A REVIEW ON SUSTAINABLE ORGANIC MATERIALS FOR OPTICAL LIMITING TECHNOLOGY

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ABSTRACT

Materials with exceptional nonlinear optical properties are critical to the continuing development of photonic and electro-optical devices, such as those used in optical communications, networking, optical computation for signal processing and data storage equipments. Currently, there exists a wide range of inorganic non-linear optical materials with varied wavelengths, damage thresholds and optical characteristics. Most technologies are based on inorganic materials with the appropriate optical properties. Using inorganic materials has some major drawbacks. Primarily, inorganic materials used in optical systems are difficult and expensive to process. In addition, inorganic materials have a high dielectric constant, requiring larger poling voltages and often suffering from changes in the material's refractive index. Finally, inorganic materials have a low electro-optic coefficient, which is less suitable for electro-optic modulation. The present best practice in Photonics technology is the usage of organic materials/dyes that exhibit exceptional nonlinear optical properties. These organic materials/dyes are easy to prepare in solution or solid form. The resulting organic material has a low dielectric constant, eliminating the need for poling while maintaining the refractive index. However, these organic materials have few of the drawbacks inherent in the processing of comparable inorganic materials like of intense light induced degradation or bleaching and aggregation at higher dye concentration. In order to overcome these drawbacks and for effective use of highly nonlinear dyes, the strategic idea for the next practice is doping the dye molecules in polymer matrix. This idea of dye-doped polymer material matrix may increase the concentration of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability. In this paper we have discussed the strategic advantages of dye-doped polymer nonlinear materials in comparison with organic and inorganic nonlinear materials for future photonics technology by considering an example of an organic dye 4-[4-(Dimethylamino)styryl]-1- docosyl pyridinium bromide, doped in a polymer matrix Polymethyl methacrylate methacrylic acid (PMMA-MA).

Keywords: Dye doped polymer films, Organic nonlinear materials, Optical limiting, Two photon absorption.

Introduction:

Materials with exceptional nonlinear optical properties are critical to the continuing development of photonic and electro-optical devices, such as those used in optical communications, networking, Optical computation for signal processing, and data storage equipments. The nonlinear optical material is a general term for the materials efficiently make appearance of nonlinear phenomenons optically as the responses to optical wavelength conversion, optical amplification as well as the refractive index changes due to its intensity. Nonlinear optical materials are largely divided into inorganic and organic materials. In 1930, the nonlinear optical effect related to optical wavelength conversion was predicted, which was said to be the first finding knowledge about the nonlinear optical phenomenon. In 1960, laser oscillation using inorganic material was reported. Since then researches of inorganic nonlinear optical materials were actively taken place, but now-a-days, probably there is no more that undiscovered [1]. With the rapid development of modern science and technology, information transmission capacity of communication increases day by day. Optical communication, which has advantages of large transmission capacity, high transmission velocity, excellent anti-jamming ability and good Signal-to-Noise value, is becoming a main method in communication researches at present. Functions like optical switching and memory by non-linear optical effects, all depending on light intensity, are expected to result in realization of a pivotal optical device in optical computing. This is a new data processing system that makes the maximum use of light characteristics such as parallel and spatial processing capabilities and high speed. All-optical networks with good performances, such as big capacity, good transparency, wavelength routing characteristics, compatibility and extensibility, has become the first choice of next generation of wide-band net with a promising application. Accompanied by the deep research of wave division multiplex (WDM), switches have drawn more and more people's attention. In the existing optical-electronic-optical conversion apparatus of present communication net, disadvantages of slow switching speed and clock displacement have lead to a "bottleneck" of optical fiber communication systems. All-optical switches which can break through the transmission speed limits of electro-optical, acousto-optical, thermo-optical and micro-electro-mechanical switches, can serve as effective methods to solve these problems. Based on the third-order nonlinear optical (NLO) effect, phase all-optical switches use a controlled light to bring changes of refraction index and make phase difference when signal light passes through sample and thus carry out the function of "on" or "off" of optical switches. Its nonlinear phase difference is proportional to $(2\pi/\lambda)n_2IL$, where I is intensity, L is length of interaction of wave and n_2 is nonlinear refraction index. The properties, such as change speed, intensity loss, sensitivity to optical polarization and insert loss, all depend on third-order NLO materials used to synthesize apparatuses. At present, it is with great enthusiasm to emphasis on exploring and synthesis of materials for all-optical switches based on the continual discovery of varies kinds of new materials. There are other applications of third-order NLO materials, including optical limiting

devices, Q-switch, passive mode locking, optical operation and light storage etc.. Laser weapons applied to military have special effects on optical-electro antagonism, aerial defense and military recovery. Laser blinding can make eyes blind temporarily or permanently, and laser can also destroy important apparatus in the satellite, such as detectors and sensors. As a result, laser protection materials and devices have become a focus. The purpose of laser protection is to protect people and devices from damage of high intensity. These optical limiting devices are mainly based on the materials' third-order NLO properties, including self-focusing, self-defocusing, two-photon absorption, reverse saturable absorption and nonlinear scattering. Comparing to earlier laser protection devices, it has advantages of fast response, wide protected band, low optical limiting threshold, large damage threshold and high linear transmission, etc. The third-order NLO properties of materials can also be used in the compression (mode-locking) and shaping of laser pulses, optical bistability, etc.. Third-order NLO materials also have many potential practical exciting applications, and motivated scientists to continually explore new materials with high third-order NLO properties. The demands of materials for all-optical information process and high-speed all-optical switches include large nonlinear refraction index, small linear and nonlinear absorption coefficient, fast response and low propagation loss [1].

Photonic and electro-optical (in which information storage or processing involves the modulation and switching of light beams) devices are used in many applications which include :

- Electro-optic modulators
- Mach-Zehnder interferometers
- Optical switches
- Optical interconnectors
- Frequency doublers for high-power lasers
- Active waveguides
- Optical memory storage devices
- Optical computing devices
- Nonlinear directional couplers
- Nonlinear Bragg reflectors
- Optical limiters
- Photorefractive memories

The global market for Non-Linear Optical Materials and Applications is in Millions of US$. There are several companies including many key and niche players worldwide such as CASIX, Inc., Cleveland Crystals, Inc., Coherent, Inc., Conoptics, Inc., Cristal Laser SA, Crystal Technology, Inc., Deltronic Crystal Industries, Inc., EKSMA OPTICS, Fujian Castech Crystals, Inc., Inrad Inc., JDS Uniphase Corporation, Laser Optics, LINOS Photonics GmbH & Co. KG, Northrop Grumman Synoptics, Nova Phase, Inc., Quantum Technology, Inc., Raicol Crystals Ltd., Saint-Gobain Crystals, and Vloc, Inc.

