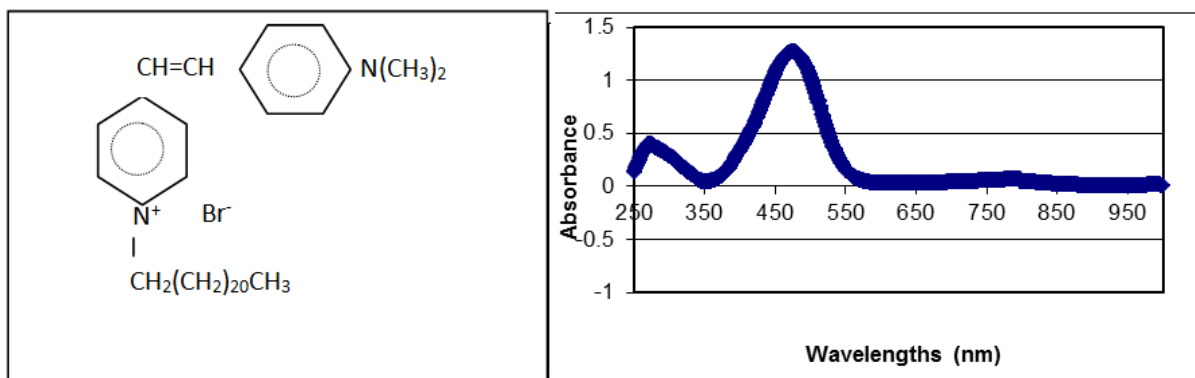


Fig-1: (a) Molecular structure of DASPB. (b) Linear absorption spectrum of DASPB.

The molecular structure of DASPB is shown in figure 1 (a). A charge-transfer between the aromatic moiety (electron donor) and bromine unit (electron acceptor) can be used to explain the third nonlinear property of this molecule. The linear absorption spectrum of DASPB dye doped in PMMA-MA polymer film is measured on a VARIAN Cary UV-VIS-IR recording Spectrophotometer. The figure 1 (b) shows the linear absorption spectrum of a DASPB in polymer

matrix with dye concentration of $d_0 = 1 \text{ mM}$. The linear absorption spectrum shows a strong absorption band with peak absorption located at 478 nm with a bandwidth of 100 nm, a medium absorption peaked at 270 nm with a bandwidth of 80 nm and no linear absorption is observed in entire spectral range of 580 to 2000 nm except IR absorption between 1200 nm to 1600 nm.

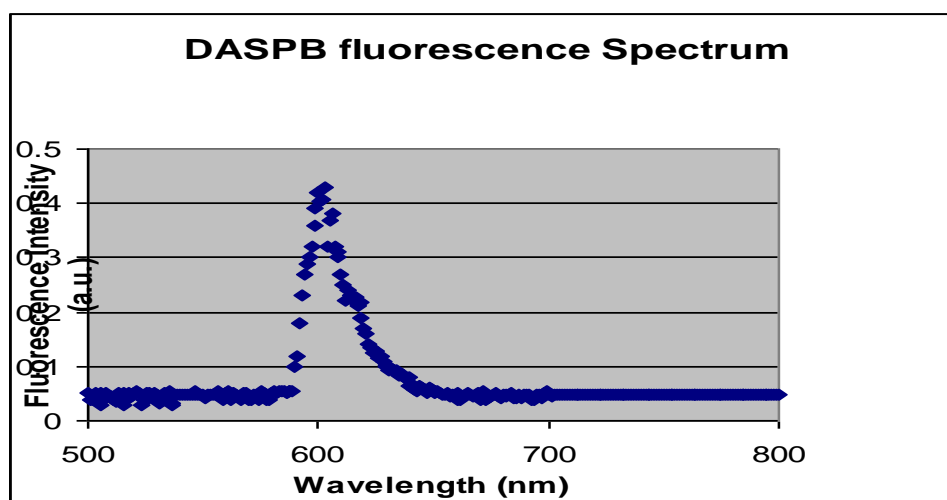


Fig-2: Fluorescence spectrum of DASPB dye-doped polymer film [20].

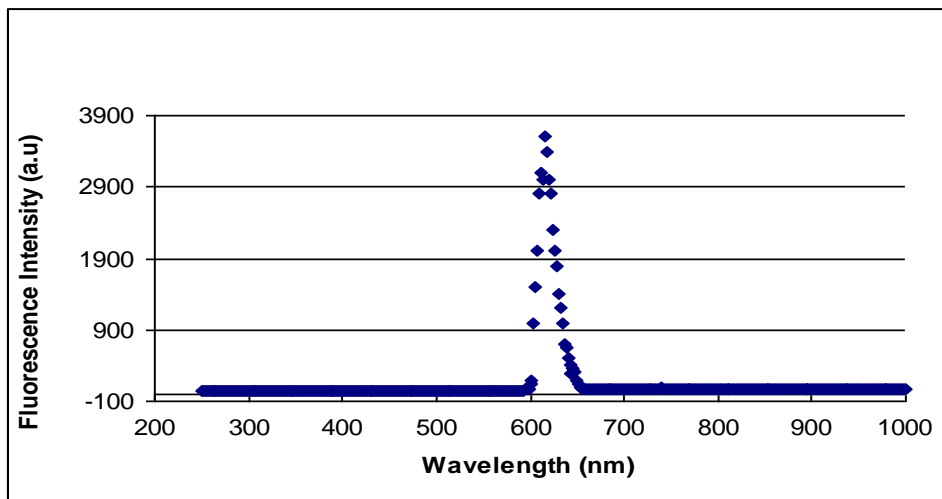


Fig-3: Fluorescence spectrum of DASPB doped polymer film at 532 nm irradiation [20].

The single photon fluorescence spectrum of the DASPB dye doped PMMA-MA polymer film sample is measured with the dye concentration of 1 mM using a spectral fluorophotometer (Rf 50000U from Schmadza) with the spectral resolution of 1 nm. The peak wavelength of the single-photon induced fluorescence is 610 nm with a bandwidth of 60 nm as shown in figure 2. Figure 3 corresponds to single photon fluorescence when DASPB is excited at 532 nm using an Nd:YAG laser beam.

The linear absorption coefficient α_0 is determined for two wavelengths 1.06 μm and 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

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

The linear absorption coefficient and refractive index are shown in table 1.

