Nonlinear Optical Characterization of Dye-doped Polymer Films for Optical Limiting and Optical Phase Conjugation

Dr. Shubhrajyotsna Aithal

Faculty, Department of Chemistry,
College of Engineering & Technology,
Srinivas University, Mangalore, INDIA

&

Dr. P. Sreeramana Aithal

Faculty, Department of Physics,
College of Engineering & Technology,
Srinivas University, Mangalore, INDIA

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Foreword

I am happy to note that the Book entitled "**Nonlinear Optical Characterization of Dye-doped Polymer Films for Optical Limiting and Optical Phase Conjugation**" by **Dr. Shubhrajyotsna Aithal** and **Dr. P. Sreeramana Aithal** is having enriched information on the latest technology of Photonics and being published by Srinivas Publication, Srinivas University, Mangalore.

Srinivas University is striving hard through its contribution for qualitative improvement in the level of education, environment, and economy of the country.We have a visionary mission to contribute to multidimensional growth and development of the society in general and all-round development of the students in particular.We hope that the inspiring students,under the guidance of dedicated teachers and a far-sighted leadership of the top administration would lend this University to a coveted and recognized position in the galaxy of higher education in the world. We aspire our University to be a world-class centre of excellence, innovation, honor, integrity, and outstanding quality and service. Our prime objective is to enrich and support the individual in his/her Endeavour towards the attainment of knowledge and wisdom to apply that knowledge in coherence with the aims and ambitions of the individuals in particular, and for the greater good of humankind in general.

I am happy to write a foreword to this book and glad that **Dr. Shubhrajyotsna Aithal** and **Dr. P. Sreeramana Aithal** are making a considerable effort in bringing out this book under Advances in Technology Series. The book contains many important introductory and advanced experimented topics on Photonics which is emerging as a multidisciplinary new frontier of Science & Technology and arranged in such a way as to improve the curiosity of the readers and think innovatively towards further contribution in the field and future endeavor in the society.Congratulations to the Authors for their determined efforts in bringing out this Book.

CA. A. Raghavendra Rao
Chancellor, Srinivas University,
President, A. Shama Rao Foundation

Contents

CONTENTS

Preface

PREPHASE

Preparation and Nonlinear Optical Characterization of Dye-doped Polymer Films for Optical Limiting & Optical Phase Conjugation

The need for nonlinear optical materials that can be used with low-intensity lasers for application such as optical phase conjugation, image processing, optical switching and optical limiting have increasingly become important. Recently, organic molecules have attracted much attention due to their large third order nonlinear optical susceptibility and the possibility of tailoring their mechanical and optical properties which allow these materials to be used to develop components for optical switching, optical memory devices, optical image processor and optical power limiters. Optical power limiters are the devices used to protect optical detection elements, such as human eyes and optical sensors, by controlling the fluency on the image plane below the desired level. Extensive research has been carried out and reported on many organic nonlinear optical materials which include single crystals of organic molecules, organic molecules in solution forms, and organics and organometallics doped in various solid matrices. The major advantages of organic optical materials compared to their inorganic counterparts are due to their low cost and easy to fabricate optical components.

A passive optical limiter designed by using organic molecule utilizes various nonlinear mechanisms such as Reverse Saturation Absorption (RSA), Two-Photon Absorption (TPA), nonlinear refraction, nonlinear scattering, and thermal nonlinearity. Out of these, two-photon induced absorption or fluorescence possesses many advantages like high initial transmission for the weak optical beam, instantaneous response to a change of input intensity of the optical beam and retention of optical quality of the input beam after passing through the nonlinear medium.

Similarly, the optical phase conjugation through four-wave mixing is demonstrated in some of the gases, organic and inorganic crystals, and films using pulsed and continuous wave (CW) lasers. Glasses and other solid matrices doped by organic dyes emerged as promising materials for optical phase conjugation (OPC) because of their large third-order nonlinear susceptibilities $\chi^{(3)}$. In these materials, the phase-conjugate wave can be generated at low light intensities of the continuous-wave lasers. Moreover, these materials can be easily prepared in the laboratories.

In this research, the nonlinear properties like the two-photon induced fluorescence and optical limiting capability of a new dye 4-[4-(Dimethylamino) styryl]-1- docosyl pyridinium bromide hereafter called as DASPB doped in Methyl methacrylate – methacrylic acid co-polymer (PMMA-MA) are carried out. The linear absorption, single photon fluorescence, and two-photon induced fluorescence behavior are studied. The intensity dependent nonlinear absorption at various wavelengths and optical limiting behavior are studied using CW laser beams. We found that the type of nonlinear absorption depends on the intensity of input beam. In linear absorption region, at a lower intensity, the dye has shown saturation absorption and with an increase in input intensity, the excited state absorption became prominent. This mechanism contributed to optical limiting behavior in the absorbing region of the dye. In the non-absorbing 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 compared to Rhodamine 6G.

The study also include the linear and nonlinear optical properties of an acceptor – donor molecule, [3-[N-ethyl-4-(4-nitrophenylazo) phynyl-amino] propionitrile also known as Disperse Orange – 25, and, 4-[4-(Phenylazo)phenylazo]-o-cresol, also known as Disperse Yellow - 7 doped in PMMA-MA for nonlinear absorption and optical limiting. These azo dye molecules generally exhibit large Reverse Saturable Absorption (RSA), which is currently considered to be the most important power limiting mechanism. It is proved theoretically that using materials with high RSA, it is possible to achieve higher nonlinear attenuation.

Phase conjugation through Degenerate four-wave mixing is studied in 4-[4-(Dimethylamino)styryl]-1- docosyl pyridinium bromide (DASPB) dye-doped in Polymethyl methacrylate – methacrylic acid (PMMA-MA) polymer films and Disperse Orange-25 dye doped in Polymethyl methacrylate – methacrylic acid (PMMA-MA) polymer films under low-power, continuous-wave laser irradiation. The effects of dye concentration, the intensity of backward, forward pump, and the inter-beam angle between the probe beam and forward pump beam on phase conjugation reflectivity are studied. The predominant phase conjugation signal is attributed to the fact that saturable absorption and two-photon induced fluorescence property of the dye molecules. Finally, the factors affecting the various determinant issues and their critical constituent elements of dye-doped polymer films to be used in Photonic applications are identified using a new framework consisting of four constructs – Advantages, Benefits, Constraints, and Disadvantages called ABCD framework.

The thesis consists of seven chapters. **Chapter 1** consists of an elaborative introduction to nonlinear optics, various nonlinear optical properties of the materials, theory of third order nonlinearity, and various experimental methods to measure optical nonlinearity, excited state nonlinearity, and optical switching, The chapter also consists of information about the concept of ideal limiter and its characteristics, design and applications of practical optical limiters in high and low power laser environment, the concept, theory and applications of optical phase conjugation using degenerate four-wave mixing in nonlinear materials using low power lasers. Finally, an elaborative discussion on the possibility of tailoring the nonlinear optical properties by considering the chemistry of organic nonlinear optical materials is presented.

An extensive literature survey on nonlinear optical materials is depicted in **Chapter 2**. This includes review of organic nonlinear material research, materials for reverse saturation absorption, molecules for two-photon and multi-photon absorption, experimental techniques for nonlinear refraction, nonlinear absorption, optical limiting, and optical phase conjugation. Finally, the various optical device configurations based on nonlinear absorption, nonlinear refraction, optical limiting and optical phase conjugation are discussed along with their advantages and limitations.

In **Chapter 3**, the objectives of present study based on a review of the literature are presented. Based on the objectives, a detailed methodology of realizing the objectives is discussed. The methodology include, Design of Nonlinear dye Molecules, Fabrication of dye-doped polymer films, Study of linear absorption of the films at different wavelengths, Study of two-photon induced fluorescence, Study of nonlinear absorption at different wavelengths/ dye concentrations, Study of nonlinear refraction at different wavelengths/dye concentrations, Study of optical power limiting characteristics, Study of Optical Phase Conjugation behavior using

Degenerate Four-wave mixing set-up of fabricated dye doped films, and Factor & Elemental Analysis of Dye-doped Polymers films in Photonic Applications using ABCD Analysis Framework.

Chapter 4 explores the structural design of organic dye molecules for better nonlinear properties and preparation of dye-doped polymer film samples of variable dye concentration and variable film thickness using the hot-press technique. Based on the molecular structural studies three dyes namely 4-[4-(Dimethylamino)styryl]-1- docosyl pyridinium bromide (DASPB), [3-[N-ethyl-4-(4-nitrophenylazo) phynyl-amino]propionitrile (Disperse Orange - 25) and 4-[4-(Phenylazo)phenylazo]-o-cresol (Disperse Yellow - 7) are chosen for further study. The linear absorption property of prepared films of these three dyes doped in Polymethyl methacrylate methacrylic acid (PMMA-MA) are studied using molecular absorption spectroscopy and the results are discussed.

In **Chapter 5,** the nonlinear absorption and nonlinear refraction properties of prepared films of these three dyes doped in Polymethyl methacrylate methacrylic acid (PMMA-MA) are studied using the Z-scan experimental method. Finally, the optical limiting properties of these films are also studied at different input power for different dye doped concentrations at 532 nm input wavelength for Type 1 and Type 2 configurations.

The optical phase conjugation property of these dye-doped polymer films are studied using degenerate four wave mixing method and the dependence of phase conjugated signal reflectivity on various parameters viz., dye concentration, intensity of backward pump beam, intensity of forward pump beam, and inter-beam angle between the probe and forward pump beam on phase conjugation reflectivity and the results are depicted and compared in **Chapter 6**.

In **Chapter 7**, the summary of the results of the research work on linear absorption, nonlinear absorption, nonlinear refraction, optical limiting, and optical phase conjugation using degenerate four wave mixing configuration are depicted and discussed. Attempts are made to explain the experimental results in terms of the structure and electronic configuration of the molecules. Application of dye-doped polymer films in Photonics is analyzed in detail by studying their affecting factors and critical constituent elements using ABCD framework. Finally, the conclusions based on the study along with the suggestions for future research are also given in **Chapter 7**.
In our experimental research, it is observed that DASPB is an optimum candidate for optical limiting due to its two-photon induced fluorescence property combined with high excited state absorption cross section. All the samples DASPB, Disperse Orange – 25, and Disperse Yellow - 7 have shown optical Phase Conjugation when they are doped in PMMA-MA polymer matrix.

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About the Authors

Mrs. Shubhrajyotsna Aithal is belonging to Mangalore, India, born on 19/11/1970. She has M.Sc. in Material Science from Mangalore University, India, M.Sc. in Chemistry from Kuvempu University, India, MA in English from Annamalai University, and M.Phil. in Chemistry, Vinayaka Mission University, India. Presently she is doing her part time Ph.D. in the field of Characterization of dye-doped polymer nonlinear optical materials in Rayalaseema University, Kurnool, India. She has 15 years teaching experience in teaching Chemistry for Pre-University & undergraduate students. Presently she is working as Principal & Senior Lecturer in Chemistry at Srinivas Pre-University College, Pandeshwar, Mangalore, Karnataka State, India. She is also elected as Joint Secretary of Dakshina Kannada Pre-University Principal Association, Mangalore. Her research interests are in nonlinear absorption, nonlinear refraction, optical limiting and generation of Phase Conjugated signal in dye-doped polymers. Mrs. Aithal has published 35 research papers in refereed international journals with 280 Google scholar citations and 30 papers in national conferences in the field of characterization of nonlinear optical materials, and innovations in higher education. She has also presented research papers in international conferences held at Kota Kinnibalu-Malaysia, Bangkok-Thailand, Penang- Malaysia, Singapore, and Grimby-United Kingdom.

Prof. Dr. P. Sreeramana Aithal has 27 years' experience in Teaching & Research and 16 years' experience in Administration. Dr. P. S. Aithal has secured the **FIRST RANK** in TOP 12,000 Business Management Authors in the Global Ranking of Elsevier's SSRN (USA) for maximum number of Research papers publications during 2016-17. He has worked as Principal at Srinivas Institute of Management Studies, Mangalore from 2001-2017. Dr. P. S. Aithal studied his B.Sc. (Physics, Chemistry, & Mathematics) from Poornaprajna College, Udupi during 1985-88. Having four Masters degrees in Physics with Electronics, Computer Science, Information Technology, and E-Business, he got his first Ph.D. degree in Physics from Mangalore University in the area of nonlinear optical materials and second Ph.D. degree in Business Management from Manipal University, Manipal, in the area of mobile banking. He worked as Post Doctoral Research Fellow at "Lasers & Quantum Optics Division, Physical Research Laboratory, Ahmedabad for two years from 1999-2000. In the year 2002, he has been selected for the prestigious Oversee Fellowship of Dept. of Science & Technology, Govt. of India – Better Opportunity for Young Scientists in Chosen Area of Science & Technology (BOYSCAST) Fellowship and did Post Doctoral Research at Centre for Research & Education in Optics & Lasers (CREOL), at University of Central Florida, Orlando, U.S.A. During his Post Doctoral Research at Ahmedabad & USA, he has worked in the area of Nonlinear Optics, Photonics, Optical Limiters and Optical Solitons. Dr. Aithal has got SERC Young Scientist Project on Nonlinear Optics funded by Dept. of Science & Technology, India. Dr. Aithal also had a visiting associateship at Physical Research Laboratory, Ahmedabad, and Visiting Professorship of Grimsby Institute of Further & Higher Studies, Grimsby, U.K. He has 42 research publications in refereed International Journals in the area of Nonlinear Optics and Photonics, and 120 in refereed International Journals publications in Business Management, Higher Education, and Information Technology. He has presented more than 200 research papers in National & International Conferences/Seminars. Presently he is guiding research scholars for their M.Phil. and Ph.D. degrees in Electronics, Information technology, and business management. Dr. Aithal has developed Teaching Materials in Operations Research, Quantitative Techniques, Research Methodology, Management Information Systems, International Business, Communication networks and Mobile Communication for MBA & MCA Courses. He has also written textbooks on Engineering Physics and Basic Electronics for Engineering Students, which has been published by ACME Publishers, New Delhi. He has research interest in Nonlinear optical absorption, Optical Phase Conjugation, Photorefractive materials, e-business, m-business, ideal business, and nanotechnology business Opportunities. Dr. Aithal is member of World Productivity Council, U.K., member of Strategic Management Forum, India, member of Photonics Society of India, CUSAT, Cochin, senior member of IEDRC.org, Singapore. Dr. P. S. Aithal has edited Twelve Conference Proceedings with ISBN numbers and recently published a book on "Quality in Higher Education" a case study of SIMS. Being a pioneer researcher, Dr. Aithal has developed a new Theory of

Organizational Behaviour in 21st Century called Theory on Accountability (Theory A). He has also developed a new model for measuring Research productivity called ABC model. He has developed a new Analysis framework for Concepts, ideas, systems, strategies and models called ABCD analysis technique. He has developed and published a new model of nanotechnology commercialization and Analyzing practical systems based on Ideal system Characteristics. Apart from teaching and research, Dr. Aithal has been involved in institution building activities since 14 years as a team member of Srinivas group and presently there are 18 institutions imparting quality education under Srinivas Group (www.srinivasgroup.com) and during 2015, Srinivas Group of Institutions became a Private University as Srinivas University and Dr. Aithal has got an opportunity to serve as first Vice-Chancellor of the University. **With the successful leadership of Dr. P. S. Aithal, Srinivas Institute of Management Studies has been Ranked #1 among Top International Business Schools other than USA and Ranked #4 among Top World Business Schools including USA in the Total number of research paper publications during last year by Elsevier's Social Science Research Network (SSRN), USA**.

CHAPTER ONE

Introduction to Nonlinear Optics & Materials

CONTENTS **PAGE No.**

1.1 INTRODUCTION TO NONLINEAR OPTICS

Science is nothing but finding Unity. When it reaches perfect unity, it would end because it would reach its goal.

Swami Vivekananda in his spiritual address in Chicago.

Photonics has certainly an important role in the future days as it emerging as a multidisciplinary new frontier of Science and Technology, capturing the imagination of Scientist and Engineers in many fields especially in optical communication, optical computation, and information processing. According to the definition, Photonics is the technology of generating and processing light and other forms of electro-magnetic energy whose quantum unit is the photon. The range of applications of photonics extends from energy generation to detection to communication and information processing using nonlinear optical properties of materials. The major challenge of photonics is identifying a right material/device to optimally process the signals for a right application using material science and chemical engineering knowledge.

1.2 NONLINEAR OPTICAL PROPERTIES OF MATERIALS

The field of nonlinear optics has been rigorously investigated for over fifty years. Since its beginning in 1960, after invention of the first Laser by T. H. Maiman [1], the field has grown to encompass a widely diverse array of phenomena such as second harmonic generation first observed by P.A. Franken, et al. in 1961, [2], the electro-optic (Pockel's) effect [3], sum and difference frequency generation [4], third harmonic generation [5], stimulated scattering [6], multi-photon absorption [7], and nonlinear refraction [8]. Each of these effects has the potential to be used for some practical application. For example, second harmonic generation is extremely useful in doubling frequency of lasers to expand their spectral coverage, while optical parametric processes similarly expand spectral range through difference frequency generation. Second harmonic generators and optical parametric oscillators represent applications that have reached some level of maturity in that they exist as commercially available products. The developments of other nonlinear optical processes are either still in their infancy or stagnant in their progress. The most notable example is the intensity-dependent refractive index and intensity-dependent absorption, which hold great promise in device applications but the development of which has stalled due to the lack of suitable materials.

Since the discovery of self-focusing in materials with an intensity-dependent refractive index, and the realization of the ability of these materials to produce intensity dependent phase shifts, all-optical devices have been a topic of rigorous investigation. Early theoretical and experimental results spurred interest in optical analogs to transistors, logic gates, switches, routers, multiplexers, de-multiplexers, and much more. The research has continued as an information-hungry society demands more information and faster transmission rates requiring high speed, increased bandwidth networks. As the internet reaches into the home of the average consumer and optical communication networks approach the tens or hundreds of gigahertz speeds, system begins to push the limits of electronic devices. Increasingly, system designers will turn to all-optical systems that are free of the data-rate constraints imposed by the use of electronic devices to transmit and receive signals.

1.3 THEORY OF THIRD HARMONIC NONLINEARITY

The general wave equation used to describe the interaction of light wave with the matter as given in many textbooks is [9]:

$$\nabla^2\vec{E} - \frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2} = \mu_0\frac{\partial^2\vec{P}}{\partial t^2} \qquad \text{----------} \quad (1.1)$$

where the vector E is the electric field component of interactive light in the form of vector and P is the polarization vector induced in the matter due to applied electromagnetic field. By ignoring the vector form of E and P, we can expand eq. (1.1) in terms of nonlinear susceptibility [10] as :

$$P(t) = \varepsilon_0\int_{-\infty}^{\infty}\chi^{(1)}(t-t_1)E(t_1)dt_1 + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi^{(2)}(t-t_1,t-t_2)E(t_1)E(t_2)dt_1dt_2$$

$$+\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi^{(3)}(t-t_1,t-t_2,t-t_3)E(t_1)E(t_2)E(t_3)dt_1dt_2dt_3+\ldots \qquad \text{---------} \quad (1.2)$$

where $\chi^{(n)}$ is the n^{th}-order susceptibility which is time-dependent. When n = 2 we get $\chi(2)$ as second harmonic susceptibility, when n=3, we get $\chi(3)$ as third harmonic susceptibility, etc. We can write the electric field component as

$$|\vec{E}(t,z)| = \mathrm{Re}\{E(t,z)\exp[i(kz-wt)]\} \qquad \text{----------} \quad (1.3)$$

Where E a complex vector function changing in time and space and contains both amplitude and phase information. It is known that $P(\omega)$ is a slowly changing function with time. For input light beam with single frequency at ω, and the expression for slowly varying polarization component at this frequency given by

$$P_{\omega}(t) = \varepsilon_0 \chi(\omega) E(t) = \varepsilon_0 \left[\chi^{(1)}(\omega) + \chi^{(3)}(\omega) \frac{|E(t)|^2}{2} + \ldots \right] E(t). \quad \text{---------- (1.4)}$$

In the above equation, it assumes that changes in the electromagnetic field and the polarization, are so slow that the material response is the same as for a continuous wave (CW) input light beam. By ignoring the degeneracy factors and the polarization properties of these nonlinearities one can get $\chi^{(3)}$ as an effective nonlinear susceptibility. It can be shown that this nonlinearity gives rise to nonlinear absorption (NLA), and nonlinear refraction (NLR). By means of external self-action [12], one can try to determine both nonlinear absorption coefficient and nonlinear refraction coefficient of a given material medium. Using Eq (1.3), one can rewrite the wave equation as [13] :

$$\frac{\partial E(z,t)}{\partial z} - \frac{n}{c} \frac{\partial E(z,t)}{\partial t} = i \frac{\omega}{2nc\varepsilon_0} P_{\omega}(z,t), \quad \text{---------- (1.5)}$$

By transforming the coordinates traveling with the wave, $\tau = t\text{-}zn/c$ and $z' = z$, and by considering only third order term, the above equation becomes :

$$\frac{\partial E}{\partial z'} = i \frac{\omega}{2n\varepsilon_0 c} P_{\omega} = i \frac{\omega}{2nc} \left(\chi^{(1)} + \chi^{(3)} \frac{|E|^2}{2} \right) E, \quad \text{---------- (1.6)}$$

where electric field E and polarization P are functions of z' and τ. Using the magnitude and the phase of Electric field E as given in equation (1.7), one can rewrite eq. (1.6) into two components as loss or gain component and phase shift components and is given in eqs. (1.8) & (1.9).

$$E = E_0 e^{i\phi}, \quad \text{---------- (1.7)}$$

$$\frac{\partial E_0}{\partial z'} = -\frac{\omega}{2nc} \left(\Im m\{\chi^{(1)}\} + \Im m\{\chi^{(3)}\} \frac{E_0^2}{2} \right) E_0 \quad \text{---------- (1.8)}$$

and

$$\frac{\partial \phi}{\partial z} = \frac{\omega}{2nc}\left(\Re e\{\chi^{(1)}\} + \Re e\{\chi^{(3)}\}\frac{E_0^2}{2}\right). \quad \text{---------- (1.9)}$$

Based on eqs. (1.8) and (1,9), one can understand how the real and imaginary parts of $\chi^{(3)}$ give to intensity dependent phase shifts and loss respectively.

Improvements in eqs. (1.8) and (1.9) using the intensity, I, and taking only the nonlinearly induced phase ϕ into consideration leads to :

$$\frac{dI}{dz'} = -\left[\frac{\omega}{2nc}\Im m\{\chi^{(1)}\}\right]I - \left[\frac{\omega}{n^2c^2\varepsilon_0}\Im m\{\chi^{(3)}\}\right]I^2 = -\alpha I - \beta I^2, \quad \text{---------- (1.10)}$$

and with $k=\omega/c$,

$$\frac{d\phi}{dz'} = k\left[\frac{1}{2n^2c\varepsilon_0}\Re e\{\chi^{(3)}\}\right]I = kn_2 I \quad , \quad \text{---------- (1.11)}$$

where β is the two-photon absorption coefficient (in m/W) and n_2 is the nonlinear refractive index (in m^2/W).

It is known that the nonlinear optical properties of materials arise due to the change in refractive index caused by the slow thermal expansion of material due to linear absorption. The effects caused by these nonlinear interactions with matter range from the reduction of transmittance from increasing absorption with increasing input intensity to beam spreading from self-defocusing to the ultimate nonlinear interaction of laser-induced damage [9, 14-19].

1.4 EXPERIMENTAL METHODS TO MEASURE NONLINEARITY

There are different constraints to determine the experimental values of nonlinear absorption coefficient β and the nonlinear refractive index n_2 to identify suitable nonlinear materials for various photonic applications. In general, the quality and shape of input laser beam used for investigation, material parameters like structure, surface quality, material defects etc. affects the experimental methods and the interpretation of results including overestimation of values of nonlinear absorption coefficient β and the nonlinear refractive index n_2 for a given material. Similarly, use of long pulse laser beam for nonlinear material characterization may result in enhanced nonlinear absorption processes like free carrier absorption which may further lead to wrong estimation of nonlinear parameters like nonlinear absorption coefficient β and the

nonlinear refractive index n_2 of the material under consideration. Further, nonlinear refraction inside the sample or on the surface of the sample may result in modification of beam size either inside the sample or propagation after the sample leads to change of irradiation area on photo detector causing loss of a portion of transmitted light from the sample leads to further error in the estimation of both nonlinear absorption coefficient β and the nonlinear refractive index n_2 [20-25]. Two experimental techniques to identify and determine optical nonlinearity in materials and their nonlinear absorption coefficient β and the nonlinear refractive index n_2 are discussed below and further used in this study for nonlinear material characterization. They are (1) Z-scan Method, (2) Four Wave Mixing Method.

(1) Z-scan Method :

The z-scan measurement technique is used to measure the magnitude of the nonlinear refractive index n_2 of any material medium which shows Kerr nonlinearity. In this method, a material sample under investigation is scanned along a long focal length lens through the focus of a laser beam, and the beam intensity along the axis is measured at some point away from the focus as a function of the sample position (Z). For a given material sample, if the nonlinear refractive index is positive, and the material sample is placed before the focus (right side of the focus), the self-focusing property of the sample reduces the beam divergence and thus increases the intensity of detected signal passed through an aperture. If the sample is moved to the after the focus (left of the focus), the focus point moves towards the left, the sample increases the beam divergence after the focus and thus decreases the intensity of detected signal passed through an aperture. By measuring the deference between maximum intensity and minimum intensity detection, one can measure the magnitude of the nonlinear refractive index. Based on similar principle, one can measure the magnitude of the nonlinear refractive index of self-defocusing material sample.

The z-scan measurement technique also allows to measure the magnitude of nonlinear absorption β either through, two-photon absorption, excited state absorption, reverse saturation absorption, or due to thermal effect in the material sample. In this case, the material sample under investigation is scanned along a long focal length lens through the focus of a laser beam, and the beam intensity along the axis is measured at some point away from the focus as a function of the sample position (Z) by collecting entire output beam intensity by means of a collecting lens without using any aperture before detection stage. By measuring the difference between

normalized maximum transmitted intensity to minimum transmitted intensity in open aperture system, one can measure the magnitude of the nonlinear absorption coefficient of the material sample. The necessary condition in closed aperture Z-scan method is controlling the values of the normalized transmittance is between $0.1 < S < 0.5$.

With the development of the Z-scan method, accurate measurements of n_2 and β in a large number of materials in various spectral regions have been possible. The Z-scan has the advantage of easily providing the sign of the nonlinearity, an important factor for the comparison of experiment with the theory. The necessary condition in open aperture Z-scan method is controlling the values of the normalized transmittance $S = 1$.

Other methods used to determine n_2 and β in materials such as degenerate four-wave mixing (DFWM), for example, are sensitive to the square of nonlinear susceptibility ($|\chi^{(3)}|^2$) so that the nonlinear absorption and nonlinear refraction effects cannot be easily separated.

The measured transmittance of a nonlinear material sample through a finite aperture placed in the far field, as a function of the sample position Z measured with respect to the focal plane of the focusing lens using a single Gaussian laser beam in a tight focus geometry, shown in Fig. 1.1.

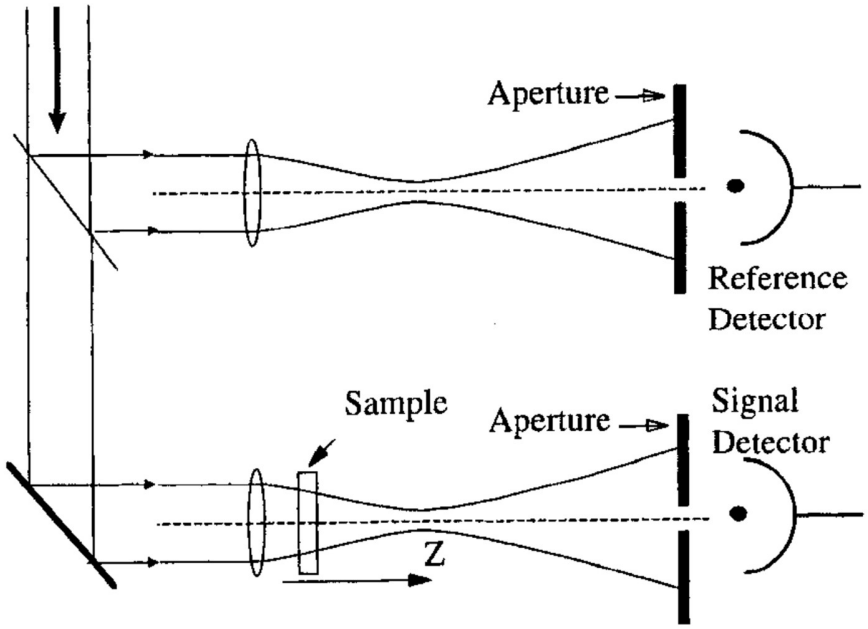

Fig. 1.1 : Experimental setup for Z-scan measurement [20]

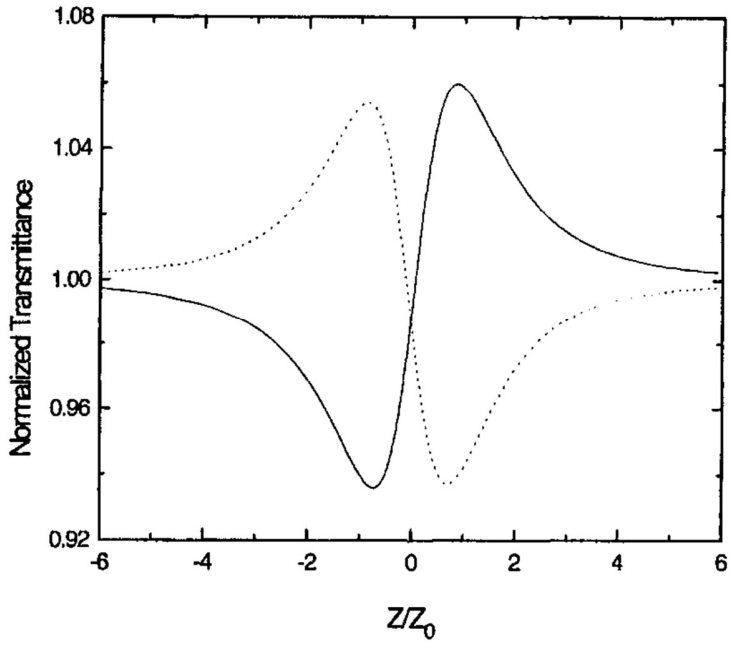

Fig. 1.2 : Z-scans (closed aperture) showing only nonlinear refraction for positive (solid line) and negative (dotted line) Δn [20].

As an example, consider a material medium with a positive nonlinear refractive index. While starting the scan from a position far away from the focus along the axis (negative Z) the beam intensity is low and week nonlinear refraction occurs hence, the transmittance remains relatively constant, and the normalized transmittance is unity as shown in Fig. 1.2. As the sample is brought closer to focus, the light beam intensity increases leading to self-focusing of beam in the sample. This positive nonlinear refraction moves the focal point closer to the lens leading to a larger divergence in the far field, thus reducing the transmittance. Moving the sample to behind focus (Z>0), the self-focusing helps to collimate the beam increasing the transmittance of the aperture. Scanning the sample farther toward the detector returns the normalized transmittance to unity. Thus, the valley followed by peak signal shown by the solid line in fig. 1.2 is indicative of positive nonlinear refraction, while a peak followed by valley shows self-defocusing shown by the dotted line in the fig. 1.2.

Advantages and Limitations of Z-scan Techniques :

Z-scan technique has many advantages, some of them are :

• **Experimental Simplicity:** The method does not need complicated set-up to carry out experiment except for keeping the light beam along the center of aperture.

• Simultaneous measurement of both sign and magnitude of third order nonlinearity.

• Data measurement and analysis is easy and quick except for some special conditions.

• The method allows to isolate the refractive and absorptive parts of nonlinearity unlike other methods including DFWM.

• The method is high sensitivity, capable of resolving a phase distortion of the beam provided the sample material has of high optical quality.

• Due to a close similarity between the Z-scan configuration and the Optical Power Limiting configuration.

However, Z-scan suffers some of the disadvantages which include :

• The requirement of high-quality Gaussian beams for absolute measurements.

• Different analysis methods should be used for non-Gaussian beams.

• Comparative measurements against standard samples allow relaxation on the quality of beam shape.

• Overestimation of parameters due to beam walk-off due to sample imperfections, tilt or distortions.

(2) Degenerate Four-Wave Mixing

Degenerate four-wave mixing (DFWM) is another method to determine the nonlinear susceptibility of a material medium [26]. One type of experimental set-up of this technique is given in Fig. 1.3 where the interference of the forward pump beam of intensity I_f and forward probe beam of intensity I_p generates a nonlinearity that is examined by the backward pump beam I_b as a function of its temporal delay. It is predicted that I_f and I_p generates a grating whose dynamics is investigated by I_b scattering off this grating into the detector shown in Fig. 1.3 referred to as the conjugate direction [27]. Figure 1.4 shows the result of such experiment carried out on ZnSe using 30 ps, 532 nm pulses [28].

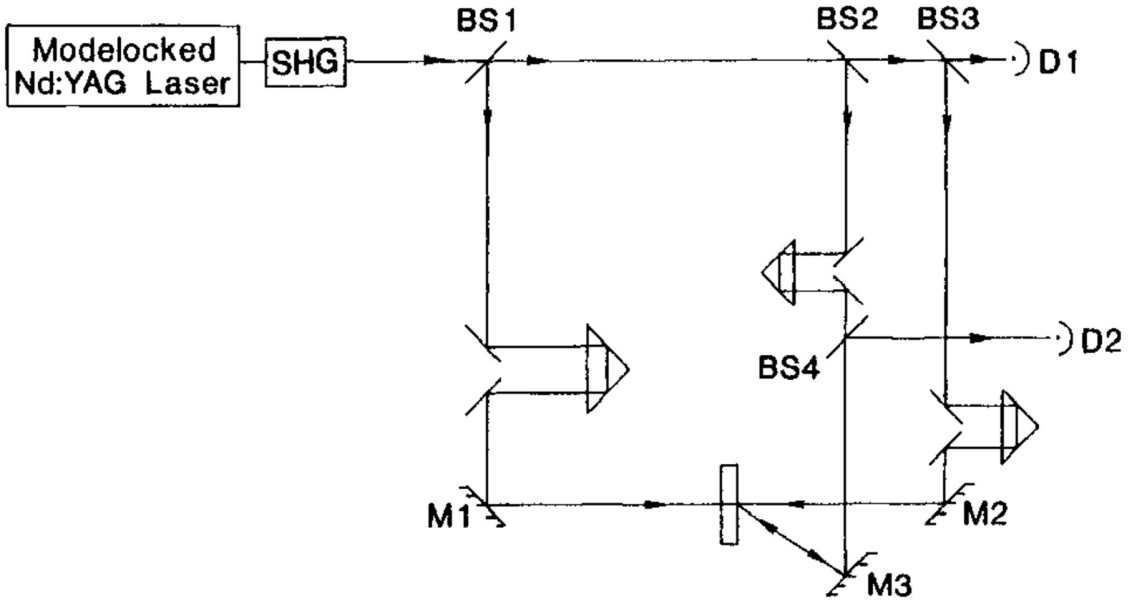

Fig. 1.3 : Experimental configuration for time-resolved DFWM [28].

This technique provides information on the nonlinear response of the sample medium both absorptive and refractive nonlinearities but it is difficult to separate into individual components.

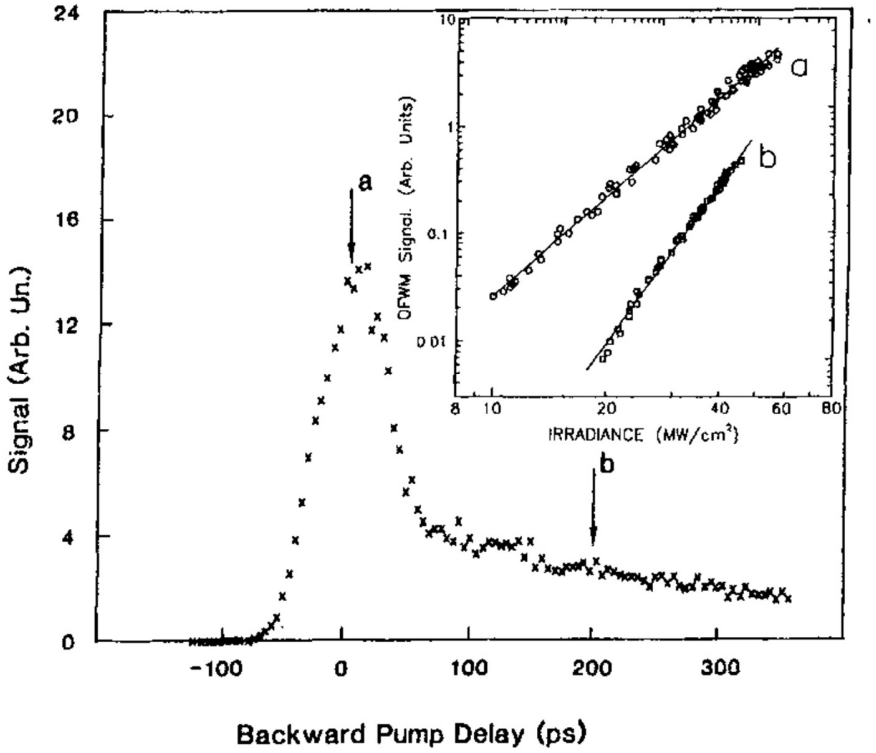

Fig. 1.4 : DFWM experiment performed on a sample of ZnSe at 532 nm. Ref. [28].

1.5 EXCITED-STATE NONLINEARITIES

In DFWM experiment, the observed nonlinear absorption and refraction induced by two-photon absorption generated carriers. Let the generation rate of these carriers of density N is given. The absorption from these carriers is referred to as free-carrier absorption (FCA), and the refraction as free carrier refraction (FCR), and both effects are linear in the carrier density. The rate of change of carrier density with time is related with two=photon absorption coefficient β as follows [28] :

$$\frac{dN}{dt} = \frac{\beta I^2}{2\hbar\omega} \quad \text{---------- (1.12)}$$

However, they are best described in terms of absorptive (σ_a) and refractive (σ_r) cross sections as

$$\left.\frac{dI}{dz}\right|_{FCA} = -\sigma_a N I$$

$$\left.\frac{d\phi}{dz}\right|_{FCR} = \sigma_r N \quad \text{---------- (1.13)}$$

The sign of σ_a is always positive while σ_r can have either positive or negative sign. In the case of low power laser beam incident, σ_r is always negative leading to self-defocusing. Once excited, these carriers can undergo a variety of processes including several types of recombination and diffusion. Combining the 3rd and 5th order responses in eq (1.13) gives,

$$\frac{d\phi}{dz} = kn_2 I + k\sigma_r N \quad \text{---------- (1.14)}$$

In the Z-scan experimental data, carrier recombination dominates the decay while in the DFWM experiment carrier diffusion between peaks and valleys of the grating dominates.

1.6 ALL-OPTICAL SWITCHING

All-optical switching is an important application of the optical nonlinearities discussed in above sections. The theory of nonlinear refractive index (n_2) and nonlinear absorption (β) allows direct determination of the ideal operating point or Q-point of a passive optical switch. For any candidate materials for optical switch, the designers have established a figure-of-merit (FOM) defined by the ratio $k_0 n_2/\beta$. The objective of good design is maximizing the FOM and for this a large nonlinear phase shift ($2\pi n/\lambda$) and a small two photon absorption loss (β) is required.

A typical procedure to determine FOM is shown in Fig. 1.5. In the figure, the absolute value of the FOM is shown as the solid line. The data shown in figure is the ratio of two experimental values, β and n2 for a candidate material [32-33].