Nonlinear Optical Materials : Best Practices:

Currently, there exists a wide range of inorganic non-linear optical materials [2-3] with varied wavelengths, damage thresholds and optical characteristics. The research focus is to develop materials that meet all requirements such as faster response, high laser damage threshold and wide transparency range coupled with adaptability, processing ability and the ability to interface with other materials. Further robust growth in demand for high bandwidth fiber optic networking infrastructure and high speed optical computing are expected to boost the demand for Non-Linear Optical Materials.

New Initiatives:

On the other hand, the 1982 ACS symposium report added momentum to the organic nonlinear optical material studies. Since then the studies have started to become active. It revealed organic compounds with the delocalized conjugated electrons which have excellent nonlinear optical property and high-speed responsiveness due to high mobility of electrons. The 21st Century is said to be an age of photonics. As one of the basic technology of photonics, improvements of the wavefront control technology using organic nonlinear optical effects are considered very important. Now R&D on the organic materials with excellent nonlinear optical properties, and vigorous applied studies have been carried out. Present developments in the field of materials chemistry show that, though inorganic materials are still the choices for many devices, interest in organic materials are growing day-by-day in view of their adaptability to various kinds of applications. The field of organic molecular materials has transformed the use of materials in the modern world in the last 20 years, and it can be seen that organic molecules provide wonderful opportunities to materials researchers to design custom-tailored materials whose properties at the macroscopic /microscopic level reflect closely to the modeled or actual behavior of individual molecules. In other words, development of novel functional organic materials is a rapidly growing area of science, which probably can replace the traditionally used materials with cheaper and better-performing new ones in the near future, and also bring out some new applications [4 - 6].

In view of the technological applications of the organic materials, the current research focus is in five technical areas, which are (1) Structural and multifunctional materials, (2) Energy and power materials, (3) Photonic and Electronic Materials, (4) Functional organic and hybrid materials, (5) Bioderived and bio-inspired materials. Among the five main technological thrust areas of the organic materials, the focus of this thesis is on "PHOTONIC MATERIALS", which can find applications in the field of linear and electric nonlinear optics (otherwise known as photonics). Some of the benefits of organic nonlinear optical materials are :

- **Easy to process**: Because they do not require electric poling or the preparation of large single crystals, these materials are easier to process than inorganic optical materials.
- **Lower cost**: The ease of processing directly translates into a lower cost to fabricate.
- **High second- and third-order susceptibility**: This technology exhibits exceptional performance in doubling and tripling the frequency of light passing through it, making it at least comparable to inorganic materials.
- **Low dielectric constant**: An optical material with a high dielectric constant requires a larger poling voltage in order to polarize the dipole moment and can suffer changes in the refractive index. This technology requires no poling voltage and maintains its refractive index.
- **High electro-optic coefficient**: Materials with a high electro-optic coefficient are more suitable for electro-optic modulation for high-speed devices.
- **Colorless**: It is believed that the clarity of the doubling material will prevent the absorption of visible light, allowing a wide variety of light frequencies to be doubled.
- **Resistant to laser damage**: The tripling material can be exposed to 432,000 20-nanosecond pulses at 20 Hz without any evidence of damage to the organic material, making it ideal for use in photonic applications.

Next Practices:

Though the present best practice in Photonics technology is the usage of organic materials/dyes that exhibit exceptional nonlinear optical properties, these organic materials have few of the drawbacks inherent in the processing of comparable inorganic materials like of intense light induced degradation or bleaching and aggregation at higher dye concentration. In order to overcome these drawbacks and for effective use of highly nonlinear dyes, the strategic idea for the next practice is doping the dye molecules in polymer matrix. This idea of dye-doped polymer

material matrix may increase the concentration of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability [7 – 8].

In this paper we have discussed the strategic advantages of dye-doped polymer nonlinear materials in comparison with organic and inorganic nonlinear materials for future photonics technology by considering an example of an organic dye 4-[4-(Dimethylamino)styryl]-1-docosyl pyridinium bromide, doped in a polymer matrix Polymethyl methacrylate methacrylic acid (PMMA-MA). We have studied the nonlinear properties like the two photon induced fluorescence and optical limting capability of a new dye 4-[4-(Dimethylamino)styryl]-1- docosyl pyridinium bromide hereafter called as DASPB both in solution form (in chloroform) as well as in Methyl methacrylate – methacrylic acid co-polymer (PMMA-MA) matrix. The linear absorption, single photon fluorescence, two photon induced fluorescence behavior are studied. The intensity dependent nonlinear absorption at various wavelengths and optical limiting behavior are studied using a picosecond laser beam.

Analysis on Next Practices:

(1) Methodology

1. Design of Nonlinear dye Molecules

2. Fabrication of dye-doped polymer films

3. Study of linear absorption of the films at different wavelengths

4. Study of two photon induced fluorescence

5. Study of nonlinear absorption at different wavelengths

6. Study of nonlinear refraction at different wavelengths

7. Study of optical power limiting

We have studied the linear, nonlinear optical properties using Z-scan and optical limiting nature of these films in continuous wave (cw), nano and pico second regime at 532 nm.

(2) Design of Nonlinear Molecule

One of design strategy is proposed recently by Albota et.al,[9] dealing with molecules based on benzene ring as π-center which is attached symmetrically by either electron-donor (D) or electron-acceptor (A) through various lengths of conjugated connectors; D-π-D or A-π-A. They concluded that σ is increased by increasing the length of conjugation; change with the D/A

strength and the extent of symmetric intramolecular charge-transfer (CT) from the D ends to the π-center or vice versa, meaning that symmetric charge redistribution effectively occurs upon excitation of such symmetric molecules.