Table 1: Linear absorption coefficient and refractive index versus wavelength of DASPB

Wavelength (nm)	Thickness (μm)	Transmittance	α_0 (μm) ⁻¹	n_0
532	10	0.7	-0.03567	2.4488
633	10	0.92	-0.0083385	1.5129
1064	10	0.98	-0.0020203	1.2234

Nonlinear Optical Properties of DASPB Two Photon Induced Fluorescence

By studying the absorption spectrum of DASPB dye-doped sample shown in the previous chapter, we can conclude that there is no linear absorption in the entire spectral range from 580 nm to 1800 nm. It is also found that DASPB shows strong frequency upconverted fluorescence when irradiated with near IR and IR light above 700 nm. This suggests

the possibility of occurrence of strong two-photon absorption process inside the DASPB dye-doped polymer film. The two-photon absorbed fluorescence spectrum of DASPB dye-doped PMMA-MA sample of dye concentration 2 mM, is excited by 1.064 μm laser beam is depicted in figure 4. VIS cutting filters are used during the measurement of the upconversion fluorescence to cut transmitted pump energy [28].

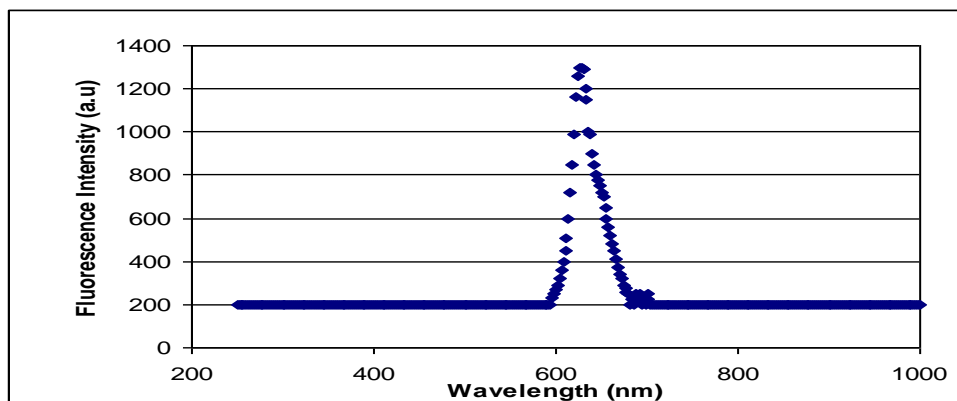


Fig-4: Two-photon induced emission spectrum of DASPb at 1.06 μm irradiation.

Nonlinear Absorption Study (Open Aperture Z-Scan):

The Z-scan technique proposed by Sheik Bahae *et al.* [30] is used for studying the nonlinear absorption properties the DASPb dye-doped PMMA-MA polymer films. The Z-scan measurement set-up uses a single Gaussian laser beam and is tightly focused on the sample polymer film. The transmittance measurement helps to determine nonlinear absorption coefficient (α), two-photon absorption coefficient (β). The schematic diagram of the experimental set-up used is shown in figure 5. A low power semiconductor laser of wavelength 532nm (BeamQ 30 mW Green Light Line) is used as the light source to produce a laser beam for the Z-scan measurement. The Gaussian profiled laser beam is focussed by means of a 3.5 cm focal length convex lens (L1), which produced a beam waist ω_0 of 15 μm . In our experiment, the Rayleigh condition, diffraction length $z_R = \pi\omega_0^2/\lambda > L$ is satisfied 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 beam transmission through an aperture placed in the far field is measured using photo detector and power meter assembly. For an open aperture Z-scan, a convex lens is used to collect the entire laser beam transmitted through the dye sample. The experimental setup used in the open aperture Z-scan is not sensitive to nonlinear refraction and hence can be used to determine the nonlinear absorption cross section of the materials. Such open aperture Z-scan trace is expected to be symmetric with respect to the focus where $Z = 0$, and at the focus, the minimum transmittance (e.g., multi-photon absorption/reverse saturation absorption) or a maximum transmittance (e.g., saturation of absorption) occurs. The nonlinear absorption coefficient (β) can be estimated from Z-scan transmittance curve (Eq. 3).

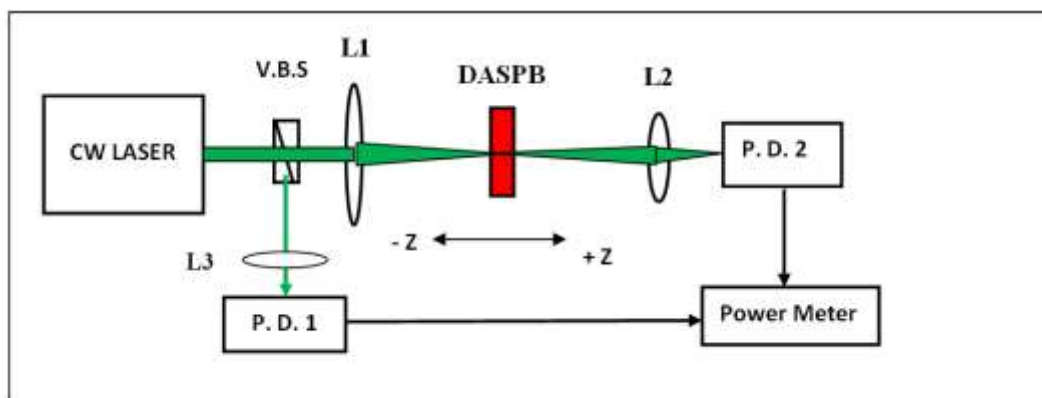


Fig-5: Experimental setup for open aperture Z scan for nonlinear samples.

The Z-scan experiment is performed for DASPb dye-doped PMMA-MA polymer films of the dye concentration 1mM, 2mM, and 5 mM using 532 nm laser beams at 10mW, 20 mW and 30 mW. The results are depicted in Fig. 6 to Fig. 8 respectively. To know the contribution of pure PMMA-MA polymer film to the observed nonlinear response, the Z-scan experiment

is performed on pure film without doping DASPb dye. There was no variation of transmittance intensity either due to nonlinear absorption or nonlinear refraction is observed as shown in figure 9. It is seen from the Z-scan plot that the DASPb sample shows strong saturable absorption at low input intensity of laser beam. From the open aperture Z-scan, it is observed

that due to nonlinear absorption, the transmittance of the DASPb film is increased initially with an increase in intensity due to saturation of absorption and as input power increases, the saturation absorption (SA) is overtaken by reverse saturation absorption (RSA) as well as two-photon absorption as seen in figure 8. Such transformation from saturation absorption to reverse

saturation absorption and two-photon absorption can be utilized as a principle for the construction of optical switches as well as optical limiters. Based on open aperture Z-scan plots of DASPb for different concentrations and at different input power, it is observed that:

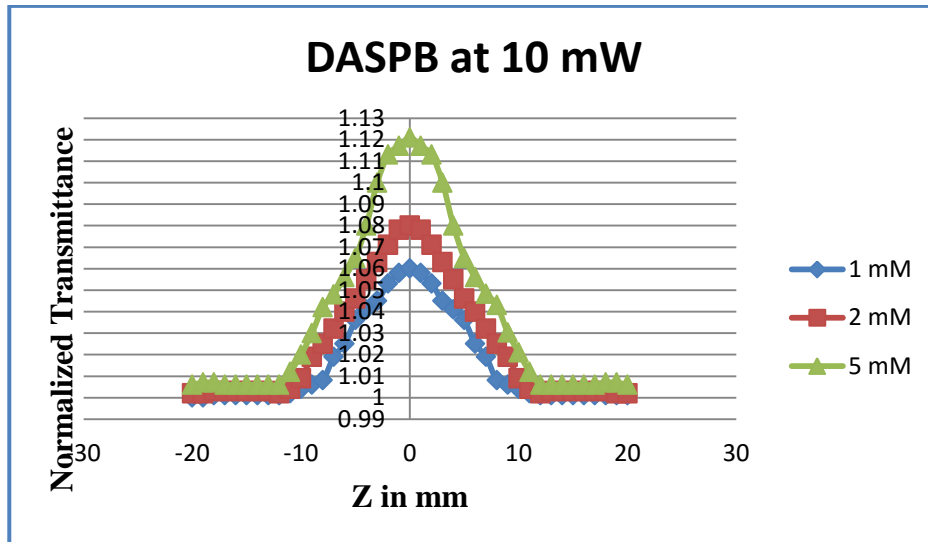


Fig-6: CW Z-scan (open aperture) of DASPb at different dye concentrations using 532 nm, 10 mW laser beam.

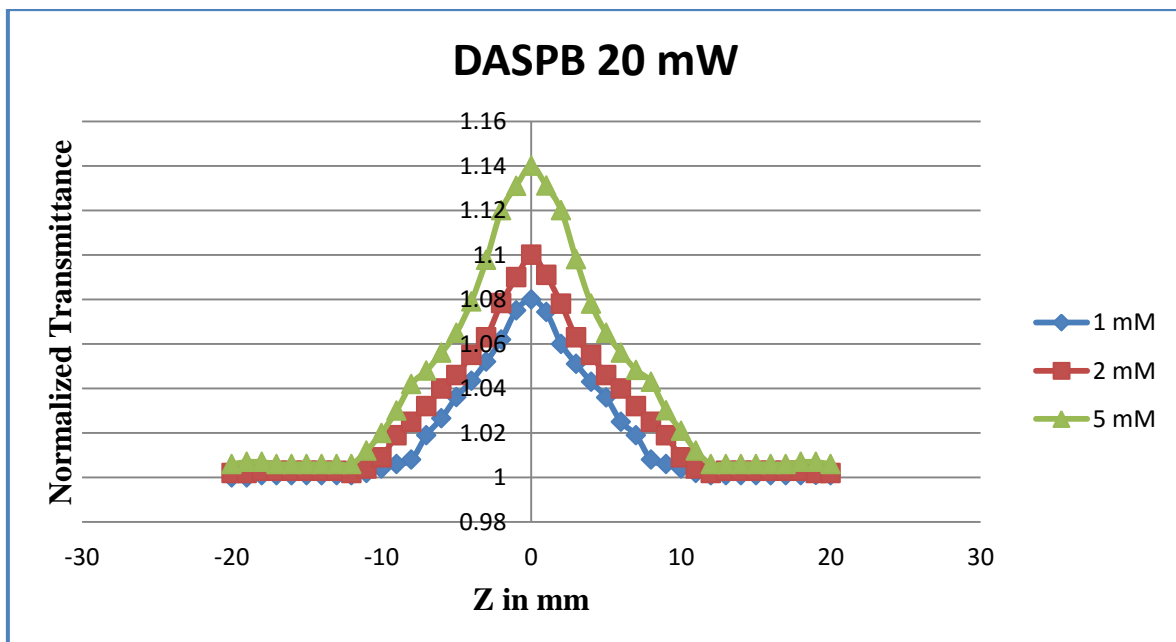


Fig-7: CW Z-scan (open aperture) of DASPb at different dye concentrations using 532 nm, 20 mW laser beam