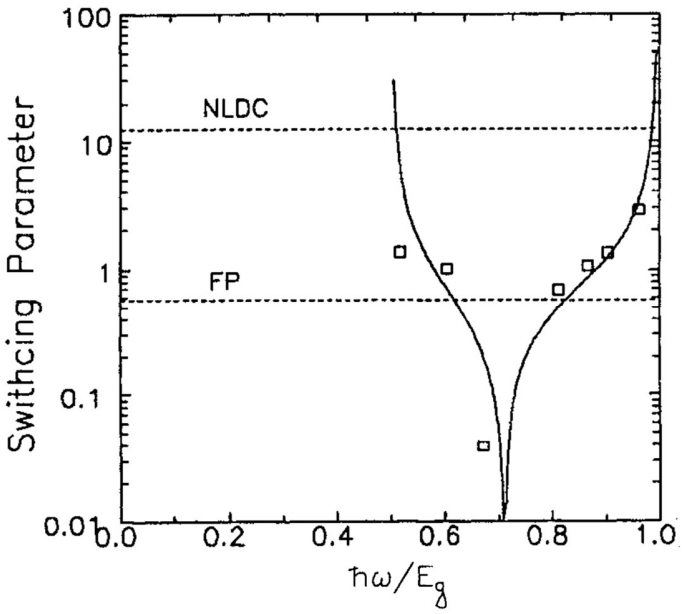

Fig. 1.5 : A typical figure of merit for passive all-optical switch [15].

All-optical switch is basic building block to realize optical computers. All-optical switch can be designed and realized by using the nonlinear optical effects of the materials. An all-optical switch is used to control light by light for optical processes in optical computation by using suitable nonlinear optical effects in the materials. The nonlinear optical effects are classified into two types namely direct effects and indirect effects. Direct effects are due to the atomic or molecular interactions in which the light changes the atomic susceptibility through variation in absorption rates of the medium. The examples for direct nonlinear optical effects are Kerr effect and saturation absorption. Indirect nonlinear effects are due to many intermediate processes takes place by interaction of light in which electric charges play a considerable role in deciding the nonlinear susceptibility. Examples for indirect nonlinear effects are photorefractive nonlinearity, nonlinearity in liquid crystals etc. There are many methods used to achieve all-optical switching devices. They are :

(1) One method of achieving optical switching is placing a Kerr medium (third order nonlinear medium by applying external electric field) on one leg of Mach-Zehnder interferometer so that when the control light is switched on and off the transmittance of the device is shifted between two states on (1state) and off (0 state) as shown in Fig. 1.6.

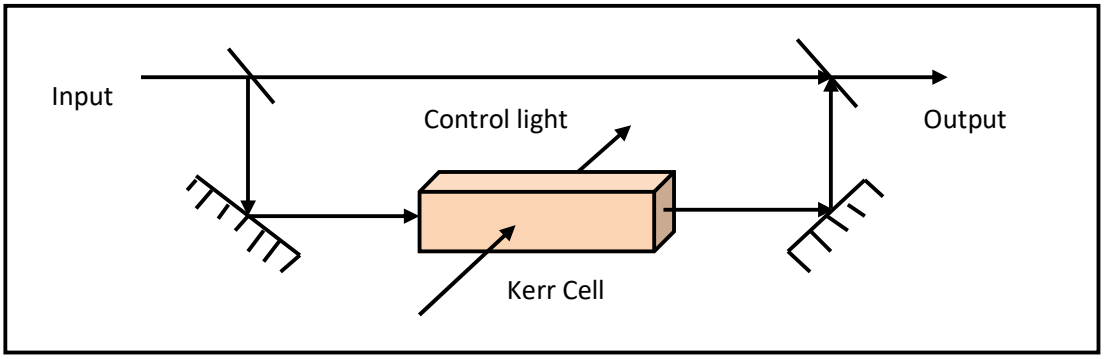

Fig. 1.6 : Block diagram of a Mach-Zehnder interferometer based all-optical switch.

(2) Another method of achieving all-optical switching is through retardation of light between two polarizations in an anisotropic nonlinear material by placing it between two crossed polarizers. (3) The third method of realizing all-optical switching is the use of an optically addressed liquid crystal spatial modulator where a controlling light beam changes the electrical field on the layer of liquid crystal and hence changes its reflectance. In all the above methods, organic materials with high value of nonlinearity are required as an active component for optical switching [34]. The speed of switching devices is determined by the response time of the material nonlinearity [35-37].

The optical switching phenomenon using third-order optical principle has advantages compared to Kerr effect. This is due to the reason that Kerr effect based on electro-optic effects requires charge separation in the medium and hence the switching speed is decided by the mobility of the carriers [36]. After 1980s, large third-order nonlinear optical responses in organic dyes, are discovered especially those possessing extended R-electron conjugation like cyanine dyes, porphyrins, carotenoids, and n-conjugated polymers which enhanced the opportunity to fabricate efficient all-optical switches [38-39].

1.7 OPTICAL LIMITING

Optical limiting is another important application of third order optical nonlinearity of materials. Nonlinear optical materials can be used for protecting sensors against high-intensity laser pulses and high-power laser beams. Devices developed for this purpose are called optical limiters. An optimum practical optical limiter can be designed and fabricated by predicting and studying the characteristics of an ideal optical limiter. An ideal optical limiter is a photonic device or component 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 input-out characteristics of an ideal optical limiter is shown in Fig. 1.7. It shows high linear transmission for low input power or energy and constant output power or energy for a large variable range of input above limiting input threshold power or energy so that such device can be also used for power or energy regulation. In practice, it is possible to realize ideal limiter characteristics at least above certain minimum input power or energy is possible using different nonlinear materials which show high nonlinear susceptibility, even though it is difficult to achieve both requirements of low limiting threshold and large constant output range simultaneously. In practice, to get high transmission at low input power or energy, the limiting material used should show low linear absorption. Based on the above discussion, we can list the characteristics of an optimum practical optical limiter as follows :

(1) Must possess high linear transmittance with wide transmission range.

(2) Should have low limiting threshold level (the input power/energy corresponding start of saturation).

(3) Should show fast response time (CW, nano to femto second signals).

(4) Should show broadband limiting response through the entire visible spectral region.

(5) Should have low light scattering inside the material medium.

Thus an optimum practical 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.

MODEL OF IDEAL OPTICAL LIMITER SYSTEM

Ideal optical limiter model is developed by considering various characteristics under 4 categories such as Input conditions, Systems requirements, Output conditions and Environmental conditions, and analyzed these characteristics with an objective to achieve the goal. An ideal

optical limiting system shall have characteristics which can be predicted and classified. Based on various factors which decide the ideal optical limiting system characteristics, a model consisting of the input conditions, output conditions, system requirements, and environmental conditions is developed by using focus group method [16-19]. The block diagram of such ideal optical limiting system and interconnection of various components is shown in figure 1.8. The ideal properties of a device can be used to improve the properties of the practical device with an objective to achieve 100% efficiency.

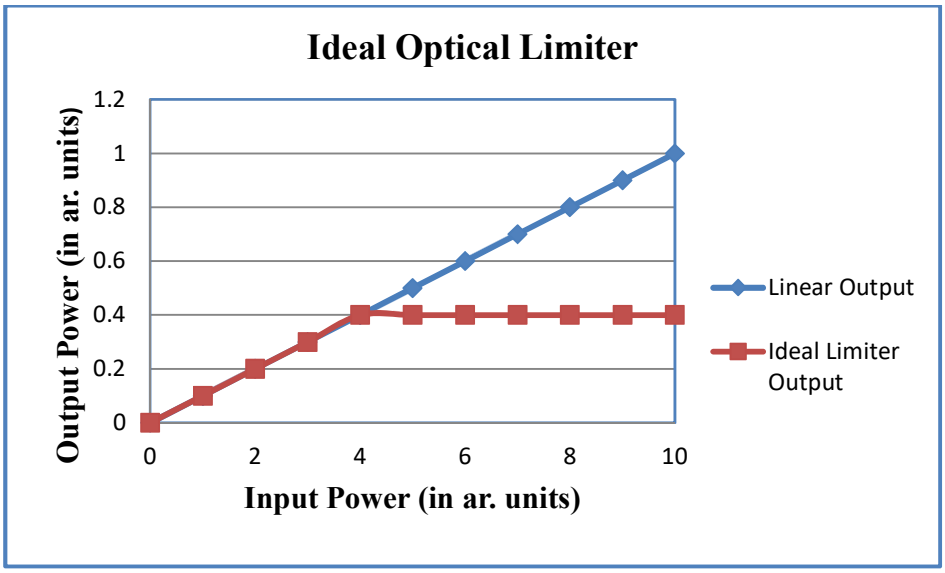

Fig. 1.7 : Input-output characteristics of an ideal optical limiter.

A. Input Conditions for Ideal Optical Limiter

(1) An ideal limiter device should capable of taking input light beam of any intensity without any material damage.

(2) An ideal limiter device should capable of accepting input light beam without any reflection or scattering from incident surface.

(3) Any variation in the input intensity or power between zero to infinity should maintain constant output intensity irrespective of input intensity variations.

(4) An ideal optical limiter device should capable of taking input light beam of any wavelength/frequency of entire electromagnetic spectrum.

(5) An ideal optical limiter device should capable of taking input light beam of continuous wave or of a pulsed wave of any time duration.

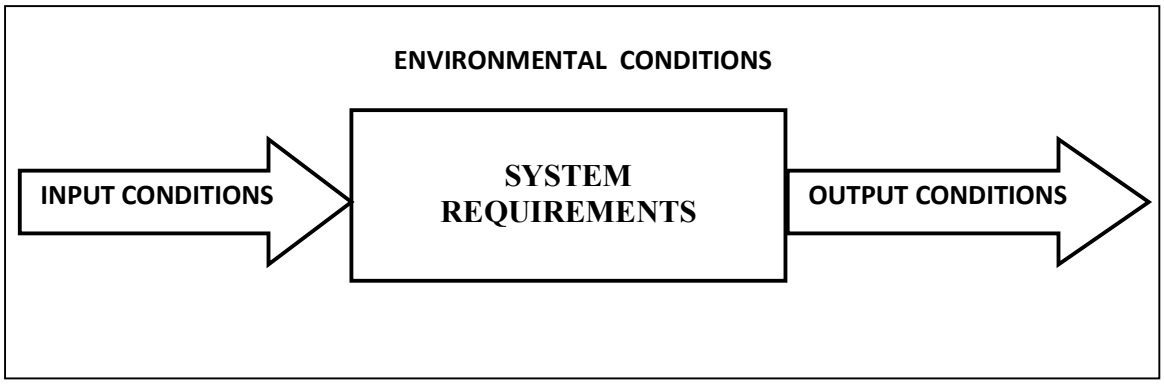

Fig. 1.8 : System model of Ideal optical limiter characteristics.

B. System Requirements

(1) An ideal optical limiter possesses high linear transmittance with wide transmission range throughout electro-magnetic spectral bandwidth. i.e., it should have infinite bandwidth.

(2) The transmission characteristics of an ideal limiter vary depending upon the incident intensity due to nonlinear properties of the active limiting material.

(3) The nonlinear material medium used for fabrication of ideal limiter should have very high nonlinearity for entire bandwidth.

(4) The nonlinear material medium used for fabrication of ideal limiter should limit any laser beam of any power of both CW and pulsed.

(5) The nonlinear material medium used for fabrication of ideal limiter should not degrade the quality of output beam.

(6) An ideal optical limiter should show immediate response time to CW, nano, pico, or femto second signals).

(7) An ideal optical limiter should have zero light scattering inside the nonlinear material medium and other optical components used.

(8) An ideal optical limiter may use any type of third harmonic nonlinearity including nonlinear absorption or nonlinear refraction and correspondingly either Type 1 or Type 2, or Type 3 optical limiting configurations.

(9) An ideal optical limiter is a simple and easily portable system.

(10) Depending on the application, the output threshold level (power/energy) of an ideal limiter should be controlled at any level between zero to infinity and the efficiency of the system is always 100%.

C. Output Conditions

(1) An ideal optical limiter shows linear transmission characteristics below a threshold level and fixes the output to a constant level above it.

(2) The output intensity/fluency of ideal optical limiter is independent on the wavelength and pulse duration of the laser beam.

(3) An ideal optical limiter should have low limiting threshold level (the input power/energy corresponding start of saturation at output).

(4) In the case of the ideal optical limiter, the output power/energy level is fixed at a constant value irrespective of variations in input power/energy between zero to infinity.

(5) An ideal optical limiter provides high-quality Gaussian output beam of constant amplitude irrespective of the quality of input laser beam.

(6) The ideal optical limiter system will be sustainable for a long time at desired output without any maintenance.

D. Environmental Conditions

(1) An ideal limiter should provide constant output for any environmental conditions like changes in temperature, pressure, and aging.

(2) An ideal limiter should provide constant output irrespective of its location in the photonic device, or its geographical location and the performance should same with time or replacement of material used for optical nonlinearity.

(3) An ideal limiter should be a low-cost device and the value it creates through its usage in photonics should far above than its cost.

(4) The Ideal optical limiter device operates in a low-cost environment. It does not need an expensive location, a huge amount of infrastructure and huge investment.

The above 25 characteristics are together constituting necessary conditions of an ideal optical limiter. The ultimate objective of any nonlinear materials research for optical limiters is to find a suitable material which can show optical limiter characteristics close to ideal optical limiter characteristics.

PRACTICAL OPTICAL LIMITERS :

To reach close to the above characteristics of an ideal limiter, the practical optical limiters can make use of nonlinear materials which show both nonlinear absorption and nonlinear refraction. For optimum nonlinear absorption, the nonlinear material can make use of two-photon

absorption property or reverse saturation absorption property and nonlinear refraction property simultaneously. Figure 1.9 shows the input-output characteristics of practical optical limiting with linear, active and saturation regions.

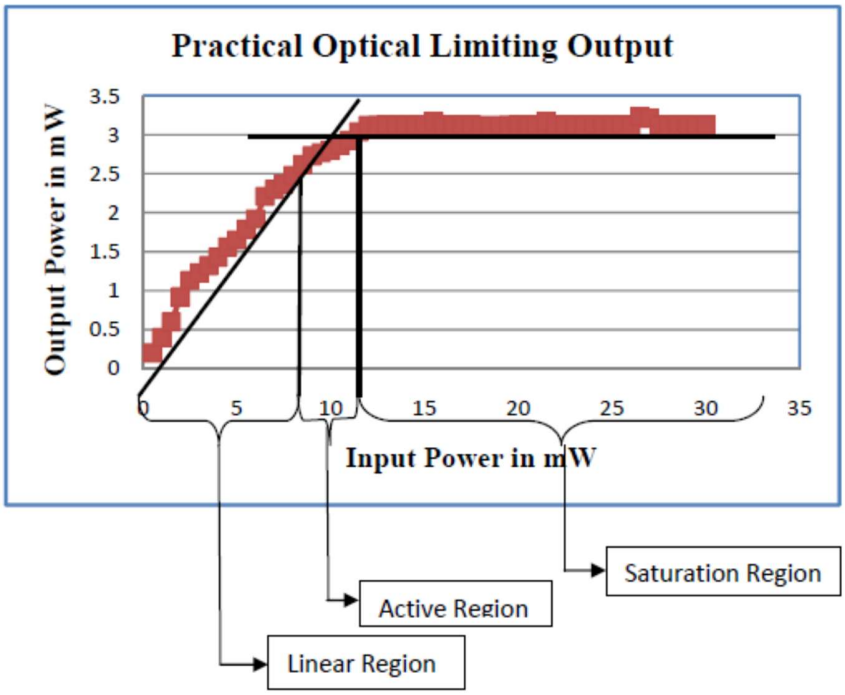

Fig. 1.9 : A Practical optical limiting behaviour with linear, active and saturation regions.

Organic materials are potential candidates for larger nonlinearities and are getting importance to be used as effective nonlinear absorbers by showing sometimes the combined effect of two-photon absorption and reverse saturation absorption in addition to effective nonlinear refraction through thermal nonlinearity [40-41]. Due to their high resultant third harmonic susceptibility, organic materials including dyes are considered to be suitable candidates for practical optimum optical limiters.

Types of Optical Limiters :

(1) Active & Passive Limiters :

Active optical limiters work based on induced scattering of the laser beam from the material medium, whereas passive optical limiters makes use of third harmonic optical property like nonlinear absorption or nonlinear refraction.

(2) Type 1, Type 2 & Type 3 Optical Limiters :

These are passive optical limiters and based on the position of nonlinear material on focus point, away from focus point towards the detector side, and away from focus point with respect to detection side are classified into Type 1, Type 2, and Type 3 optical limiting configurations respectively. Type 1 optical limiter make use of nonlinear absorption property of the limiting material, Type 2 optical limiter make use of nonlinear refractive defocusing property of the limiting material, and Type 3 optical limiter make use of nonlinear refractive focusing property of the limiting material.

(3) Tandem Optical Limiters :

These optical limiters make use of multiple nonlinear elements in the device geometry to make use of combined effect of these individual effects as well as to enhance the range of effective bandwidth.

(4) Reflective Optical limiters :

Reflective optical limiter blocks light beam with excessively high total energy by reflecting them back to space, instead of absorbing them so that the output energy remains constant.

(5) Energy Spreading types Optical limiters :

These limiting devices work using principles of self-focusing, self-de-focusing, induced scattering, induced refraction, or induced aberration.

(6) Energy Absorbing type Optical limiters :

These limiting devices work using principles of nonlinear absorption or optical bistability. Nonlinear absorption includes Two-Photon Absorption (TPA), Excited State Absorption (ESA), and Free-Carrier Absorption (FCA).

(7) Cascaded optical limiters :

By cascading many limiting elements in a single geometry, one can decrease the activating threshold and damage threshold while increasing the limiting bandwidth. The cascaded optical limiter shows a low activating threshold, a high optical damage threshold, and broadband limiting properties [42].

Optical Limiting Configurations :

(1) Type 1 Optical Limiting Configuration :

In this experimental setup, the nonlinear sample is placed in a fixed position at the focus of the Z-scan setup. The emergent beam from the nonlinear sample is collected to a photo detector by means of a collecting lens 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 configuration will make use only the nonlinear absorption property of the nonlinear sample. In this case, both self-focusing and self-defocusing materials can be used as nonlinear sample.

(2) Type 2 Optical Limiting Configuration :

This experimental setup is designed only for self-defocusing nonlinear materials used as nonlinear sample. The nonlinear sample is placed in a fixed position at the valley point of Z-scan plot of the Z-scan setup and an aperture of fixed hole size is used between the nonlinear sample and the collecting lens before measuring output intensity by photo detector. 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 for negative nonlinearity* or ***Type 2 optical limiting***. This type of optical limiting study will take care of nonlinear refraction property of the nonlinear sample.

(3) Type 3 Optical Limiting Configuration :

This experimental setup is designed only for self-focusing nonlinear materials used as nonlinear sample. The nonlinear sample is placed in a fixed position at the peak point of Z-scan plot of the Z-scan setup and an aperture of fixed hole size is used between the nonlinear sample and the collecting lens before measuring output intensity by photo detector. 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 for positive nonlinearity* or ***Type 3 optical limiting***. This type of optical limiting study will take care of nonlinear refraction property of the nonlinear sample.

As discussed in earlier sections many techniques are used to measure nonlinear refraction which includes Nonlinear interferometry, three-wave mixing, degenerate four-wave mixing (DFWM), beam distortion, nearly-degenerate ellipse rotation, beam deflection, and third-harmonic generation for direct or indirect measurement. Similarly, various techniques used to measure nonlinear absorption include transmittance, calorimetry, photoacoustic, and pump-probe methods. However, the Z-scan technique can be used for measuring both nonlinear absorption and nonlinear refraction simultaneously but separately.

1. 8 OPTICAL PHASE CONJUGATION

In optics, by using suitable nonlinear optical process, a time-reversed wave for an incident wave called phase-conjugate wave can be generated. This concept is proposed theoretically in the early 1970s by many researchers [43-45]. Thereafter, many techniques were developed to generate optical phase conjugated signal in practice using different nonlinear optical media. This includes degenerate four-wave mixing, three-wave mixing, scattering from saturated sources, stimulated Raman scattering, photon echoes, and stimulated Brillouin scattering.

Generating phase conjugated signal using DFWM is a comparatively new method with potential applications in several area of technology, science, and related fields including optical image transmission & processing, optical filtering, laser resonators, real-time holography, adaptive optics, optical interferometry, high resolution spectroscopy, laser fusion, laser-induced instabilities, wave propagation in the atmosphere, etc. [46 – 48]. In the degenerate four-wave mixing technique, two counter-propagating and intense light beams are made to interact with a nonlinear medium, together with a less intense third beam, results in a fourth beam generated from the nonlinear medium, which is found to be in phase conjugation with the third beam. One of the unique properties of the phase-conjugated beam is that the aberration noise generated on the forward beam propagating in material medium can be automatically nullified by the backward P.C. beam propagating in the same material medium [49]. The attractive uses of DFWM technique are generation of phase conjugation beam, real-time holography, and nonlinear spectroscopy. Phase conjugation by DFWM has been shown in many organic molecular materials including organic dyes, inorganic materials, composites, nanomarerials etc. using continuous-wave (CW) or pulsed lasers [50, 51].

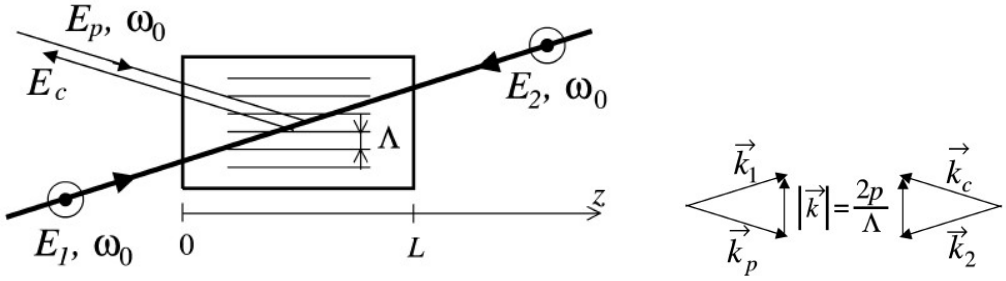

Fig. 1. 10 : Geometry of degenerate four-wave mixing interaction to generate a phase conjugate wavefront [43].

Generation of optical phase conjugation beam using four-wave mixing is a third-order nonlinear process and as the name implies, four waves interact in a given nonlinear optical medium as identified below :

(1) The forward pump beam with an amplitude E_1
(2) The backward pump beam with an amplitude E_2
(3) The probe beam with an amplitude Ep
(4) The conjugate beam denoted as C with amplitude Ec, resulting from the interactions of other three beams.

The geometrical model of phase conjugation system consists of two counter-propagating light waves called the forward pump beam and backward pump beam having amplitudes E_1 and E_2 interact with a third light beam called probe beam of amplitude E_p then with certain conditions nonlinear material medium gives rise to the fourth beam called conjugated beam which is in phase with pump beam. In this geometry, it is necessary that all the light beams should be comparable in terms of their polarization state, and the inter-beam angle between the pump beam and probe beam and the probe beam on recording medium with third-order nonlinear susceptibility is called inter-beam angle θ as shown in figure 1.10 [52-53].

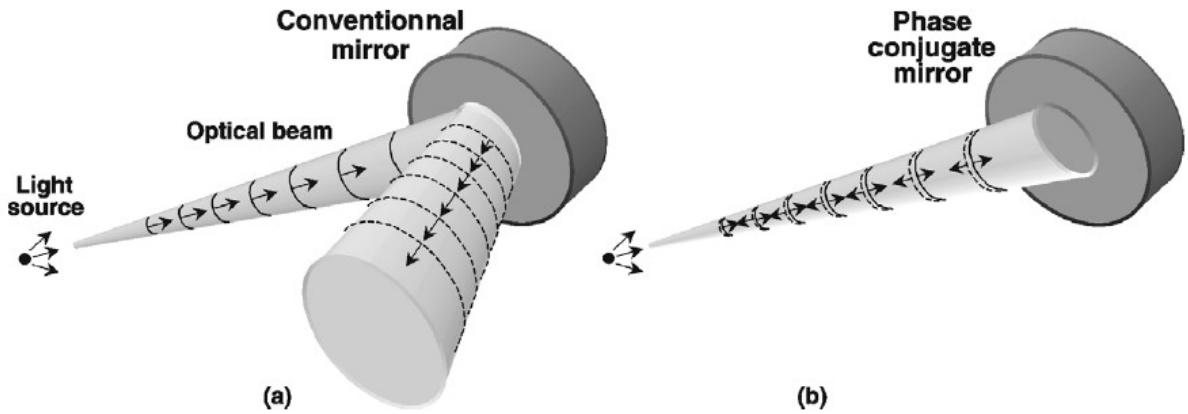

Fig. 1.11 : An example of beam reflection by (a) a conventional mirror and (b) a phase conjugate mirror [54].

It is observed that the phase conjugated beam has both phase and propagation direction exactly reverse of the probe beam. This is demonstrated in fig. 1.11 where the first part (a) shows the reflection by a regular mirror where the angle of incident is equal to the angle of reflection. In

the second part (b) the direction of phase conjugated wave reflection direction is shown which traces the original incident path in reverse direction.

Properties of Optical Phase Conjugate Waves :

The phase conjugate light shows a number of properties not seen in normal light as listed below [73] :

(1) Phase compensation property

If the PC waves are passed to a phase conjugate mirror, the reflected wave is re-propagated through the medium then phase distortion of the wave is compensated.

(2) Multiple waves interaction through Space domain

When two or more laser light beams are used in the generation of P.C. light the resultant polarization and hence the interaction of their intensity is proportional to the product of these interacting light waves in their temporal domains.

(3) Intensity-dependent phase shift property

In a nonlinear medium, due to the optical Kerr effect, the phase shift of the electric field vectors of P.C. beam depends on the instantaneous wave intensity.

(4) Inversion of Time property

The P.C. light beam can be considered as a time inverted light beam due to the reason that the direction of propagation of the P.C. beam is exactly opposite direction to the probe beam and the wave-front of the P.C. beam is identical to the wave-front of the probe beam.

(5) Dependence on frequencies property

The reflectance of a P.C. mirror is proportional to the detuning between the probe beam and pump beam frequencies.

(6) Interaction of Multiple waves

When two or more laser light beams are used in the generation of P.C. light the resultant polarization and hence the interaction of their intensity is proportional to the product of these interacting light waves in their temporal domains.

(7) Photon correlation nature

While quantum mechanical analysis is used to correlate the forward and backward waves theoretically, the interacting P.C. waves and probe are regarded respectively as the photon creation and annihilation operators.

Many organic molecules show large polarizabilities using their delocalized π-bond electrons for external intense light beam [55]. Such systems exhibit large third-order susceptibilities which may give rise to saturation absorption of laser beams. The saturable absorption property of organic dyes plays a very important role when used for the production of phase conjugation light because χ^3 is inversely proportional to the saturation intensity [56]. OPC has been reported in many organic dyes which are doped in glasses and other solid matrices like polymers and hence such doped matrices are emerged as promising materials for optical phase conjugation generation. One of the advantages of organic dye-doped materials is that the phase-conjugate wave can be generated at low light intensities obtained by the continuous-wave lasers. However, these materials can be easily prepared in the laboratories [57-58]. The following nonlinear processes like nonlinear refraction, thermal grating, Saturation and Reverse Saturation absorption, two-photon induced fluorescence, photorefraction, and stimulated Brillouin scattering lead to the formation of a laser-induced grating in the medium are associated with the generation of phase conjugated wave.

(a) Nonlinear Refraction :

In nonlinear refraction, the refractive index of the material varies with the intensity of light used. Materials with positive nonlinear refractive index show self-focusing and materials with negative nonlinear refractive index give rise to self-defocusing. For a purely third order response with input irradiance I_0,

$$\Delta n = n_2 I_0 \quad \text{----------} \quad (1.15)$$

where n_2 is nonlinear refractive index and n_2 is positive for self-focusing materials and n_2 is negative for self-defocusing materials. The nonlinear optical properties of materials range from the index change due to the high speed interaction of light with bound electrons of the materials to the index change caused by the relatively slow thermal expansion of a liquid due to linear absorption. The effects caused by these nonlinear interactions with matter range from the reduction of transmittance from increasing absorption with increasing irradiance (e.g. two-photon absorption) to beam spreading from self-defocusing to the ultimate nonlinear interaction of laser-induced damage.

(b) Thermal Gratings :

When the irradiated light beam passes through a nonlinear medium, the temperature of the material at illuminated regions increases due to the thermal effect on the medium and hence the refractive index decreases [62]. Such change in refractive index along the path of light beam depends on the change in the intensity of the propagating light beam and results in self-diffraction effects in liquids or solids leads to phase conjugate beam generation. Using heat equations one can prove that the steady-state refractive index modulation varies as the square of the grating period and is inversely proportional to the thermal conductivity of the material. For small grating periods, thermal diffusion tends to decrease both the modulation of the photoinduced refractive index and the diffraction efficiency of thermal holograms. Thus, thermal nonlinearities of organic dyes doped in polymer matrix will support using small pump-probe beam angle or a longer wavelength for four-wave mixing experiments [63-65].

(c) Saturation and Reverse Saturation Absorption :

Nonlinear absorption in dyes can be of two types as saturation absorption and reverse saturation absorption. Depending on the intensity of pump beam and on the absorption cross section of the dye material at the excitation wavelength, most molecules show nonlinear absorption. By increasing intensity, if the excited states show saturation of absorption owing to their long lifetimes, the transmission of light in dye will show saturation absorption characteristics. Saturation absorption is believed to be an effective mechanism for efficient phase conjugation. If, however, in such nonlinear material medium, the excited state has strong absorption compared with that of the ground state, then the transmission of light in dye will show reverse saturation absorption characteristics. The absorption characteristics of the nonlinear materials are highly dependent on the wavelength, intensity, and excited-state lifetime. The availability of intense light sources made it possible to understand the absorption characteristics of the dyes as material medium [66]. Reverse saturation absorption appears as a result of excited-state absorption, two-photon absorption or both.

(d) Two photon Induced Florescence :

Some of the organic and inorganic nonlinear materials are capable of absorbing two photons simultaneously to go to excited state and from there they relax to ground state by means of

emitting the difference in energy in the form of fluorescence. Using the basic theory of two photon absorption, one can write the expression for decreased transmitted intensity as

$$I(L) = \frac{I_0}{(1+ I_0 L\beta)} \qquad \text{--------} \quad (1.16)$$

where I_0 is the incident beam intensity, L is the thickness of the sample, and β is the two-photon absorption coefficient of the nonlinear medium. Using the intensity equation (1.16), the value of β can be measured by determining the ratio of transmitted intensity with the input incident intensity for a nonlinear medium with a given length L. Furthermore, the TPA coefficient β (in units of cm/GW) of a given sample is determined by

$$\beta = \sigma_2 N_o = \sigma_2 N_A d_o \times 10^{-3.} \qquad \text{----------} \quad (1.17)$$

Here, N_o is the molecular density of the dopant (in units of 1 cm^3), σ_2 is the molecular TPA coefficient (or cross-section) of the same dopant (in units of cm^4 /GW), d_o is the concentration of the dopant compound in the matrix (in units of M), and finally N_A is Avogadro's number. For known values of β and d_o, the value of σ_2 can be calculated from Equation (1.17).

(e) Photorefraction :

Photorefraction is a kind of nonlinearity exhibited by certain type of materials which generally shows linear or quadratic electro-optic properties. Photorefraction is observed when the material is illuminated by a two-beam interference pattern which generates a photoinduced charge distribution. This allows trapping of photo-generated carriers (electrons or holes) and gives rise to a space-charge field in the volume of the material which modulates the refractive index through the electro-optics coefficient. Photorefractive materials have a dark storage time constant, equivalent to memory effect [71–72]. Photorefractive materials have demonstrated their importance in experiments based on the recording and erasure of holograms for high-gain wave mixing, optical information processing, and phase conjugation with low-power visible or near-infrared laser beams. Most of the experiments were performed with different types of Electro-Optical (EO) materials such as $LiNbO_3$, $BaTiO_3$, and $Bi_{12}(Si,Ge,Ti)O_{20}$, semiconductors such as GaAs, InP, and CdTe, PLZT ceramics, doped EO polymers, and liquid crystals [73].

(f) Stimulated Brillouin Scattering

The origin of this effect is from the electrostrictive effect generated by the transparent dielectric media such as liquids, gases or solids. The incident and spontaneous scattered optical fields in the material creates an interference patterns in the form of traveling acoustic wave that modulates the material refractive index through the elasto-optic effect. Stimulated Brillouin Scattering is a phenomenon that exhibits a threshold, and its typical response time in nanoseconds due to the phonon lifetime. Stimulated Brillouin Scattering is studied in many materials which include, high-pressure gases like N_2, SF_6, Xe, etc., liquids like CCl_4, CS_2, $SiCl_4$, $TiCl_4$, acetone, etc., or solids like quartz, silica fibers or bulk, some organic crystals etc. [73].

Applications of Optical Phase Conjugation Techniques

As per G. S. He [74], Optical Phase Conjugation techniques require certain attributes like (i) the simplicity and compactness of optical experimental arrangements, (ii) low input power laser beam as pump beam, (iii) high conversion efficiency from the input pump beam to the output phase-conjugate beam, (iv) fast time response of the nonlinear material medium, and (v) high wave-front restoration fidelity for the phase-conjugate beam.

Optical Phase Conjugation is considered as a tool to identify the nonlinear optical properties of any given material and to study various physical processes happening in such materials during the irradiation of strong coherent laser beam. Based on their wavefront-reconstruction ability or phase-distortion compensation capability, the Optical Phase Conjugation techniques are useful and attractive for many applications in photonics [75 - 83]. Some of the applications of Optical Phase Conjugation techniques are [74] :

(1) Phase-conjugate reflector based laser oscillator

(2) Laser amplifier devices with a phase-conjugate reflector.

(3) Auto-focusing devices and laser-based target-finding systems.

(4) Laser directed weapons for military.

(5) Identification and rescue systems based on lasers.

(6) Optical amplifier and oscillator systems using Stimulated Brillouin Scattering Mirror.

(7) Nonlinear spectroscopy based on optical phase conjugation to find the energy state structure, spectral width, and population relaxation of materials.

(8) Optical phase-locking based on phase conjugation.

(9) Optical interferometry based on phase conjugation.

(10) Optical data processing using optical phase conjugation.

(11) Devices based on optical phase conjugation for fiber-optic communication systems.

(12) Optical signal frequency filters based on phase conjugation.

(13) Phase conjugation based optical pulse compression.

(14) Laser Fusion Experiments using Phase conjugation.

1.9 CHEMISTRY OF NONLINEAR OPTICAL MATERIALS

Many varieties of inorganic nonlinear optical materials are identified which can show optical nonlinearity for a different range of wavelengths, laser damage thresholds, and other optical properties [85-86]. Further, there exists an enhanced research focus to invent nonlinear materials which satisfy all necessary device requirements such as faster nonlinear response, high laser damage threshold for both CW and pulsed laser input beam, and wide transparency range coupled with adaptability, processing ability, higher efficiency, and the possibility to interface with other materials. Currently, an increased demand for wide bandwidth fiber optic networks and high-speed optical computing infrastructure are expected to boost the requirements for nonlinear optical materials.

Parallelly, from 1980 onwards the organic nonlinear optical material research got accelerated due to the announcement of many organic molecular materials with substantial nonlinear optical properties. Since then the research studies have focused on finding suitable organic compounds which show excellent nonlinear optical properties through their delocalized conjugated electrons for high nonlinear susceptibility and high-speed switching responsiveness due to the high electrons mobility. Based on further developments in researching organic systems for enhanced nonlinearities and other material related benefits, the 21st Century is considered to be an age of photonics with organic molecules as a building block of photonic systems.

Currently, though inorganic materials are still used for many devices of in the field of materials chemistry, interest in organic materials for using in photonic devices are growing continuously in view of their adaptability to various types of applications. The area of organic molecular materials provides potential opportunities to materials researchers to design customized materials whose characteristics can be tailored t0 the macroscopic and /microscopic level to be modeled or actual behavior of individual molecules [87 – 89]. From the device frame of reference, the nonlinear optical materials are preferred to be in solid forms and must possess some physical characteristics such as hardness and stability for practical use. They should also meet various

processing requirements such as for pattern or shape definition and integration with additional dissimilar materials.

Molecular materials consist of chemically bonded molecular units that interact in the bulk material through weak Vander Wall forces interactions. Examples of this class of materials are many organic crystals and polymers. For such materials, the optical nonlinearity is mainly derived from the molecular structure. The nonlinear efficiency of these materials is highly dependent on the geometrical structural arrangements of the molecules in the condensed medium in the case of second-order nonlinear process, but much less for the third-order nonlinear process. Thus, the molecular structure modifications is the primary step in optimizing optical nonlinearities in this class of materials, which requires a detailed understanding of the relationship between molecular electronic structure in molecular materials and the nonlinear polarization that can be induced in a molecule [90, 91].

The nonlinearities in the case of bulk materials are thought of as arising from electrons not associated with individual nuclei, such as those in metals and semiconductors. The optical nonlinearity in this class is determined by the electronic characteristics of the bulk medium and thus requires different theoretical frameworks to account for the origins of nonlinear optical effects. Examples of these category materials are quantum well structures derived from GaAs and II-IV semiconductors such as CdSe. Inorganic crystals such as potassium dihydrogen phosphate (KDP), Potassium titanyl phosphate (KTP), $LiNbO_3$, BaB_2O_4, SrB_2O_4 etc are also regarded as bulk materials because no single molecular unit in the ionic lattice can be identified. However, in these systems, the nonlinear responses are related to individual bond polarizabilities. The first crystal used for second harmonic generation (SHG) experiment in 1961 was quartz [92]. Because of phase matching property and large conversion efficiency, ADP and then KDP replaced quartz [93-94]. During 1965, the first major advance in the development of nonlinear materials came with the announcement of the properties of $LiNbO_3$ [95], which became interesting due to its nonhygroscopic and easy polishable nature. For a short period, it looked as almost an ideal material for NLO in visible and near IR regions [96]. However, when really good quality crystals became available, it was discovered that the crystals suffer from hitherto unknown damage effect [97]. Following lithium niobate, a host of related ferroelectric niobate crystals were grown and studied. Thereafter, a number of inorganic materials were grown in the form of crystals for SHG applications. These include rubidium hydrogen arsenate,

ammonium dihydrogen arsenate, lithium iodate, beryllium sulphate, some formates, some borates like barium meta borate, lithium triborate, KTP, rubidium titanyl phosphate, potassium titanyl arsenate, GaAs etc. A survey on inorganic NLO crystals studied till 1990 is reported by Dmitriev et al [98] and Nikogosyan [99].

The advantages of organic nonlinear materials over classical inorganic nonlinear materials are summarized below :

(1) Organic structures can be grown into large crystals, their crystalline layers fabricated into structures that can be deposited into thin films, layer by layer as in- the Langmuir - Blodgett technique, or incorporated into polymers for deposition and processing as highly oriented thin film structures. The resulting structure can exhibit optimized orientations for many types of nonlinear behaviors especially those of interest for waveguide formats.

(2) Many organic materials especially high-performance polymers have high mechanical strength as well as excellent environmental and thermal stability. Recent developments have produced materials with thermal stabilities in excess of 350°C. In contrast to misconceptions about the fragility of organic materials, the optical damage threshold for polymeric materials can easily be greater than 10^8 Hz/cm^2 with pico and nanosecond pulses. In contrast, multiple - quantum well structures derived from BaAs will undergo optical damage at power densities many order of magnitude lower.

(3) The dielectric constants of organic crystals are considerably lower than those of inorganic crystals. This feature has important implications for electro-optic devices in which a low-frequency AC field is used to modulate the refractive index. The low dielectric constant yields a low RC time constant, thus permitting a large operating bandwidth < (10^8 Hz) modulation. Furthermore, for organic materials, the dielectric constants at low frequency are comparable to those at optical frequencies, which lead to minimization of phase mismatch between electrical and optical pulses in high speed traveling wave photonic devices.