A similar approach was made in designing molecules by Reinhardt [10] and his coworkers. 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. In fact, an asymmetric structure, D-π-A. This seems to suggest that there must be more crucial molecular factors other than structural symmetry involved. In this study we have considered dye molecule as 4-[4-(Dimethylamino)styryl]-1-docosyl pyridinium bromide with π centre is used.

(3) Sample Preparation

Commercially available DASPB (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 was used as polymer matrix. The thin films of DASPB doped in PMMA-MA is prepared using hot press technique. Thin films of variable thickness are obtained between two glass slides.

(4) Linear Optical Properties of DASPB

The molecular structure of DASPB is shown in Figure 1. A charge-transfer in between the aromatic moiety (electron donor) and bromine unit (electron acceptor) can be proposed to explain large χ^3 value measured using Z-scan technique. The linear absorption spectrum of DASPB in chloroform is measured on a VARIAN Cary UV-vis-IR recording Spectrophotometer by using quartz cuvete with one cm path length as well as doping it in Polymethyl methacrylate methacrylic acid (PMMA-MA) film. The Figure 2 shows the linear absorption spectrum of a DASPB in chloroform with solute concentration of d_0 = 0.0001 mol/L, in which the solvent influence is not included. The spectral curve has shown that there is 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.

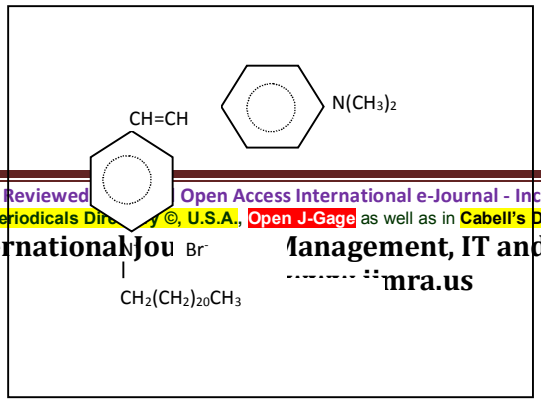
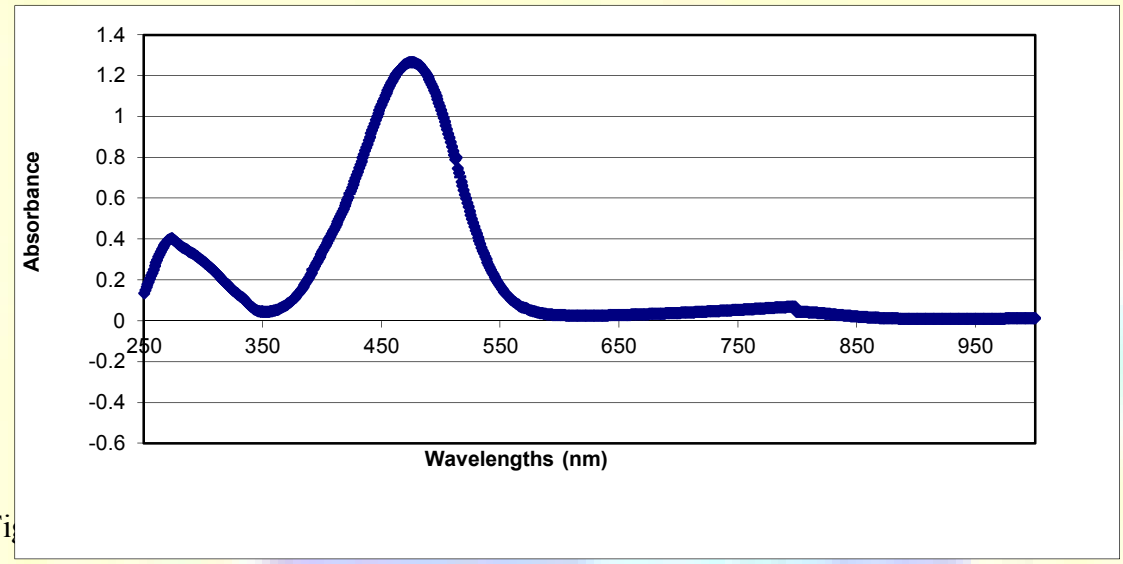


Figure 1 : Molecular structure of DASPB.



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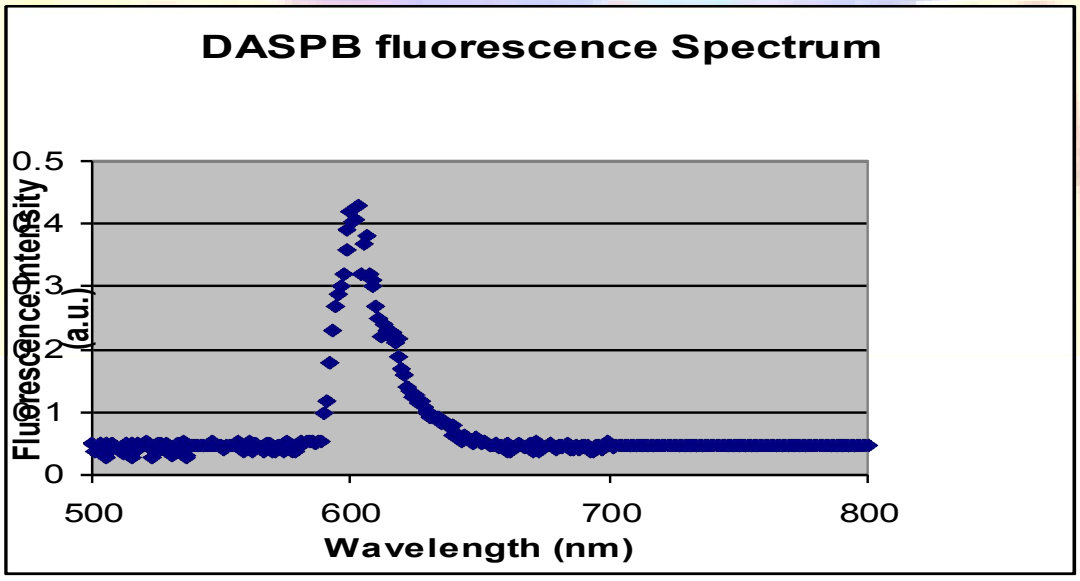

Figure 3 : One photon induced emission spectrum of DASPB in chloroform.