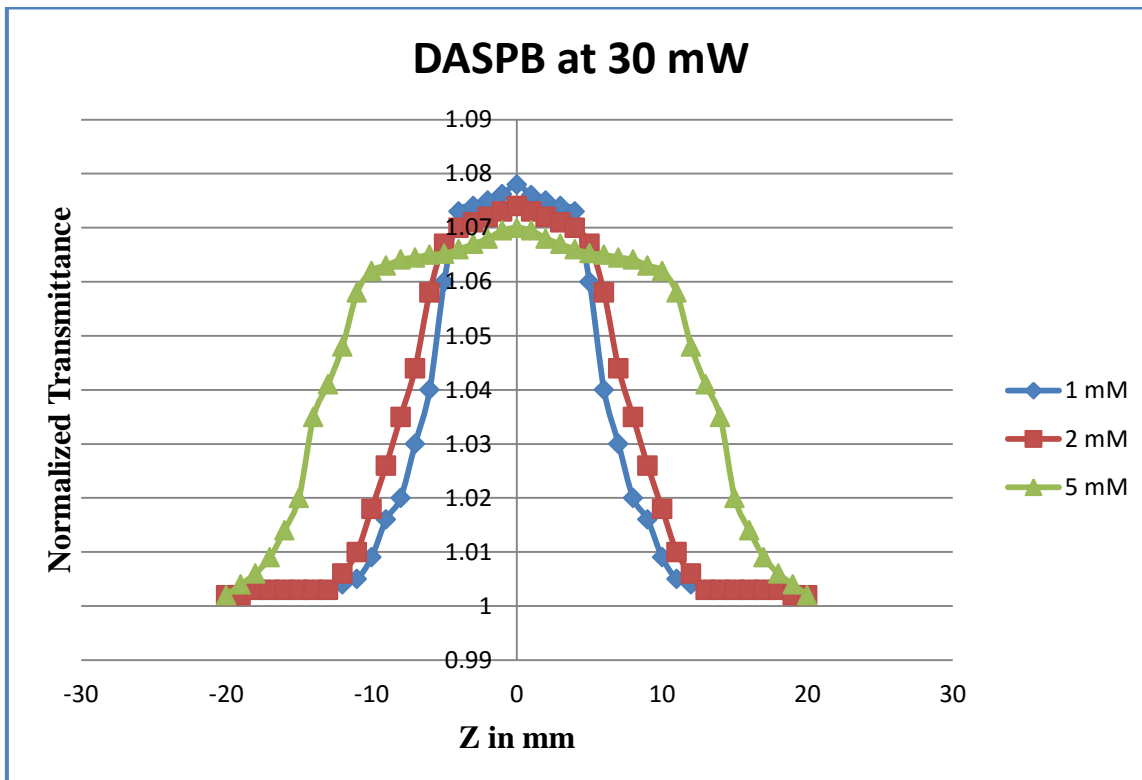


Fig-8: CW Z-scan (Open aperture) of DASPB at different dye concentrations using 532 nm, 30 mW laser beam.

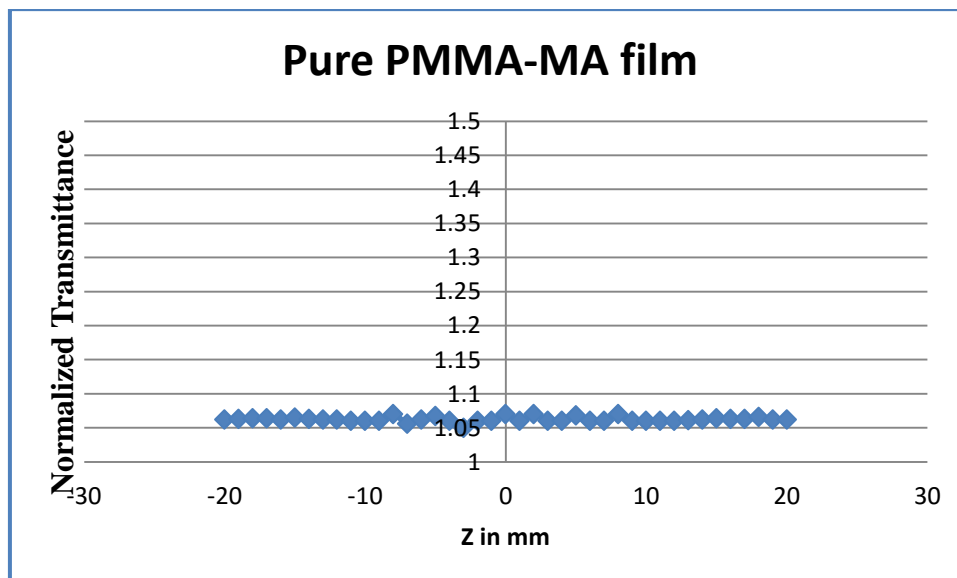


Fig-9: Z-scan transmittance of PMMA-MA film without dye sample

- At the higher intensity of input light, DASPB has shown two-photon absorption and reverse saturation absorption so that saturation absorption (SA) of the sample is decreased.
- At low input power, saturation absorption (SA) increased with increase in the concentration of dye in the sample.

From the graphs (figure 7 and figure 8), reverse saturable absorption (RSA) is seen in the open aperture Z-scan trace for DASPB dye doped in PMMA-MA film as it shows minimum transmittance with increase in intensity of input laser beam. The nonlinear absorption coefficient β can be estimated from the open aperture Z-scan data, where

$$\beta = (2\sqrt{2} \Delta T) / (I_0 L_{eff}) \text{ ----- (3)}$$

Here, I_0 is the intensity at the focal spot and is given by

$$I_0 = 2P_{peak}/\pi\omega_0^2 \text{ ----- (4)}$$

The effective length of the sample can be determined from the formula

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

For low input intensity, the transmittance increases with the increase in excitation intensity and has a maximum value at the focus. As input power is increased, the sample has shown a decrease in transmittance which is the signature of reverse saturation absorption according to Sheik-Bahae's theory [29-30]. When reverse saturation absorption occurs, the absorption coefficient β is no longer a constant. Instead, it becomes a function of the excitation intensity as in the relation,

$$\alpha = \alpha_0 + I\beta \text{ ----- (6)}$$

here, α is the total absorption coefficient of the material, α_0 is the linear absorption coefficient of the material, β is the nonlinear absorption coefficient of the material, and I is the input intensity of the laser beam.

By considering only third-order nonlinearities in the sample, the total refractive index of the sample (n) becomes:

$$n = n_0 + n_2 I. \text{ ----- (7)}$$

where $\Delta n = n_2 I$ is change in refractive index, n_0 is the linear refractive index of the sample, n_2 is the nonlinear refractive index for third-order nonlinear sample, and I is the input intensity of the laser beam.

The experimental values of nonlinear absorption coefficient β at different dye concentrations for DASPb dye-doped PMMA-MA films are listed in table 2.

Table-2: Nonlinear absorption coefficient values for DASPb dye-doped PMMA-MA film at 20 mW input power

Wavelength (nm)	Concentration	ΔT	I_0 (KW/cm ²)	β (cm/W) × 10 ⁻³
532	1 mM	0.08	3.5	0.64
532	2 mM	0.1	3.5	0.81
532	5 mM	0.14	3.5	1.13

Nonlinear Refraction Study (Closed Aperture Z-Scan)

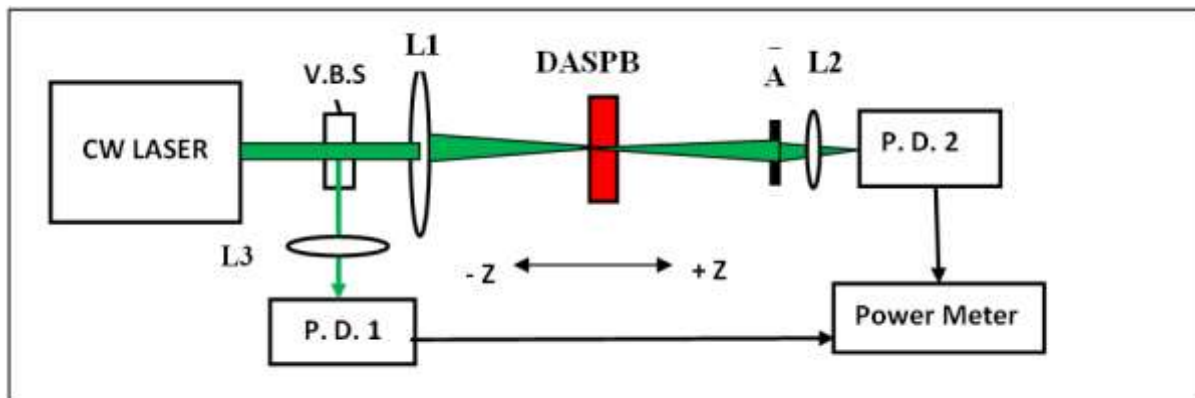


Fig.-10: Experimental setup for closed aperture Z-scan for DASPb sample film.