(4) Because of their unique chemical structures (π - bonding), organic molecular materials exhibit the largest nonresonant (non-absorptive) optical nonlinearities. For many device applications, such as in all - optical signal processing, the nonlinear optical response time is an important consideration. But a nonresonant electronic optical nonlinearity, in organic materials by its nature, would have the fastest response time limited only by the width of the driving laser

pulse. For inorganic systems, the higher nonlinear optical effects are resonant (absorptive). Thus, heat dissipation tends to limit the response time of devices derived from these materials. Other disadvantages of inorganic materials associated with resonant optical nonlinearities are beam depletion due to absorption and thermal damage. Further complications arise from thermally induced nonlinearities associated with refractive index changes, which often can dominate the intrinsic electronic optical nonlinearity.

The approach towards material optimization in the field of organics runs surprisingly parallel with that of inorganic materials. Molecular features responsible for the enhancement of three-photon effects were initially identified after scanning a large number of organic compounds [100 -102] using the SHG powder test [103]. It has helped to show the basic features of nonlinear molecules namely (1) the presence of highly conjugated and polarizable electronic molecules or systems, either linear, cyclic, or a combination of both, and (2) the occurrence of intermolecular charge transfer, which could be modulated by a suitable choice of donor and acceptor substituents. Moreover, one can in a similar way adjust the transparency of the system.

Certain classes of organic molecules have been identified for their interest in NLO such as (1) disubstituted aromatic molecules : exemplified by meta-dinitro benzene (m-DNB), meta-bromonitro benzene (m-BNB), and nitroaniline derivatives like m-NA, p-NA, MAP, NPP and NPAN ; (2) Pyridine family: POM ; (3) Stilbene family: AMA [104]. Some of other potential organic materials reported recently are 2-methoxy-nitro phenol [105], p-toluene sulphonate [106], CMHB [107], MBANP [108], MNA [109], sulfonyl group compounds [110], organometallic compounds [111], organic polymers [112], 5-nitro-uracil [113], APDA [114], indole-3-aldehyde [115], LNNL [116], DAD [117] etc. Even though the polymers became interesting candidates in second order NLO active materials, the general problem in NLO active polymeric system is the decay of orientational order with time. Miyata et al [118], Fainman et al [119], Zang et al [120], Bailey et al [121], Ledonx et al [122] and Shu Shi [123] have reviewed the use of different types of organic materials in optoelectronics and photonic devices.

The two approaches are followed to enhance the nonlinear properties of a system are (1) increasing the third-order nonlinearity of the material by enhancing local field effects [124] and (2) tailoring the molecules for excited states absorption [125–126]. The first approach can be used to design and structure the nonlinear medium to get higher effective nonlinearity than that offered by a bulk sample of the same material. The second approach of increasing nonlinearity

by adding excited states to the material is difficult. Though the present best practice in Photonics technology is the usage of organic materials/dyes that exhibit exceptional nonlinear optical properties, some of the 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. To minimize these limitations and for effective use of highly nonlinear dyes, the strategic idea for the next practice is doping the dye molecules in the polymer matrix. The idea of dye doping in polymer material may increase the concentration of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability [127] and used in this thesis work as a motivator.

Other materials recently considered for the use of their third-order nonlinear optical properties incorporate π-electron rich structures not necessarily of polymeric nature. An example for such a structure is buckminsterfullerene, C^{60} [128–130] which has a reasonably high third-order nonlinearity by itself and also influences properties of other nonlinear materials. Porphyrin and phthalocyanine structures [131-132] and dyes such as squaraines [133–135] continue to receive the attention of researchers. A research publication on third-harmonic generation in squaraines [135] brings an interesting discussion of the excited states contributing to the nonlinearity of squaraine and endeavours to predict the complex degenerate nonlinearity $x^{(3)}$ as a function of frequency. The nonlinear optical properties of certain films of polymers are found to depend strongly on the way the material is prepared. It is also estimated that the two-photon merit factor should be less than unity for the good nonlinear materials. From above discussion, it is understood that organic molecular materials and polymeric system have emerged in recent years as a new class of promising nonlinear optical materials compared to their inorganic counterparts [136 -152]. Many books have been published during last four years in the field of theory and experiments on Nonlinear Optical Phenomena, Materials, and Devices which explains the importance of research in nonlinear optical materials for Photonic Applications [153- 160].

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CHAPTER TWO

Literature Survey on Nonlinear Optical Materials

CONTENTS **PAGE No.**

2.1 INTRODUCTION

Basically, all materials exhibit nonlinear optical phenomena. This includes all forms of matter – gases, liquids, and solids. The power of the optical fields required to observe these effects varies over many orders of magnitude, depending on the detailed nature of the electronic structure of the atomic and molecular arrangements of the medium, their dynamical behavior, as well as the symmetry and details of their geometrical arrangement in the medium. The important nonlinear optical materials from the device point of view are generally in solid formats and must meet a wide variety of ancillary material requirements for practical use. In general, they require extraordinary stability with respect to ambient conditions and high intensity light sources. They will have to meet many processing requirements for device pattern, and integration with additional dissimilar materials. Some of the affecting mechanisms studied to explain the optical power limiting effect in materials are identified as reverse saturation absorption, multi-photon absorption, photo-refractivity (due to beam fanning), linear and nonlinear scattering, self-focusing and defocusing, free carrier absorption, intermolecular charge transfer absorption, photo-chromics, and liquid crystal fibre arrays.

Several conferences have been held on this topic of optical power limiting and their proceedings have been published [161-162]. There have been reviews by Tutt and Boggess [163], Perry [164] and Van Stryland et. al. [165]. The various requirements for an effective optical power limiter have been outlined by Justus et al [166], Miles [167], and Miller et. al [168], as given below :

(1) A reduction of laser fluence (energy per area) by a factor of 10^4 to 10^5. This is a big order to fill. ANSI standard prescribe a maximum fluence of 0.5 $\mu J/cm^2$ for laser pulses shorter than 17μs. This reduction in fluence has not been demonstrated with any material till date.

(2) For eye protection, we need a broad spectral range of response, that is we need to protect from 400nm to 700 nm device at low light intensity levels. High transmission of 50% to 70%, for any limiting is also required.

(3) A fast temporal response and rapid recovery time is needed.

(4) High threshold for optical damage and recovery is needed.

(5) A solid based device with a large index change is much preferred over any liquid based device.

These are difficult conditions to be met, but this survey is limited to visible range. In general, the nonlinear absorption is associated with the decrease of the intensity, I, of high beam travelling

through a nonlinear medium in the z-direction, which can be described by the following equation:

$\delta I/\delta z = -\alpha I - \beta I^2 - \gamma I^3 - \ldots\ldots\ldots$ (2.1)

Where α, β, and γ are the linear absorption coefficient, two-photon absorption coefficient, and three-photon absorption coefficient respectively. Higher terms in equation (2.1) can also contribute through higher order photon absorption, but usually are insignificant.

Reverse Saturation Absorption :

In the late 1960's Giuliano and Hess [169], were looking for better saturation absorbers for Q switching a laser. Under high intensity the ground state to first excited state transition is saturated and no longer absorbs, opening a way for high pulse of radiation to be emitted from the laser cavity. Although they found many compounds for saturation absorption, they found at least one compound, platinum dithizonate, which exhibited both positive and negative saturation effects [170]. It is also found that the optical transmission as a function of incident power density goes through a maximum and decreases at higher power densities. The effect is very pronounced and should be useful in laser applications i.e., in passive power limiting devices. Historically this is one of the first references to Reverse Saturation Absorption (RSA).

In 1935 Jablonski [171] was the first researcher to draw a schematic energy diagram for dye molecules as shown in Figure 2.1. For good RSA behavior, the transition probability for the first excited state to high states must be significantly higher than the absorption probability from the ground singlet state to the first excited singlet state. This ratio (σ_2/σ_1) of the two absorption probabilities should be greater than 30 for good RSA process. Approximate values for the relaxation of the first excited state to the ground state is of the order of 10 ns, while intersystem crossing to the triplet state can be slower at least one order of magnitude. On the other hand, relaxation times from the second excited state to the first excited state can be in the picosecond range, a very much faster process. For an efficient RSA process both the excited state absorption in the singlet manifold and the absorption from the lowest triplet state are required. Usually if $\sigma_2 >> \sigma_1$ the RSA process is dominated by a multiphoton absorption mechanism.

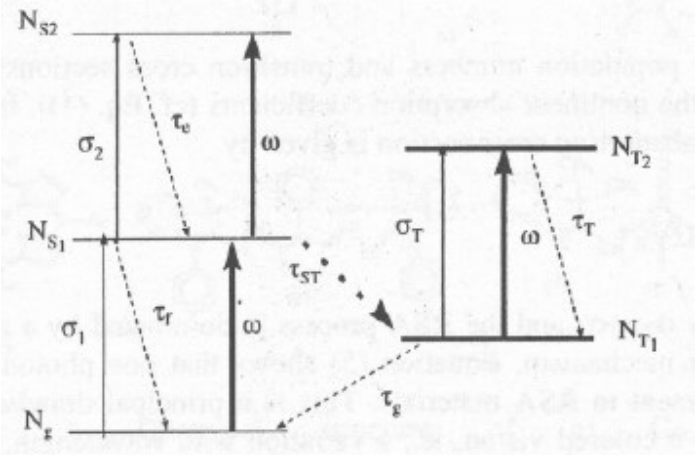

Fig. 2.1 : Schematic representation of RSA Process.

Two and Multi Photon Absorption :

Two-photon absorption is another effective and impressive way to realize optical limiting. The possibility of a simultaneous absorption of two photons is assumed theoretically during the beginning of the twentieth century by Maria Goppert [172]. According to Maria Goppert, the excited levels of a centrosymmetric molecule can be classified into gerade and ungerade levels which are differing each other in terms of their total angular momentum quantum number by an integral multiple of an odd number. Since photons bear a spin of 1, the illuminated light induces only allowed transitions between states of opposite symmetry (gerade to ungerade or opposite). But, by illuminating any even number of photons it is possible to excite electrons between states of the same symmetry. In such cases the transition involving the lowest number of photons called a two-photon transition, which is a simultaneous absorption of two photons.

The first transition is to a virtual state, followed by excitation to a final state with symmetry like that of the ground state (Fig. 2.2). The states accessible by absorption of two (or any even number) photons from the ground or any other state are called two-photon states. The interesting thing here is that the transitions to a two-photon state are forbidden for one (or any odd number of photons) photon. As a result, the molecule is transparent for photon energies corresponding to the transition energy between fundamental and the two-photon state. In noncentrosymmetric molecules, such as charge transfer molecules, due to the presence of a permanent electric dipole, the selection rules are relaxed and two-photon transitions are possible between all states. In such case, the molecule absorbs light for photon energies corresponding to the transition energy

between the fundamental and the two-photon state, however, it corresponds to half of the two-photon excitation transition energy. Thus, these materials are similar to centrosymmetric materials, that is, the molecules are mainly transparent and do not show any absorption when excited by two photons.

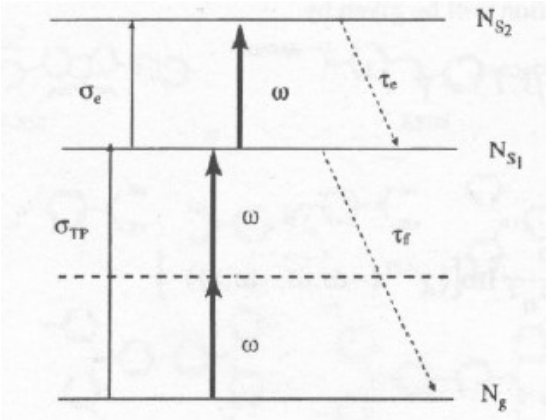

Fig. 2.2 : Schematic representation of a two and three photon absorption process.

2.2 ORGANIC NONLINEAR OPTICAL MATERIALS RESEARCH

The requirement for nonlinear materials to be used with low power lasers for application such as optical power limiting, optical image processing, optical signal switching and optical phase conjugation, are becoming important [173-174]. Nonlinear organic materials are attracting many researchers due to their exceptionally high third order nonlinear optical susceptibility and the potentiality to tailor their mechanical, dielectric and optical characteristics which help the organic materials to be utilized to develop components for optical signal switching, optical memory devices, optical image processor and optical power limiters. Optical power limiters are the devices developed to protect laser beam detectors, such as light sensors and human eyes, by maintaining the laser light intensity below the required level. Many research studies are being carried out and published on many organic nonlinear optical materials which include molecular single crystals [175-176], organic molecules in solution forms [177-180], and organic dyes and organometallics doped in different solid matrices [181-183]. The major advantages of organic optical materials compared to their inorganic counterparts are due to their low cost and easy to fabricate optical components.

An optical power limiter designed by using organic molecules uses different nonlinear principles such as Two-Photon Absorption (TPA), Reverse Saturation Absorption (RSA), nonlinear refraction, nonlinear scattering, and thermal nonlinearity. Amongst these mechanisms, two-photon induced fluorescence or absorption has many benefits like high initial transmission for the low power optical beam, quick reply to input power variations of the optical beam and maintaining the quality of the input beam at the output after passing through the nonlinear material.

The two-photon absorption process depends on spatial and temporal overlap of the input light and is proportional to the magnitude of quadratic nonlinear property of the molecules of the material which in turn depends on the incident light intensity. The quadratic nonlinear dependence of absorbed input light intensity results in various characteristics like localized photo-excitation, 3D spatial resolution, two-photon absorption, enhanced transparency of materials at longer wavelengths, low photobleaching, and photodamage. The advantages of two-photon absorption and two-photon fluorescence can be utilized for protection against high-intensity for optical devices and for stabilizing high variations of laser power or intensity [184].

Many methods are used to study two-photon absorption cross-sections which include measuring the optical fluorescence from the decay of a species excited by absorption of two photons. This method has several disadvantages associated with spatial and temporal properties of the laser beams. This method includes considerable amount of errors in the measurement due to its section's dependence on the quadratic power of intensity and also need the exact knowledge of quantum yield of fluorescence intensity. These factors add considerable uncertainties in the measured values of two-photon cross section. Several years ago, Levenson, Bloembergen, and co-workers, [185-186] suggested that measurement of a liquid's third order susceptibility helps to calculate the two-photon absorption cross section. Hochstrasser et al. [187] demonstrated that this method can be also used for gaseous molecules. During 1985, J. Burris et al. [188] used a four-wave mixing technique to determine two-photon absorption cross section of diatomic molecules. Later many other techniques are also developed which include nonlinear interferometry [189-190], degenerate four-wave mixing [191], nearly-degenerate three-wave mixing [192], ellipse rotation [193], and beam distortion measurements [194-195]. Four-wave mixing, nonlinear interferometry, and three-wave mixing methods are optically sensitive

techniques but require relatively complex instruments and experimental set-up. The beam distortion measurement techniques are insensitive and require detailed analysis of light wave propagation through the material medium. During 1989, Sheik-Bahae, Van Strayland, and co-workers from CREOL, University of Central Florida [196-197] demonstrated a new simple method for calculating the value of nonlinear refractive index n_2 of a material and its two-photon cross section and named it as Z-scan technique. The principle of working of the Z-scan method is based on the spatial beam distortion by the nonlinear sample. This technique offers simplicity as well as very high sensitivity for measuring the nonlinear refractive index of the material.

2.3 MATERIALS FOR REVERSE SATURABLE ABSORPTION

The currently studied materials for RSA can be conveniently divided into three types: carbon related materials, aromatic ring structures commonly containing a metal ion complex at the center, and dyes. The carbon related materials are a subject of an intense study for optical power limiting. In particular carbon black in solution (inks) [198-199] and nigrosin [200] (a black staining dye for biological systems) show excellent performances. But concerning nonlinear absorption fullerenes (C_{60} and C_{70}) [201-203] belong to a class of better RSA materials. All these materials absorb over a broad visible wavelength range - a good attribute. The fullerenes, on the other hand, are frequently chemically modified with side groups to make them more soluble in a solvent or to be efficiently adsorbed onto a solid, like sol-gel. Recently charge transfer complexes are also under research for optical power limiting such as combinations of C_{60} compounds and zinc phthalocyanine [204]. The phthalocyanine [204-208], naththalocyanine [207] and porphyrin [209-213] systems are ring systems comprised of four aromatic ring systems joined together with either two hydrogen atoms in the middle or a metal ion which forms a complex. Some of the metals are zinc, silicon, cadmium, lead, tin, gallium, indium, and germanium, to name a few. As mentioned above, the complexes with heavier metals seem to function more efficiently.

2.4 MOLECULES FOR TWO AND MULTI PHOTON ABSORPTION

Two types of molecules were studied for two (and multi) photon absorption :

(i) Small molecules composed of a conjugated backbone (π) and electron donating (D-π-D), electron attracting (A-π-A) or mixed electron donating - electron attracting side groups (D-π-A) [214-215] : Small molecules usually exhibit a sufficiently large optical band, thus are transparent

over a large part of the visible spectrum. However, they are difficult to process and are used mainly in solution form. Theoretical calculations, as well as experimental results, indicate that A-π-A type molecules are the most efficient TP absorbers [216-217].

(ii) Conjugated π electron polymers [218-223] : The main advantage of conjugated polymers is that some of them are soluble and can be processed into good optical quality films or slabs. Also, often, due to the large electron-electron correlation the two-photon states lies below the one-photon state. The main disadvantage is that they have usually a small optical gap which limits the applicability of these polymers for the optical power limiting in the visible spectral region.

Two-photon absorption based optical power limiting mechanism has been studied in many organic dyes both in solution form and in solid form. But, when we use the organic dyes directly for two-photon absorption applications, they show bleaching and aggregation of dye molecules at higher dye concentration. To solve this problem and for effective use of highly nonlinear dyes for different photonic applications, they can be doped in a suitable polymer matrix. This may even increase the density of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability [223].

2.5 EXPERIMENTAL TECHNIQUES

2.5.1 Third order nonlinearity Study

Direct Techniques :

Clearly, the simplest and most direct method is to measure the output fluence as a function of input fluence. This gives the reduction directly. In this single beam technique developed by Sheik Bahae and Van Strayland of the University of Central Florida to measure the magnitude of nonlinear absorption as well as the sign and magnitude of nonlinear refraction and called Z-scan method. In the Z-scan technique, a CW laser light beam with Gaussian profile is passed through a nonlinear medium will experience both amplitude and phase distortions. In the experimental set-up, if the intensity of transmitted light beam is measured through an aperture having fixed hole diameter placed in the far field with respect to focal region, the technique is called closed aperture Z-Scan. In this case, the transmitted light beam is sensitive to both nonlinear absorption and nonlinear refraction of material medium. If the measurement is done without an aperture, the process of measurement is referred to as open aperture Z-Scan. Nonlinear susceptibility is a complex quantity and Z-Scan methods yield the real and imaginary parts of nonlinear

susceptibility $\chi^{(3)}$. In figure 2.3 (a), which shows a Schematic representation of an experimental setup for nonlinear transmission and open aperture z-scan measurements, for the determination of real and imaginary parts of the nonlinear index of refraction one uses an aperture in order to limit the beam diameter, placed before the focusing lens. When working with short laser pulses the use of boxcar integrator is required for detection.

Usually closed aperture Z-scan data are divided by open aperture Z-scan data to nullify the effect of nonlinear absorption noted in the closed aperture experiment. The new graph called closed aperture Z-scan contains information on nonlinear refraction alone.

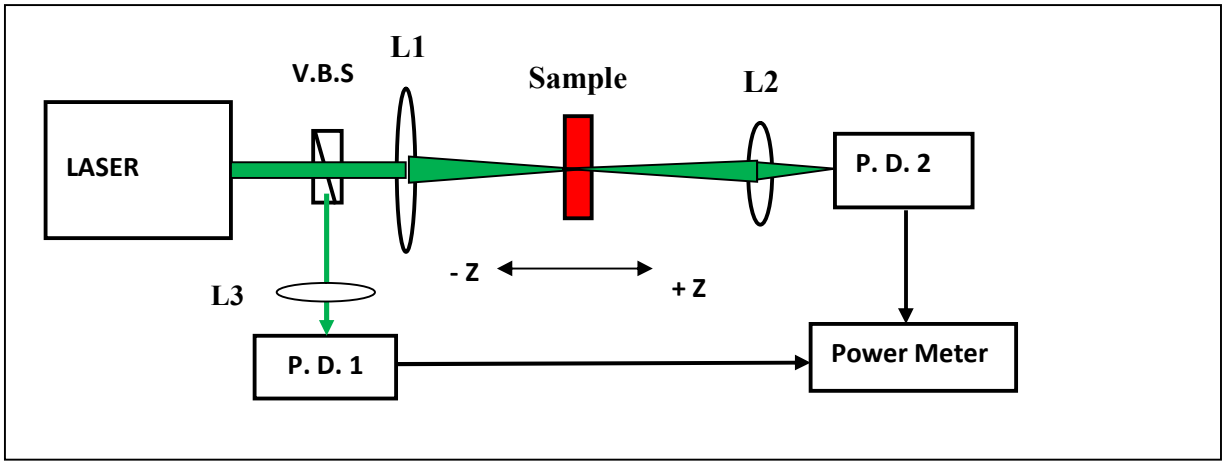

Fig. 2.3 (a) : Schematic representation of an experimental setup for nonlinear transmission and open aperture z-scan measurements.

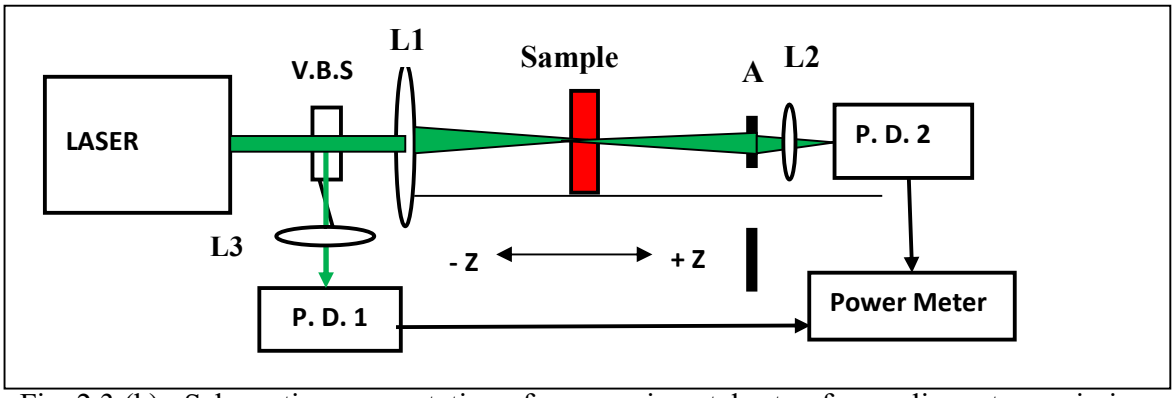

Fig. 2.3 (b) : Schematic representation of an experimental setup for nonlinear transmission and closed aperture z-scan measurements.

Two approaches are used here:

(i) Nonlinear transmission (Fig. 2.3 (a)). In that case by using a set of filters the output intensity is measured as a function of the incident one. By fitting Eq. (2.1) (with $\alpha=0$) one can determine the coefficients β and γ.

However, usually, the separation is not conclusive if both contribute similarly. In that case, another experiment, such as two-photon induced fluorescence could discriminate [224]. Also, the measurements over a large energy range would be helpful. The nonlinear transmission curve is more sensitive to the TPA process at lower incident fluences while it is more sensitive to three-photon (or higher order) processes at higher intensities.

(ii) Z-scan (Fig. 2.3 (b)). In this case, the sample is located at the focal point of the focusing beam and when translated experiences a variable beam intensity. The beam diameter is limited by using an aperture.

The technique allows one to determine both the real and the imaginary part of $\chi^{(3)}$, that is the nonlinear absorption k_2 and nonlinear refraction n_2 [225-228], and both are linked to the Kerr susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ through the following equation

$$n_2 = n_2' + ik_2 = \frac{3}{4\varepsilon_0 c\, n_0^2}\chi^{(3)}(-\omega;\omega,-\omega,\omega) \qquad \text{----------} \quad (2.2)$$

where n_0 is the medium refractive index at low light intensity. The nonlinear absorption coefficient is directly connected to the two-photon absorption coefficient

$$\beta = \frac{2\pi}{\lambda} k_2 \qquad \text{----------} \quad (2.3)$$

where λ is the operation wavelength. β can be also expressed in terms of two-photon absorption cross section :

$$\beta = \frac{N_0}{\omega}\sigma_{TP} \qquad \text{----------} \quad (2.4)$$

where N_0 is the number density of molecules.

The main drawback of both techniques is that they give only the global two (or multi) photon absorption coefficient without discriminating the origin. Although this is not important from the point of view of the practical application of studied materials in optical power limiting devices, it does limit the understanding of the origin of the nonlinear absorption and the possibility of material optimization. Indeed, different physical effects may contribute to the variation of beam transmission through a nonlinear medium. Only time-resolved techniques or use of ultrafast laser pulses could lead to a resolution.

Indirect Techniques

Pump-probe techniques have been used to measure the temporal characteristics [229]. The most useful is the Kerr ellipsometric technique which allows one to measure the dispersion of nonlinear refraction and absorption coefficients. Degenerate four wave mixing (DFWM) also gives the same information. The Kerr $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ susceptibility can be used to derive the β coefficient and subsequently the two photon absorption cross section. Finally, $\chi^{(3)}$ can be measured by third harmonic generation (THG). The main advantage of this technique is that it measures the fast, electronic part of real and imaginary part of $\chi^{(3)}$ susceptibility. These may be the used to calculate the Kerr susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ via multilevel quantum models. Single photon spectroscopic results are also useful to characterize potential materials.

2.5.2 Study of Phase Conjugation Wave generation using Four-Wave Mixing

During last five decades, optical phase conjugation (OPC) has been identified as one of the major research subjects in the field of nonlinear optics and photonics. OPC defines a special relationship between two optical light beams which are coherent and propagating in opposite directions with reversed wave-front and same transverse amplitude distributions. The unique characteristic of these two phase-conjugate waves is that the aberration influence imposed on the forward light beam passed through an inhomogeneous or disturbing medium can be automatically removed from the backward light beam passed through the same disturbing medium. The majority of experimental studies to generate optical phase conjugation light have been carried out by using the degenerate four-wave mixing method due to the reason that method is simple and clear, the required laser facilities are relatively inexpensive, and most importantly, a huge number and variety of materials can be used as nonlinear optical media for examination. It is seen that a considerable amount of such experiments have been focused on determining the nonlinearity of materials rather than studying the phase-conjugate properties of backward generated optical beams [230].

Fig. 2.4 shows two typical experimental arrangements for observing phase conjugation wave via degenerate four-wave mixing configuration. In this experimental arrangement, the incident beam from a laser source is divided into three beams using necessary mirrors and beam splitters. These two beams are used as the pump beams and passed through a nonlinear material medium in a

counter-propagating direction, while the third beam containing certain spatial information is incident upon the nonlinear material medium with a crossing angle of incident to one of the pump beams. In such arrangements, the backward phase conjugate wave can be measured in the direction opposite to that of the incident signal beam. To ensure a longer interaction length in the sample film, the angle between the signal beam and one of the pump beams should be relatively small.

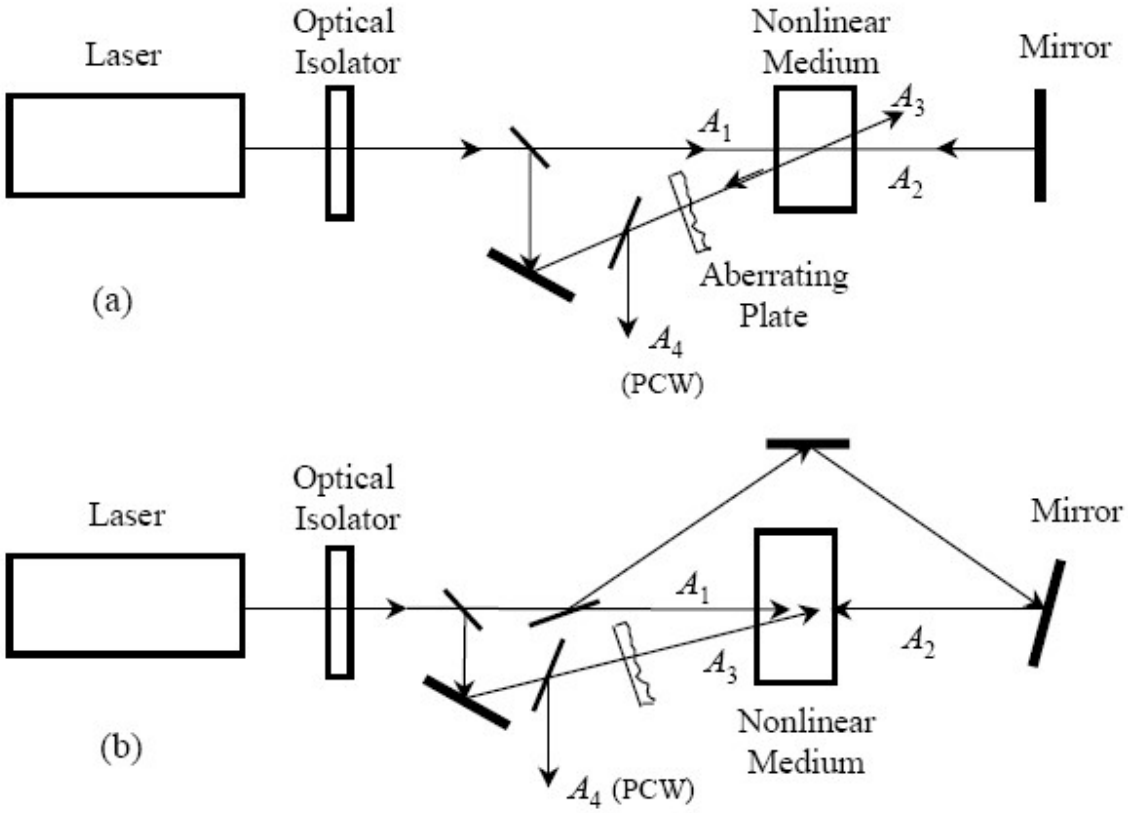

Fig. 2.4 : Two experimental configurations for PCW generation using DFWM [230].

In various parameters to be determined related to PCW are:

(1) The nonlinear P.C. reflectivity (R)

The nonlinear P.C. reflectance or reflectivity is defined as the intensity ratio between the incident signal beam and the backward phase-conjugate beam. The value of R and related coupling parameter γ can be approximately expressed as

$$R \approx [|\gamma| l]^2 \propto |\chi_e^{(3)} A_1 A_2|^2 l^2 \propto |\chi_e^{(3)}|^2 I_1 I_2 \, l^2 \quad \text{---------- (2.5)}$$

Here, $\chi^{(3)}$ is the effective third-order nonlinear susceptibility value of the material medium, I_1 and I_2 are intensity values of the two pump waves, l is the effective interaction length in the nonlinear medium, and γ is assumed [230].

(2) Fidelity of the phase-conjugate beam

To study the aberration-correction possibility of the phase-conjugate beam, an aberrating plate, which is usually a glass slide etched by hydrofluoric acid solution, can be placed on the incident path of the signal beam. After passing back through the same aberrating plate, the aberration influence on the phase-conjugate beam might be entirely or partially removed depending on the fidelity of wavefront reconstruction of that beam [230].

(3) Polarization property of the phase-conjugate beam

The polarization property of PCW is dependent on the polarization states of the three incident beams. Hence, from the study on effect of various polarization combinations for the three input waves, researchers may get a better understanding of the related processes [230].

(4) Temporal behavior of the pulsed phase-conjugate wave

To test the dynamic response of the phase conjugation light wave generation via FWM arrangements, an ultrashort-pulse laser source should be used to provide the three input pulses. By allowing two writing laser pulses be incident on the sample simultaneously to produce a phase-grating, and delaying the third reading beam, one can study whether the four-photon parametric interaction or the induced phase-grating effect is the main possible mechanism that leads to PCW generation under given experimental conditions [229].

2.6 PHOTONIC DEVICES

Much of the work has been done on solutions, clearly unacceptable for any device in the field, unless in thin film form [231]. Both sol-gels and polymers have been proposed and are being actively studied. Unfortunately, their damage thresholds are lower, and they could lack a good means for recovery. Liquid just flows to another region and adjust. Currently, most of device development has been on tandem structures or density variations. Hopefully, other device configurations and different solid hosts will be discovered in the near future. The best reported

results, that we have seen, have a 500 deduction in signal with a 50% transmission at low intensity with a lead phthalocyanine complex. Clearly, these are some of the most promising materials. Indeed, Perry et. al. [232] reported an attenuation of 540 for a system based on bottleneck idea [233] and using an Indium phthalocyanine. Similar results were reported by Xu et al. [234] with lead phtalocyanine (attenuation of 500) in solid (thin films) and liquid solutions [235-237].

2. 7. MATERIALS FOR OPTICAL PHASE CONJUGATION Via FOUR WAVE MIXING

The most experimental studies on optical phase conjugation study using FWM technique can be divided into three categories: (1) based on nonresonant media, (2) Four wave mixing based on resonant media, and (3) Four wave mixing based on photorefractive materials.

(1) **Degenerate FWM in nonresonant media**

In this case, a nonresonant nonlinear material say CS_2 liquid is used for the DFWM experiment. It is found that the spatial resolution of the wavefront reconstruction for the phase-conjugate beam generated could be up to 30 lines/mm [238-241], and the measured nonlinear reflectivity was R ≈ 10% [239].

(2) PCW generation in resonant media

In this case, a large third-order nonlinear susceptibility medium has to be used. For this reason, many researchers choose resonant material in which certain types of resonance enhancements of χ^3 can be utilized. In early experiments, the metal vapors were used as resonant nonlinear media [242-243].

There are many resonant media that can be utilized for degenerate FWM studies with one-photon resonant enhancement [244-250]. It is known that certain dye solutions or dye-doped solid materials have shown very strong linear one-photon absorption or nonlinear two-photon absorption energy bands in appropriate spectral regions, hence, they are good candidates for degenerate or partially degenerate Four Wave Mixing (FWM) studies due to their largely enhanced third-order nonlinearity [250].

Based on literature review, the various types of optical materials commonly used for FWM studies are summarized below :

(1) Absorbing liquid and solid materials : This kind of materials shows a strong one-photon or two-photon absorption. The mechanism causing the induced refractive-index change is either population change or due to opto-thermal effect. The typical materials in this category include dye solutions [251-255] or dye-doped matrices [256-262], impurity-doped glasses [263-269] and crystals [270-273], fullerenes (e.g. C^{60}) related materials [274-276], and liquid crystals [277 – 280].

(2) Lasing gain media : Various pumped lasing media such as Nd:YAG and others are used to achieve degenerate FWM and phase-conjugation experiments [281-286]. One of the mechanisms used to explain the induced gratings in material medium could be the periodic spatial modulation of density distribution. As per published reports, the nonlinear reflectivity currently reached up to ~ 2500 for a small signal intensity and multi-pass geometry [282-286].

(3) Metal vapors : Four wave mixing can be efficiently generated in various metal vapors, including Na, K, Rb, Cs, and others [287-293]. Compared with liquid or solid absorbing media, metal atoms in the vapor phase shows narrower absorption line width, therefore the frequency of incident laser beams have to be tuned close to the selected spectral transition to reach the expected resonant enhancement. Currently reported nonlinear reflectivity has reached as high as ~ 300 [294].

(4) Photorefractive materials : Degenerate four-wave mixing technique is a common method to investigate the optical phase conjugation properties of photorefractive materials. The photorefractive effect is result of the combination of photoconductivity-induced charge separation and subsequent electro-optic response in a second-order nonlinear material [295-297]. In this sense, the mechanisms of induced refractive-index change are mostly different from the above discussed third-order nonlinear media. Hence most of the photorefractive materials used for FWM and phase conjugation studies are impurity-doped inorganic crystals, such as $LiNbO_3$, $LiTaO_3$, $BaTiO_3$, $KNbO_3$, SBN, KNSBN, $Bi_{12}(Si\ Ge)O_{20}$, KH_2PO_4, CdS, GaAs, InP, etc. [298]. In the recent decade, organic crystals and dc-field poled polymer materials have also been used as optimum photorefractive materials for FWM studies [299]. Photorefractive materials can be

used to get high efficiency light-induced gratings with low power CW laser beams in OPC experiments [300 – 301]. The main disadvantage of this type of nonlinear material for FWM applications is their slow response time (usually in 1–10^{-3} s range).

2.8 Present Work

Many researchers have studied nonlinear absorption, nonlinear refraction, optical limiting and all-optical switching of organic molecules doped in various matrices during last four years [277 - 302] with an intension to further improve the properties and efficiencies. Similarly, many studies have been published in the field of generation of optical phase conjugation using degenerate four-wave mixing in many organic materials and dyes during last four years [303-311] for application in optical storage, memory devices and for optical special soliton generation [312-338].

The result of experimental investigations carried out on third-order nonlinear optical properties of some organic dye materials doped in polymer material is the theme of the present thesis. The organic dye materials including 4 – (4-(Dimethylamino)styryl)-1- docosyl pyridinium bromide (DASPB), 3 –(N-ethyl-4-(4-nitrophenylazo)phynyl-amino) propionitrile (DO-25) and 4-[4-(Phenylazo)phenylazo]-o-cresol (DY–7) are doped in PMMA-MA polymer matrix and used as samples for nonlinear absorption, nonlinear refraction, optical limiting and optical phase conjugation studies. Open aperture and closed aperture Z-scan techniques, Type 1 and Type 2 optical limiting configurations, and Degenerate Four-wave mixing (DFWM) set-up are used as experimental techniques. Nonlinear absorption coefficients of the samples are calculated, and the results are compared. The optical limiting and optical phase conjugation behavior of the dye-doped PMMA-MA polymer samples are analyzed and the determined nonlinear optical parameters are tabulated. Application of dye-doped polymer films in Photonics is analyzed in detail by studying their affecting factors and critical constituent elements using ABCD framework.

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CHAPTER THREE

Objectives & Research Methodology

CONTENTS PAGE No.

3.1 INTRODUCTION

Nonlinear optics is expected to play an important role in the field of photonics which is emerging as a multi-disciplinary new frontier of science and technology capturing the imagination of scientists and engineers worldwide because of its potential applications in the field of optical communication, and optical computation. Photonics is the technology of generating and harnessing light and other forms of radiant energy whose quantum unit is the photon. The wide range of applications of photonics extends from energy generation to detection and to communication to information processing using nonlinear optical properties of materials. The major challenge of photonics is identifying a right material and developing a right device to optimally process the signals for a right application using material science and chemical engineering knowledge. Materials with exceptional 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 equipment. The nonlinear optical material is a general term for the materials efficiently makes the appearance of nonlinear phenomenon optically as the responses to optical wavelength conversion, optical amplification, refractive index changes etc. which are intensity dependent. Nonlinear optical materials are largely divided into inorganic and organic materials. In 1930, the nonlinear optical effect related to optical wavelength conversion is predicted, which is said to be the first finding knowledge about the nonlinear optical phenomenon. In 1960, for the first time, laser oscillation using inorganic material is reported. Since then research of inorganic and organic nonlinear optical materials are actively taken place, but nowadays, probably there is no more that undiscovered [339] except optimization of these phenomenon using the suitable material [340]. Thus, the present focus of research in nonlinear optical materials focus on two areas as (1) Optical switching for all-optical devices, and (2) Optical limiting for protection of Eyes and photo detectors.

All-optical networks with good performances, such as good transparency, big capacity, wavelength routing characteristics, compatibility, and extensibility have become the first choice of next generation wide-band network for information communication technology. In the existing optical-electronic-optical conversion devices of the present communication network, disadvantages of slow switching speed and clock displacement have led to a “bottleneck” for

optical fiber communication systems. All-optical switches which can break the transmission speed limits of electro-optical, acousto-optical, thermo-optical, and micro-electro-mechanical switches, can function as effective tools to solve these problems. The third-order nonlinear optical (NLO) effect based all-optical switches can be used to control light to bring changes in refractive index and hence phase difference when signal light passes through the sample and thus carry out the function of "on" or "off" of optical switches. It id found that many properties, such as change speed, intensity loss, sensitivity to optical polarization and insert loss, etc. depend on third-order nonlinear properties of the material used for the fabrication of the device. The other applications of third-order NLO materials include optical power limiting devices, Q-switching and passive mode locking for pulsed lasers, optical light storage etc. One of the main applications of optical limiter is in avoiding laser blinding. Laser blinding can make eyes blind temporarily or permanently, and laser can also destroy important apparatus in the satellite, such as detectors and sensors. The purpose of laser protection is to protect people and devices from the damage of high intensity laser light beam. Hence, laser protection materials and devices are finding importance in photonics research.