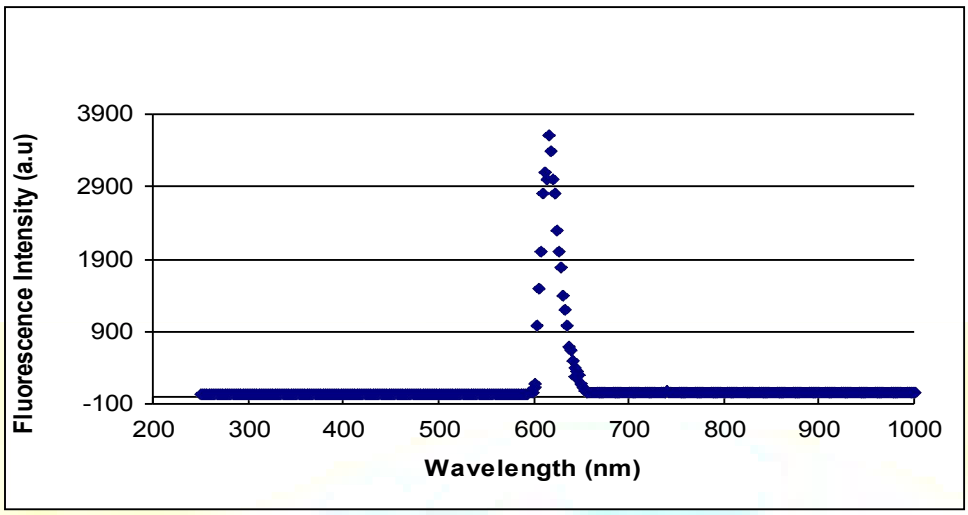

Figure 4 : One photon induced fluorescence at 532 nm irradiation.

The single photon fluorescence spectrum of the sample is measured for a 1 cm –path DASPB in chloroform with the solute concentration of 0.0001 mol/L using a spectral fluophotometer (Rf 50000U from Schmadza) with the spectral resolution of 1 nm. The peak wavelength of the single-photon induced fluorescence was 610 nm with a bandwidth of 60 nm (Figure 3). Figure 4 corresponds to single photon fluorescence when DASPB is excited at 532 nm using an Nd:YAG laser beam.

5.4 NONLINEAR OPTICAL PROPERTIES

5.4.1 Nonlinear Optical Properties of DASPB

TPA Cross-section Measurement :

From absorption spectrum of DASPB, we can see that there is no linear absorption in the entire spectral range from 580 nm to 1800 nm except the fact that IR radiation between 1,200 nm to 1,600 nm is strongly absorbed by DSAPB solution. It has been observed that this dye shows quite strong frequency upconverted fluorescence when exposed to near IR and IR laser beam above 700 nm. This suggests that a very strong TPA process may occur inside the sample.

Two-photon Excited Fluorescence Emission

The TPA induced emission spectrum of 0.0005 mol/L DASPB in chloroform with 1 cm path length excited with 1064 nm laser beam is shown in Figure 5. In the measurement of the upconversion efficiencies, VIS cutting filters were used to cut transmitted pump energy.

Comparing Figure 5 with Figure 4, we can see that the TPA induced emission spectrum of DASPB with much higher concentration has a red-shift as compared to that in much lower concentration single photon absorption study. This can be explained by reabsorption of Dye material [11].

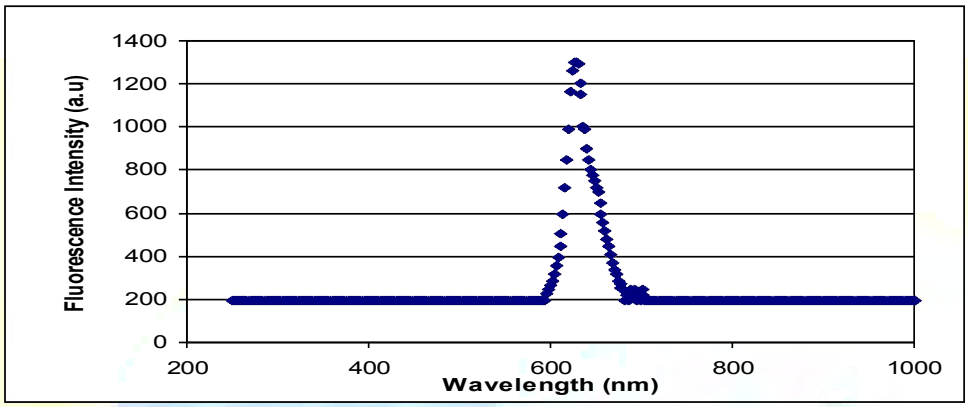

Figure 5 : Two-photon induced emission spectrum of DASPB at 1.06 μm irradiation.

Z-scan technique is used to study the nonlinear optical properties of the sample [12-13]. In Z-scan approach, a single beam is tightly focused into a thin nonlinear medium. The transmittance through a small aperture in the far-field is measured and this allows the measurement of nonlinear refractive index n_2. By removing the aperture, measurement of the transmittance allows the determination of the two photon absorption coefficient β. Figure 6 shows the experimental setup for the measurement of nonlinear absorption including saturation absorption in linear absorbing region and two-photon absorption in transmitting region of DASPB. 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.

To study the behavior of DASPB at its linear absorptive region, both pico (32 ps, 10 Hz.) and nano second laser (6 ns, 20 Hz.) beams (from second harmonic of a Q-switched, mode-locked Nd:YAG laser system and operating at 532 nm) are used.