The experimental setup used for the closed aperture Z-scan measurement 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 whole 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 is focused by means of a 3.5 cm focal length convex lens (L1), which produced a beam waist ω_0 of 15 μ m. The peak intensity of the incident laser beam is calculated as $I_0 = 3.5 \text{ kW/cm}^2$ and the

diffraction length (Z_R) is calculated as 2.5 mm. The schematic diagram of the experimental setup used is shown in figure 10. The DASPb dye-doped PMMA-MA sample is translated across the axial focal region along the direction of propagation of the laser beam. The transmission of the emergent 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 at different dye concentrations at 20 mW input power is shown in figure 11.

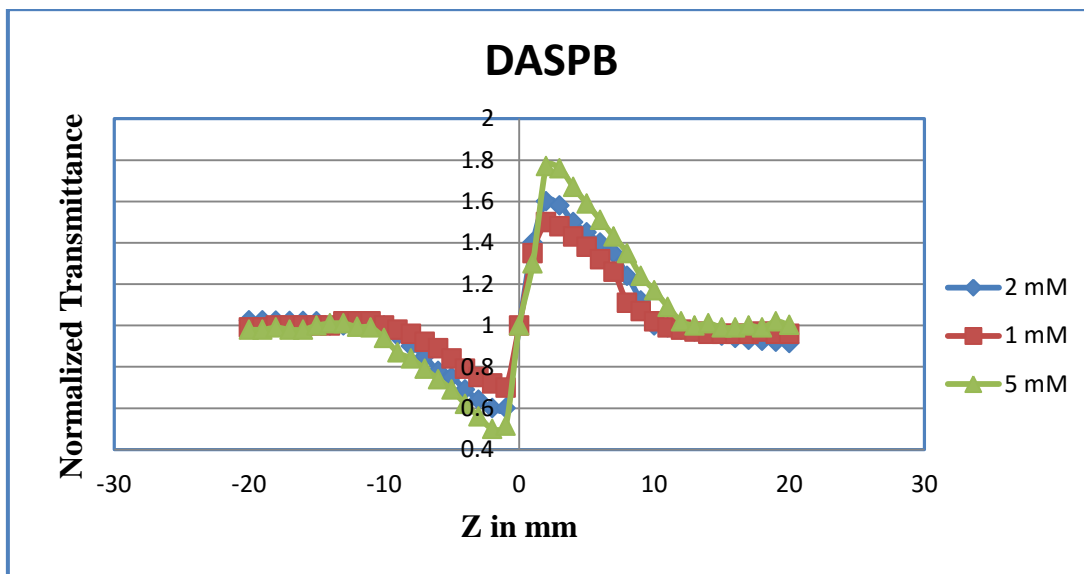


Fig-11: Closed-aperture CW Z-Scan with both refractive and absorptive nonlinearity at 532 nm for DASPB sample (20 mW).

The normalized transmittance curve for DASPB doped PMMA-MA film drawn from the closed aperture Z-scan data contains a negative valley followed by a positive peak, which shows that the sample DASPB has positive nonlinearity (self-focussing nonlinearity). This self-focussing effect is mainly due to the local variation in refractive index of DASPB dye sample with variation in light intensity. From the normalized nonlinear refraction graph, the difference between the normalized peak transmittance (T_p) and valley transmittances (T_v) is denoted as ΔT_{p-v} , since the closed aperture transmittance is affected by the nonlinear refraction and nonlinear absorption, to determine nonlinear refractive coefficient, it is necessary to separate the nonlinear refraction effect from nonlinear absorption effect. As per Sheik-Bahae

[29-30], 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 refraction for all the three concentrations of DASPB dye doped samples are shown in figure 12 at the input laser beam intensity of 20 mW. Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in finding the absolute value of the third-order nonlinear optical susceptibility [31-32]. 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 DASPB dye. Neither nonlinear absorption nor nonlinear refraction is observed.

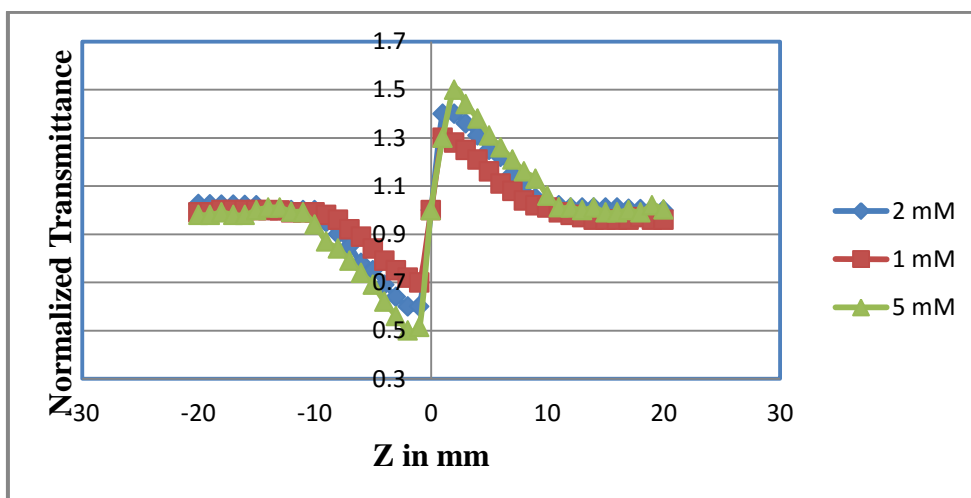


Fig-12: Closed-aperture CW Z-Scan with pure refractive nonlinearity at 532 nm for DASPB (20 mW).