These optical power limiting devices are mainly based on the materials with third-order NLO properties such as self-focusing, self-defocusing, two-photon absorption, reverse saturation absorption, and nonlinear scattering. Comparing to earlier laser protection devices, optical power limiting devices have 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. so that they find important application in the development of optical computers. Third-order NLO materials also have many potential practical exciting applications and motivating scientists to continually explore new materials with high third-order NLO properties. The demands of materials for all-optical information process and all-optical high-speed switches include a large nonlinear refractive index, fast switching response, small linear and nonlinear absorption coefficient, and low propagation loss are increasing in the field of photonics [339-341].

Currently, many devices use a wide range of inorganic non-linear optical materials [340-341] with varied wavelengths, laser damage thresholds, and nonlinear optical characteristics. The

research focus is to develop materials that meet all requirements such as faster response, high laser damage threshold, wide transparency range coupled with adaptability, processing ability, and the ability to interface with other materials/devices. Further, the enhanced demand for high bandwidth fiber optic networking infrastructure and high-speed optical computing are expected to boost the demand for nonlinear optical materials [339]. Doped inorganic nonlinear crystals are also shown better optical power limiting properties [342-345]. Studies also showed that by means of heavy ion irradiation, one can improve the material properties of both inorganic and organic nonlinear crystals [346-349].

Optical power limiters based on Two-Photon Absorption properties have been researched and reported in organic dyes in solution form as well as in solid films. But, directly using nonlinear organic dyes with two-photon absorption or two-photon fluorescence capability is prohibited due to their disadvantage of bleaching and aggregation of dye molecules at higher dye concentration with intense light beam irradiation. To resolve this limitation and at the same time, to use such highly nonlinear dyes effectively by improving their physical properties in photonic applications, they can be doped in the polymer matrix. This idea of doping in the polymer matrix may increase the concentration of absorptive or fluorescence centers as well as the opto-chemical and opto-physical stability. Organic molecules of Azo dyes are widely identified and used as attractive candidates for many nonlinear and photonic applications due to the fact that their highly deformable & distributed π - electrons gives rise to very large molecular optical nonlinearities. [350-352].

In this chapter, the objectives of present study based on a review of the literature are presented. Based on the objectives, a detailed methodology of realizing the objectives is discussed. The methodology include, Design of Nonlinear dye Molecules, Fabrication of dye-doped polymer films, Study of linear absorption of the films at different wavelengths, Study of two-photon induced fluorescence, Study of nonlinear absorption at different wavelengths, Study of nonlinear refraction at different wavelengths, Study of optical power limiting, and Study of Optical Phase Conjugation using Degenerate Four-wave mixing set-up on fabricated dye doped films, and analysis of dye-doped polymers use in Photonic device applications using ABCD analysis framework.

3.2 OBJECTIVES OF PRESENT STUDY

The present study is based on following four objectives :

(1) To study the nonlinear properties like the two-photon absorption (TPA), reverse saturation absorption (RSA) and optical power limiting capability of a new dye 4-(4-(Dimethylamino) styryl)-1- docosyl pyridinium bromide (DASPB) doped in a neutral polymer Methyl methacrylate – methacrylic acid (PMMA-MA) matrix. The linear transmission spectrum, single photon fluorescence spectrum, two-photon induced fluorescence behavior are to be recorded and studied. The nonlinear absorption at different intensities have to be studied for different dye concentrations and optical power limiting response are also to be studied at different wavelengths and dye concentrations using continuous wave laser beams.

(2) To study the linear absorption spectrum/properties, nonlinear absorption, nonlinear refraction properties, and optical power limiting properties of two electron donor- acceptor azo dye molecules, 3-(N-ethyl-4-(4-nitrophenylazo) phynyl-amino) propionitrile (Disperse Orange-25) and 4-(4-(Phenylazo)phenylazo)-o-cresol (Disperse Yellow–7). It is found that the azo dye molecules generally show considerably large reverse saturation absorption (RSA), a mechanism which is commonly used for many optical limiters. It is proved theoretically that materials having high reverse saturation absorption properties, one can show higher nonlinear attenuation.

(3) To study Optical Phase Conjugation (OPC) properties of these dyes doped in PMMA-MA polymer films using Degenerate Four Wave Mixing (DFWM) experimental set-up using continuous wave 532 nm laser beam and continuous wave 633 nm beam of semiconductor diode lasers. To investigate the reflectivity of phase conjugated wave as a function of various parameters which include the concentration of dyes, the thickness of films, intensity of the pump beams and the probe beams, the angle between the pump beams and the probe beams etc., and to verify the suitability of the dyes for interferometric applications.

(4) Finally, to study the factors affecting the various determinant issues and their critical constituent elements of dye-doped polymer films usage in Photonic applications, by means of using a new framework consisting of four constructs – Advantages, Benefits, Constraints, and Disadvantages called ABCD analysis framework.

The optical limiting property of dye-doped polymers may arise mainly due to two reasons apart from thermal absorption. They are either Two-Photon Absorption (TPA) and/or Reverse Saturation Absorption (RSA). In the case of dye molecular medium with molecules of high RSA, when a high power laser beam propagates through the medium, the number of the molecules in

the excited state increases. Such increase in number of excited state molecules is proportional to the ground state cross section and the incident photon flux. The increase in excited state molecules in dye medium will limit the transmission of light in the medium. This phenomenon is called reverse saturation absorption. For effective optical limiting devices, the required characteristics of RSA materials are :

(1) The ratio of the excited state absorption cross-sections and ground state absorption cross-sections should be much larger than one so that the material will limit the power of the incoming light at output to a safe level and prohibits damage to the material.

(2) The dye material should possess comparatively high transmission at the lower intensity incident light beam.

(3) The spectral response of dye material should be wide to cover the substantial amount of the visible region.

(4) The dye material should have a fast response time for laser light beam.

As per the objectives of the present research work, we have identified three dyes which show nonlinear absorption either due to Two-Photon Absorption property and/or Reverse Saturation Absorption property. The physical properties of these dyes are improved by doping them in transparent polymer PMMA-MA. The resultant samples are characterized by studying their linear and nonlinear absorption, nonlinear refraction and the resultant ability of optical limiting. The samples are also characterized by studying their optical phase conjugation property by means of the degenerate four-wave mixing experiment as shown in the block diagram of the plan of Research Methodology (Figure 3.1.).

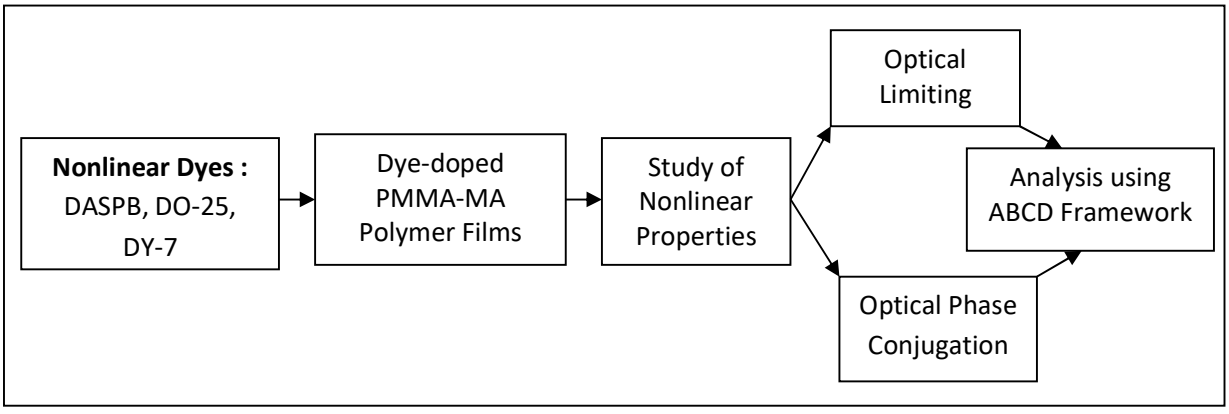

Fig. 3.1 : Block diagram of the Plan of Research Methodology for the proposed study.

3.3 METHODOLOGY

1. Design of Nonlinear dye Molecules.
2. Fabrication of dye-doped polymer sample films.
3. Study of linear absorption of the dye-doped sample films at different wavelengths.
4. Study of two-photon induced fluorescence of sample films.
5. Study of nonlinear absorption at different wavelengths/dye concentrations using Z-scan techniques.
6. Study of nonlinear refraction at different wavelengths/dye concentrations using Z-scan technique.
7. Study of optical power limiting behavior of the samples for type 1 and type 2 configurations.
8. Study of Optical Phase Conjugation (OPC) using Degenerate Four-wave mixing method using these dyes doped in PMMA-MA polymer films.
9. Factor & Elemental Analysis of Dye-doped Polymers films in Photonic Applications using ABCD Analysis Framework.

It is proposed to study the linear optical properties, nonlinear optical properties of these dye-doped polymer films using open aperture and closed aperture Z-scan technique and optical limiting properties of these sample films in CW regime. The phase conjugation properties are planned to study using continuous wave (CW) laser at 532 nm and 633 nm.

Description of Methodology :

3.3.1 Methodology for Design of Nonlinear dye Molecules :

Most of molecular design schemes underlying the design and the optimization of efficient molecules for nonlinear optical (NLO) applications are based on intramolecular charge transfer (ICT) processes from a donor species toward an acceptor moiety through a π-electron conjugated chain, such as in benzene, azobenzene, polyene, stilbene, or thiophene derivatives [353-354]. Significant progress has been made recently in finding a compromise between aromaticity and thermal stability of highly conjugated dyes in photonic device applications [355]. It is found that in the organic molecular systems the delocalized π-electrons that governs various macroscopic arrangements and thereby show characteristic nonlinear optical responses.

For real applications, these materials can be grown into molecular crystals, either in bulk or in the form of thin films on substrates or as amorphous polymeric systems. Molecules with high NLO responses must possess small differences between the ground and low excited states; the

corresponding electronic transitions should also correspond to strong absorptions and there must be a large difference between the dipole moments of the ground and excited states [354]. These properties can be accomplished by compounds with a D-π-A structure, where an electron donor (D) group and an electron acceptor (A) group are placed away from each other in the molecule through a π-conjugated system, therefore creating a high asymmetry in the electronic density. Many organic compounds with extensive π-delocalisation have identified as promising NLO materials instead of inorganic solids, due to their ultrafast NLO responses, good processability as thin-film devices and enhanced nonresonant NLO responses [356].

3.3.2 Methodology for Fabrication of dye-doped polymer films :

To fabricate dye-doped PMMA-MA films two methods were used :

In the first method, dye-doped PMM-MA polymer thin films were prepared between two glass slides. The dye-doped PMMA-MA films were prepared by dissolving PMMA-MA and the dye separately in chloroform and then the solution of dye and that of PMMA-MA are mixed, heated (up to 50°C) and stirred for 2 hours, thus the mixed solutions of dye and PMMA-MA were obtained. After the solutions were filtrated, the films were prepared on a clean glass slide by the repeat-spin-coating method and dried at room temperature (300K) for 24 hours. In the second method, hot press technique is used. In this method also dye-doped PMMA-MA polymer films were prepared between two glass slides by means of hot pressing of the mixture.

3.3.3 Methodology of Study of linear absorption of the films at different wavelengths :

Linear optical absorption measurements of the samples can be performed in the air at room temperature using light beams of different wavelengths. The linear absorption, α can be calculated by measuring output power with a sample (P_S) as a function of the power without the sample called input power (P_i) in low power regime at different wavelengths. The linear absorption is obtained from Eq. (3.1).

$$\alpha_0 = -\frac{1}{t}\ln\left[\frac{P_s}{Pi}\right] \quad \text{----------} \quad (3.1)$$

or $$\alpha_0 = -\frac{1}{t}\ln\left[\frac{1}{\mathrm{T}}\right] \quad \text{----------} \quad (3.2)$$

where (t) is the thickness of sample and T is the transmittance.

The linear absorption spectrum of the samples can be measured on a UV-VIS-IR recording Spectrophotometer. The dye-doped samples in Polymethyl methacrylate methacrylic acid

(PMMA-MA) films can be used. One photon fluorescence spectrum of the dye sample films can be studied using a spectral fluorophotometer with the specified spectral resolution.

3.3.4 Methodology of Study of Two-Photon induced Fluorescence :

The multi-photon induced fluorescence emission spectrum of the sample dye in chloroform with 1 cm path length or doped in PMMA-PA matrix can be recorded by exciting the sample with 1064 nm laser beam using a spectral fluorophotometer with the known spectral resolution.

3.3.5 Methodology of Study of Nonlinear Absorption property :

When a beam of light passes through a nonlinear material medium, the medium induces a variation in the nonlinear refractive index of the material which is proportional to the variation in the light beam intensity and hence the total refractive index of the material changes. In a simple model of such system, when only third-order nonlinearities are considered, the resultant change in the total refractive index becomes :

$$n = n_0 + n_2 I. \quad \text{--------} \quad (3.3\ (a))$$

Here n is the total refractive index of the sample medium, n_0 is the linear refractive index of the sample medium, n_2 is the third order nonlinear refractive index of the sample medium, and I is the incident beam intensity. If the incident beam has Gaussian profile, then the variation in the intensity of the beam will induce a nonlinear refractive index profile which acts like a focusing or defocusing lens to the light beam itself. Thus, it is concluded that the light beam propagating in nonlinear material medium induces a refractive index lens in the medium.

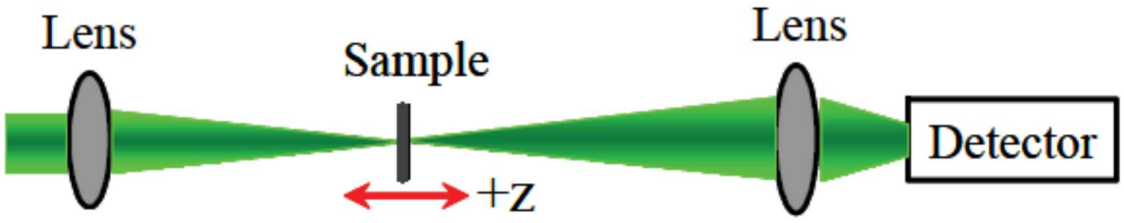

Fig. 3.2 Open aperture Z-scan measurement configuration

The Z-scan method is also used to determine the coefficient of nonlinear absorption β. The whole absorption is defined

$$\alpha = \alpha_0 + \beta I \quad \text{----------} \quad (3.3\ (b))$$

where α_0 is the linear absorption coefficient, β is the nonlinear absorption coefficient, α is the total absorption coefficient, and I is the intensity of the incident laser beam. The Z-scan technique is performed by translating a nonlinear sample medium along with the beam waist of a focused laser beam and then measuring the output power transmitted through the sample medium. While translating the sample with respect to the focus of the light beam (Z-scan), the incident intensity changes due to the change in the spot dimension of the beam inside the sample. By monitoring the entire transmission through the sample during its scan one can study the transmission profile. In this configuration, since no aperture is placed in front of the photo detector the technique is called open aperture Z-scan. From the Z-scan graph, it is found that the absorption of the sample medium depends on the incident beam intensity. The theoretical function that interrelates this phenomenon is given below [341]:

$$T(z) = \frac{\ln[1 + q_0(z)]}{q_0(z)},$$

Where,

$$q_0(z) = \frac{\beta I_0 \left[\frac{1 - \exp(-\alpha_0 L)}{\alpha_0}\right]}{1 + z^2 / z_0^2}$$

The above general formulae is valid only for the third-order nonlinear optical processes and have to be further improved when the higher-order processes are taken into account. In case of the saturation of the changes in nonlinear refractive index in a medium, one can write:

$$\Delta n_0(I_0) = \frac{n_2 I_0}{1 + I_0 / I_{sat}}. \qquad \text{---------- (3.3 (c))}$$

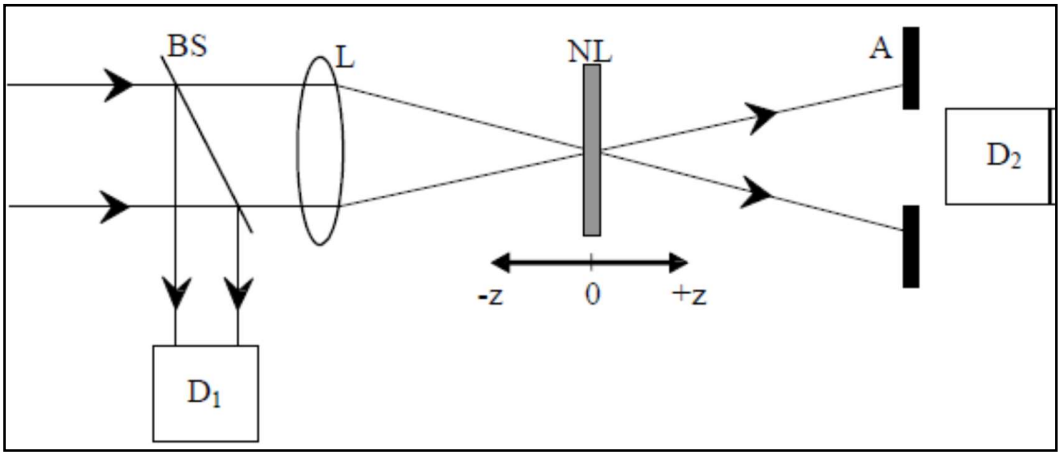

Fig. 3.3 : Experimental configuration for Z-scan technique. BS- Beam Splitter, L-Lens, NL-Dye-doped Polymer sample, A- Aperture, D1 & D2 – Photo-detectors.

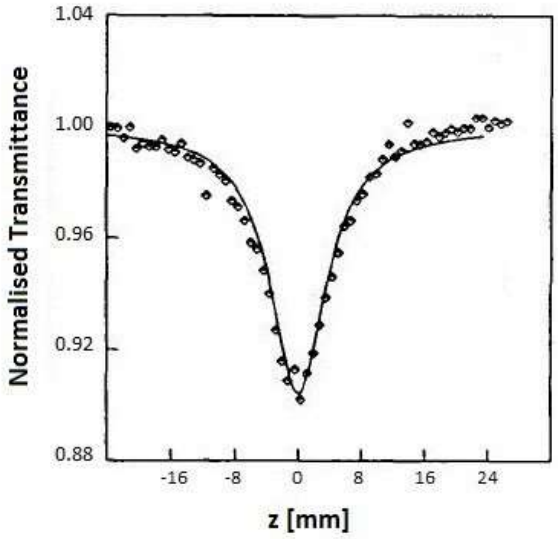

Fig. 3.4: Typical T(z) graph for ZnSe with open aperture (λ = 532 nm) [341]

The final graph is represented in figure 3.5. As we can see, the peak and the valley are asymmetric and this is the sign of the nonlinear absorption.

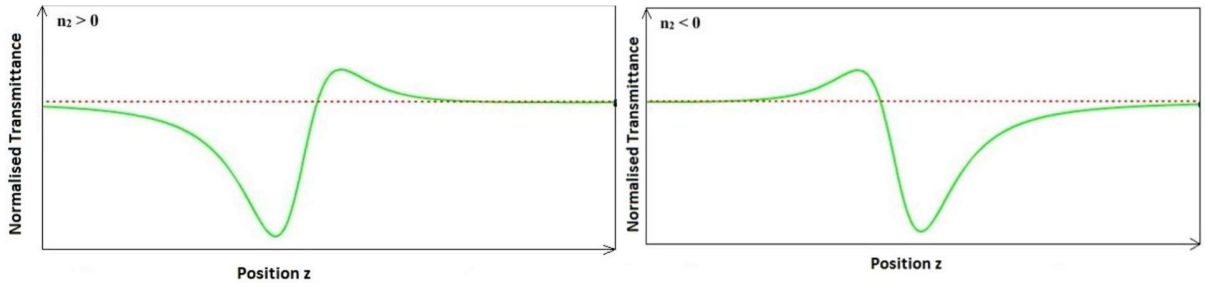

Fig. 3.5: Typical Z-scan graph (closed aperture) for the material with the nonlinear absorption ($\beta \neq 0$) for $n_2 > 0$ and $n_2 < 0$

It is quite remarkable that we can determine the sign of n_2 and the presence of the nonlinear absorption only from the form of the transmittance graph.

3.3.6 Methodology of Study of Nonlinear Refraction property :

To characterize the optical nonlinearities of dye-doped films, a time-averaging technique has been used successfully in Z-scan measurements due to its practical and experimental simplicity and high sensitivity [341]. This technique gives not only the signs but also the magnitudes of the nonlinear refraction and absorption coefficients.

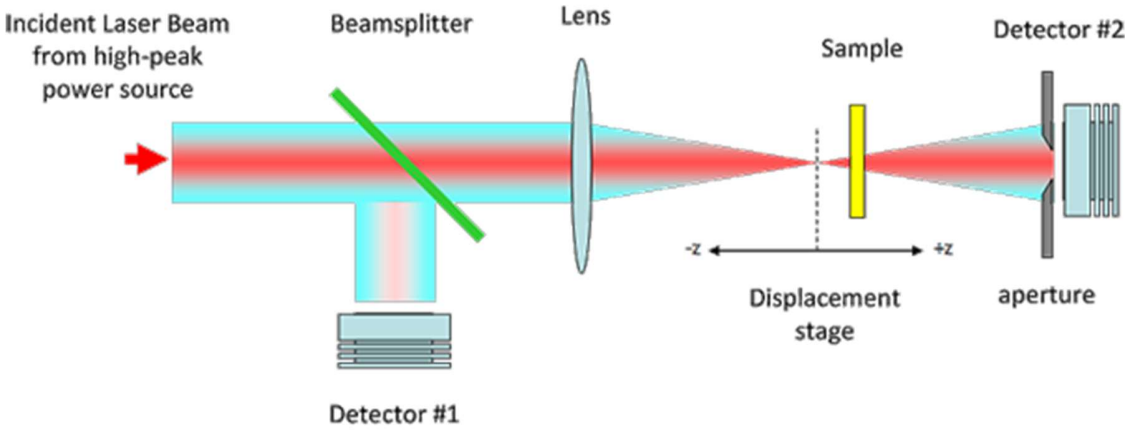

Fig. 3.6 : Schematic drawing of the Z-scan technique [357]

The nonlinear refractive index n_2 can be measured by a Z-scan technique, which can simultaneously measure both nonlinear absorption and nonlinear refraction of any material including solids, liquids, and liquid solutions. On the basis of the principle of spatial beam distortion, the Z-scan technique make use of the spatial variation of intensity distribution in transverse can create an induced lens-like effect due to the presence of space-dependent refractive-index change via the nonlinear effect, affect the propagation behaviour of the light beam within the sample material, and generate a self-focusing or defocusing effect. This phenomenon generates a change in the far-field diffraction pattern. Z-scan is a single-beam technique that provides us both the sign and magnitude of refractive index nonlinearities. It is found that Z-scan method is rapid, simple to perform and accurate in measurement, therefore it is used extensively. This technique is found to be adequate for the determination of a nonlinear coefficient n_2 for a particular wavelength. Hence this technique is used by many researchers to study nonlinearities in semiconductors, glasses, semiconductor-doped glasses, liquid crystals, biological materials and everyday liquids e.g. tea [358].

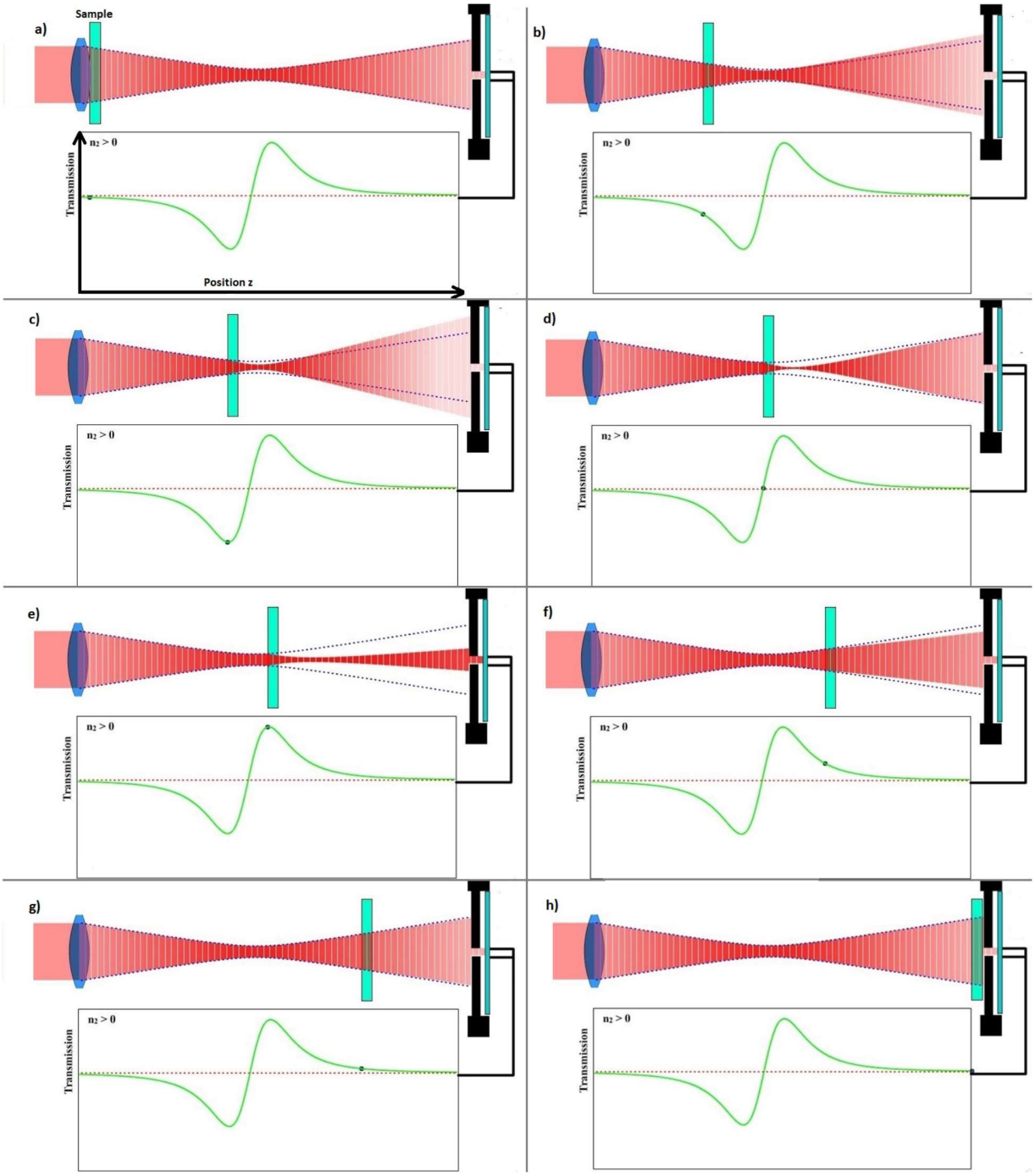

Fig. 3.7: The Z-scan measurement as represented in an online animation. http://www.optics.unm.edu/sbahae/z-scan.htm; we can see the change of the laser beam and the change of the transmittance at the same time.

The measurement of Z-scan starts far away from the focus along beam axis (negative z), where the transmittance is relatively constant (figure 3.7 a). Then the sample is moved towards the

focus and then to the positive z (figure 3.7 b to h). If the material has a positive nonlinearity ($n_2 > 0$), the T(z) graph has a valley first and then a peak. For the sample with $n_2 < 0$ the graph is exactly the opposite (first the peak and then the valley) (figure 3.8). When self-focusing in the sample occurs, this tends to collimate the beam and causes a beam narrowing at the aperture which results in an increase in the measured transmittance as shown and when self-defocusing takes place the beam broadens at the aperture and the transmittance decreases. The scan is finished when the transmittance becomes linear again (figure 3.9).

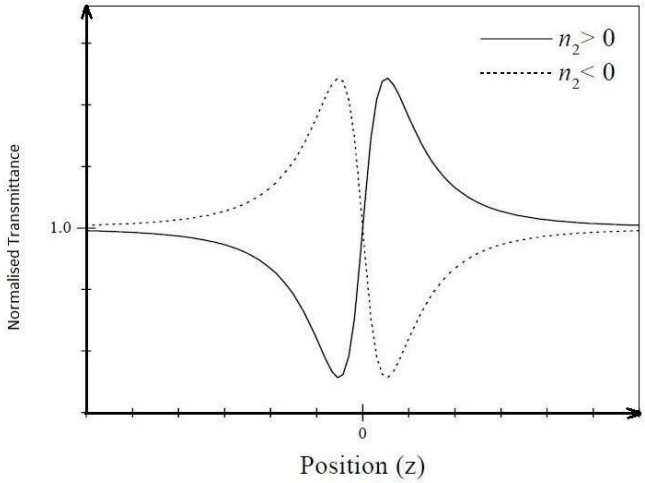

Fig. 3.8: Determination of the sign of the n_2 from a graph of transmittance T(z) [359]

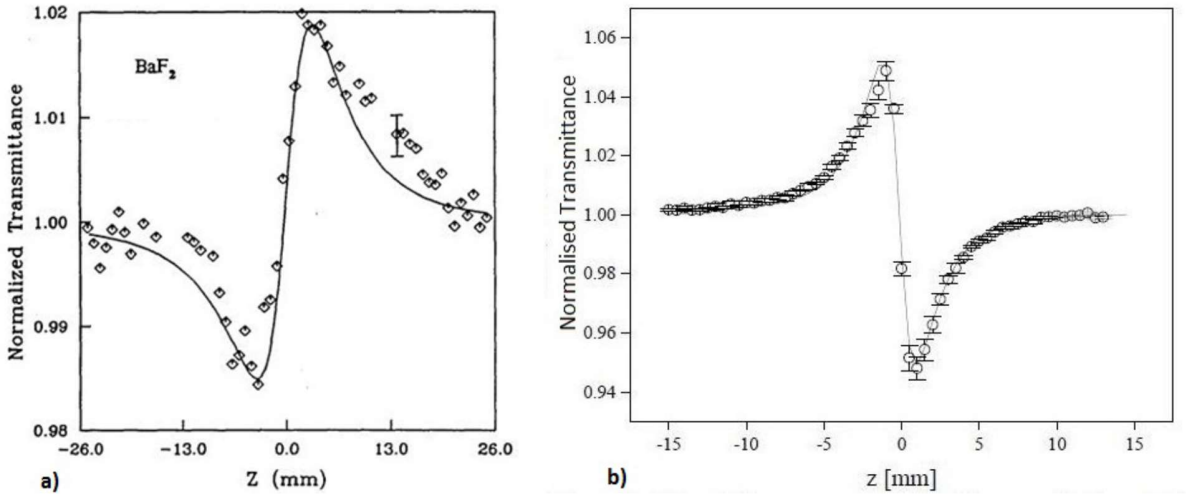

Fig. 3.9: Typical Z-scan curve; (a) for $n_2 > 0$ (barium chloride) [360, 322] and (b) for $n_2 < 0$ a lyotropic liquid crystals [361]

There are not many materials with $n_2 > 0$, the negative n_2 is much more common. (This is attributed to a thermal nonlinearity [360]).

3.3.7 Methodology of Study of Optical Power Limiting :

The practical optical power limiters can be optimized by defining and identifying the characteristics of an ideal limiter. 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. The minimum criteria identified for a material to act as an effective practical optical power limiter are :

(1) Having high linear transmittance with broad transmission range.

(2) Having low limiting threshold level (the input corresponding to the breakpoint in the curve).

(3) Having fast response time (e.g. picoseconds or faster).

(4) Having broadband limiting response (e.g. the entire visible spectrum).

(5) Low optical scattering inside the material.

Effective optical power limiting can be achieved in many materials by means of various nonlinear optical mechanisms which include self-focusing, self-defocusing, light-induced scattering, light-induced refraction, light-induced aberration, excited state absorption, two-photon absorption, multi-photon absorption, photo-refraction, and free-carrier absorption. Although there are many varieties of optical power limiting devices, most of them can be divided into two categories such as the energy-spreading type of devices and the energy-absorbing type of devices. Energy-spreading devices works using principles like self-focusing, self-de-focusing, induced scattering, induced refraction, or induced aberration. Energy-absorbing type of devices work using principles of nonlinear absorption or optical bistability. Nonlinear absorption includes Two-Photon Absorption (TPA), Excited State Absorption (ESA), and Free-Carrier Absorption (FCA).

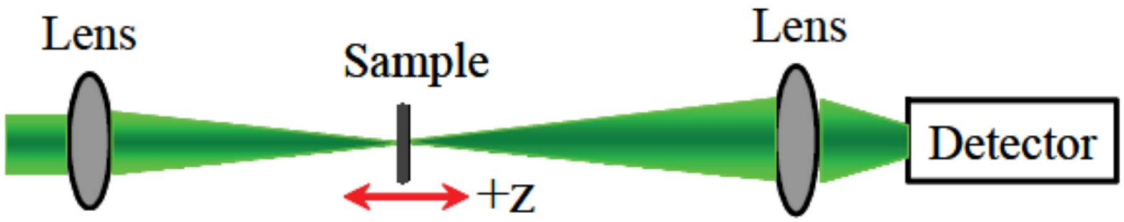

Fig. 3.10 Open aperture Z-scan measurement configuration

The experimental set-up for the demonstration of optical limiting under both CW illumination as well as pulsed illumination is very similar to the z-scan geometry. The schematic representation is shown in Figure 3.10. A variable beam splitter or variable beam filter is used to vary the input power. The continuous wave semiconductor diode laser beam of wavelength 532 nm with suitable power is used as the excitation source. The laser beam is focused normally onto the sample by a convex lens of suitable focal length. The dye-doped polymer sample is to be moved forth and back along the optic axis in order to change the position of the focal point of the lens with respect to the sample medium. The dye-doped sample film is to be placed either at the focal point (type 1 optical limiting configuration) or after the focal point to get the optimum result (type 2 limiting configuration) depending on the nature of optical nonlinearity of the sample medium. A lens of suitable diameter is used to collect the output beam emerging out from the dye-doped polymer film. This beam is then focused on a photo detector-power meter assembly. The intensity of the input laser beam is varied gradually using a variable beam splitter (VBS) and the corresponding output intensity values are measured by means of the photo detector-power meter assembly. In order to study the optical limiting behavior of the dye sample which has negative nonlinearity, the dye-doped polymer film is translated along the direction of propagation of the laser beam at the various position around the focus of the lens (z = 0) forward and backward. The transmittance is recorded using a power meter. It is found that the limiting occurs when the sample is placed beyond the focus of the lens. Hence the sample is placed beyond the focus of the lens i.e. closer to the valley point (Type 2 optical limiting configuration). The output power should be noted for different input power. The graph has to be drawn between transmitted output intensity/power versus input intensity/power to study the optical power limiting behaviour of the sample.

3.3.8 Methodology of Study of Optical Phase Conjugation :

During last fifty, phase conjugation in optics has been identified as a very important research subject in the area of photonics [362-369]. Optical phase conjugation (OPC) defines a special relationship between two optical light beams which are coherent and moving in opposite directions with reversed wave-front and same amplitude. Three different methods are commonly used to generate the backward phase-conjugate light beam in a given optical medium [371]. The first method uses the degenerate four-wave mixing technique, the second method uses backward

stimulated scattering processes like Raman, Brillouin, Rayleigh-wing, Kerr etc., and the third method uses one photon or multi-photon pumped stimulated backward emission processes. These methods can be successfully used for the construction of high-brightness laser oscillator/amplifier systems, laser target-aiming systems, cavity-less lasing equipment, aberration correction devices, long distance optical fiber communications systems, optical phase locking and coupling devices, and photonic data storage and data processing devices.

Hellwarth in 1977 [370] proposed a popular method to generate a backward degenerate phase conjugated wave (PCW). The configuration of such method is shown in Fig. 3.11. In this method, a third-order nonlinear medium is illuminated with two counter-propagating strong plane waves simultaneously and a third signal beam is generated internally which has an arbitrary wavefront distortion but different propagation direction. Incidentally, if these three waves have the same frequency (ω), then a newly generated wave can be observed with the same frequency ω but propagating along the opposite direction as shown in figure 3.11. It is found that the newly generated wave is the backward frequency-degenerate version of phase conjugated wave of the incident beam [371].

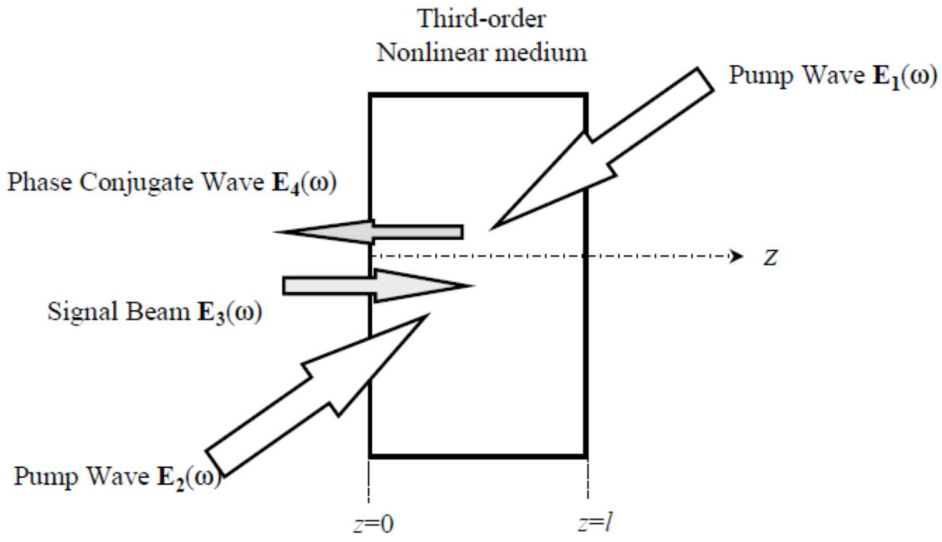

Fig. 3.11. Configuration for phase-conjugate wave generation by DFWM [371].

Many experimental studies have used the degenerate FWM method to generate Phase conjugated waves using third harmonic nonlinear materials. This is because the method is simple and relatively inexpensive. Most importantly, many nonlinear materials can be used as nonlinear

optical media in solid, liquid, and gasses form. Many of these studies have been focused on determining third harmonic nonlinearity of materials instead of studying the phase-conjugate properties of backward generated optical beams [371].

Fig. 3.12 shows two types of experimental configurations for generating phase conjugated waves by considering degenerate four wave mixing method. The similarity in these two arrangements is that the incident laser beam is divided into three light beams using suitable mirrors and beam splitters. Two beams out of three are used as pump beams and pass through a nonlinear medium in a counter-propagating direction, while the third beam containing certain spatial information is allowed to incident on the nonlinear sample with certain crossing angle to one of the pump beams. The resultant backward phase conjugated wave can be identified and studied in the direction opposite to that of the incident signal beam. By making the angle between the signal beam and one of the pump beams relatively small one can ensure a longer interaction length [371].