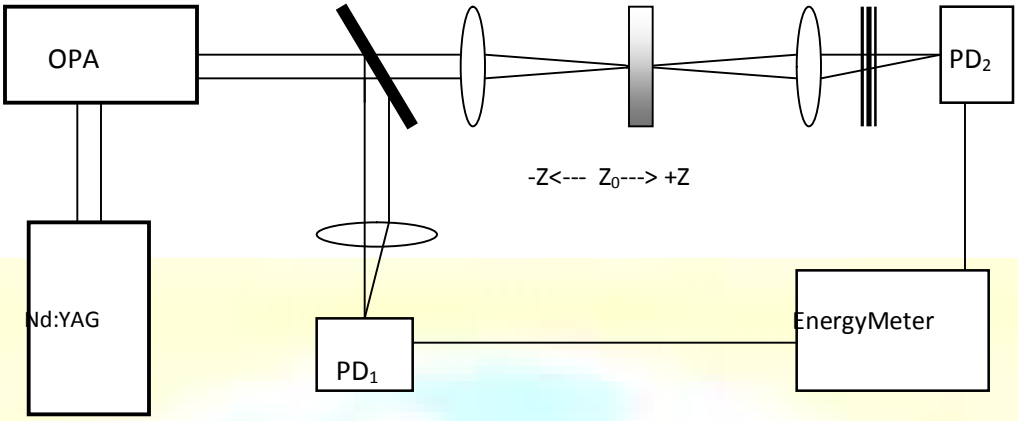

Figure 6 : Experimental set-up used for the measurement of the total transmittance and overall energy conversion efficiencies.

Figure 7 & 8 show the Z-scan results for DASPB at 532 nm using cw and pico second pulses at low energy and the material shows strong saturable absorption. Even if the linear transmittance of the sample is low, it is observed that due to nonlinear absorption, transmittance of the sample is increased initially with increase in intensity. But it is interesting to note that, the saturation absorption is over taken by reverse saturation absorption effect at higher input irradiance (figure 9). The transformation from SA to RSA is with increase in fluency level is first observed in organic dyes and this behavior can be used for optical limiting as well as optical switching. From the figure 10, it can be noted that the nonlinear transmission of the sample at 600 nJ input energy is about 16 times larger than the value of linear transmission. Similar behavior is observed with nano-second laser beam except the fact that a dip is observed close to the focus due to overlapping of reverse saturation absorption on saturation absorption.

The normalized energy transmittance for a temporal Gaussian pulse can be written as [12]

$$T(Z,S=1) = \frac{1}{\sqrt{\pi}\, q_0(Z,0)} \int_{-\infty}^{+\infty} \ln(1+q_0(Z,0))\, e^{-\tau 2}\, d\tau$$

Where $q_0(Z,t) = \beta I_0(t) L_{eff} / (1+Z^2/Z_0^2)$, $L_{eff} = (1 - e^{-\alpha L})/ \alpha$, Here, L is the sample length and α is the linear absorption coefficient, S is the aperture linear transmittance, Z is the distance of the sample from the focus and Z_0 is the Rayleigh length. When there is no linear absorption, $\alpha \rightarrow 0$ and L_{eff} equals to L.

For $|q_0| < 1$, the transmittance can be expressed in terms of peak irradiance in a summation form that is more suitable for numerical evaluation, as

$$T(Z,S=1)=\sum_{m=0}^{\infty}\frac{[-q_0(Z,0)]^m}{(m+1)^{3/2}}$$

Once an Open aperture Z-scan with S =1 is performed, the two photon absorption coefficient β can be deduced. By knowing the concentration of dopent, the molecular two photon cross-section σ'_2 can be determined by using following relationship, with d_0 as molecular density of the dye.

$$\beta = \sigma_2 N_0 = h\nu\sigma'_2 N_A d_0 \times 10^{-3}$$

The nonlinear absorption coefficient β is estimated from the data in Fig. 8 by studying the best fit according to the relationship, I(L) = [ln (1 + I0Lβ)] /Lβ where I(L) is the transmitted beam intensity, I0 is the incident beam intensity, L is the thickness of the sample.

Two photon absorption cross section is measured for 0.0005 mol/L DASPB with sample thickness 1 mm in cuvete as well as incorporating it in PMMA-MA polymer of thickness 0.1 mm by using a focused 32 ps mode-locked Nd:YAG laser at wavelength range 800 nm to 1000 nm [14]. The pump laser beam from the output of OPA was focused by a convex lens (f = 15 cm) on to the centre of the DASPB film. The pump energy and the output energy were recorded simultaneously by a two-channel energy meter. In the measurement of nonlinear absorption, IR cutting filters were used to cut the upconverted energy. All the experiments were done at room temperature. Table 1 gives the value of nonlinear coefficient β and corresponding TPA cross section σ'_2 at different wavelengths and corresponding peak irradiance.

Table 1 : Experimental values of TPA coefficient and TPA cross section at different wavelengths.

Wavelength (nm)	β in cm/GW	σ'_2 in $cm^4.s/photon$
800	5.6	3.91×10^{-47}
900	6.4	4.23×10^{-47}
1000	5.9	3.98×10^{-47}

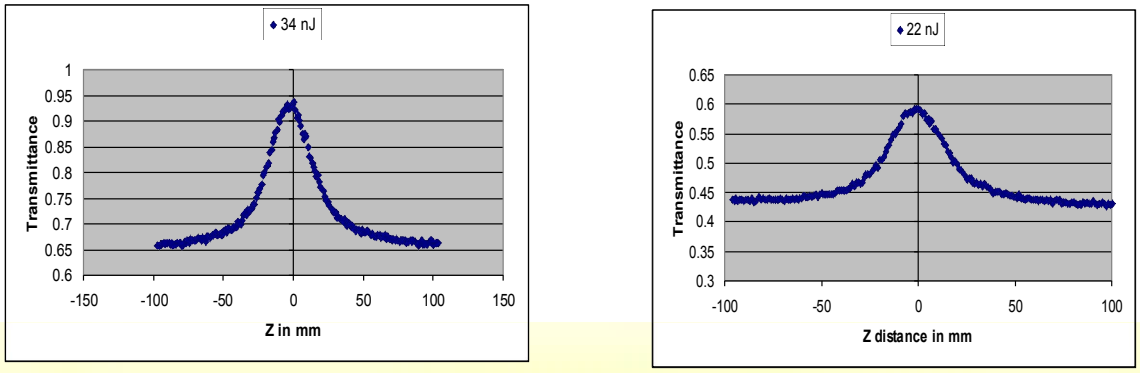

Figure 7 : Picosecond 532nm open aperture Z-scan curves at energies (a) 34 nJ (b) 22 nJ.