The nonlinear refractive index n_2 can be calculated using the formula

$$n_2 = \frac{\Delta\phi \lambda}{2\pi I_0 L_{eff}} \quad (8)$$

and

$$|\Delta\phi| = \Delta T_{(p-v)} / [0.406 (1-S)^{0.25}] \quad (9)$$

where ΔT_{p-v} is the peak-valley transmittance difference from the closed aperture plot, $|\Delta\phi_0|$ is the on axis nonlinear phase-shift and S is the aperture linear transmittance given by $S = [1 - \exp(-2r_a^2/w_a^2)]$ 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

adjusted to 0.5 for our 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 index Δn can be calculated using the formula,

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

Table 3 contains experimental values of nonlinear phase shift and nonlinear refractive index for DASPB dye-doped PMMA-MA film.

Table-3: Nonlinear refractive index and nonlinear phase shift for DASPB film at 20 mW.

Wavelength (nm)	Concentration	ΔT_{p-v}	I_0 (KW/cm ²)	$\Delta\phi_{rad}$	n_2 (cm ² /W) $\times 10^{-7}$
532	1 mM	0.81	3.5	2.37	+ 0.69
532	2 mM	1.02	3.5	2.99	+ 0.87
532	5 mM	1.28	3.5	3.75	+ 1.09

Third-order Nonlinear Optical Susceptibility $[\chi^{(3)}]$

The Z- scan plot of DASPB dye in PMMA-MA polymer film, show a pre-focal transmittance minimum (valley) followed by a post-focal transmittance maximum (peak). This indicates that DASPB has a positive non-linearity due to self-focussing. Self-focussing is due to variation in refractive index with the two-photon absorption or/and reverse saturation absorption. The nonlinear refractive index n_2 can be calculated using the equation (6) and change in refractive index, Δn can be calculated using equation (10). Experimentally determined nonlinear refractive index n_2 can be used to find the real part of

the third-order nonlinear optical susceptibility $[\chi^3]$ according to the following relation [31-32],

$$\text{Re } \chi^{(3)} = |\chi^3| = \frac{10^{-4} \epsilon_0 (n_0^2) c^2 n_2}{\pi} \quad (\text{cm}^2/\text{W}) \quad (11)$$

Experimentally determined nonlinear absorption coefficient β can be used to find the imaginary part of the third-order nonlinear optical susceptibility $[\chi^3]$ according to the following relation

$$\text{Im } \chi^{(3)} = \frac{10^{-2} \epsilon_0 (n_0^2) c^2 \lambda}{4\pi^2} \quad (\text{cm}^2/\text{W}) \quad (12)$$

Table-4: Third harmonic susceptibility for DASPB film at 20 mW.

Wavelength (nm)	Concentration	n_2 (cm ² /W) $\times 10^{-7}$	$[\chi^3]$ (esu) $\times 10^{-6}$
532	1 mM	+ 1.09	9.149
532	2 mM	+ 0.87	10.998
532	5 mM	+ 0.69	13.349

The absolute value of the third-order nonlinear optical susceptibility is given by the relation

$$|\chi^3| = [(\text{Re } \chi^{(3)})^2 + (\text{Im } \chi^{(3)})^2]^{1/2} \quad (13)$$

Where ϵ_0 is the vacuum permittivity and C is the light velocity in vacuum.

The nonlinear parameters, such as nonlinear refractive index (n_2), change in refractive index (Δn), the nonlinear absorption coefficient (α) and nonlinear susceptibility ($\chi^{(3)}$) are calculated and listed in Table 4.

CW Optical Limiting Study

The optical limiting effect of the DASPB dye-doped polymer film is studied at 532 nm by means of a 30 mW CW semiconductor diode laser beam (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 photo detector 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 whole size is used between the dye sample and the collecting lens & photo detector. The dye sample film is kept at a point along the beam axis where the transmitted light intensity shows a valley in closed aperture Z-scan curve [33-38]. The input laser intensity is varied systematically and the corresponding output intensity values are measured by the photo detector. 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-doped 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 DASP B dye-doped PMMA-MA films are studied by using a CW laser source. The experimental set-up for the demonstration of type-1 optical limiting is shown in figure 13. The dye sample is kept fixed at the focal point of the convex lens L1 of open aperture Z-scan set-up. A variable beam splitter (VBS) is used to change the power input beam. By means of a convex lens, the entire output light beam is focused to a photo-detector-power meter assembly. In the experiment, the input intensity of light is increased gradually in steps and the corresponding output intensity is noted by means of photo detector-power meter assembly. A graph is drawn between variations in input power and corresponding variations in output power for different dye concentrations and is shown in figure 14.

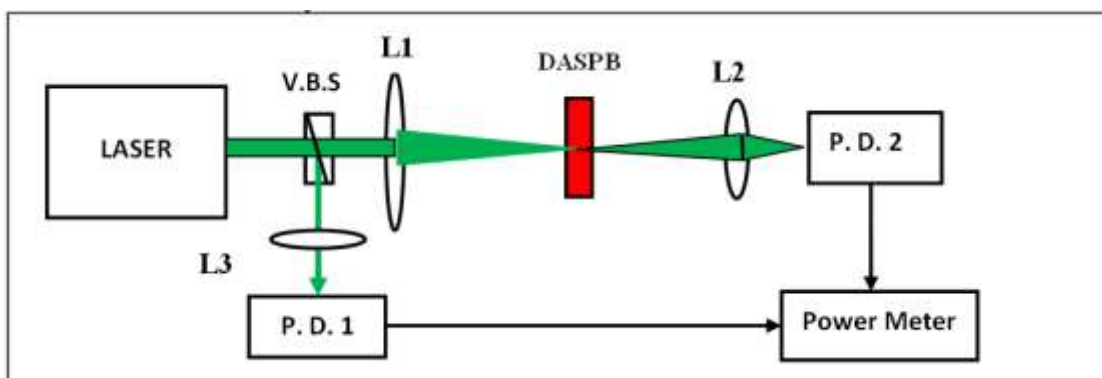


Fig-13: Experimental setup for Optical limiting (Type 1) due to pure absorptive nonlinearity