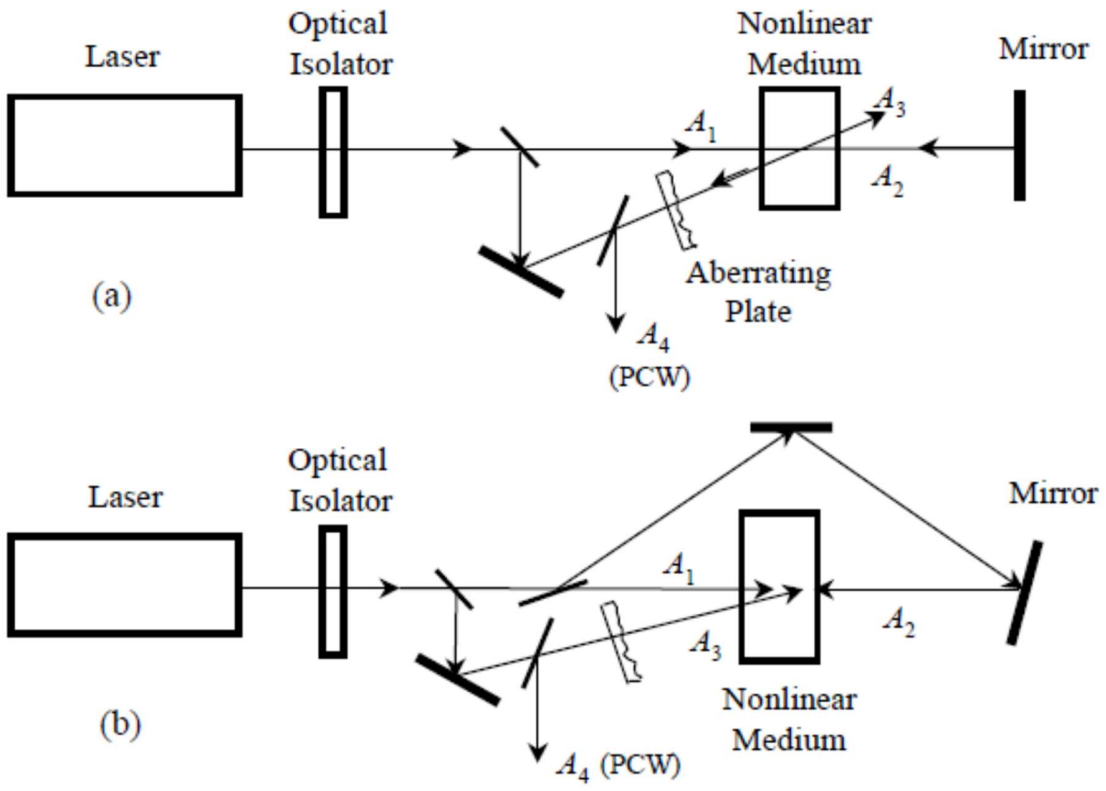

Fig. 3.12. Two experimental configurations to generate PCW using DFWM [371].

In the above two configurations, the first configuration generates the backward pump beam by using a vertically placed mirror, whereas the second method generates two counter-propagating pump beams by a ring type optical path. Compared to the second configuration, the first configuration is simple and easy whereas the second configuration is more convenient to study the effect of various factors on the strength of P.C. reflectivity. An optical isolator may be used to block any possible optical feedback of backward PC signal into laser device [371].

In the present experiment, using three dye-doped PMMA-MA samples, the dependence of phase conjugated signal reflectivity on following parameters are studied using continuous wave (CW) semiconductor diode laser beams at 532 nm & 633 nm :

(1) Maximum Phase Conjugation Reflectance at different dye concentrations.

(2) Phase Conjugation signal recording time at different concentrations.

(3) Phase Conjugation reflectance as a function of an angle between the probe beam and forward pump beam.

(4) Dependence of Phase Conjugation reflectance on backward pump beam intensity.

(5) Transmission Phase Conjugation signal as a function of Time.

(6) Phase Conjugation Reflectance is studied at different values of the probe beam intensity.

(7) Phase Conjugation Reflectance is measured at different values of the forward pump beam intensity.

3.3.9 Methodology of Factor & Elemental Analysis using ABCD Framework :

Application of dye-doped polymer films in Photonics can be analyzed in detail by studying their affecting factors and critical constituent elements using ABCD framework [372-373]. The methodology of ABCD framework contains identification of the factors affecting the various determinant issues like (1) Material Issues, (2) Commercialization Issues, (3) Application Issues, (4) Production/Service providing Issues, (5) Customer Issues, and (6) Environmental/Social Issues and finding critical constituent elements for each affecting factors of dye-doped polymer films to be used in Photonic applications under four constructs :

(1) Advantages,

(2) Benefits,

(3) Constraints, and

(4) Disadvantages

ABCD analysis framework allows to study a system, concept, or an idea from various frame of reference called determinant issues. Further it provides an opportunity to identify various affecting factors under the constructs Advantages, Benefits, Constraints, and Disadvantages based on some key issues for each determinant issues. Finally, the framework allows to list number of critical constituent elements for each affecting factors. Thus, ABCD analysis framework is also called factor and elemental analysis technique for analysis systems, concepts, ideas, materials, strategies, theories etc.

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CHAPTER FOUR

Design, Preparation, & Linear Optical Properties of Dye-Doped Polymer Films

CONTENTS PAGE No.

4.1. INTRODUCTION

The design of effective third-order nonlinear materials is possible by knowing the relationship between electronic structure and molecular geometry, particularly the length of the π-electron structure in the molecule. In the organic materials, the relaxation of molecular geometry is possible by exciting an electron in the molecule leads to nonlinear excitations. Usually, the relaxation of the molecular geometry due to photon irradiation is much slower than the change in π-electron distribution and the related shift in π-electron density. Such variation in π electron density is responsible for the huge molecular polarizabilities of π-electron structures [374]. Thus by tailoring the molecular geometry, one can modify the polarizability of the molecules and hence third order optical susceptibility of the material.

Among the various classes of multiphoton absorbing materials, one-photon absorption is a linear process in any material, and two-photon absorption is the nonlinear process that involves the unusual ability of some molecules to absorb two photons together to populate an energy level within the molecule with total energy equal to the sum of the energies of the two photons absorbed. Some molecules like fluorene and benzene derivatives have generated interest for two-photon absorption during last many years due to their utility or potential in multiple applications such as nondestructive type fluorescence imaging, two-photon induced optical power-limiting devices, and two-photon induced photodynamic therapy. In the 1990s, the research in nonlinear optical materials targeted on the design, preparation, and characterization of new nonlinear organic dyes and the measurement of their two-photon absorption cross sections [375]. Several papers have been published from various research groups revealed to the design strategies for efficient two-photon absorption molecules by a systematic variation of chromophores with various electron acceptor (A) and electron donor (D) moieties, which are attached symmetrically or unsymmetrically to a conjugated electron bridge (π). The effect of changing the electron-donating or/and electron-accepting groups on the strength of nonlinear absorptivity, the effect of adding new groups in the center of the molecule to modify the charge redistribution on the strength of nonlinear absorptivity, and the consequence of altering the conjugation length on nonlinear susceptibility have been investigated by many researchers to understand design criteria for fabricating structures with increased two-photon absorptivity.

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 [376-379]. 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 [380 382]. A similar effect can be expected in dipolar chromophores of the D- π- π - π -A and D-π- π- π- π-A type. By modifying 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 Rodamine B, Rodamine 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 [380-389]. The strategy for the construction of molecules with large TPA cross sections has been studied both experimentally [390-391], and theoretically by many researchers [392-393], 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 [375].

Although a considerable amount of efficient two-photon absorption chromophores are available already in the literature, many of them contain only of substituted conjugated aromatic rings, such as benzene or fluorene, and depend on the electronic properties of simple electron donating and/or electron-withdrawing functionalities. Replacement of these aromatic systems with more easily delocalizable π-excessive or π-deficient heteroaromatics has been demonstrated as a reason for increased intramolecular charge transfer results in enhanced two-photon absorption,

without affecting the chemical and photochemical stabilities of these systems [394-396]. Moreover, modification of the structure by incorporation of heteroaromatics into π-conjugated systems allows for fine-tuning of the electronic and optical properties and often results in strong fluorescence emission, which is an essential prerequisite for certain two-photon based applications [397].

This chapter explores the structural design of organic dye molecules for better nonlinear properties and preparation of dye-doped polymer film samples of variable dye concentration and variable film thickness using the hot-press technique. Based on the molecular structural studies three dyes namely 4-(4-(Dimethylamino)styryl)-1-docosyl pyridinium bromide [DASPB], 3-(N-ethyl-4-(4-nitrophenylazo) phynyl-amino)propionitrile (Disperse Orange, DO- 25), and 4-(4-(Phenylazo)phenylazo)-o-cresol [Disperse Yellow, DY-7)] are chosen for further study.

4.2 DESIGN OF NONLINEAR MOLECULE

There is another way of looking into molecular electronic structures required for third order nonlinear organic materials and systems. Even though the understanding of structure – property relationship in organic molecules for third order optical effect is highly limited, the microscopic theoretical models developed to explain the effect, predict that large nonresonant third-order optical nonlinearity is associated with delocalized π-electron systems. Such molecules must possess anharmonicity to give rise to high optical nonlinearity. Conjugated polymer molecules with alternate single and double bonds in their backbone structure provide a molecular frame for extensive conjugation and hence are most widely studied and attractive group of χ^3 organic materials. From both of the above arguments, it is observed that the strength of optical nonlinearity is strongly dependent on the extent of π-electron delocation from one unit to another unit of the organic molecule.

Albota et al. [375] 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 [398], 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. Since there is no clear evidence 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 3 molecules as 4-(4-(Dimethylamino)styryl)-1-docosyl pyridinium bromide (DASPB), Disperse orange-25, and Disperse Yellow-7 with π centre for studying third order optical properties.

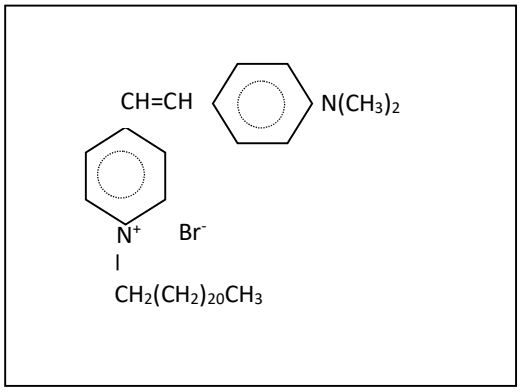
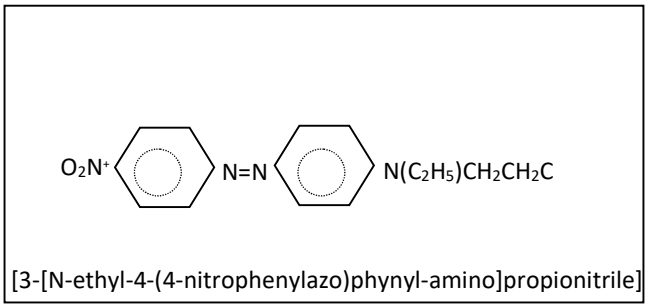


Fig. 4.1 : Molecular structure of DASPB.



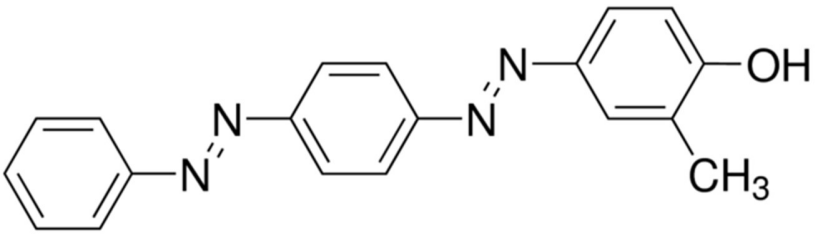


Fig. 4.2 : Molecular structure of Disperse Orange – 25.

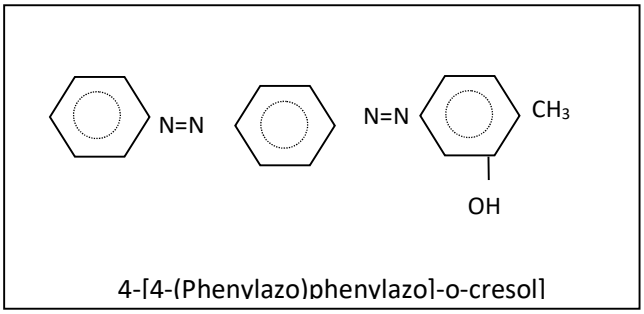


Fig. 4.3 : Molecular structure of Disperse Yellow – 7.

4.3 SAMPLE PREPARATION

Even though DASPB can be prepared in the laboratory, to maintain high quality, DASPB is purchased from Aldrich Chemical Company, USA., and further filtered and recrystallized using spectrograde ethanol. The research grade chloroform is used as the solvent for DASPB. The thin films of DASPB doped in polymer matrix by dissolving both DASPB and PMMA-MA in specified quantity in chloroform. The solution mixture is poured between two micro glass slides in a clean laboratory environment and thin films of specified thickness are prepared using hot press technique [399]. Thin films of 10 μm thickness of DASPB dye-doped samples are prepared between two glass slides.

Similarly, commercially available Disperse orange-25 and Disperse yellow-7 are purchased by Aldrich Chemical Company, USA. and further filtered and recrystallized using spectrograde ethanol. The research grade chloroform is used as the solvent. The thin films of DO-25 and DY-7 doped in polymer matrix by dissolving both DO-25 and PMMA-MA and DY-7 and PMMA-MA respectively in specified quantity in chloroform. The solution mixtures are poured between two micro glass slides in a clean laboratory environment and thin films of both the dye samples of specified thickness are prepared using hot press technique [399]. Thin films of 10 μm thickness of both DO-25 and DY-7 dye-doped polymer films are prepared between two glass slides separately.

The thickness of the films is determined by gravimetric weighing method [400 426]. The film thickness is determined to be 10 μm for the solution molarity 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 [401].

4.4 LINEAR OPTICAL PROPERTIES OF THE SAMPLES

4.4.1 LINEAR OPTICAL PROPERTIES OF DASPB

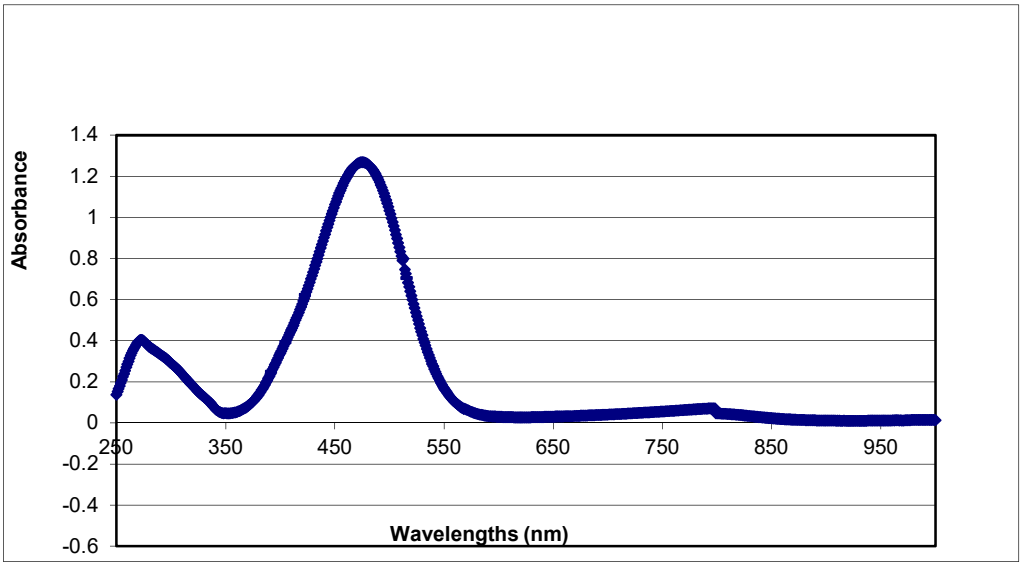


Fig. 4.4 : Linear absorption spectrum of DASPB doped PMMA-MA polymer films.

The molecular structure of 4-(4-(Dimethylamino)styryl)-1-docosyl pyridinium bromide (DASPB), is shown in figure 1. The molecular structure discloses a charge-transfer in DASPB between the electron donor (the aromatic moiety) and the electron acceptor (bromine unit) can be considered to express the third nonlinear property of this molecule. The linear absorption spectrum of DASPB dye-doped polymer film is recorded using UV-VIS-IR Spectrophotometer (VARIAN Cary). The linear absorption spectrum of a DASPB in the polymer matrix with a dye concentration of 2 mM. The linear absorption spectrum of DASPB in the polymer matrix shows a strong absorption band with peak absorption situated at 478 nm with a bandwidth of 100 nm, a medium absorption peaked at 270 nm with a bandwidth of 80 nm is observed. Also no linear absorption is observed in the spectral range of 580 to 2000 nm.

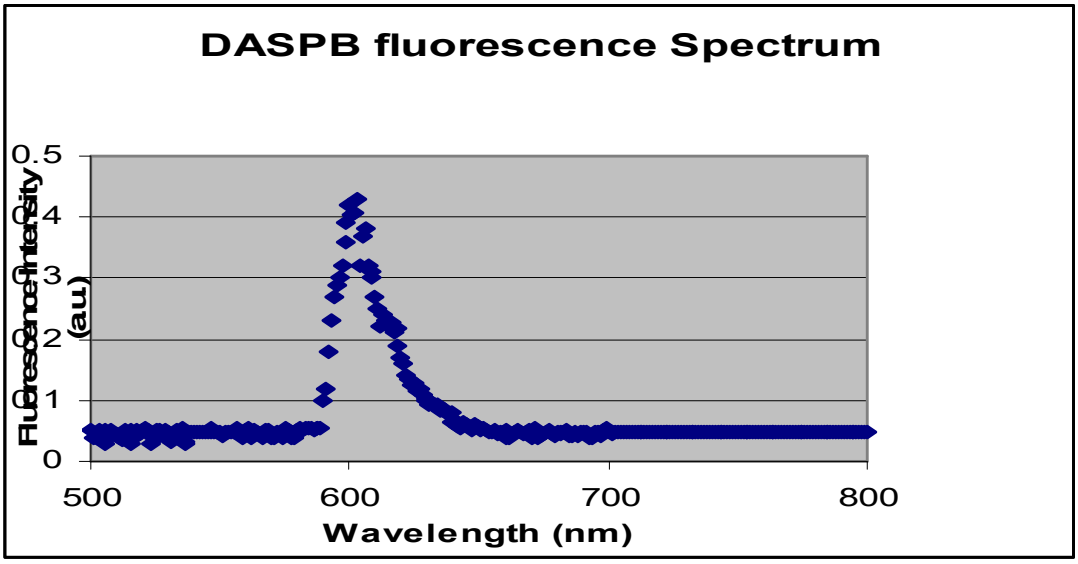


Fig. 4.5 : Fluorescence spectrum of DASPB dye-doped polymer film.

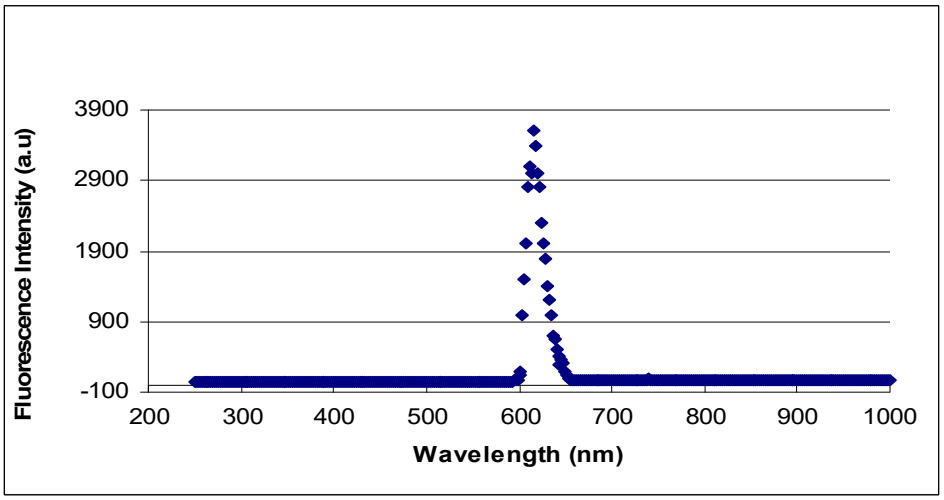


Fig. 4. 6 : Fluorescence spectrum of DASPB doped polymer film at 532 nm irradiation.

One photon fluorescence spectrum of the DASPB dye doped PMMA-MA polymer film sample of 1 mM dye concentration is recorded by a Rf 50000U from Schmadza spectral fluophotometer with the resolution of 1 nm. The peak wavelength of 610 nm is observed for the single-photon induced fluorescence with a bandwidth of 60 nm as shown in Figure 4.5. Figure 4.6 depicts a single photon fluorescence spectrum of DASPB doped film when excited at 532 nm using a Nd:YAG laser beam.

The linear absorption coefficient α_0 is calculated for two wavelengths 1.06 µm and 532 nm by using formula $\alpha_0 = -\frac{1}{t}\ln\left[\frac{1}{T}\right]$ ---------- (4.1)

where (t) is the thickness of sample and T is the transmittance [402].

The refractive index n_0 can be calculated from transmittance spectrum of the film according to the following equation [403]

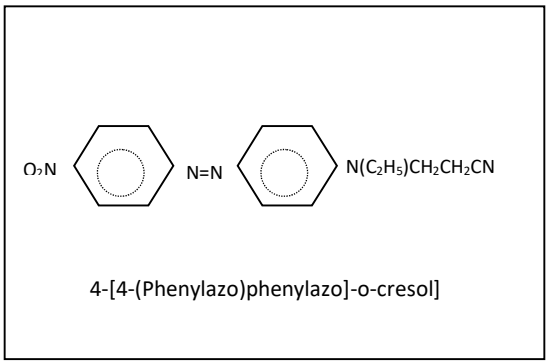
$$n_0 = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)\right]^{1/2} \quad \text{--------} \quad (4.2)$$

The linear absorption coefficient and the refractive index of DASPB doped PMMA-MA film are listed in table 4.1.

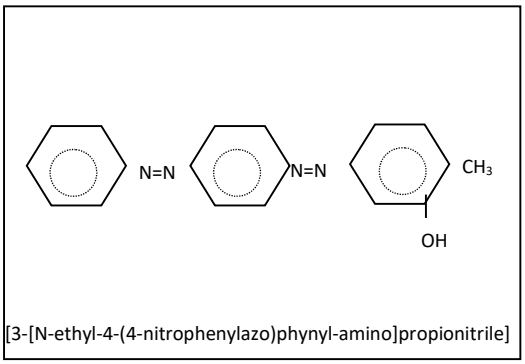
Table 4.1: Linear absorption coefficient and refractive index versus wavelength of DASPB.

Wavelength (nm)	Thickness (µm)	Transmittance	α_0 $(\mu m)^{-1}$	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

4. 4. 2 LINEAR OPTICAL PROPERTIES of DO-25 & DY-7



Disperse Orange - 25



Disperse Yellow – 7

Table 4.2: Linear absorption coefficient and refractive index versus wavelength of DO-25.

Wavelength (nm)	Thickness (µm)	Transmittance	α_0 $(\mu m)^{-1}$	n_0
532	10	0.6	-0.0510786	2.999
633	10	0.9	-0.010536	1.8070
1064	10	0.98	-0.0020195	1.22345

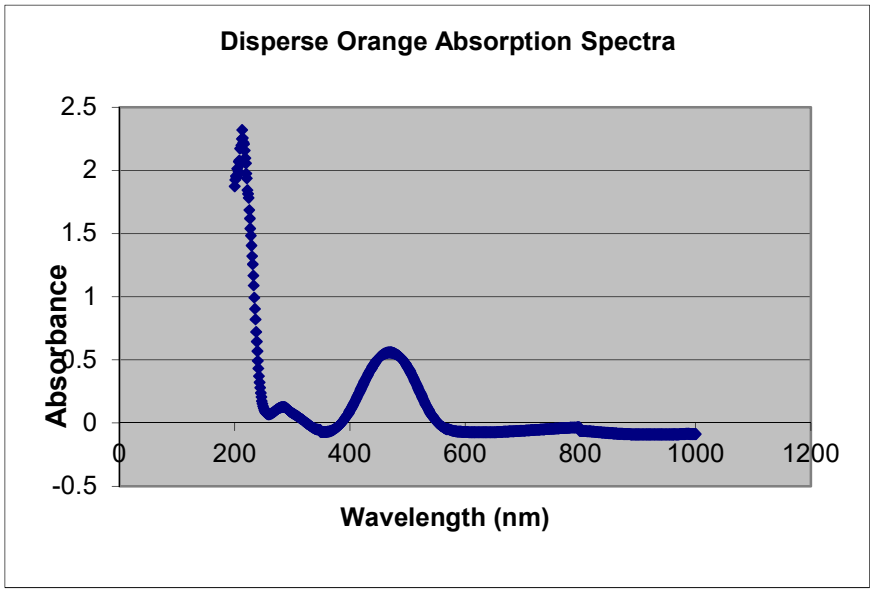


Fig. 4.7 : Ground state absorption spectrum of Disperse Orange.

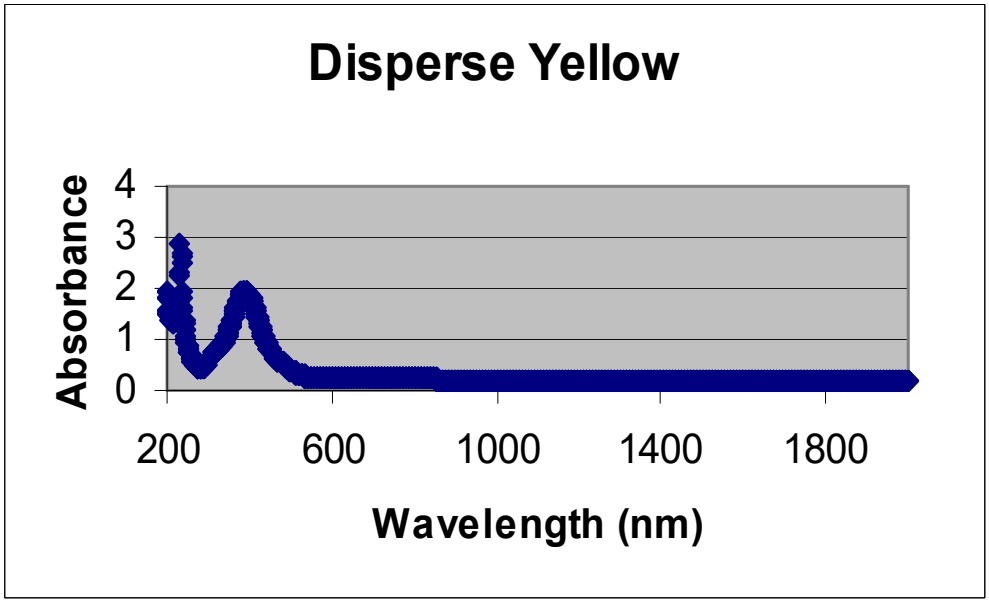


Fig. 4. 8 : Ground state absorption spectrum of Disperse Yellow.

Table 4.3: Linear absorption coefficient and refractive index versus wavelength of DY-7.

Wavelength (nm)	Thickness (µm)	Transmittance	α_0 $(\mu m)^{-1}$	n_0
532	10	0.58	-0.05447226	3.12864
633	10	0.9	-0.010536	1.59543
1064	10	0.98	-0.00202026	1.22347

To study the linearity of the prepared sample films, the samples are placed in front of a Nd-YAG CW laser beam of 532 nm and the beam is passed through the sample films. By varying input power of the laser beam, the output power of the beam transmitted through the sample films is measured. A typical plot of output power versus input power for DY-7 dye-doped PMMA-MA sample is shown in figure 4.9.

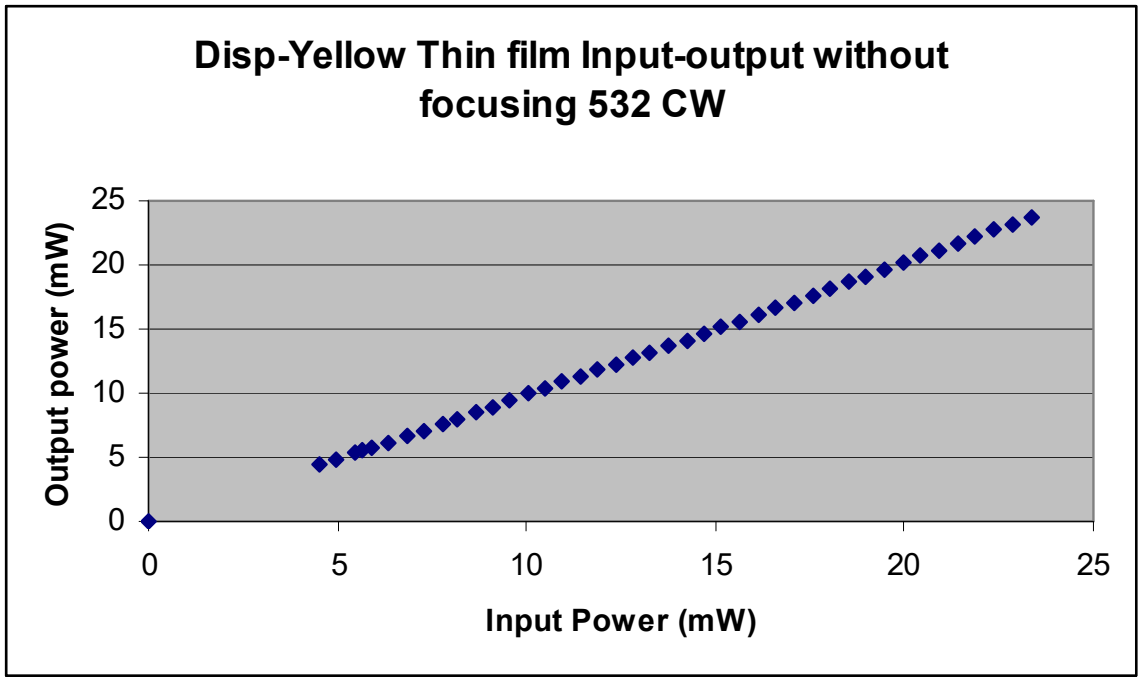


Fig. 4.9 : Linear Transmission study of DY-7 in PMMA-MA matrix Film.

The absorption spectra of the thin dye-doped films of three samples shown above infer that transmission through these films is relatively low at below band gap region, indicating a high concentration of defects, free carriers. The transmittance increases abruptly in the short wavelengths which are due to the band edge absorption. A sudden increase at a particular wavelength indicates the presence of optical band gap in these samples. The incoming photons get sufficient energy to excite electrons from the valence band to the conduction band, which results in strong absorption in dye samples. The optical absorption edge is determined by the optical absorption, a simple and common method used that provides an explanation for the features concerning the band structure of the films [403-405].

4.5 CONCLUSION

In this Chapter, the structural design of organic dye molecules for better nonlinear properties and preparation of dye-doped polymer film samples of variable dye concentration and variable film thickness using the hot-press technique is explored. Based on the molecular structural studies three dyes namely 4-(4-(Dimethylamino)styryl)-1-docosyl pyridinium bromide [DASPB], 3-(N-ethyl-4-(4-nitrophenylazo) phynyl-amino)propionitrile (Disperse Orange, DO- 25), and 4-(4-(Phenylazo)phenylazo)-o-cresol [Disperse Yellow, DY-7)] are chosen for further study.

The linear absorption property of prepared films of these three dyes doped in Polymethyl methacrylate methacrylic acid (PMMA-MA) are studied using molecular absorption spectroscopy and the results are discussed. The results of the physical parameters and linear optical properties are summarized in table 4.4.

Table 4.4 : Comparison of Physical parameters and Linear Absorption properties of dye-doped samples.

S. No.	Parameter/Property	DASPB in PMMA-MA	DO-25 in PMMA-MA	DY-7 in PMMA-MA
1	Linear absorption range (bandwidth)	100 nm	100 nm	80 nm
2	Linear absorption peak (nm)	479 nm	468 nm	468 nm
3	Linear Transmission Range (nm)	480 – 1,600	530 – 1,600	528 – 1,600
4	Linear Transmittance (T) at 532 nm	0.7	0.6	0.58
5	Linear absorption coefficient (α_0) at 532 nm	-0.03567	-0.0510786	-0.05447226
6	Linear Refractive index (n_0) at 532 nm	2.4488	2.999	3.12864
7	Dye concentrations in prepared films	1 mM, 2 mM, & 5 mM	1 mM, 2 mM, & 5 mM	1 mM, 2 mM, & 5 mM
8	Dye concentration in the solution (Chloroform)	0.0001 mol/L	0.0001 mol/L	0.0001 mol/L
9	Film Thickness	10 µm	10 µm	10 µm
10	Single photon florescence Peak	610 nm	Not applicable	Not applicable

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CHAPTER FIVE

Experimental Study & Results of Nonlinear Refraction, Nonlinear Absorption, and Optical Limiting of Dye-doped Polymer Films

CONTENTS PAGE No.

5.1 INTRODUCTION

The search for optimum nonlinear material is active since forty years, through the combined efforts of physics, material science, and chemistry researchers by carrying out continuous nonlinear experiments on various possible materials, this fields seems to be still very active in research and a promising tool for future photonics technology. Molecules with high two-photon absorption (TPA) cross section and the molecules which have reverse saturation absorption (RSA) cross section are of great interest today because of their application to three-dimensional optical data storage and electronic switches. For more than four decades several techniques have been used to determine the two-photon absorption cross sections and reverse saturation absorption cross sections of materials. They include direct methods, such as nonlinear transmission and Z-scan methods, and indirect methods, such as two-photon excited fluorescence and two-photon pump-probe transient absorption spectroscopy. In this chapter, the nonlinear optical properties like nonlinear absorption and nonlinear refraction of sample films of these three dyes doped in Polymethyl methacrylate-methacrylic acid (PMMA-MA) are studied using open aperture and closed aperture Z-scan experimental method. Finally, the optical limiting properties of these films are also studied for type 1 and type 2 optical limiting configurations at different input intensity using CW laser beam.

5.2 THERMAL SELF-DIFFRACTION STUDY

The ray diagram of an experimental configuration for self-diffraction study is shown in Fig. 5.1. A CW semiconductor diode laser beam is used as an incident illumination beam. The laser beam is focused by a convex lens with focal length of 5 cm. The dye-doped sample film is placed closely behind the focus and the beam is projected onto a screen for observation, which is placed 25 cm away from the focal point of the lens. The output beam pattern is recorded on observation screen using a digital camera. Multiple concentric rings appeared on the screen when the power of laser beam exceeds a certain value (threshold value = 10 mW). The number of rings and the size of the outermost ring are both increased with increasing illuminating laser power. This shows that the number and the size of the rings are intensity dependent and the rings are produced due to thermally induced refractive index change in the dye-doped film medium and are responsible for the observed diffraction. When the Gaussian beam illuminates the film, the dye medium absorbs the light and its temperature rises. The increased temperature results in the

variation of local refractive index and hence induces the self-diffraction. Thermally induced pattern of such diffraction rings for the dye concentrations 1 mM and 2 mM are shown in Fig. 5.2. The increasing of the number of diffraction rings and the size of the outmost ring with increasing the concentration are due to the fact that the increase in aggregation of the dye molecules at the point of focus at higher concentrations. The diffusivity of light extends to a larger region thereby causing more interference to take place leading to an increased number of rings [406].

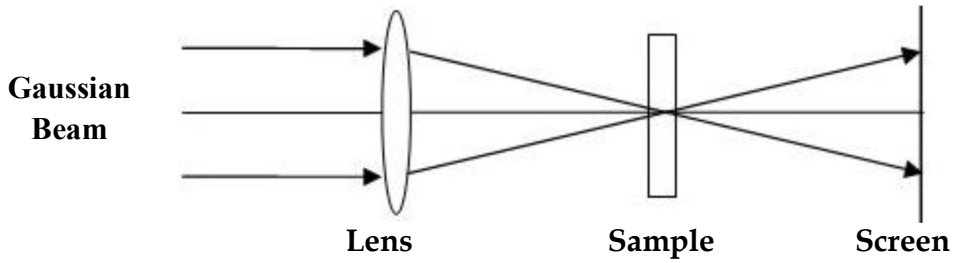

Fig. 5.1 : Ray diagram of self-diffraction study

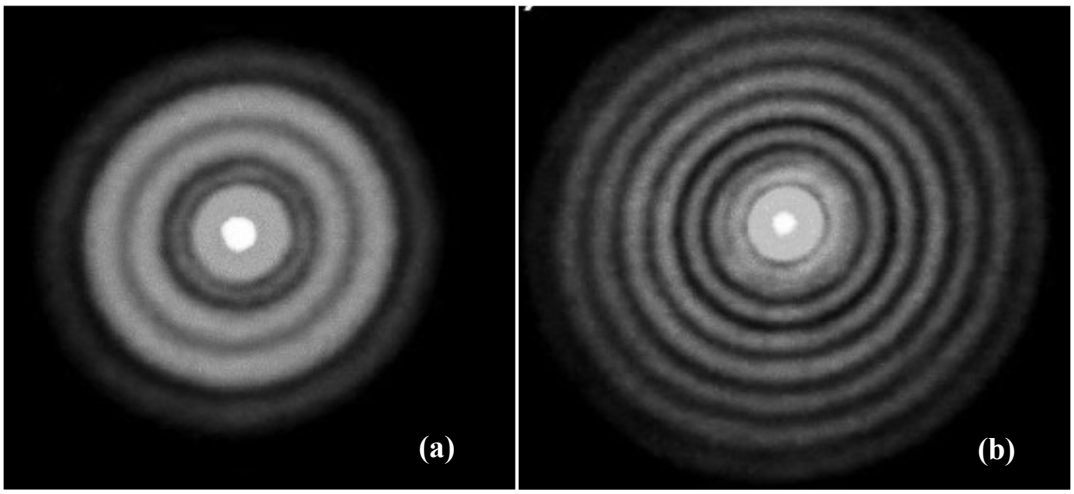

Fig. 5.2 : A typical diffraction rings pattern obtained by illuminating laser beam of λ = 532 nm on dye-doped films of concentrations: (a) 1 mM and (b) 2 mM.

5. 3 NONLINEAR OPTICAL PROPERTIES

Many dyes have shown considerable third order nonlinearity for intense laser light like Phthalocynamines (Perry et al. 1994, [407]), porphyrins (Blau et al. 1985 [408], Sevian et al. 1996 [409]). Castillo et al. (1994 [410]) observed the thermal lensing effect resulting from one and two-photon. Muto et al. (1998 [411]) 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. Brzozowski et al. (2001[412]) 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. Venugopal Rao et al. (2002) [413] reported the non-linearity of Rhodamine B dye in methanol. Umakanta Tripathy et al. (2002) [414] published a few parameters of IR 140 dye in dimethyl sulphoxide (DMSO) using Z-scan techniques. Chen et al. (2003) [415] reported the third-order optical nonlinearity of fullerene-containing polyurethane films at telecommunication wavelengths. Dharmadhikari et al (2004) observed the higher-order optical nonlinearities in 4-dimethylamino-N-methyl-4-stilbazoliumtosylate [416] and Ganeev et al. (2004) observed the fifth order optical nonlinearity of pseudoisocyanine solution [417]. 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 [418]. Aithal et al. studied two photon absorption cross section and nonlinear absorption properties of DASPB [419], Singh et al. [420] DO-25, and DY-7 at picoseconds regime in solution from. Reports show that there has been less work carried on the study of nonlinearities of dyes in solid medium. It is expected that by studying nonlinear properties of dye in solid medium one can fabricate new elements, which have potential application in optical limiting and optical switching.

5. 3. 1 NONLINEAR OPTICAL PROPERTIES OF DASPB

(A) Measurement of TPA Cross section :

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 5.3. VIS cutting filters are used during the measurement of the upconversion fluorescence to cut transmitted pump energy [421].

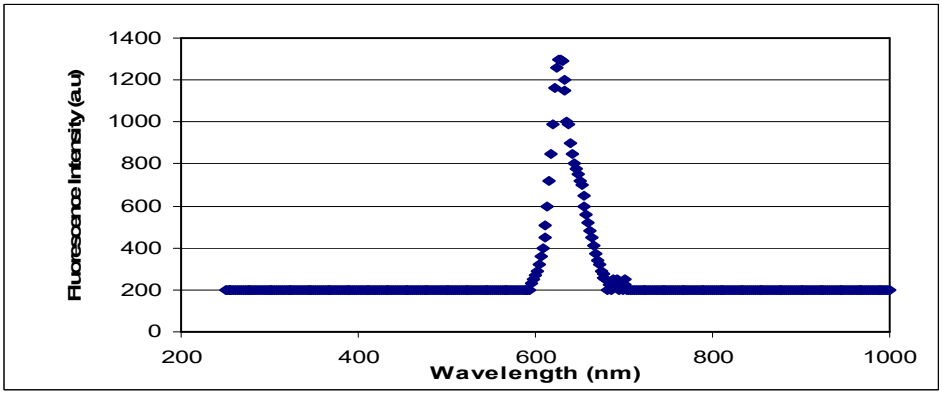

Fig. 5.3. 1.06 µm irradiated two-photon induced emission spectrum of DASPB.