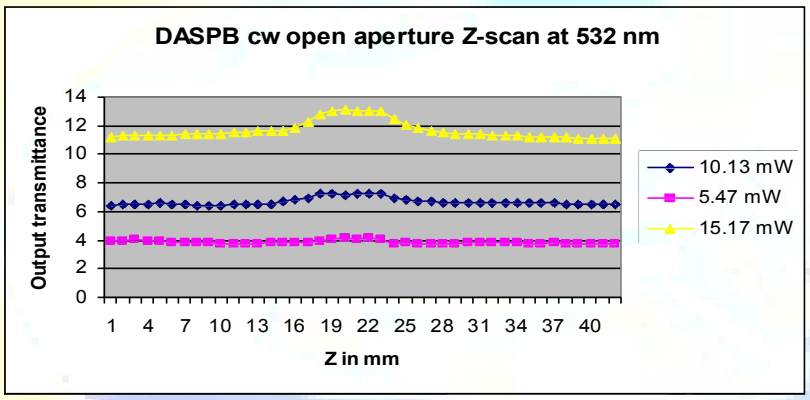

Figure 8 : CW 532 nm open aperture Z-scan at different input power.

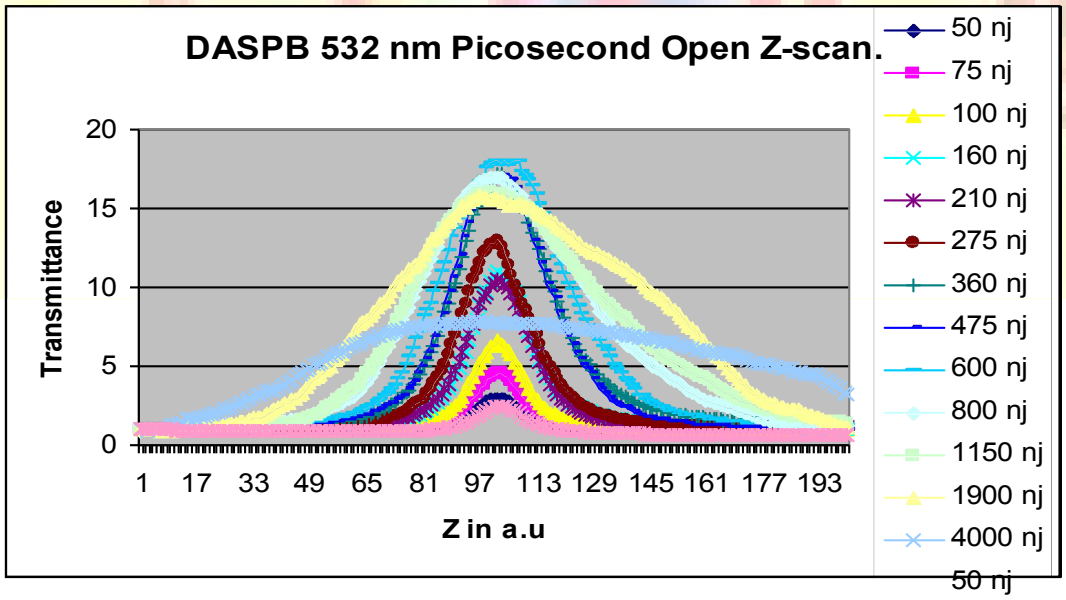

Figure 9 : Pico second 532 nm open aperture Z-scan of DASPB at different energies.

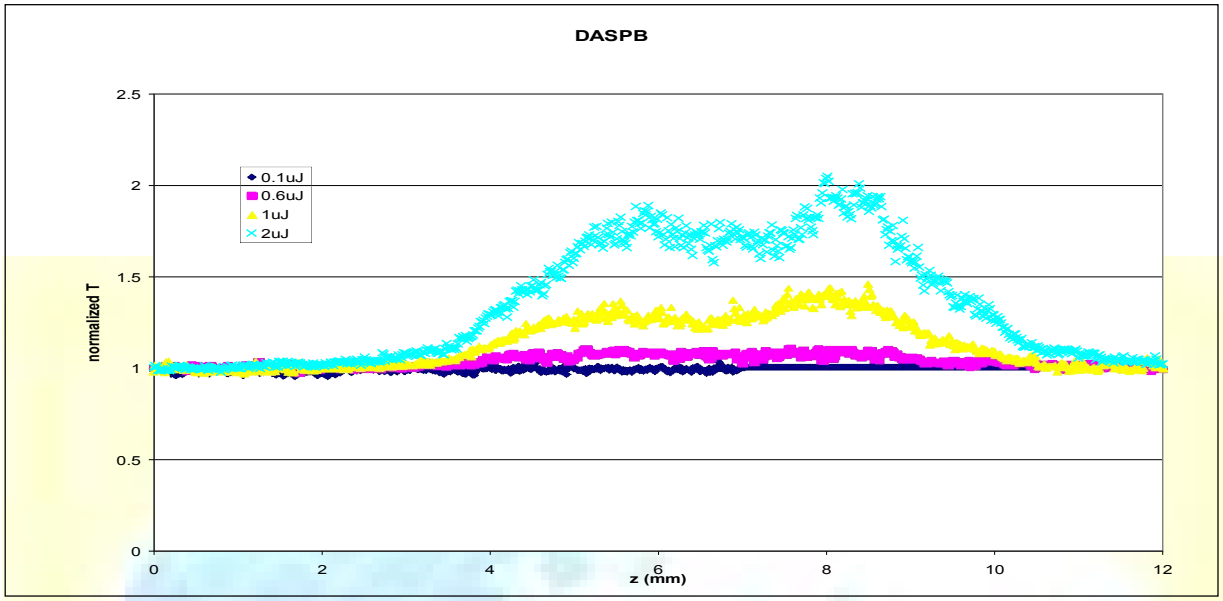

Figure 10 : Nanosecond 532 nm open aperture Z-scan of DASPB at different energies.