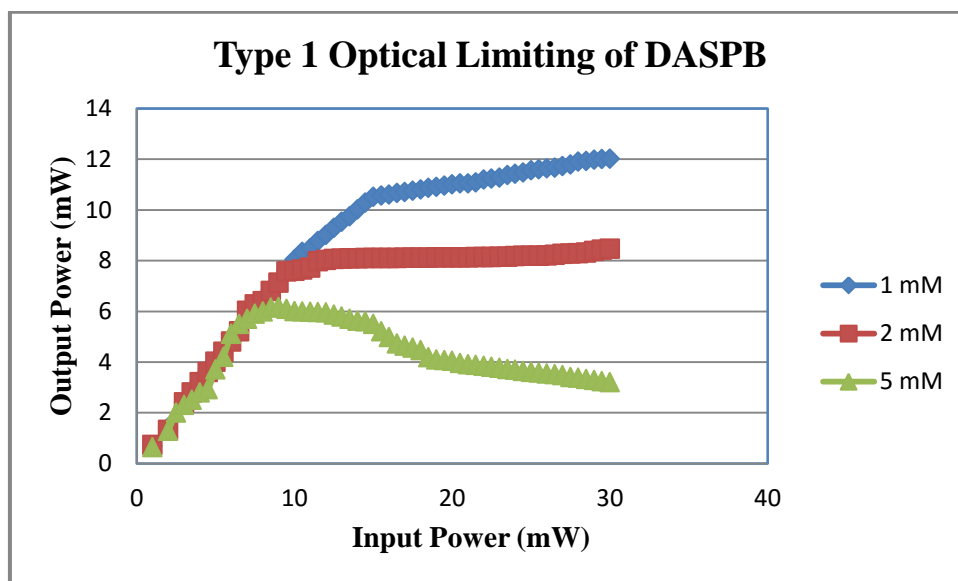


Fig-14: Open aperture (Type 1) Optical limiting behavior of DASP B dye-doped PMMA-MA film at CW 532 nm

In this case, the power of the output transmitted beam is found to change linearly with the change in input power for low values of input power but starts to saturate at high incident input power beam due to combined nonlinear effect of two-photon absorption and reverse saturation absorption. Hence, after a certain threshold value of the input intensity, the nonlinear absorption of the DASPb dye sample becomes dominant, resulting in a limiting of the intensity of output beam. Thus the transmittance recorded by the photo detector remained almost constant showing a saturation region in the optical limiting graph.

Case (2)

Optical Limiting with Aperture (Type 2)

The pure nonlinear refraction property of the dye-doped sample is measured using this method of optical limiting with an aperture at the output side

(Type-2 optical limiting). The light beam from CW semiconductor diode laser of wavelength 532 nm (BeamQ 30 mW Green Light Line) 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 DASPb 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 15. The dye-doped 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 different input power and corresponding output power for different dye concentrations and is shown in figure 16.

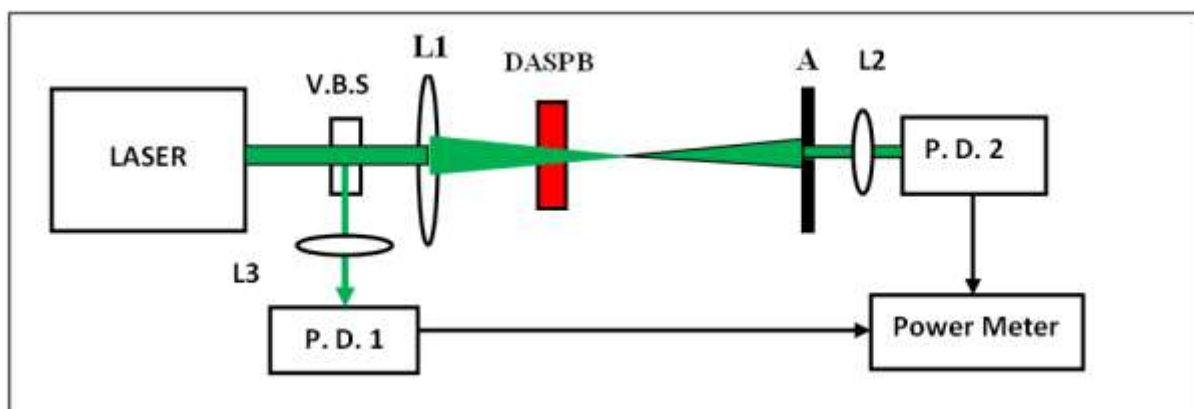


Fig-15: Experimental setup for closed aperture Optical limiting for DASPb doped PMMA-MA using nonlinear refraction

In this case of DASPb dye-doped sample, with focusing nonlinearity (positive nonlinearity), the intensity of transmitted output beam is observed to change linearly with low values of the incident input intensity, but appears to saturate after a certain threshold value due to the fact that the dye sample starts focusing the transmitting beam, resulting blocking of the part of the beam by the aperture A placed in between the dye sample and the collecting lens before the photo-detector. Thus the light intensity received by the photo detector remained almost constant showing a saturation region as shown in figure 16.

RESULTS & DISCUSSION

The optical nonlinearity of DASPb doped PMMA-MA polymer film is studied using open aperture and closed aperture Z-scan techniques by means of low power CW laser at different dye-doping concentrations. The open aperture Z-scan study shows

that the dye-doped sample shows a considerable amount of saturable absorption property. But at higher input intensity, the two-photon absorption and the reverse saturation absorption properties of the dye in polymer film becomes prominent as shown in Z-scan graph of figure 8. From figure 6, it is seen that the transmission at the focus decreases with increasing sample concentration. At higher concentration, the dye-doped sample shows better nonlinear absorption properties. As shown in the closed aperture Z-scan graph, absorption saturation in the sample enhances the peak and decreases the valley 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 [33-38]. Table 4 shows the experimentally calculated Nonlinear optical parameters of DASPb dye-doped PMMA-MA film at 532 nm.