(B) Nonlinear Absorption Study (Open Aperture Z-Scan) :

The Z-scan technique proposed by Sheik Bahae et al. (1990 [422-423]) 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 5.4. 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 focused 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. 5.1).

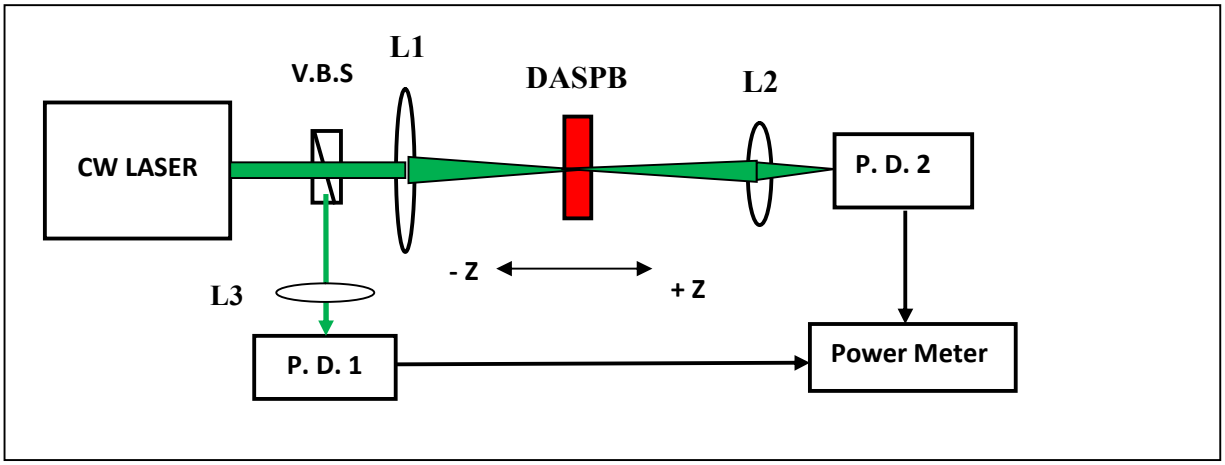

Fig. 5.4 Experimental setup for open aperture Z scan for nonlinear samples.

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 beam at 10mW, 20 mW and 30 mW. The results are depicted in Fig. 5.5 to Fig. 5.7 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 5.8. 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 5.7. 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 :

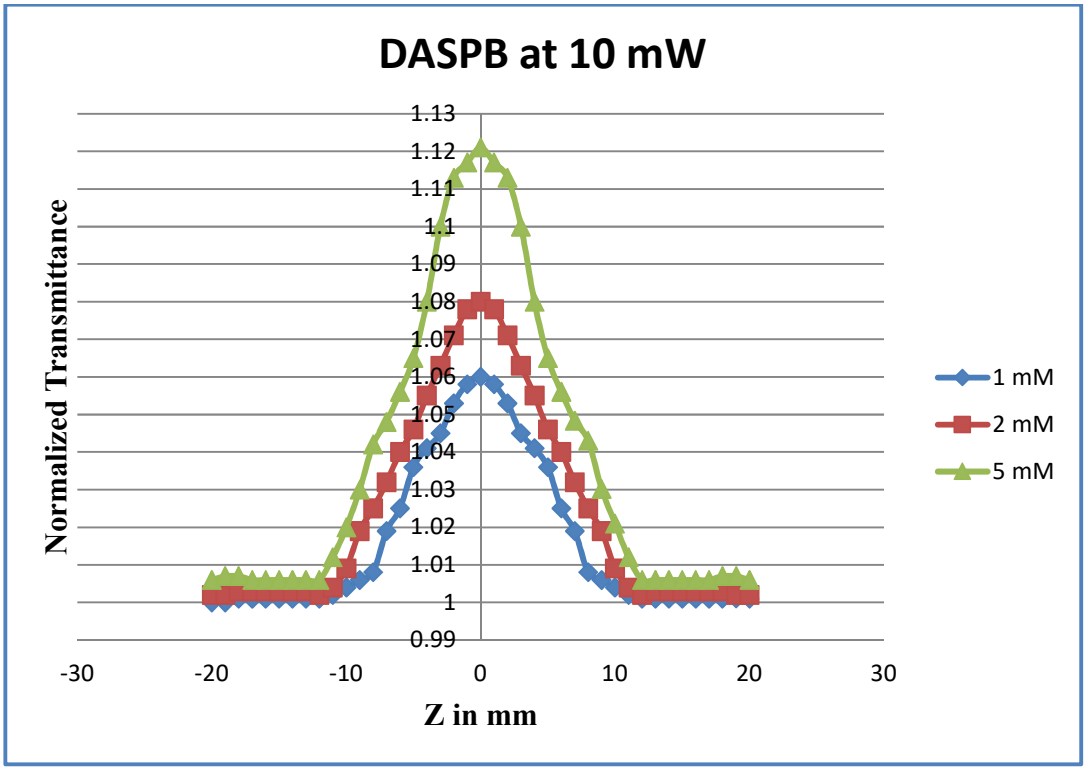

Fig. 5.5 : CW Z-scan (open aperture) of DASPB at different dye concentrations using 532 nm, 10 mW laser beam.

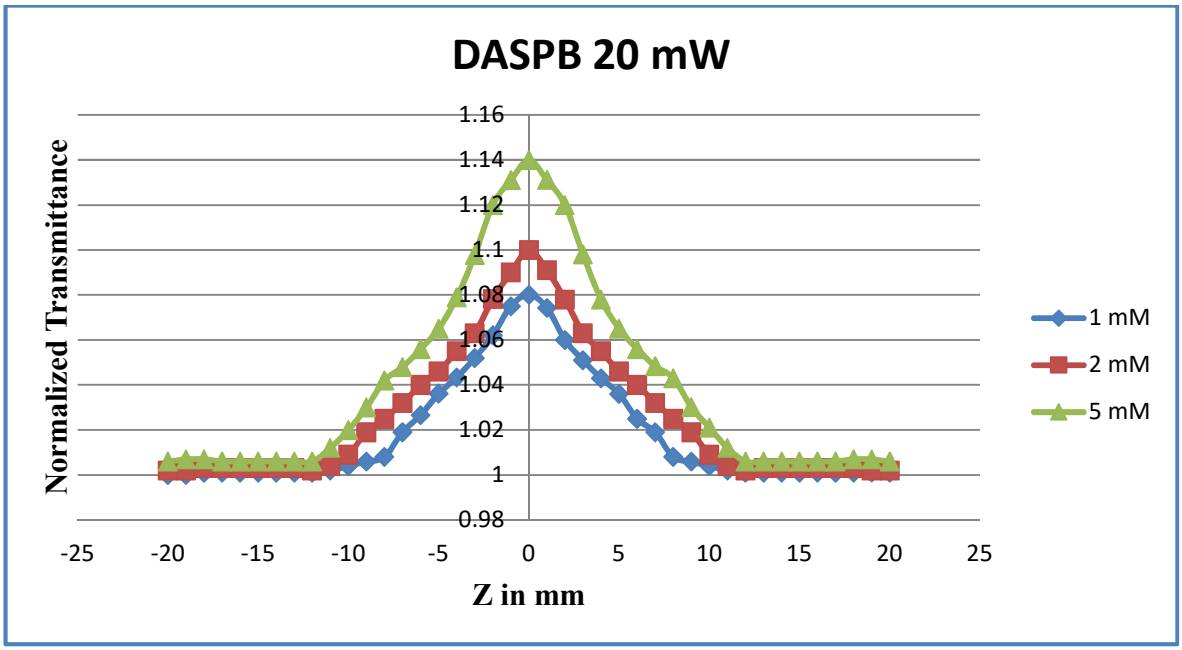

Fig. 5.6 : CW Z-scan (open aperture) of DASPB at different dye concentrations using 532 nm, 20 mW laser beam.

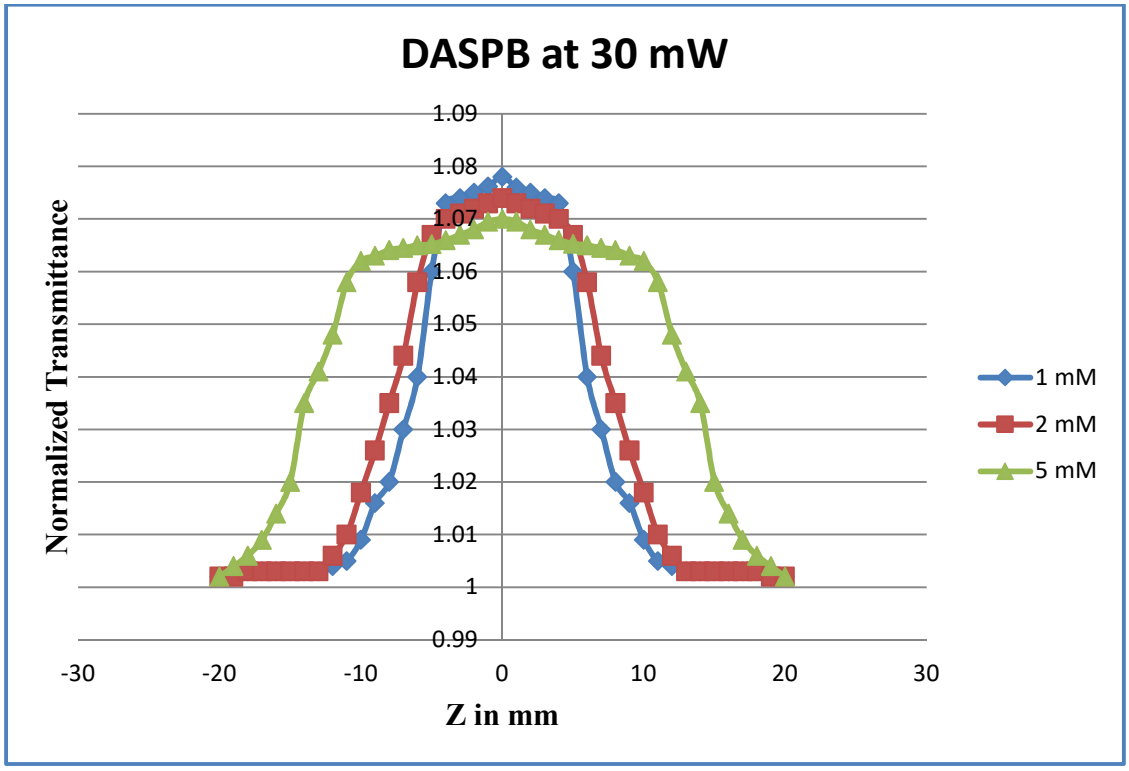

Fig. 5.7 : CW Z-scan (Open aperture) of DASPB at different dye concentrations using 532 nm, 30 mW laser beam.

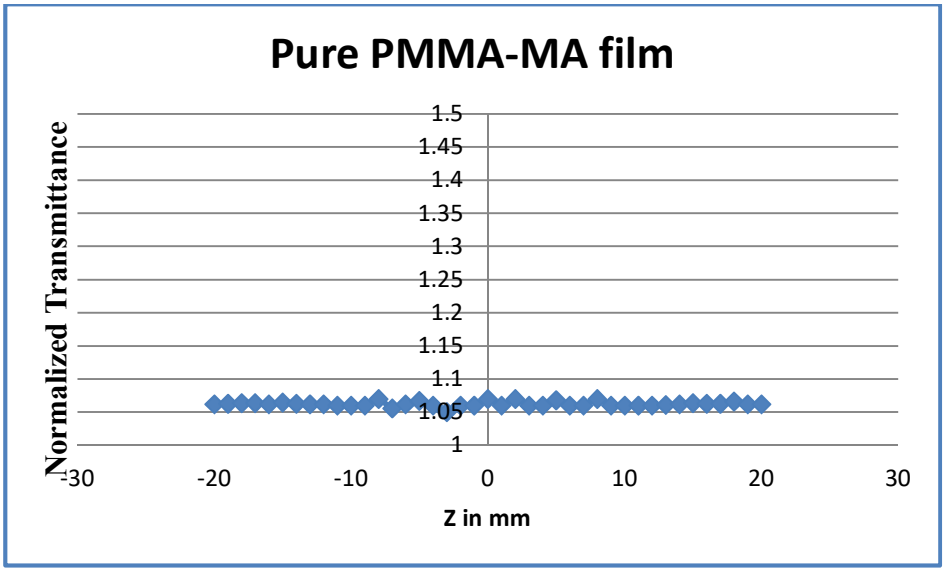

Fig. 5.8 : Z-scan transmittance of PMMA-MA film without dye sample

(i) 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.

(ii) At low input power, saturation absorption (SA) increased with increase in the concentration of dye in the sample.

From the graphs (figure 5.6 and figure .5.7), 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

$\beta = (2\sqrt{2}\,\Delta T) / (I_0 L_{eff})$ ----- (5.1)

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

$I_0 = 2P_{peak}/\pi\omega_0^2$ --------- (5.2)

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

$L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0$ ------- (5.3)

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 [422-423]. 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,

$\alpha = \alpha_0 + I\beta$ ------- (5.4)

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:

$n = n_0 + n_2 I.$ -------- (5.5)

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 5.1.

Table 5.1 : 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

(C) Nonlinear Refraction Study (Closed Aperture Z-Scan) :

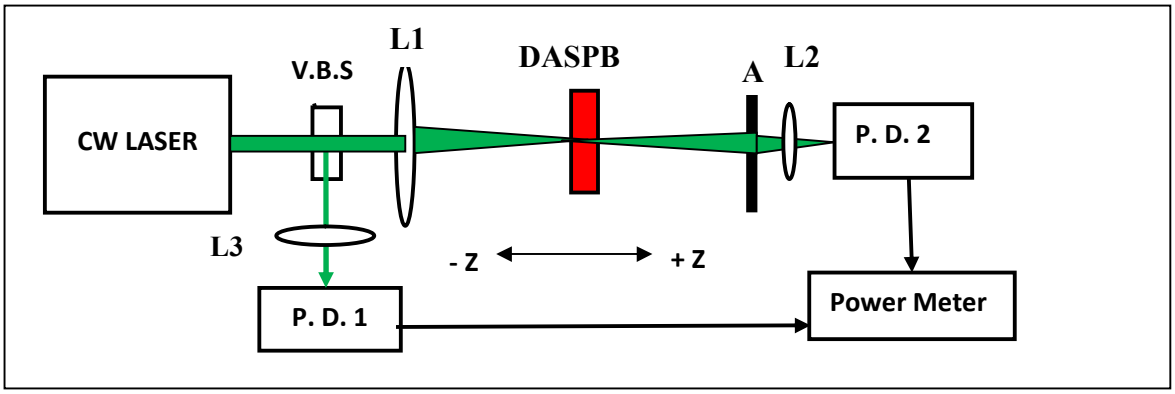

Fig. 5.9 : Experimental setup for closed aperture Z-scan for DASPB sample film.

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 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 is focused by means of a 3.5 cm focal length convex lens (L1), which produced a beam waist ω_0 of 15 μm. The peak intensity of the incident laser beam is calculated as I_0 = 3.5 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 5.9. 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 5.10.

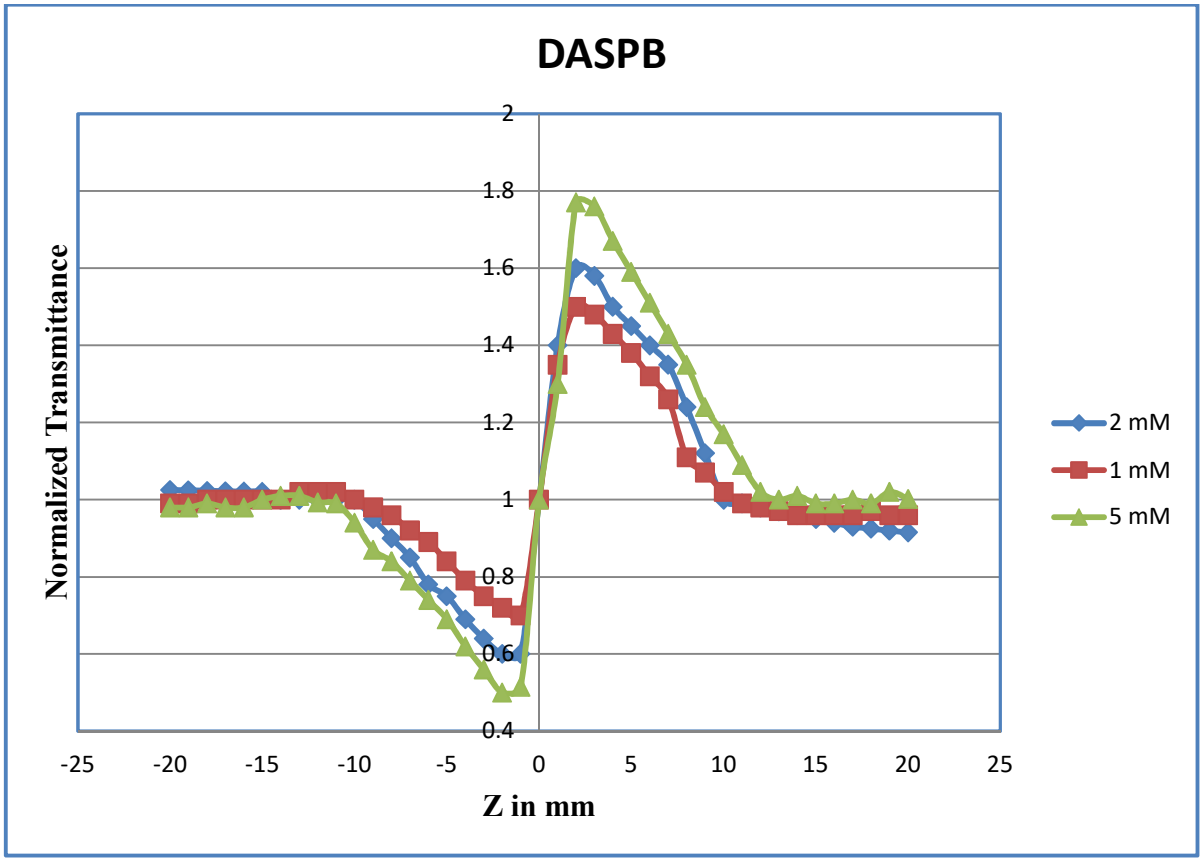

Fig. 5.10 : Closed-aperture CW Z-Scan with both refractive and absorptive nonlinearity at 532 nm for DASPB sample (20 mW).

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-focusing nonlinearity). This self-focusing 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 [422-423], 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 5 mM concentration DASPB dye doped sample is shown in figure 5.11 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 [424-425]. 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.

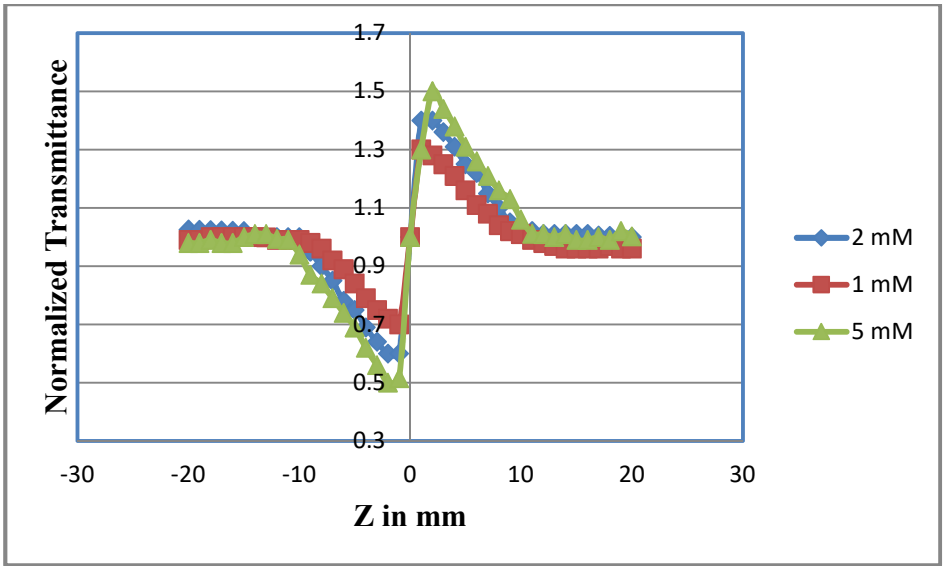

Fig. 5.11 : Closed-aperture CW Z-Scan with pure refractive nonlinearity at 532 nm for DASPB (20 mW).

The nonlinear refractive index n_2 can be calculated using the formula $n_2 = \frac{\Delta\emptyset\,\lambda}{2\pi I_0 L_{eff}}$ ------ (5.6)

and $|\Delta\emptyset| = \Delta T_{(p\text{-}v)} / [0.406\,(1\text{-}S)^{0.25}]$ --------- (5.7)

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 aperture linear 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 0.5 for closed aperture configurations used in our experiment. In eq. (5.6), I_0 is the intensity at the focal spot as per eq. (5.2) and L_{eff} is the effective length of the sample and is given by eq. (5.3).

The change in refractive index Δn can be calculated using the formula,

$\Delta n = n_2 I_0$ ------- (5.8).

Table 5.2 contains experimental values of nonlinear phase shift and nonlinear refractive index for DASPB dye-doped PMMA-MA film.

Table 5.2 : Nonlinear refractive index and nonlinear phase shift for DASPB film at 20 mW.

Wavelength (nm)	Concentration	ΔT_{p-v}	I_0 (KW/cm^2)	$\Delta\emptyset_{rad}$	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

(D) 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-focusing. Self-focusing 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 (5.6) and change in refractive index, Δn can be calculated using equation (5.8). Experimentally determined nonlinear refractive index n_2 can be used to find the real part of the third-order nonlinear optical susceptibility [χ^3] according to the following relation [424-425],

$$\text{Re } \chi^{(3)} = |\chi^3| = \frac{10^{-4}\,\epsilon_0\,(n_0^2)c^2\,n_2}{\pi} \quad (\text{cm}^2/\text{W}) \quad \text{---------} \quad (5.9)$$

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

$$\text{Im } \chi^{(3)} = \frac{10^{-2}\,\epsilon_0\,(n_0^2)c^2\,\lambda}{4\pi^2} \quad (\text{cm}^2/\text{W}) \quad \text{---------} \quad (5.10)$$

Table 5.3 : Third harmonic susceptibility for DASPB film at 20 mW.

Wavelength (nm)	Concentration	n_2 (cm^2/W) $\times 10^{-7}$	Δn ($\times 10^{-4}$)	[χ^3] (esu) $\times 10^{-6}$
532	1 mM	+ 0.69	2.415	9.149
	2 mM	+ 0.87	3.045	10.998
	5 mM	+ 1.09	3.815	13.349

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

$|\chi^3| = [(\text{Re}\,\chi^{(3)})^2 + (\text{Im}\,\chi^{(3)})^2]^{1/2}$ --------- (5.11)

Where ϵ_0 is the vaccum permitivity 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 5.3.

5.3.2 NONLINEAR OPTICAL PROPERTIES OF DISPERSE ORANGE-25

(A) Nonlinear Absorption Study (Open Aperture Z-Scan) :

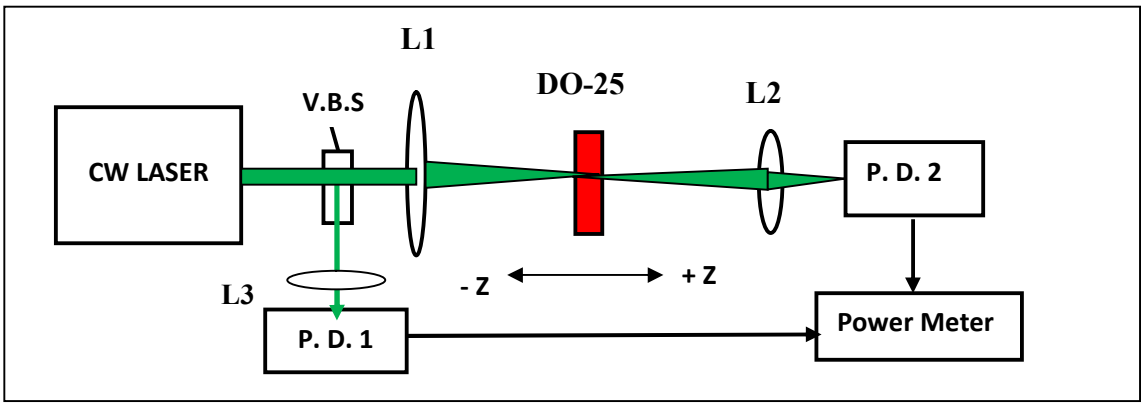

Fig. 5.12 : Experimental setup for open aperture Z scan for DO-25 samples.

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 5.12. The CW 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 μm. The peak intensity of the incident laser beam is calculated as I_0 = 3.5 kW/cm^2 and the diffraction length (Z_R) is calculated as 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. 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. 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. 5.1). 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. The results are depicted in Fig. 5.13, to Fig. 5.15 respectively.

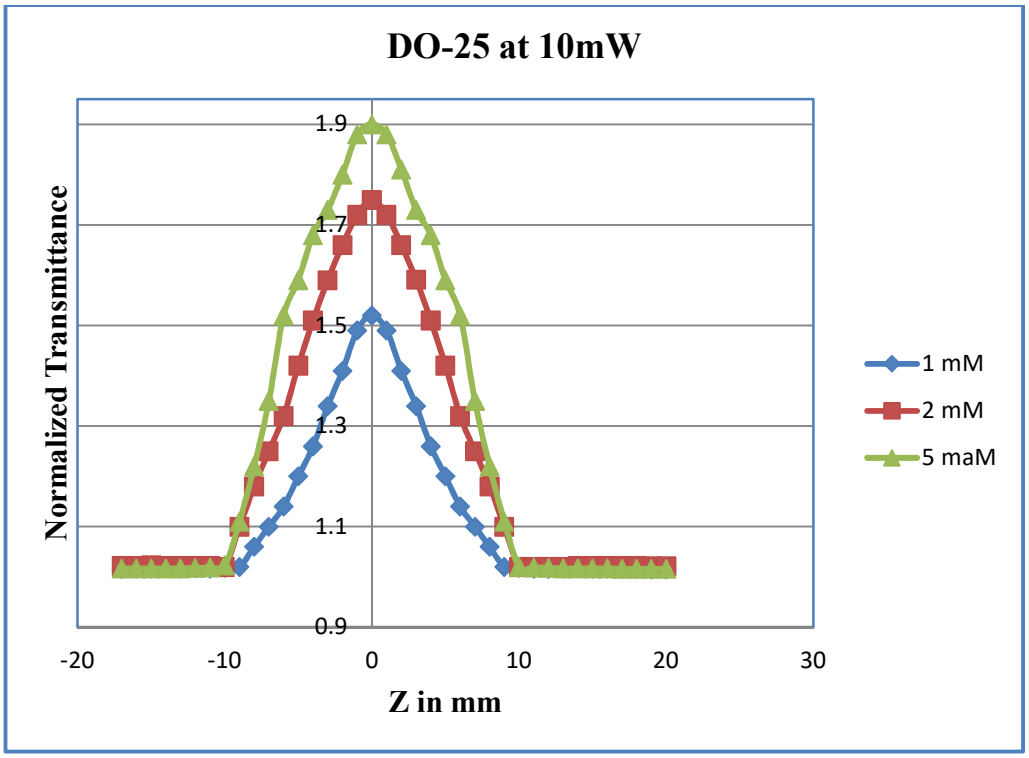

Fig. 5.13 : CW Open aperture Z-scan plot of DO-25 at different dye concentrations using 532 nm, 10 mW laser beam.

In Z-scan open aperture graph, the dye sample DO-25 has shown a decrease in transmittance with an increase in irradiance/input intensity due to reverse saturation absorption [426-427]. It is seen from the Z-scan plot that the DO-25 shows strong saturable absorption at low input intensity of laser beam.

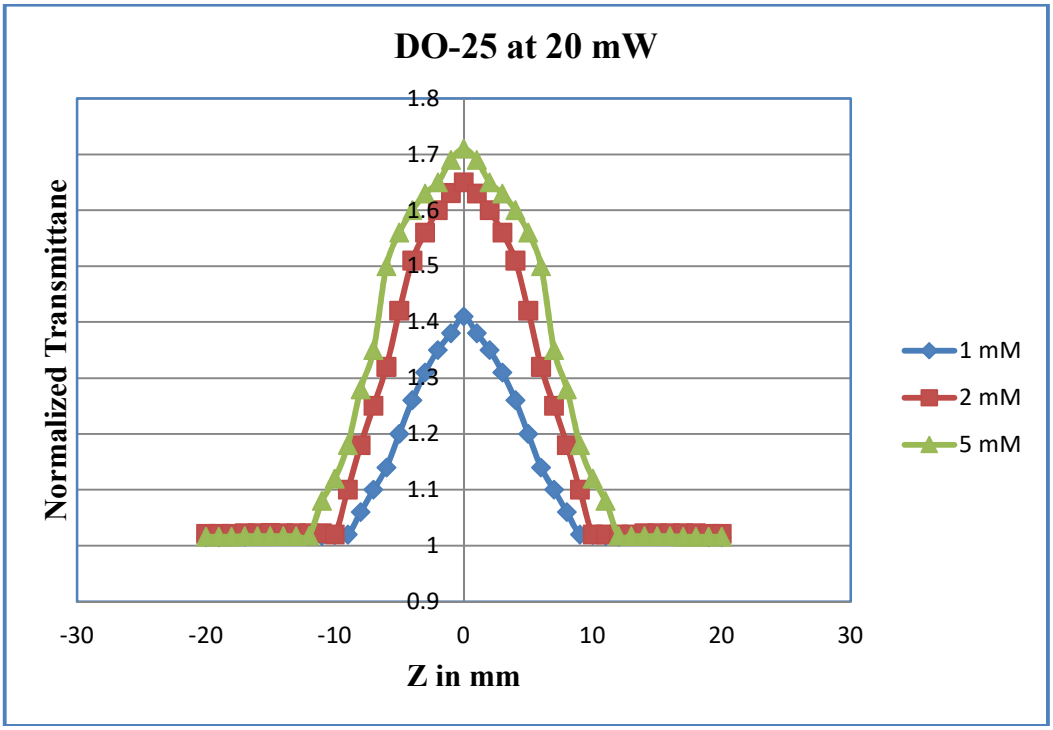

Fig. 5.14 : CW Open aperture Z-scan plot of DO-25 at different dye concentrations using 532 nm, 20 mW laser beam.

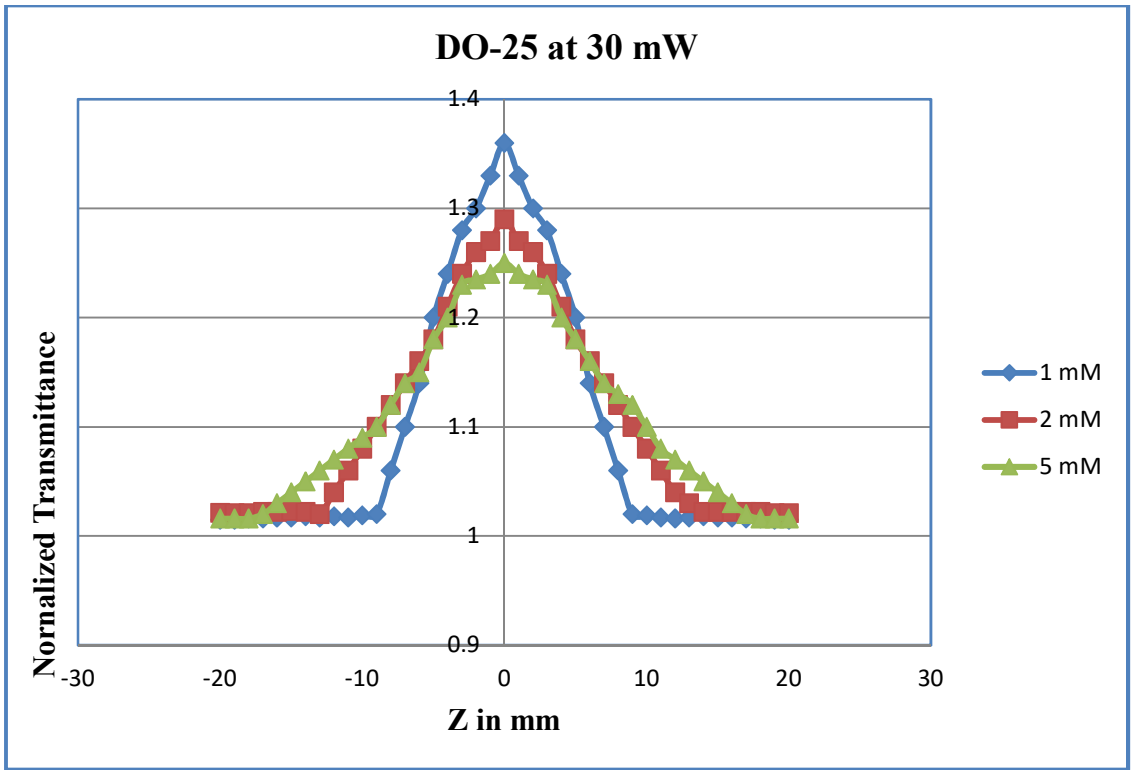

Fig. 5.15 : CW Open aperture Z-scan plot of DO-25 at different dye concentrations using 532 nm, 30 mW laser beam.

From the open aperture Z-scan, it is observed that due to nonlinear absorption, the transmittance of the DO-25 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 seen in figure 5.15. Such transformation from saturation absorption to reverse saturation 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 DO-25 for different concentrations and at different input power, it is observed that :

(i) At low input power, saturation absorption (SA) increased with increase in the concentration of dye in the sample.

(ii) 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 seen 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 using eq. (5.1). The transmittance increases with the increasing input intensity and has a maximum value at the focus where Z=0, which is the sign of saturation absorption according to Sheik-Bahae's theory. In eq. (5.1), ΔT is maximum transmittance at the focus (at Z = 0). When saturation absorption occurs, the absorption coefficient α will not become a constant. Instead, it will become a function of the excitation intensity as in the relation, $\alpha = \alpha_0 + I\beta$ where α_0 is the linear absorption coefficient and β is its nonlinear counterpart.

The experimental values of nonlinear absorption coefficient β at different dye concentrations for DO-25 dye-doped PMMA-MA films at 20 mW input power are listed in table 5.4.

Table 5.4 : Nonlinear absorption coefficient values for DO-25 dye-doped PMMA-MA film.

Wavelength (nm)	Concentration	ΔT	I_0 (KW/cm^2)	β (cm/W)× 10^{-3}
532	1 mM	0.14	3.5	-0.74
532	2 mM	0.11	3.5	-0.88
532	5 mM	0.092	3.5	-1.13

(B) Nonlinear Refraction Study (Closed Aperture Z-Scan) :

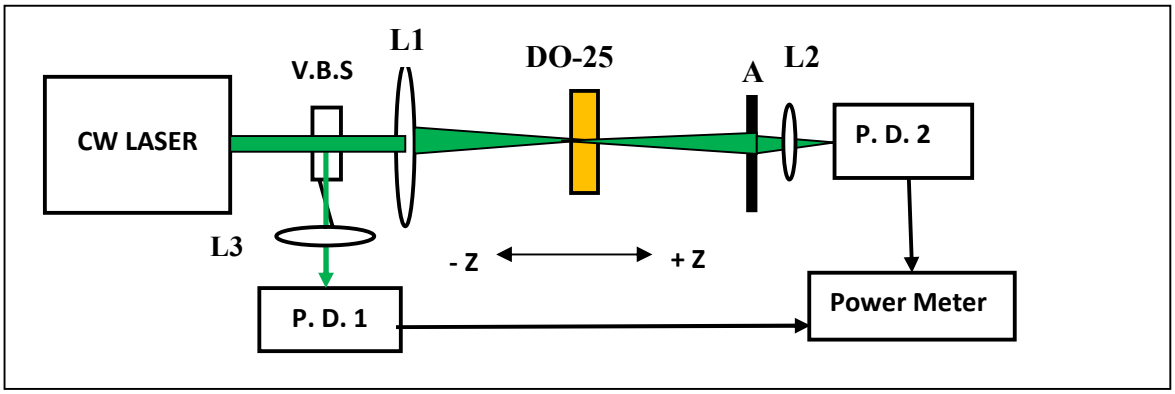

Fig. 5.16 : Experimental setup for closed aperture Z scan for DO-25 sample film.

The experimental set-up used for the closed aperture *Z*-scan measurement 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 is focused by means of a 3.5 cm focal length convex lens (L1), which produced a beam waist ω_0 of 15 μm. The peak intensity of the incident laser beam is calculated as I_0 = 3:5 kW/cm^2 and the diffraction length (Z_R) is calculated as 2.5 mm. The schematic of the experimental setup used is shown in figure 5.16. The dye sample is translated across the axial focal region along the direction of the propagation laser beam. The transmitted laser 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 5.17.

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 changes in the refractive index with variation in temperature. It can be argued that the defocusing effect for the dye in polymer film shown in figure 5.17 is attributed to a thermal nonlinearity resulting from the absorption of radiation at 532 nm. From the normalized nonlinear refraction graph, the measurable quantity ΔT_{p-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 determine nonlinear refractive coefficient, it is necessary to separate the nonlinear refraction

effect from nonlinear absorption effect. As per Sheik-Bahae [422-423], 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 5 mM concentration DO-25 dye doped sample is shown in figure 5.18 at the input laser beam intensity of 20 mW. Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used to calculate the absolute value of the third-order nonlinear optical susceptibility [426-427].

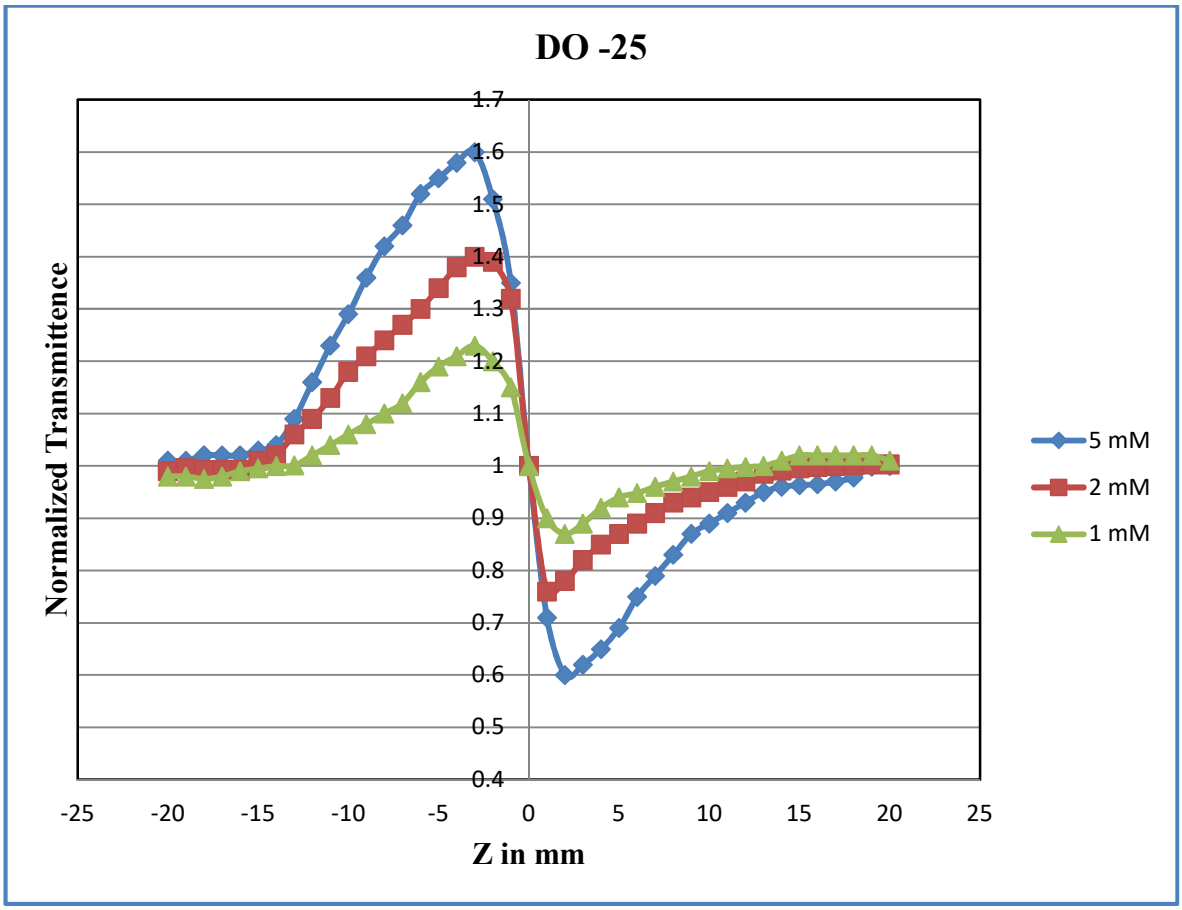

Fig. 5.17 : Closed-aperture CW Z-Scan with both refractive and absorptive nonlinearity at 532 nm for DO-25 (20 mW).