5. 5 OPTICAL LIMITING STUDY

Optical limiting study is performed at absorbing region using cw, nanosecond and picosecond 532 nm laser beams and in two photon absorbing region using pico-second 800 nm, 900 nm and 1,000 nm laser beam. The linear transmission of dye in the form of film was about 10 %. The limiting curves using 532 nm pico second and nano second pulses are shown in figure 11 and figure 12 respectively. From the figures it can be noted that at very low input intensity, linear transmission is preserved, with increase in input intensity DASPB starts to contribute to saturation absorption which increases the transmission above linear level and at higher intensities the excited state absorption starts to contribute and it dominates with further increase in intensity. This kind of behavior has interesting applications in Optical switching [15].

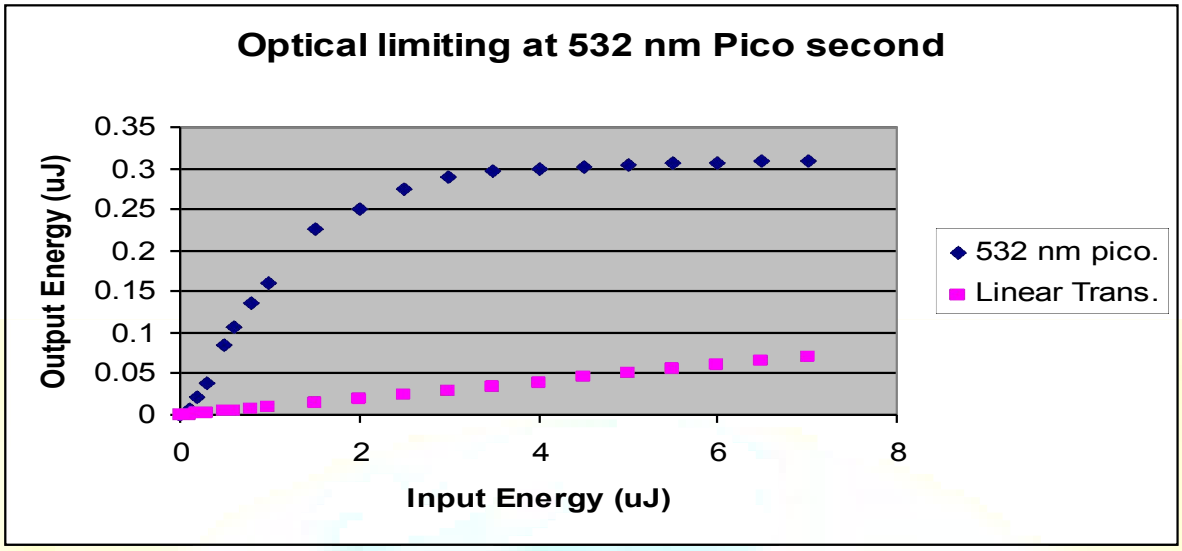

Figure 11 : Optical limiting behavior at 532 nm pico second pulses.

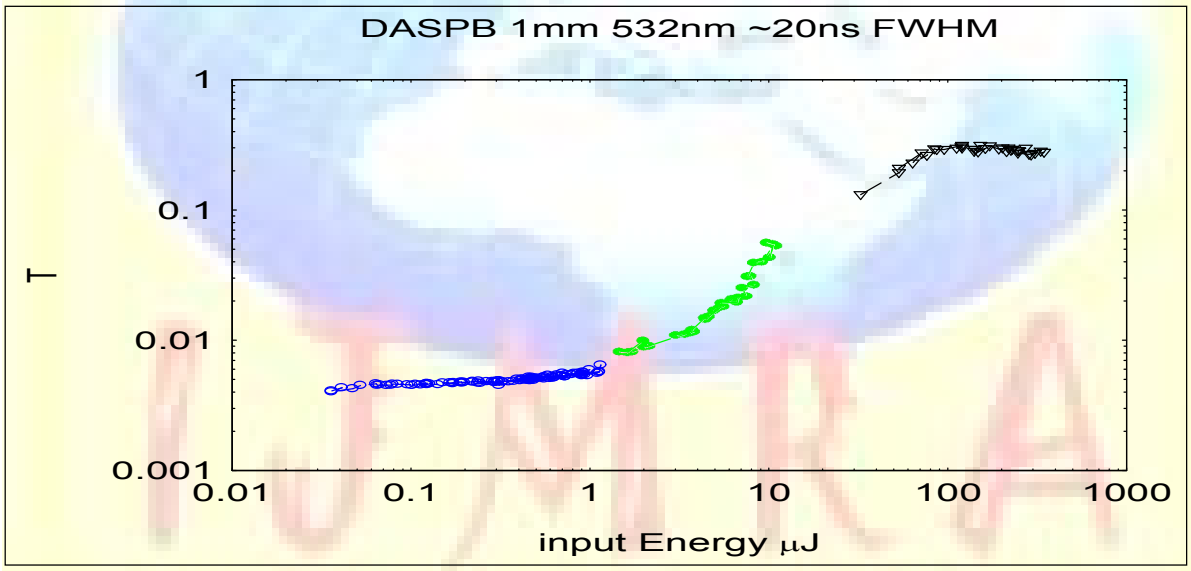

Figure 12 : Optical limiting behavior of DASPB at 532 nm nano second pulses.

The input – output characteristics of DASPB in PMMA-MA matrix with CW 532 nm laser beam without focusing is shown in Fig. 13. The beam spot on the film is maintained around 3 mm in diameter using an aperture. We could not see any thermal damage on the spot. It is observed that as input increased, the output power exceeded well above the linear transmission range.