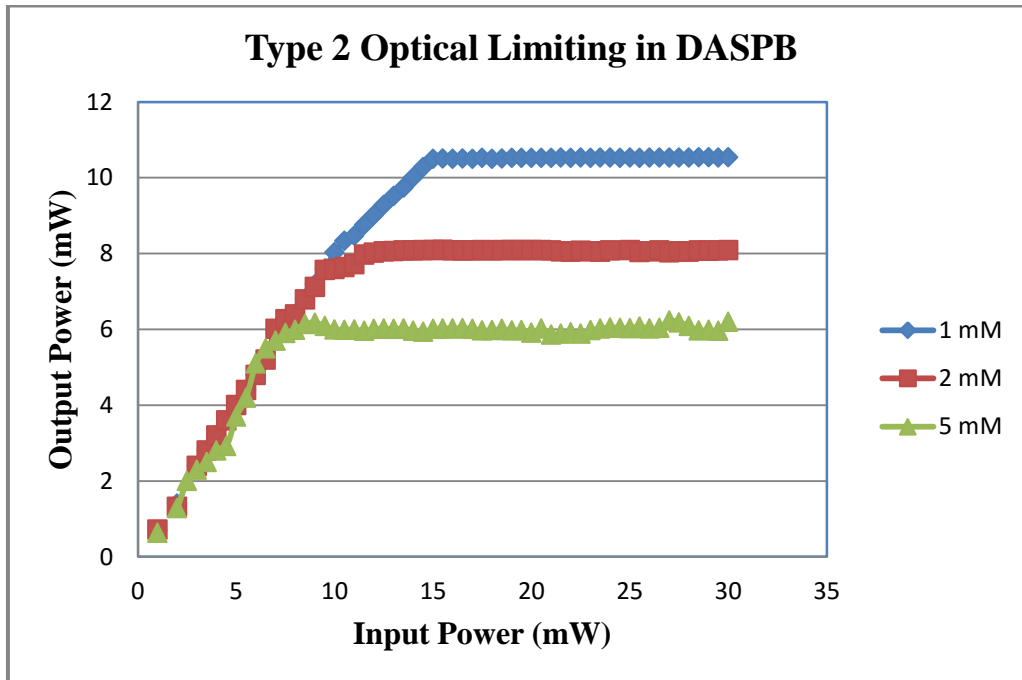


Fig-16: Closed aperture (Type 2) Optical limiting behavior of DASP B dye-doped PMMA-MA film at CW 532 nm.

Table-5: Nonlinear parameters for DASP B dye-doped PMMA-MA film at 532 nm

S. No.	Parameter	Dye concentration	DASP B
1	α_0 (Linear absorption coefficient) (Using equation 1)	2 mM	-0.03567
2	n_0 (Linear refractive index) (Using equation 2)	2 mM	2.4488
3	ΔT_{p-v} (The difference between the normalized peak and valley transmittance)	1 mM	0.81
		2 mM	1.02
		5 mM	1.28
4	$n_2 \times 10^{-7}$ (cm ² /W) Nonlinear refractive index n_2	1 mM	0.69
		2 mM	0.87
		5 mM	1.09
5	$\beta \times 10^{-3}$ (cm/W) (Using equation 3)	1 mM	0.64
		2 mM	0.81
		5 mM	1.13
6	$\Delta n = n_2 I_0$ ($\times 10^{-4}$)	1 mM	2.415
		2 mM	3.045
		5 mM	3.815
7	$\alpha = \alpha_0 + I_0 \beta$ (Using equation 4)	1 mM	2.2043
		2 mM	2.7993
		5 mM	3.9193
8	$ \chi^{(3)} \times 10^{-6}$ esu (Using equation 11)	1 mM	9.149
		2 mM	10.998
		5 mM	13.349

Optical limiting behavior DASP B dye-doped PMMA-MA polymer films under low power CW laser input for different dye concentrations are studied. Optical limiting Regions in DASP B-doped Polymer film at 532 nm CW laser beam are identified and listed in table 5. The mechanism responsible for type 1 optical limiting is mainly attributed to the combined effect of

reverse saturation absorption and two-photon absorption in case of DASP B dye-doped sample, which further increased with thermally induced nonlinear refraction. The focussing effect observed in DASP B dye samples under CW illumination is utilized to demonstrate their optical limiting action of type 2. Based on its high nonlinear refractive index, the

DASPB dye-doped in PMMA-MA matrix behaves as good type 1 optical limiters even at low powers. These

results are quite encouraging for possible applications in nonlinear optical devices [39-40].

Table-6: Optical limiting Regions in DASPB-doped Polymer film at 532 nm CW laser beam

S. No.	Sample & Type of Limiting	DASPB dye Concentration	Linear Region (mW)	Active Region (mW)	Saturation Region (mW)
1	DASPB in PMMA-MA Type 1 Limiting configuration	1 mM	1 – 15 mW	15 – 28 mW	28 mW onwards
		2 mM	1 – 9 mW	9 – 11 mW	11 mW onwards
		5 mM	1 – 7 mW	7 – 9 mW	9 mW onwards
2	Type 2 Limiting configuration	1 mM	1 – 14 mW	14 – 15 mW	15 mW onwards
		2 mM	1 – 9 mW	9 – 11 mW	11 mW onwards
		5 mM	1 – 7 mW	7 – 8 mW	8 mW onwards

Table-7: Concentration dependence of limiting Input threshold of dye-doped in PMMA-MA films

S. No.	Sample	Dye Concentration (mM)	Type 1 Optical Limiting Input Threshold (mW)	Type 2 Optical Limiting Input Threshold (mW)
1	DASPB in PMMA-MA	1 mM	14.5	15.0
		2 mM	11.5	8.02
		5 mM	8.0	5.90

Both type 1 and type 2 optical limiting effects show an increase with increasing the concentration of the doped dye in the polymer film as shown in figure 14 & figure 16 and the input threshold power for limiting are listed in table 7. The optical limiting responses of the low dye concentration films are generally much weaker than those of high concentrated films, and hence high concentrated films exhibit strong optical limiting. This indicates an inverse relationship between the number densities of dye molecules in the laser beam with the output clamping level. From the graph, it can be seen that the threshold intensity for optical limiting is inversely proportional to the dye concentration in the PMMA-MA film. The limiting experiment shows that as the concentration increases, both the linear

transmittance as well as the output clamping level decreases. The experimentally determined optical limiting saturated output power values are shown in Table 8. The results are comparable to some of the reports of low power optical limiting [41-47]. In the case of 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 very low powers as the self-defocussing effect is enhanced by the thermal effect which is closely related to the absorptive properties of the DASPB dye used. Thus it can be suggested that the best position for a sample, when used for optical limiting based on self-defocusing (type 2) is at the valley point of the Z-scan curve.

Table-8: Concentration dependence of saturated output power in DASPB 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	11	10.5
2	2 mM	8.0	8.06
3	5 mM	4.0	6.10

CONCLUSION

The nonlinear absorption, nonlinear refraction properties of DASPB dye-doped in Polymethyl methacrylate methacrylic acid (PMMA-MA) polymer film are studied at low power CW laser beam of 532 nm using the Z-scan experimental method. The optical limiting properties of these films are also studied by

increasing input power at different dye doping concentrations. It is found that the type of nonlinear absorption depends on the intensity of input beam. DASPB has shown saturation absorption at lower input irradiance and then combined effect of two-photon absorption and reverse saturation absorption at higher irradiance. Optical limiting studies using type 1 and

type 2 setups is carried out and is found that type 2 has shown better limiting characteristics for DASPb doped PMMA-MA polymer films.

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