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 Eq. (5.6). The experimental values of nonlinear phase shift and nonlinear refractive index for DO-25 dye-doped PMMA-MA film are listed in Table 5.5.

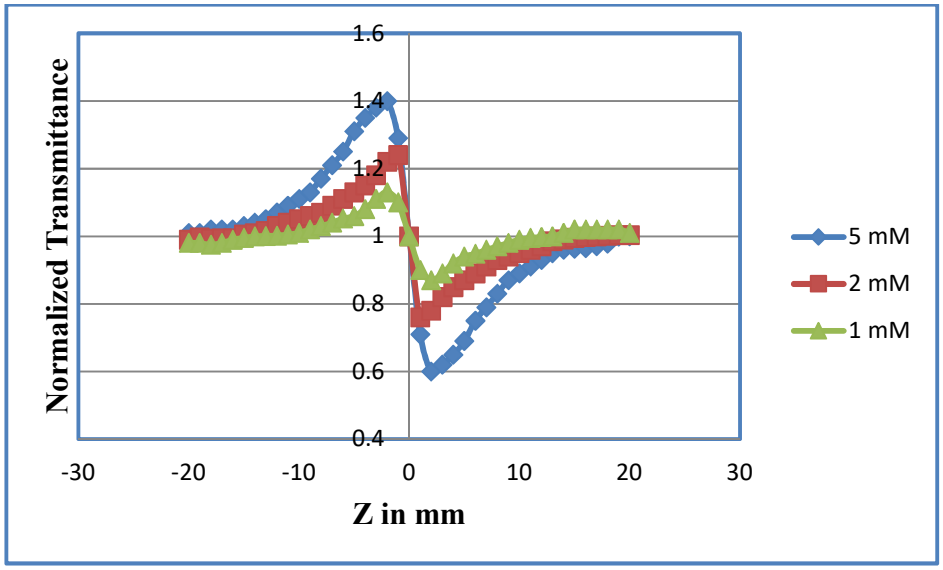

Fig. 5.18 : Closed-aperture CW Z-Scan with pure refractive nonlinearity at 532 nm for DO-25 (20 mW).

Table 5.5 : Nonlinear refractive index and nonlinear phase shift for DO-25 film.

Wavelength (nm)	Concentration	ΔT_{p-v}	I_0 KW/cm²	$\Delta\emptyset_{rad}$	n_2 (cm²/W) × 10^{-8}
532	1 mM	0.38	3.5	1.113	-3.25
532	2 mM	0.65	3.5	1.904	-5.57
532	5 mM	1.0	3.5	2.929	-8.36

(C) Third-order Nonlinear Optical Susceptibility $|\chi^{(3)}|$:

The Z- scan plot of DO-25 dye in PMMA-MA polymer film, show a pre-focal transmittance maximum (peak) followed by a post-focal transmittance minimum (valley). This indicates that DO-25 has a negative non-linearity due to self-defocusing. Self-defocusing is due to variation in refractive index with the thermally agitated dye molecules along with reverse saturation absorption. The nonlinear refractive index n_2 can be calculated using the equation (5.6) and change in refractive index, Δn can be calculated using equation (5.8). Experimentally determined nonlinear refractive index n_2 can be used to find the real part and imaginary part of the third-order nonlinear optical susceptibility [χ^3] using Eq. (5.9), (5.10), and (5.11).

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 5.6.

Table 5.6 : Third harmonic susceptibility of DO-25 film.

Wavelength (nm)	Concentration	n_2 (cm^2/W) $\times 10^{-8}$	Δn ($\times 10^{-4}$)	$[\chi^3]$ (esu) $\times 10^{-6}$
532	1 mM	- 3.25	-1.138	5.69
	2 mM	- 5.57	-1.950	7.45
	5 mM	- 8.36	-2.926	9.73

5.3.3 NONLINEAR OPTICAL PROPERTIES OF DISPERSE YELLOW-7

(A) Nonlinear Absorption Study (Open Aperture Z-Scan) :

The block diagram of the experimental setup used for the open aperture Z-scan study of DY-7 doped in PMMA-MA film is shown in figure 5.19. A CW diode laser of wavelength 532nm (BeamQ 30 mW Green Light Line) is used as the light source. The Gaussian profiled laser beam is focused by a convex lens (L1) of focal length f (f = 3.5 cm) to create 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 dye-doped sample is 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 transmitted beam is collected by means of a convex lens and the output intensity measured using photo detector - digital power meter assembly.

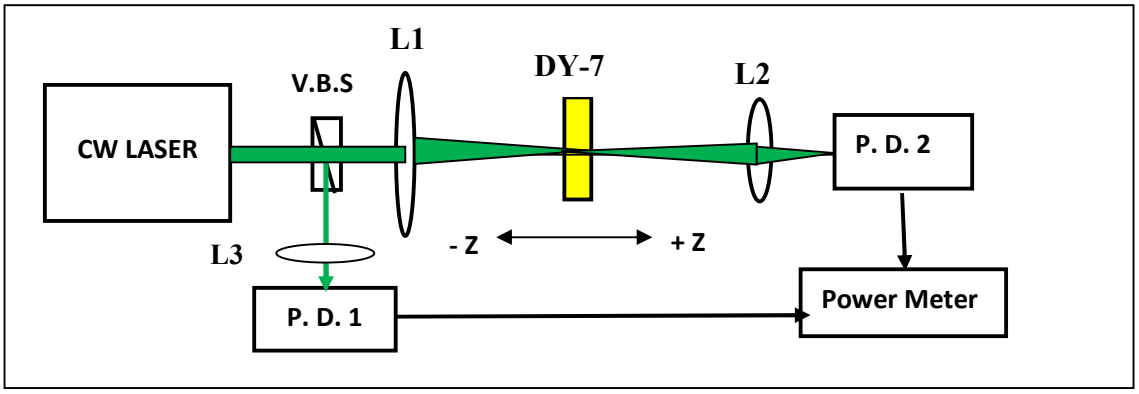

Fig. 5.19 : Experimental setup for open aperture Z scan for DY-7 samples.

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. 5.1). 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) and Photo detector (P.D.1). The DY-7 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.

The Z- scan experiment is performed for DY-7 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. The results are depicted in Fig. 5.20, to Fig. 5.22 respectively. In open aperture Z-scan, DY-7 has shown a decrease in transmittance with an increase in irradiance/input intensity due to reverse saturation absorption [426-427].

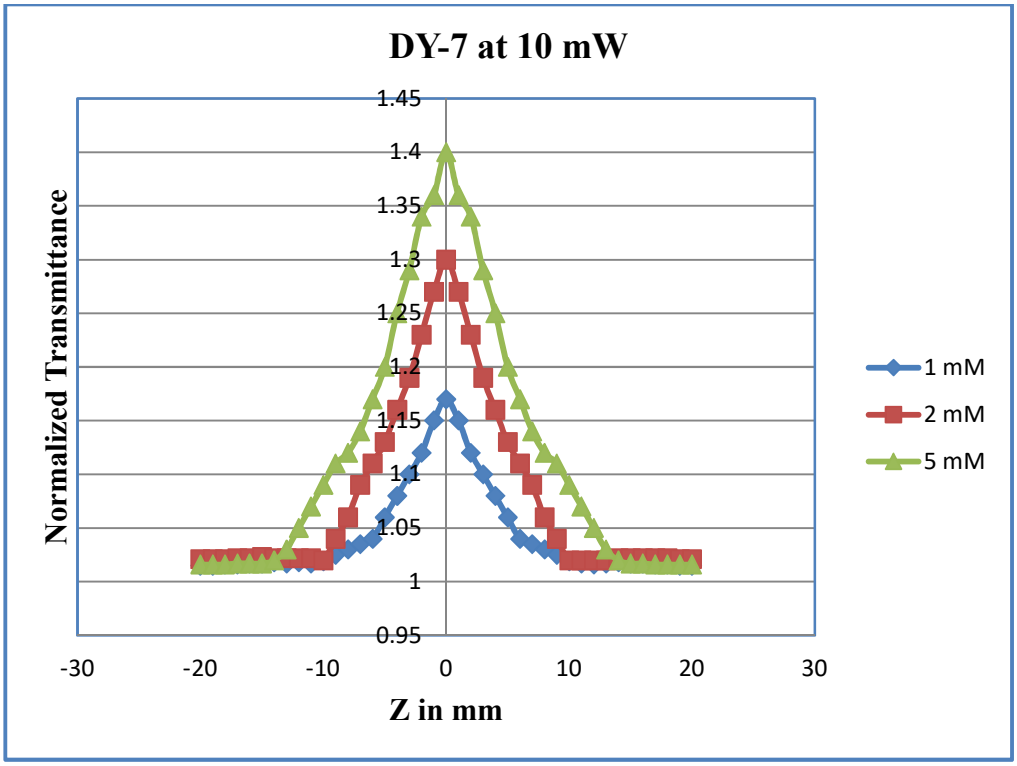

Fig. 5.20 : CW Open aperture Z-scan plot of DY-7 at different dye concentrations using 532 nm, 10 mW laser beam.

It is seen from the Z-scan plot that the DY-7 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 DY-7 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 seen in figure 5.22. Such transformation from saturation absorption to reverse saturation 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 DY-7 for different concentrations and at different input power, it is observed that :

(i) At low input power, saturation absorption (SA) increased with increase in the concentration of dye in the sample.

(ii) At the higher intensity of input light, DY-7 has shown reverse saturation absorption (RSA) so that saturation absorption (SA) of the sample is decreased.

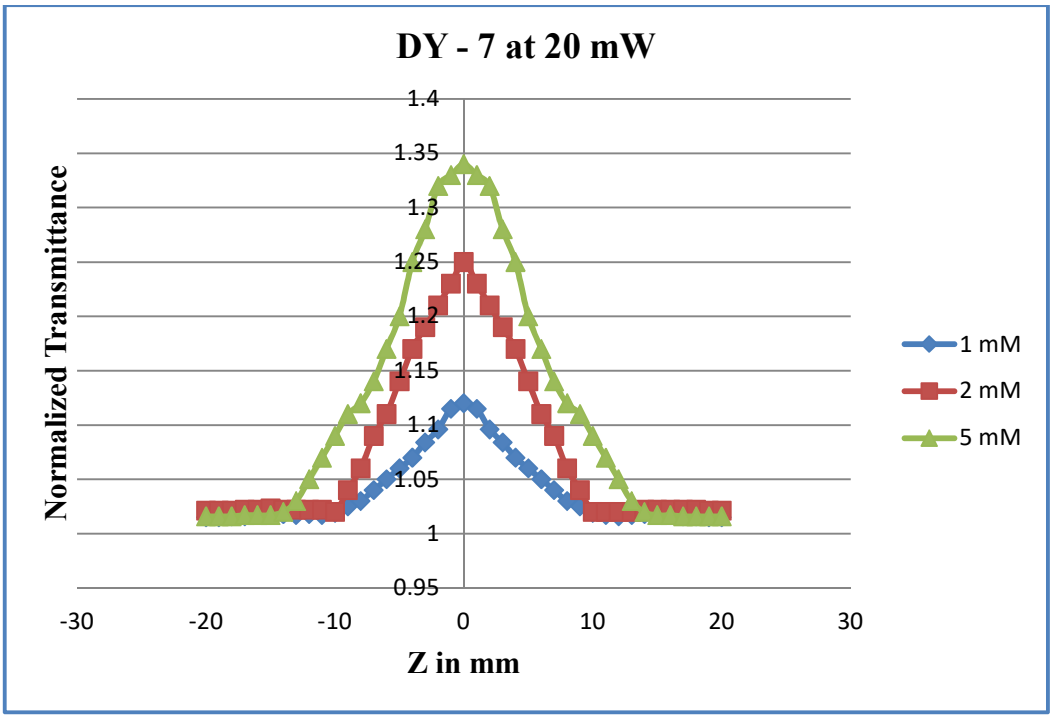

Fig. 5.21 : CW Open aperture Z-scan plot of DY-7 at different dye concentrations using 532 nm, 20 mW laser beam.

Reverse saturation absorption is found in the open aperture Z-scan graph of DY-7 dye-doped in PMMA-MA film as it shows a decrease in peak transmittance as increase in input power. The nonlinear absorption coefficient (β) can be calculated from the open aperture Z-scan data using eq. (5.1). At lower input intensity it is observed that the transmittance increases with the increasing input intensity as Z-scan progress and has a maximum value at the focus where Z=0,

which is the signature of saturation absorption according to Sheik-Bahae's theory. In eq. (5.1), ΔT is maximum transmittance at the focus (at Z = 0). When saturation absorption occurs, the absorption coefficient α will become a function of the excitation intensity as in the relation, $\alpha = \alpha_0 + I\beta$ where α_0 is the linear absorption coefficient and β is its nonlinear counterpart.

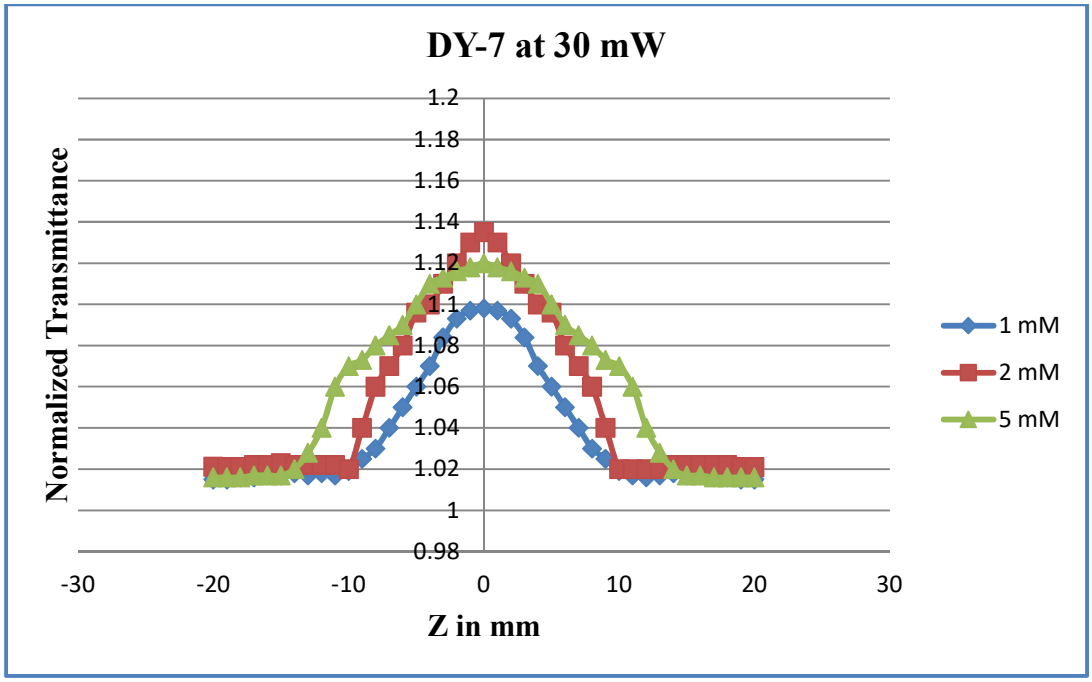

Fig. 5.22 : CW Open aperture Z-scan plot of DY-7 at different dye concentrations using 532 nm, 30 mW laser beam.

The experimental values of nonlinear absorption coefficient β at different dye concentrations for DY-7 dye-doped PMMA-MA films are listed in table 5.7.

Table 5.7 : Nonlinear absorption coefficient values for DY-7 dye-doped PMMA-MA film.

Wavelength (nm)	Concentration	ΔT	I_0 (KW/cm²)	β (cm/W)× 10^{-3}
532	1 mM	0.12	3.5	- 0.97
532	2 mM	0.26	3.5	- 2.10
532	5 mM	0.34	3.5	- 2.75

(B) Nonlinear Refraction Study (Closed Aperture Z-Scan) :

The experimental set-up used for the closed aperture *Z*-scan technique is same as the set-up used for open aperture Z-scan except for the output beam from the DY-7 dye-doped 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 is focused by means of a 3.5 cm focal length convex lens (L1), which produced a beam waist ω_0 of 15 μm. The peak intensity of the incident laser beam is calculated as I_0 = 3.5 kW/cm^2 and the diffraction length (Z_R) is calculated as 2.5 mm. The schematic of the experimental set up used is shown in figure 5.23. The dye sample is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The intensity of transmitted light through an aperture kept in the far field is measured using photo detector and the digital power meter assembly. The closed aperture Z-scan plot between Z in mm and normalized transmittance for different dye concentration is shown in figure 5.24.

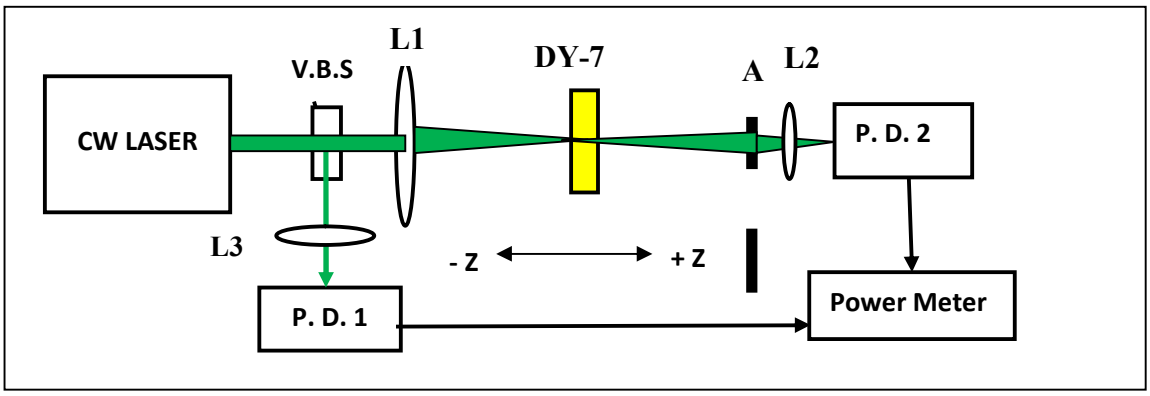

Fig. 5. 23 : Experimental setup of closed aperture Z scan for DY-7 sample.

The observed peak amplitude followed by a valley amplitude of normalized transmittance curve in the closed aperture *Z*-scan plot shows that the sign of the refractive nonlinearity is negative, i.e. the DY-7 dye-doped sample is self-defocusing property. The self-defocusing effect is due to the local variation of the refractive index with temperature. The defocusing effect for the DY-7 dye in polymer film shown in figure 5.24 is attributed to a thermal nonlinearity originating from intensity dependent absorption of light at 532 nm. The change in transmittance ΔT_{p-v} can be measured as the difference between the normalized peak transmittance value and valley transmittance value. Since the closed aperture transmittance is affected by the nonlinear refraction and absorption, the determination of nonlinear refraction is not easy and direct. To

solve this, one has to separate the effect of nonlinear absorption from that of the nonlinear refraction. The simple solution to get purely refractive nonlinearity is to divide the closed aperture transmittance data by the corresponding open aperture transmittance data [418].

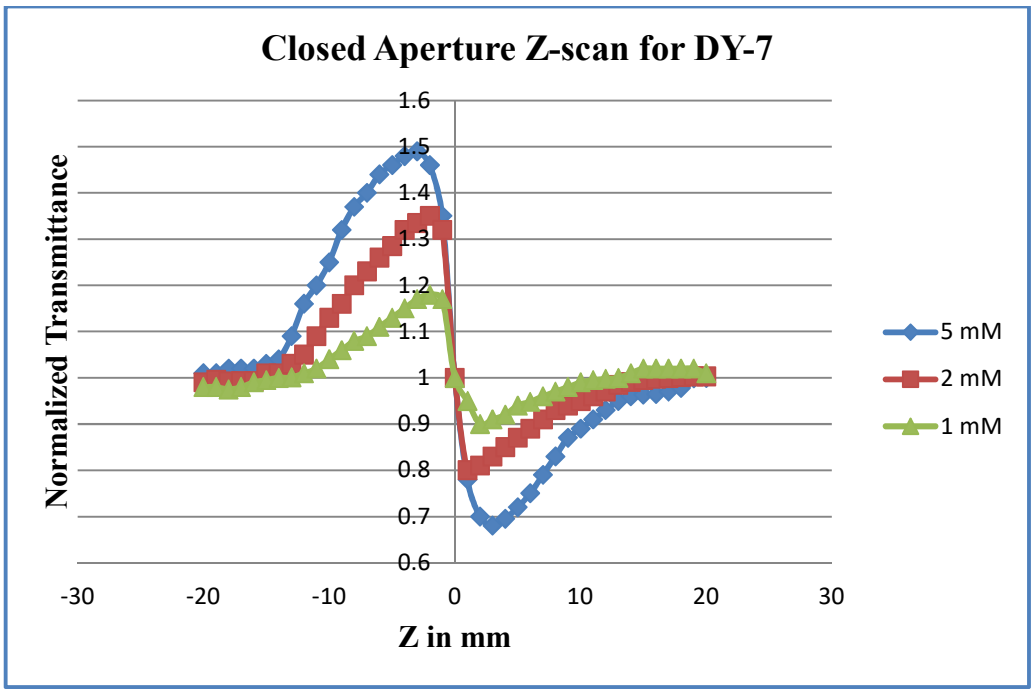

Fig. 5.24 : Nonlinear refraction of DY-7 using CW 532 nm 20 mW laser beam.

The pure nonlinear refractive *Z*-scan curves are shown in figure 5.25 for the Dy-7 dye in the polymer film. 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 DY-7 dye doping. Neither nonlinear absorption nor nonlinear refraction is observed. The nonlinear refractive index n_2 can be calculated using the Eq. (5.6). The experimental values of nonlinear phase shift and nonlinear refractive index for DY-7 dye-doped PMMA-MA film are listed in Table 5.8.

Table 5.8 : Nonlinear refractive index and nonlinear phase shift for DY-7 film.

Wavelength (nm)	Dye Concentration	ΔT_{P-V}	I_0 mW/cm^2	$\Delta\emptyset_{rad}$	n_2 (cm^2/mW) $\times 10^{-8}$
532	1 mM	0.29	3.5	0.8494	- 2.48
532	2 mM	0.55	3.5	1.6110	- 4.71
532	5 mM	0.82	3.5	2.4010	-7.02

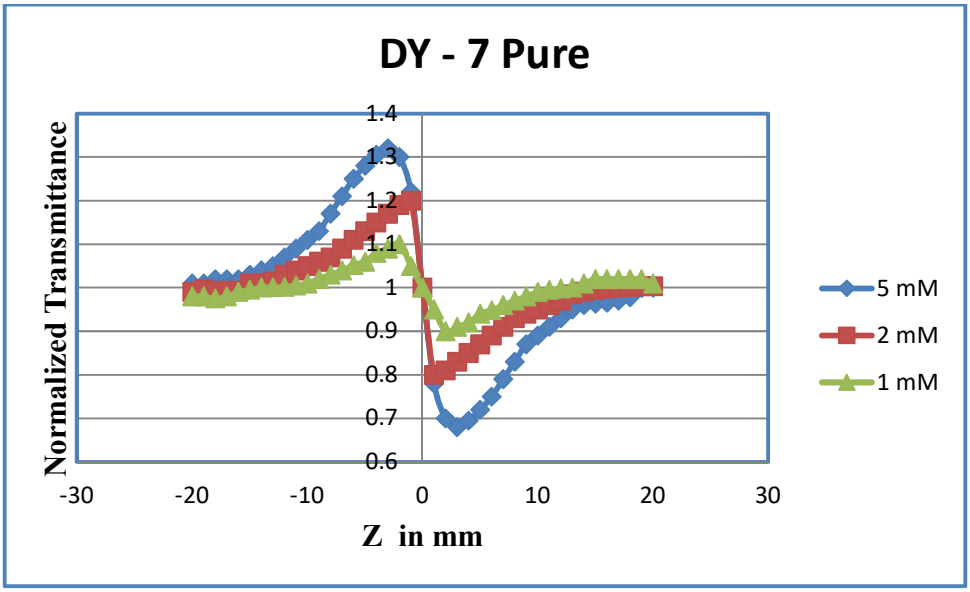

Fig. 5.25 : Pure nonlinear refraction plot of DY-7 using CW 532 nm 20 mW laser beam.

(C) Third-order Nonlinear Optical Susceptibility $|\chi^{(3)}|$:

The Z- scan plot of DY-7 dye in PMMA-MA polymer film, show a pre-focal transmittance maximum (peak) followed by a post-focal transmittance minimum (valley). This indicates that DY-7 has a negative nonlinearity due to self-defocusing. Self-defocusing is due to variation in refractive index with the thermally agitated dye molecules along with reverse saturation absorption. The nonlinear refractive index n_2 can be calculated using the equation (5.6) and change in refractive index, Δn can be calculated using equation (5.8). Experimentally determined nonlinear refractive index n_2 can be used to find the real part and imaginary part of the third-order nonlinear optical susceptibility $[\chi^3]$ using Eqs. (5.9), (5.10), and (5.11).

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 5.9.

Table 5.9 : Third harmonic susceptibility for DY-7 film.

Wavelength (nm)	Concentration	n_2 (cm^2/W) $\times 10^{-8}$	Δn ($\times 10^{-4}$)	$[\chi^3]$ (esu) $\times 10^{-6}$
532	1 mM	- 2.48	-0.868	5.12
	2 mM	-4.71	-1.649	6.82
	5 mM	-7.02	-2.457	8.52

5. 4 OPTICAL LIMITING STUDY

5.4.1 OPTICAL LIMITING STUDY OF DASPB :

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 hole 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 [418-430]. 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 DASPB 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 5.26. 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 5.27.

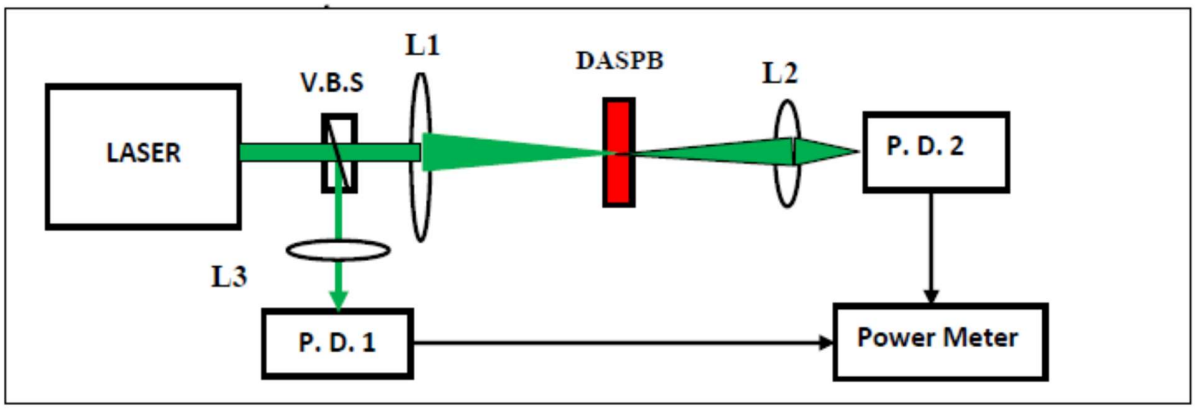

Fig. 5.26 : Experimental setup for Optical limiting (Type 1) due to pure absorptive nonlinearity.

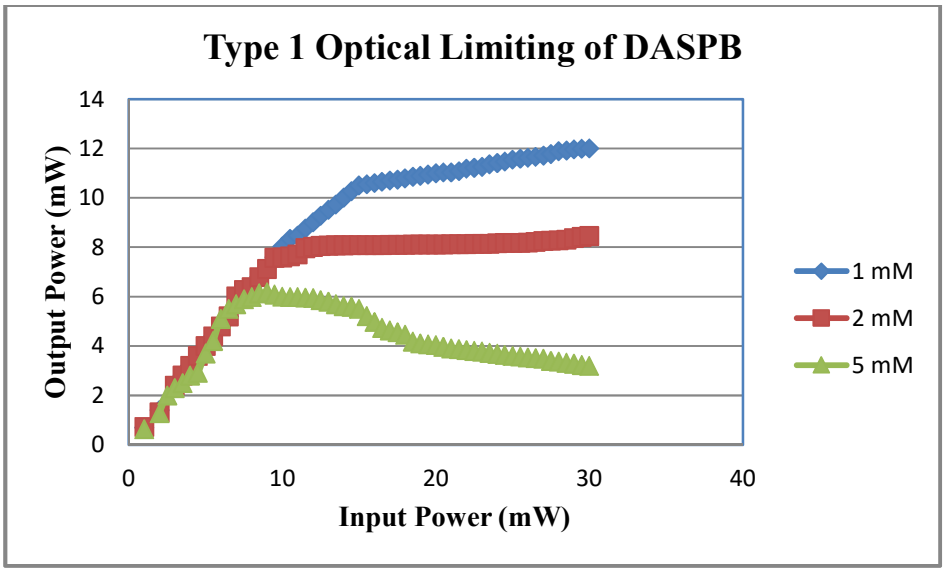

Fig. 5.27 : Open aperture (Type 1) Optical limiting behavior of DASPB dye-doped PMMA-MA film at CW 532 nm.

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 5.28. 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 5.29.

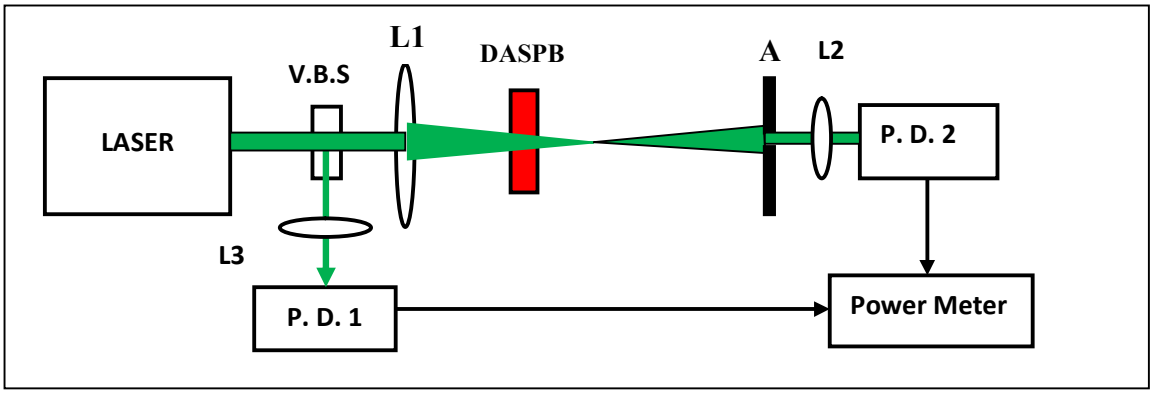

Fig. 5.28 : Experimental setup for closed aperture Optical limiting for DASPB doped PMMA-MA using nonlinear refraction.

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 5.29.

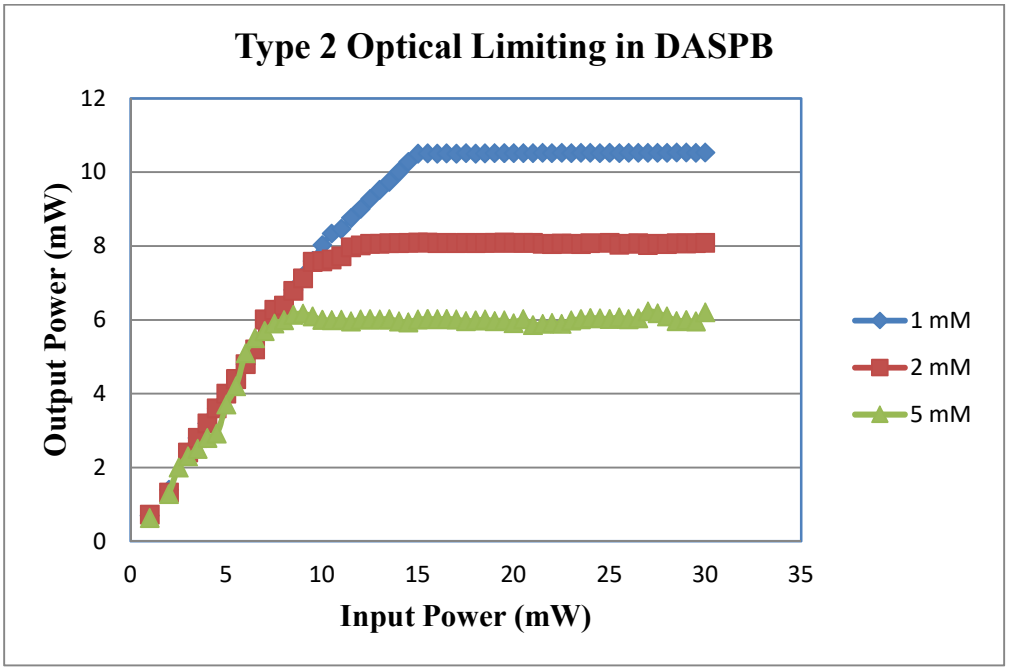

Fig. 5.29 : Closed aperture (Type 2) Optical limiting behavior of DASPB dye-doped PMMA-MA film at CW 532 nm.

5.4.2 OPTICAL LIMITING STUDY OF DISPERSE ORANGE-25

The optical limiting effect of the DO-25 dye-doped polymer film is studied by means of a 30 mW CW semiconductor laser beam at 532 nm (BeamQ 30 mW Green Light Line). Two experimental set-ups 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 hole size is used between the dye sample and the collecting lens & photo detector. The DO-25 dye film is kept at a point along the beam axis where the transmitted light intensity shows a valley in closed aperture *Z*-scan curve [418-430]. The input intensity of laser beam is varied and the corresponding output intensity is noted by a photo detector power meter assembly. 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 5.30. The dye sample is kept fixed at the focal point of a convex lens L1 of open aperture Z-scan setup. A variable beam splitter (VBS) is utilized to change 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 5.31.

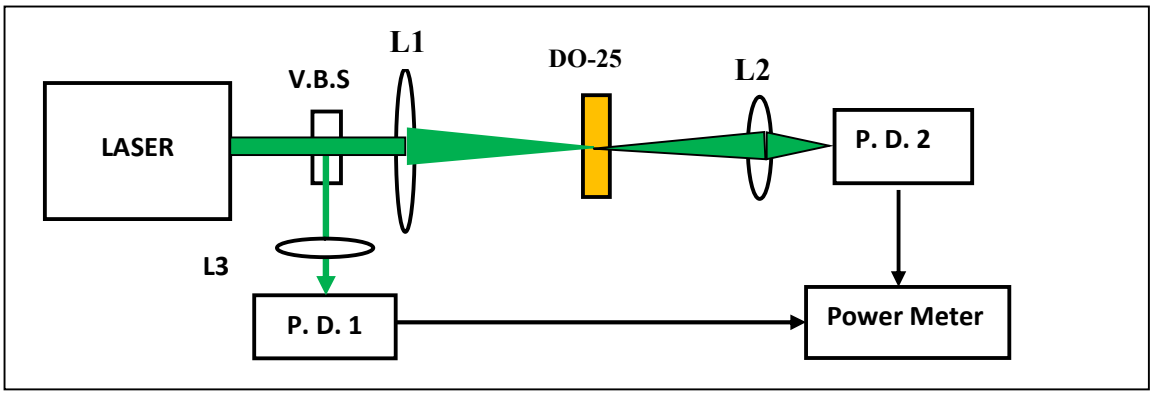

Fig. 5.30 : Experimental setup for Optical limiting (Type 1) due to pure absorptive nonlinearity.

In this case, the intensity of the transmitted output beam from the DO-25 dye-sample is observed to change linearly at lower values of the input intensity but observed to saturate at higher incident intensities due to nonlinear reverse saturation absorption and thermal lensing. Hence, after a certain threshold value of the input intensity, the nonlinear absorption of the DO-25 dye sample becomes dominant, resulting in the limiting of the intensity of output beam. Thus, the transmittance recorded by the photo detector remained reasonably constant showing a saturation region in the graph.

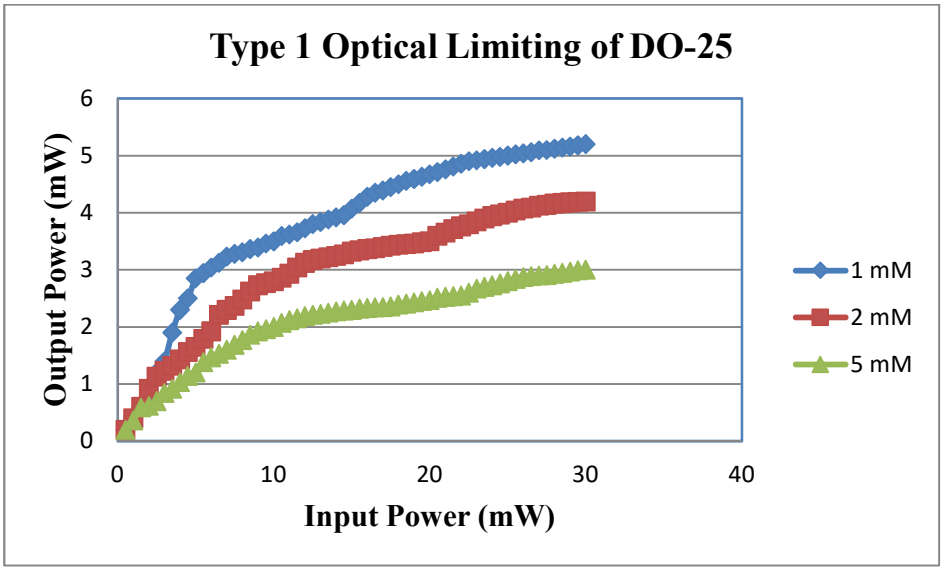

Fig. 5.31 : Open aperture (Type 1) Optical limiting behavior of DO-25 dye-doped PMMA-MA film at CW 532 nm.

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 5.32. 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 5.33.

In this case of DO-25 dye sample with defocusing nonlinearity (negative nonlinearity), the intensity of transmitted beam at output is observed to change linearly at low values of the input intensity but appears to saturate after a certain threshold value due to the fact that the dye sample starts defocusing 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 5.33.