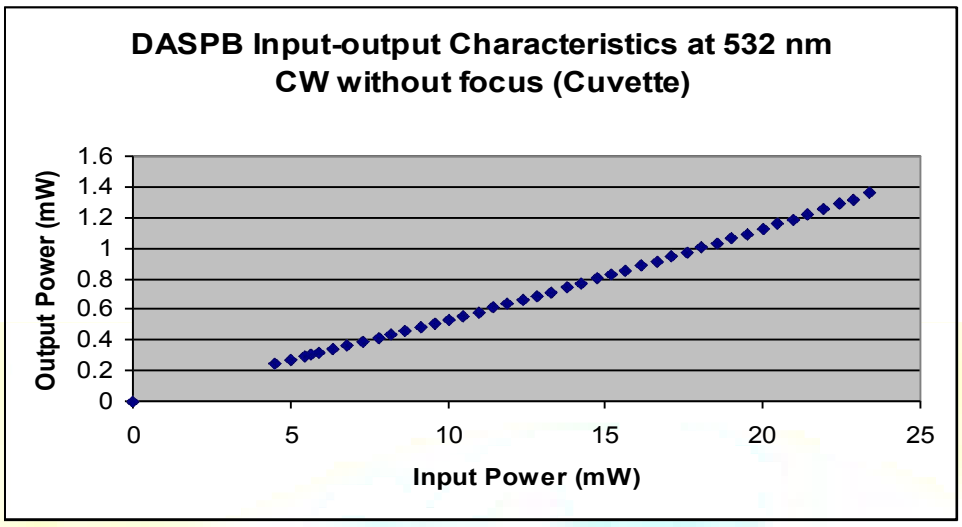

Figure 13 : Input – output characteristics of DASPB with CW 532 nm beam without focusing (4 mm beam spot).

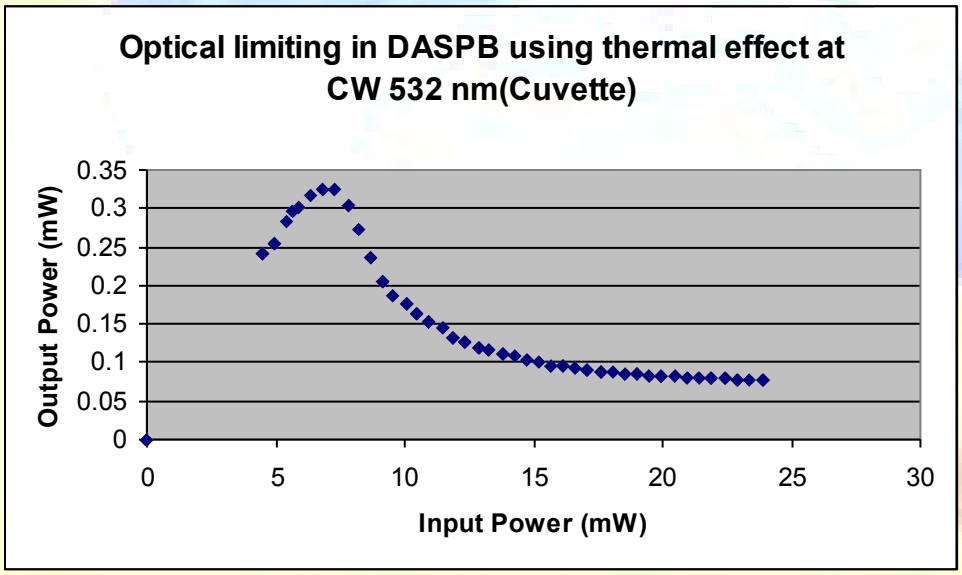

Figure 14 : CW optical limiting at 532 nm (sample is placed at focus).

The CW optical limiting study is also performed on DASPB in chloroform in 1 mm thick cuvette by keeping it at the focus of a convex lens. As increase in input power the output emerging beam spot is increased due to defocusing thermal effect. The output power is measured through a 4 mm aperture and the limiting behavior is shown in Fig. 14. In this case, the output initially increased due to saturation of absorption, decreased thereafter due to defocusing effect and finally became constant.

Conclusion:

We have characterized the nonlinear optical properties of DASPB in PMMA-MA polymer matrix at its linear absorbing region and linear transmitting region. We found that the type of nonlinear absorption depends on the intensity of input beam. In linear absorption region, at lower intensity, the dye has shown saturation absorption and with increase in input intensity, the excited state absorption became prominent. This machanisum contributed to optical limiting behavior in absorbing region of the dye. In nonabsorbing region, the two photon induced fluorescence along with excited state absorption contributed for optical limiting. It is also found that DASPB has a much larger TPA cross-section of Rhodamine 6G listed in literature [16-17] as 10^{-48} – 10^{-50}, at least one order of magnitude larger. More detailed understanding of the behavior in entire spectral region in terms of different nonlinear processes require further investigation. Efforts are under way to study the two-photon pumped cavity lasing using this dye doped polymer material. Based on the result, it is expected that dye doped polymers are going to be the next practice as effective nonlinear materials.

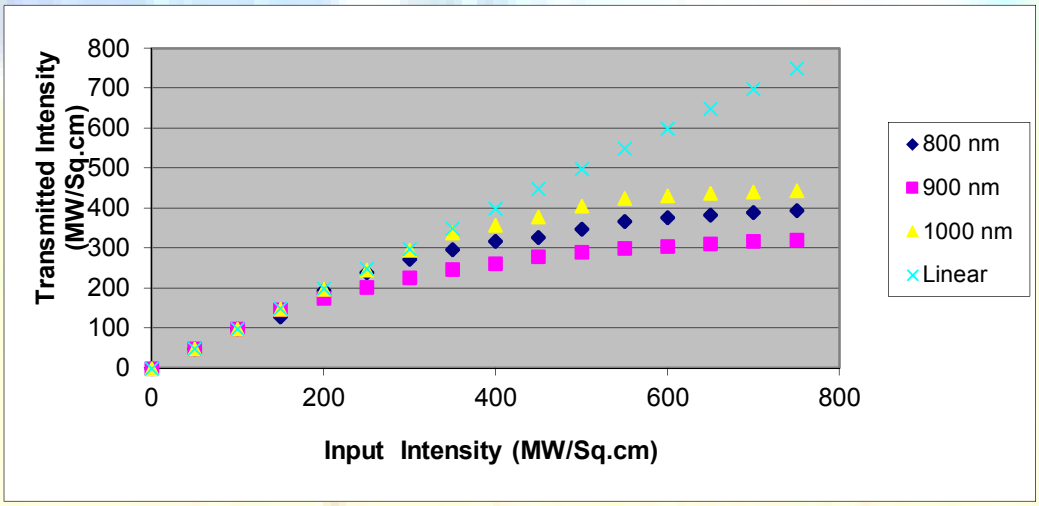

Figure 15 : Optical limiting behavior of DASPB at 800 nm, 900nm and at 1000 nm.

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