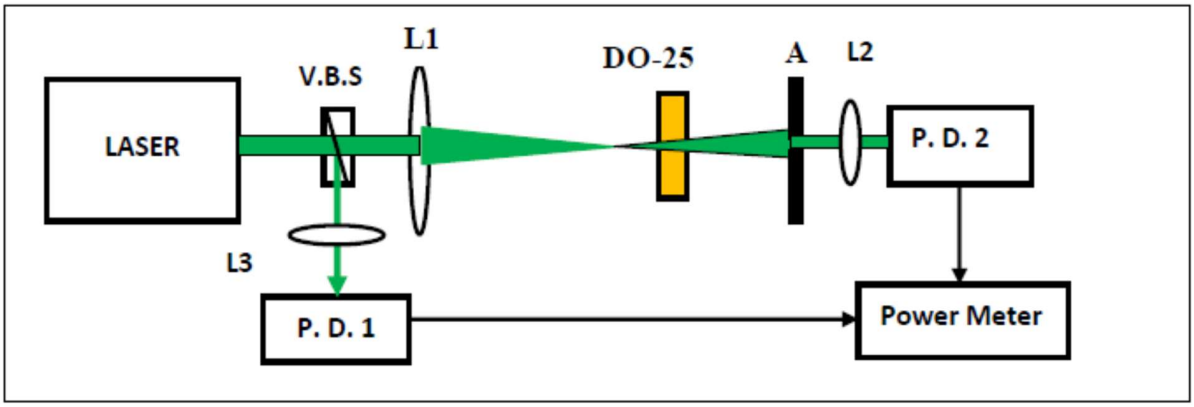

Fig. 5.32 : Experimental setup for closed aperture Optical limiting for DO-25 doped PMMA-MA using nonlinear refraction.

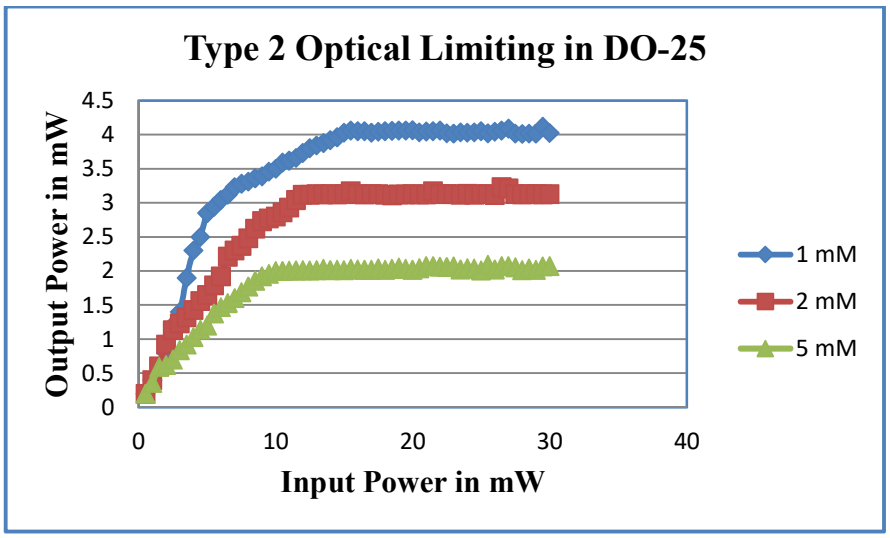

Fig. 5.33 : Closed aperture (Type 2) Optical limiting behavior of DO-25 dye-doped PMMA-MA film at CW 532 nm.

5.4.3 OPTICAL LIMITING STUDY OF DISPERSE YELLOW-7

The optical limiting effect of the DY-7 dye-doped polymer film is analysed by means of using a 532 nm, 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 hole size is used between the dye sample and the collecting lens & photo detector. The dye sample film is kept at a position where the transmitted intensity shows a valley in closed aperture *Z*-scan curve [418-430]. The input laser beam intensity is varied, and the corresponding output laser beam intensity values are noted by a photo detector and power meter assembly. 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) :

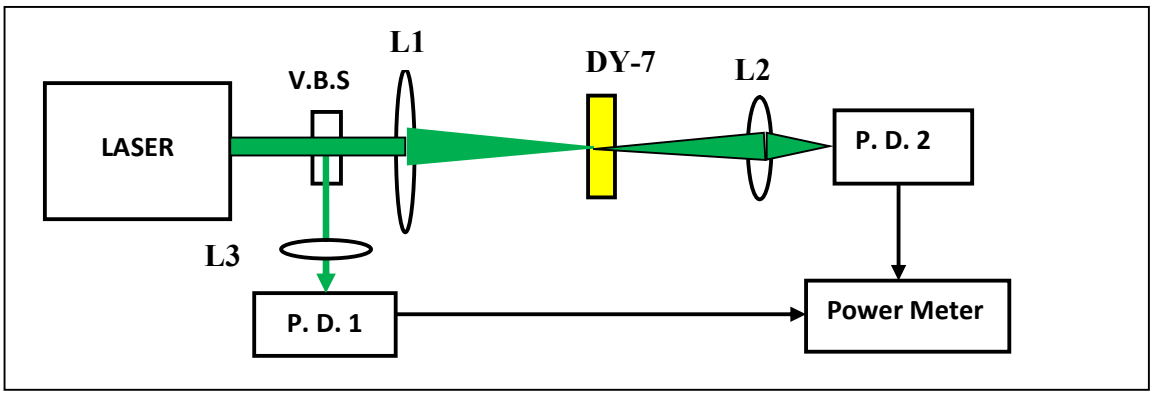

Fig. 5.34 : Experimental setup for Optical limiting (Type 1) due to pure absorptive nonlinearity.

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 DY-7 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 5.34. The dye sample is kept fixed at the focal point of the convex lens L1 of open aperture Z-scan setup. The input power is changed by means of a variable beam splitter (VBS). By means of a convex lens, the output light beam intensity is measured using a photo detector-power meter assembly.

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 5.35.

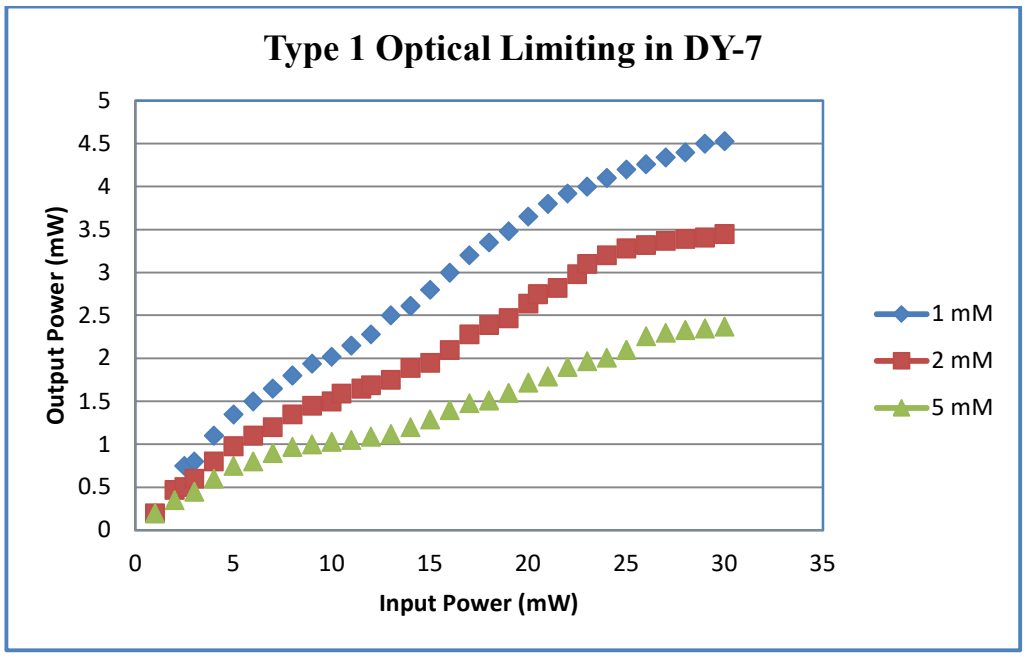

Fig. 5.35 : Open aperture (Type 1) Optical limiting behavior of DY-7 dye-doped PMMA-MA film at CW 532 nm.

In this case, the intensity of the transmitted beam at the output is observed to change linearly at low incident input intensity but found to saturate at higher value of input intensities due to nonlinear reverse saturation absorption and thermal lensing effect. Hence, after a certain threshold value of the input light intensity, the nonlinear absorption of the DY-7 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.

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

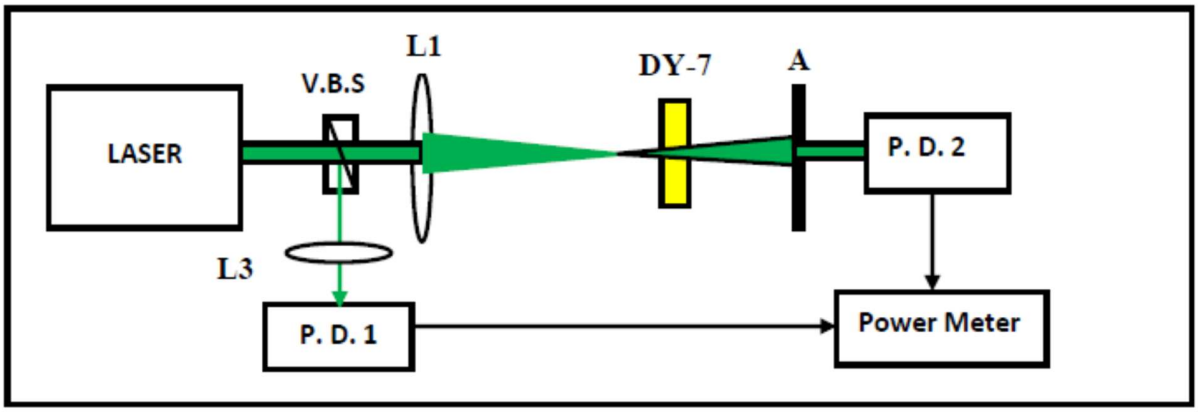

Fig. 5.36 : Experimental setup for closed aperture Optical limiting for DY-7 doped PMMA-MA using nonlinear refraction (Type 2).

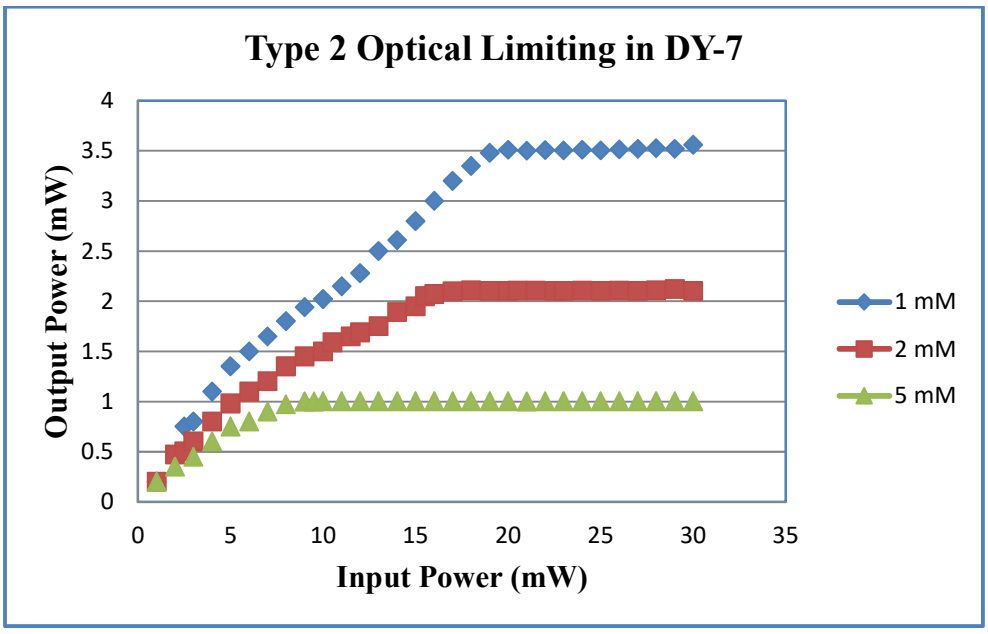

Fig. 5.37 : Closed aperture (Type 2) Optical limiting behavior of DY-7 dye-doped PMMA-MA film at CW 532 nm.

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 DY-7 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 5.36. 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 5.37.

In this case of DY-7 doped PMMA-MA film with defocusing nonlinearity (negative nonlinearity), the intensity of transmitted output laser beam is observed to change linearly with low values of input intensity, but found to saturate after a certain threshold value of input power due to the reason that the dye sample starts defocusing 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 5.37.

5.5. RESULTS AND DISCUSSION

In this section, we have studied the nonlinear optical properties of three organic dye materials DASPB, DO-25, and DY-7 in PMMA-MA polymer matrix for their nonlinear absorption using open aperture Z-scan, nonlinear refraction using closed aperture Z-scan, and for optical limiting using type 1 and type 2 optical limiting configurations. Based on our study we observed that the nature of nonlinearity shown by these dyes depends on the intensity of input laser light beam. At the lower intensity of input beam, the saturation absorption became prominent and with an increase in input intensity further, the excited state absorption in the form of either through two-photon absorption & reverse saturation absorption or thermally induced absorption became prominent. On the basis of two-photon absorption fluorescence study, it is argued that in the nonabsorbing region of DASPB, the two-photon induced nonlinearity along with reverse saturation absorption contributed for optical limiting [419]. From literature survey, it is also observed that DASPB has a much larger TPA cross-section (at least one order of magnitude larger) compared to other well-known organic dyes [413, 443].

It is also observed from other studies [423-433] that the value of ΔT_{p-v} has increased in the case of dye-doped polymer films when compared to the dyes in the solvent. This shows that the change in refractive index due to reverse saturation absorption as well as thermal effect in solid media is larger compared to that of the liquid media. The heat dissipation rate in the liquid is more than that in the film because of the poor thermal conductivity of the polymer film. This

leads to increase in temperature in solid media compared to temperature rise in liquid media which might increase nonlinear absorption. So, the nonlinear refractive index change is more in solid media than in liquid media.

In this study, it is observed that the value of the nonlinear refractive index and nonlinear absorption coefficient of these three dye-doped polymer films depends on the concentration of the dyes in the polymer film. It is seen that there is an increasing trend in values of n_2, β, and $|\chi^{(3)}|$ as the concentration increases. This may be explained by the fact that the number of dye molecules increases when the concentration increases, more dye molecules get involved in the nonlinear process (two-photon absorption/reverse saturation) due to thermal agitation resulting in an enhanced effect. Thus Z-scan measurements indicate that these dyes exhibit large nonlinear optical properties.

Table 5.10: Nature of Nonlinearity of dye samples doped in PMMA-MA polymer films.

S. No.	Dye	Medium	Nature of Nonlinearity
1	DASPB	PMMA-MA polymer film	Positive Nonlinearity Focusing effect
2	Disperse Orange DO-25	PMMA-MA polymer film	Negative Nonlinearity Defocusing effect
3	Disperse Yellow DY-7	PMMA-MA polymer film	Negative Nonlinearity Defocusing effect

Table 5.11 : Nonlinear parameters for dye-doped samples at 532 nm.

S. No.	Parameter	Dye concentration	DASPB	DO-25	DY-7
1	β ($\times 10^{-3}$) (cm/W)	1 mM	0.64	-0.74	- 0.97
		2 mM	0.81	-0.88	-2.10
		5 mM	1.13	-1.13	-2.75
2	n_2 ($\times 10^{-7}$) (cm^2/W)	1 mM	0.69	-0.325	-0.248
		2 mM	0.87	-0.557	-0.471
		5 mM	1.09	-0.836	-0.702
3	$\Delta n = n_2 I_0$ ($\times 10^{-4}$)	1 mM	2.415	-1.138	-0.868
		2 mM	3.045	-1.950	-1.649
		5 mM	3.815	-2.926	-2.457
8	$\|\chi^3\|$ ($\times 10^{-6}$) (e.s.u.)	1 mM	9.149	5.69	5.12
		2 mM	10.998	7.45	6.82
		5 mM	13.349	9.73	8.52

Optical limiting behavior of three dye-doped PMMA-MA polymer films under low power CW laser irradiation are studied for different dye concentrations. In case of DASPB doped PMMA-

MA films, the mechanism responsible for type 1 optical limiting is mainly attributed to the combined effect of reverse saturation absorption and two-photon absorption which further increased with thermally induced nonlinear refraction. The self-focusing effect observed in DASPB dye-doped samples under CW illumination is utilized to demonstrate their optical limiting action of type 3. Based on its high nonlinear refractive index, the DASPB dye-doped in PMMA-MA matrix behave as good type 1and type 3 optical limiters even at low powers.

The mechanism responsible for type 1 optical limiting is mainly attributed to reverse saturation absorption in case of DO-25 and DY-7, which further increased with thermally induced nonlinearity. The defocusing effect observed in DO-25 and DY-7 dye-doped samples under CW illumination is utilized to demonstrate type 2 optical limiting action. Based on their nonlinear refractive index, these dyes in PMMA-MA matrix behave as good optical limiters even at low powers. These results are quite impressive and encouraging for possible applications in nonlinear optical devices.

Table 5.12 : Optical limiting Regions in Dye-doped Polymer films at 532 nm CW laser beam.

S. No.	Sample	Dye Concentration	Linear Region (mW)	Active Region (mW)	Saturation Region (mW)
1	DASPB in PMMA-MA Type 1	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	DASPB in PMMA-MA Type 2	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
3	DO-25 in PMMA-MA Type 1	1 mM	1 – 5 mW	5 – 22 mW	22 mW onwards
		2 mM	1 – 8 mW	8 – 25 mW	25 mW onwards
		5 mM	1 – 10 mW	10 – 27 mW	27 mW onwards
4	DO-25 in PMMA-MA Type 2	1 mM	1 – 5 mW	4 – 14 mW	14 mW onwards
		2 mM	1 – 8 mW	8 – 11 mW	11 mW onwards

		5 mM	1 - 7 mW	7 – 9 mW	9 mW onwards
5	DY-7 in PMMA-MA Type 1	1 mM	1 – 5 mW	5 – 23 mW	23 mW onwards
		2 mM	1 – 8 mW	8 – 25 mW	25 mW onwards
		5 mM	1 – 10 mW	10 – 26 mW	26 mW onwards
6	DY-7 in PMMA-MA Type 2	1 mM	1 - 18 mW	18 - 19 mW	19 mW onwards
		2 mM	1 – 15 mW	15 – 17 mW	17 mW onwards
		3 mM	1 – 8 mW	8 – 9 mW	9 mW onwards

Table 5.12 lists details on various optical limiting regions in Dye-doped Polymer films at 532 nm CW laser beam. In all three types of dyes used in the present study, 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 5.29, figure 5.33 & figure 5.37. 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 5.13, 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 5.14. The results are comparable to some of the reports of low power optical limiting [428-443].

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-focusing/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-focusing/self-defocusing position is at the valley point of the Z-scan curve.

Table 5.13 : 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
2	DO-25 in PMMA-MA	1 mM	22	15
		2 mM	25	12
		5 mM	27	10
3	DY-7 in PMMA-MA	1 mM	23	19
		2 mM	25	17
		5 mM	26	09

Table 5.14 : Concentration dependence of saturated output power in dye-doped PMMA-MA films.

S. No.	Sample	Dye Concentration (mM)	Type 1 Optical Limiting Saturated Output Power (mW)	Type 2 Optical Limiting Saturated Output Power (mW)
1	DASPB in PMMA-MA	1 mM	11	10.5
		2 mM	8.0	8.06
		5 mM	4.0	6.10
2	DO-25 in PMMA-MA	1 mM	5.10	4.0
		2 mM	4.0	3.10
		5 mM	2.92	1.99
3	DY-7 in PMMA-MA	1 mM	4.3	3.50
		2 mM	3.5	2.10
		5 mM	2.2	0.95

5.6. CONCLUSION

The nonlinear absorption, nonlinear refraction properties of prepared films of these three dyes DASPB, Disperse orange–25, and Disperse yellow-7 are studied by doping them in an optically neutral polymer matrix Polymethyl methacrylate methacrylic acid (PMMA-MA) at low power CW laser beam of 532 nm by using the Z-scan experimental method. The optical power limiting properties of all these three sample dye films are also studied for different input power at different dye doping concentrations.

In case of all the three dyes, it is observed that the type and nature of nonlinear absorption depends on the input intensity. 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.

Both azo dyes Disperse orange-25 and Disperse yellow-7 have shown saturation absorption at lower input irradiance and then have shown reverse saturation absorption at higher input irradiance. The optical limiting properties of these films are also studied at different input power using continuous wave (CW) laser beams of 532 nm wavelength. The 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 and DY-7 doped PMMA-MA polymer films.

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CHAPTER SIX

Experimental Study & Results of Optical Phase Conjugation

CONTENTS **PAGE No.**

6.1. INTRODUCTION

Optical phase conjugation (OPC) in nonlinear materials by degenerate four-wave mixing (DFWM) is considered to be an important technique with applications in many fields of technology and science which include image transmission, optical image processing, optical filtering, and laser resonators [444-446]. In a nonlinear medium, when two intense light beams moving in opposite direction interact with a third beam of comparatively less intensity, a fourth beam is generated from the medium, which will be the phase conjugation of the third beam. The technique used for achieving this is called four-wave mixing. The unique characteristic of generated pair of phase-conjugate beams is that the aberration influence passing through the nonlinear medium can be removed automatically from the backward phase-conjugated beam [447]. The degenerate four-wave techniques are mainly used in nonlinear spectroscopy, real-time holography, and phase conjugation mirrors. The OPC by DFWM has been observed in many organic and inorganic materials using a light beam of pulsed or continuous-wave (CW) lasers. [448-449].

The special characteristics of phase conjugate light beam which are not observed with normal light beam [450] are listed below :

(1) Multiplicative interaction through space domain : Since phase conjugate waves are produced by interaction in a nonlinear medium, the spatial multiplicative effect among the interacting light waves appears in the phase conjugate waves.

(2) Compensation of Phase : The phase distortion of the wave is compensated if is re-propagated through the medium.

(3) Inversion of Time : The P.C. light beam can be considered as a time inverted light beam due to the reason that the direction of propagation of the P.C. beam is exactly opposite direction to the probe beam and the wave-front of the P.C. beam is identical to the wave-front of the probe beam.

(4) Intensity dependent phase shift : In a nonlinear medium, due to the optical Kerr effect, the phase shift of the electric field vectors of P.C. beam depends on the instantaneous wave intensity.

(5) Dependence on frequencies : The reflectance of a P.C. mirror is proportional to the detuning between the probe beam and pump beam frequencies.

(6) Photon correlation nature : While quantum mechanical analysis is used to correlate the forward and backward waves theoretically, the interacting P.C. waves and probe are regarded respectively as the photon creation and annihilation operators.

(7) Interaction of Multiple waves : When two or more laser light beams are used in the generation of P.C. light the resultant polarization and hence the interaction of their intensity is proportional to the product of these interacting light waves in their temporal domains.

The optical phase conjugation property of these dye-doped polymer films is studied using degenerate four-wave mixing method and the dependence of phase conjugated signal reflectivity on various parameters viz., dye concentration, the intensity of backward pump, forward pump, and inter-beam angle between the probe and forward pump beam on phase conjugation reflectivity are studied and presented in this Chapter.

6.2 EXPERIMENTAL CONFIGURATION FOR DEGENERATE FOUR-WAVE MIXING

The ray diagram of phase-conjugate wave generation by DFWM is shown in figure 6.1. The probe beam E_3 and the forward-pump beam E_1 are interfere in the nonlinear material medium gives rise to a periodic interference pattern [450]. The amplitude of resulting grating vector is written as $k = 2\pi/\Lambda$. Then the fringe period (Λ) can be calculated using formula :

$\Lambda = \lambda/2 \sin(\theta/2)$ ---------- (6.1)

where, λ is the laser wavelength and θ is the angle between forward-pump and probe beam with respect to the normal to the nonlinear medium. The backward-pump beam E_2 is then diffracted under Bragg conditions by the dynamic volume hologram and generates a backward phase conjugate wave whose amplitude can be written as E_4.

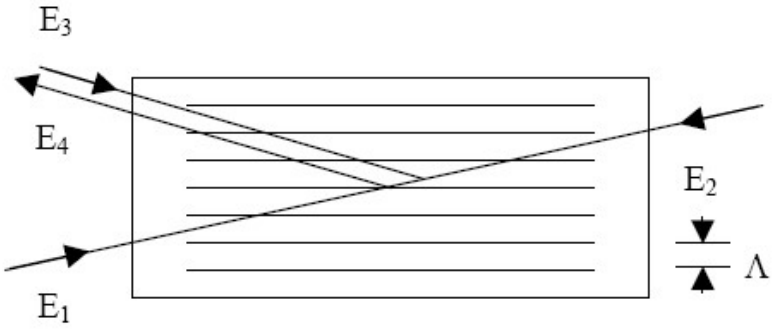

Fig. 6.1. Ray diagram of P.C. wave production by DFWM.

6.3 EXPERIMENTAL SET-UP FOR DEGENERATE FOUR WAVE MIXING

The schematic diagram of the experimental setup to study phase conjugation effect is shown in figure 6.2. A He-Ne/Semiconductor Diode laser (20 mW) beam at wavelength 633 nm/532nm is considered as input and is divided into three laser beams, two counter-propagating beams E_1 and E_2 namely forward-pump and backward-pump beams respectively and third beam E_3 is a probe beam to form the degenerate four-wave mixing configuration. The spot dimension of the individual beam at the nonlinear medium is 1.10 mm in diameter. The constant power ratio of the forward-pump beam (E_1), the backward-pump beam (E_2), and the probe beam (E_3), used in this experiment is ≈ 10 : 10 : 1. The inter-beam angle can be adjusted to a specific angle θ. The sample is exposed to all these three beams simultaneously. The optical path lengths of all the three beams are made equal so that they were coherent in the sample. The phase-conjugate wave follows the path in the opposite direction to that of the probe beam E_3 and is detected by using a photo-detector and a power meter assembly. The experimental set-up is mounted on a vibration isolation table to avoid the mechanical disturbances on the laser-induced gratings formed in the DASPB dye-doped polymer matrix.

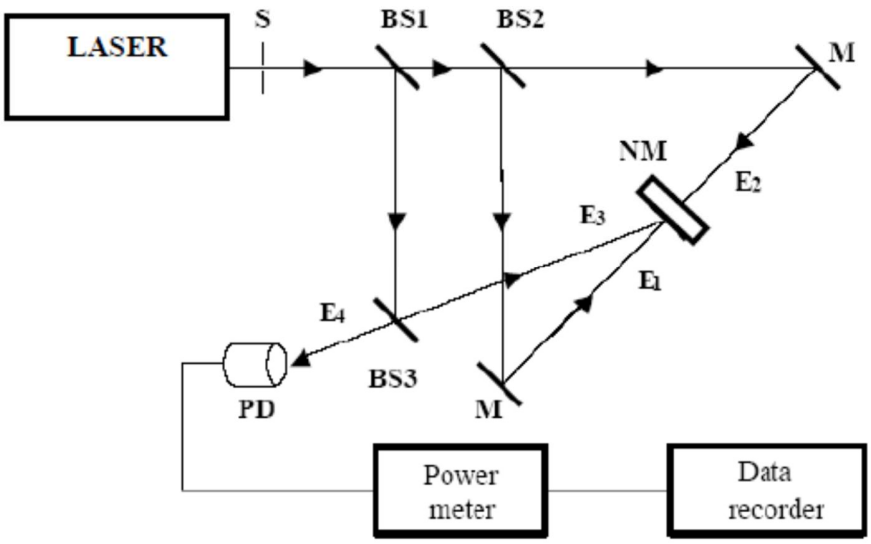

Fig. 6.2. Experimental set-up for Phase Conjugated wave generation using Degenerate Four-Wave Mixing configuration. S (Shutter), M (Mirror), BS1–BS3 (Beam splitters), NM (Nonlinear medium), PD (Photo-detector).

6.4. PROCEDURE FOR PHASE CONJUGATED SIGNAL GENERATION & STUDY

After generating the phase conjugated waves using experimental set-up described in the previous section, the dependence of phase conjugated signal reflectivity on various parameters viz., dye concentration, the wavelength of input laser beam, the intensity of forward pump beam, the intensity of backward pump beam, inter-beam angle between the probe beam and forward pump beam on phase conjugation reflectance are studied for all the three samples. The graphs are drawn between two variable as listed below :

(1) Maximum P.C. Reflectivity at different dye concentrations.

(2) Phase conjugated signal recording time at different concentrations.

(3) Phase conjugated signal reflectivity as a function of angle between probe and forward pump beam.

(4) Dependence of phase conjugated signal reflectivity on backward pump beam intensity.

(5) Transmission of phase conjugated signal as a function of Time.

(6) Phase conjugated signal reflectivity as a function of probe beam intensity.

(7) Phase conjugated signal reflectivity as a function of forward pump intensity.

6.4.1 Degenerate Four-Wave Mixing Property of DASPB

In the case of DASPB dye in PMMA – PA polymer matrix to explain the optical phase conjugation property, a three-level energy system with energy level diagram consisting of ground singlet state, excited singlet state, and triplet states are considered. Absorption of photons by DASPB dye-doped film sample results in transition of the electrons of DASPB from ground state to the first excited state which is singlet. Based on the allowed transition from singlet to triplet, the DASPB molecule will jump to triplet state. Since, the triplet to singlet transition is not allowed and molecule will not absorb energy from the ground state. As a result, saturation of absorption occurs and the absorption becomes a function of intensity. If two writing beams, say probe & pump, interfere, the modulated intensity pattern creates a complex grating due to variation in refractive index [451-452]. The volume hologram develops in the material due to this change in refractive index in Kerr media or due to saturable absorbers or two-photon absorption. Such dynamic volume hologram generates a backward conjugate wave-front and is named as the conjugate image beam. The geometry is known as four-wave mixing geometry [451-453].

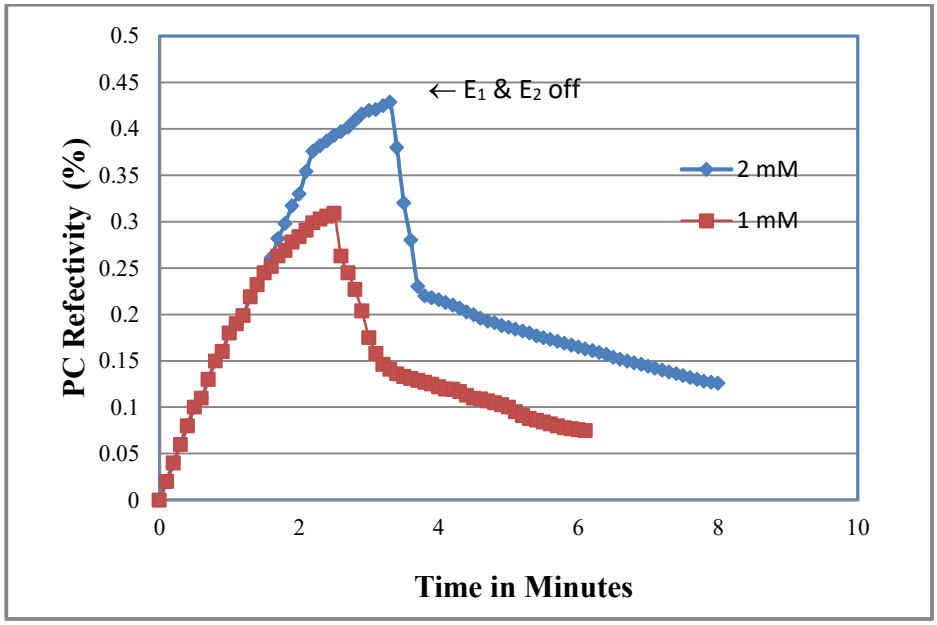

Fig. 6.3 (a) : P.C. signal versus recording time for 1mM and 2 mM concentrations at 633 nm.

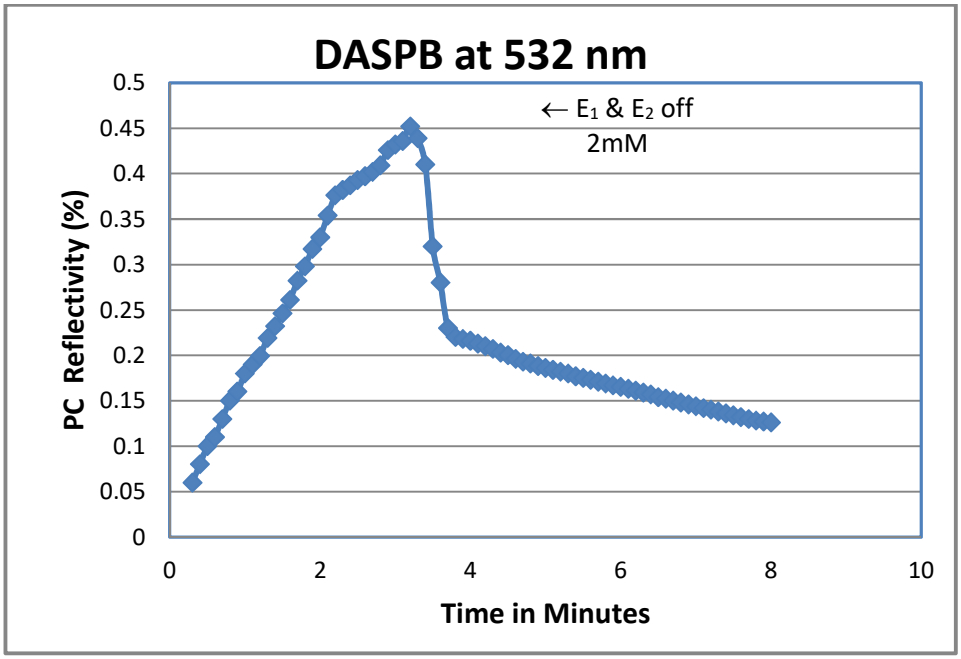

Fig. 6.3 (b) : P.C. signal versus recording time for 2 mM concentrations at 532 nm.

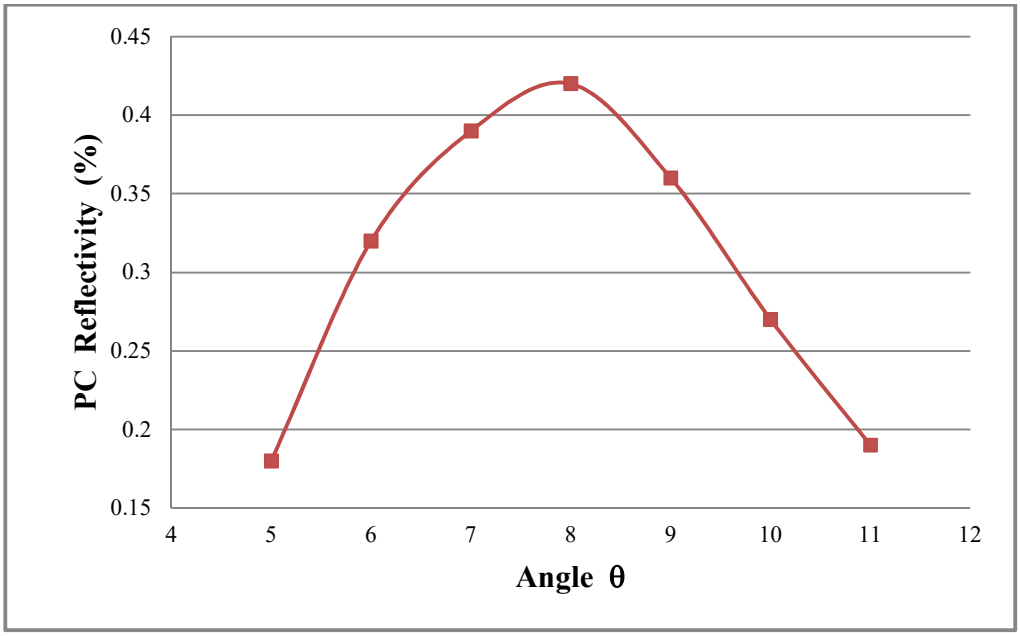

Fig. 6.4 (a) **:** Variation of P.C. reflectance with the angle between the probe and forward pump beams at 633 nm.

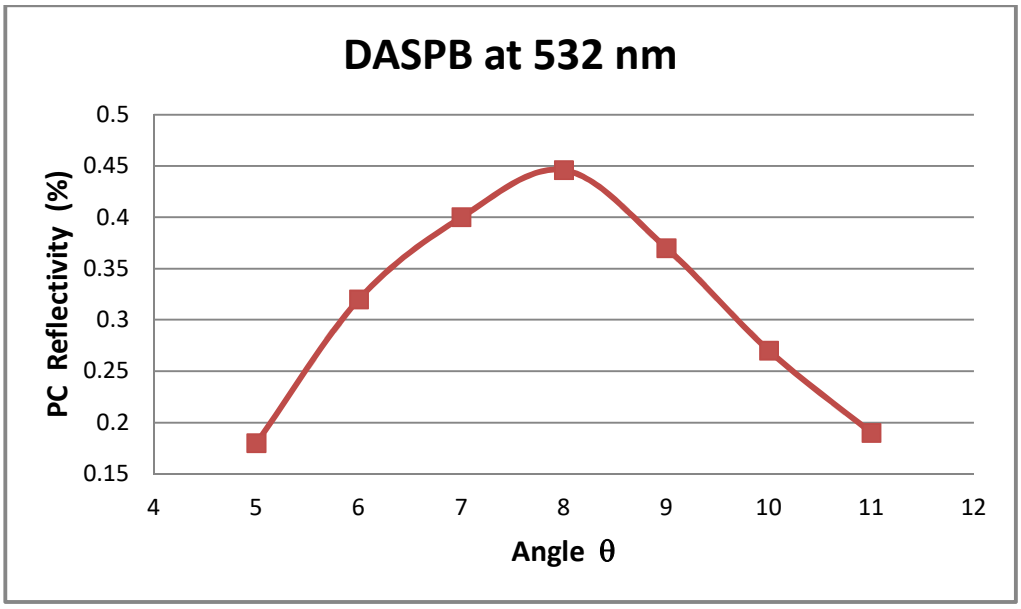

Fig. 6.4 (b) **:** Variation of P.C. reflectance with the angle between the probe and forward pump beams at 532 nm.

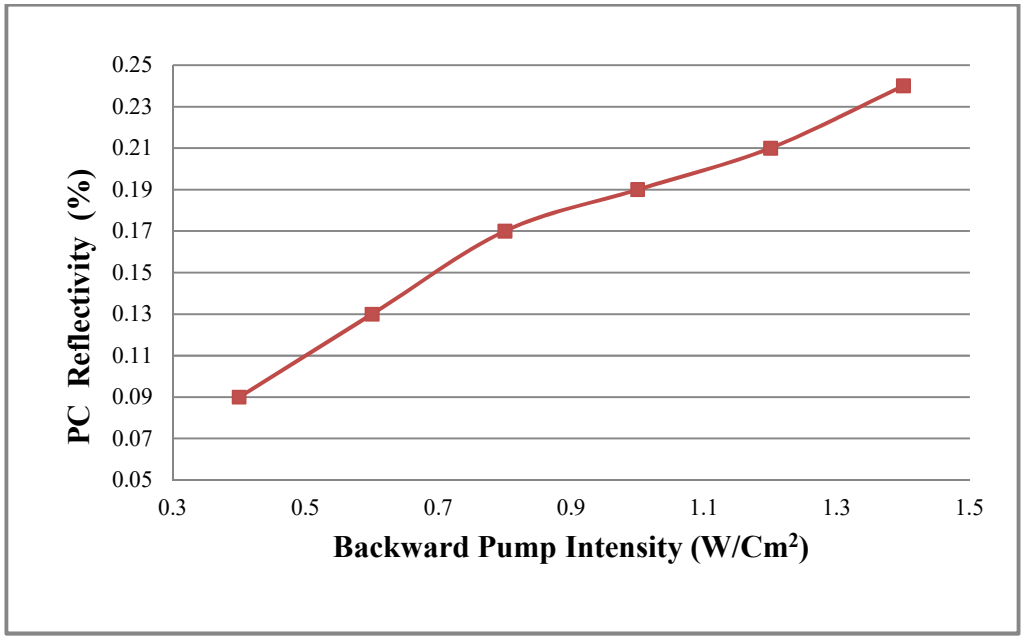

Fig. 6.5 (a) : Dependence of P.C. reflectivity on backward pump Intensity at 633 nm.

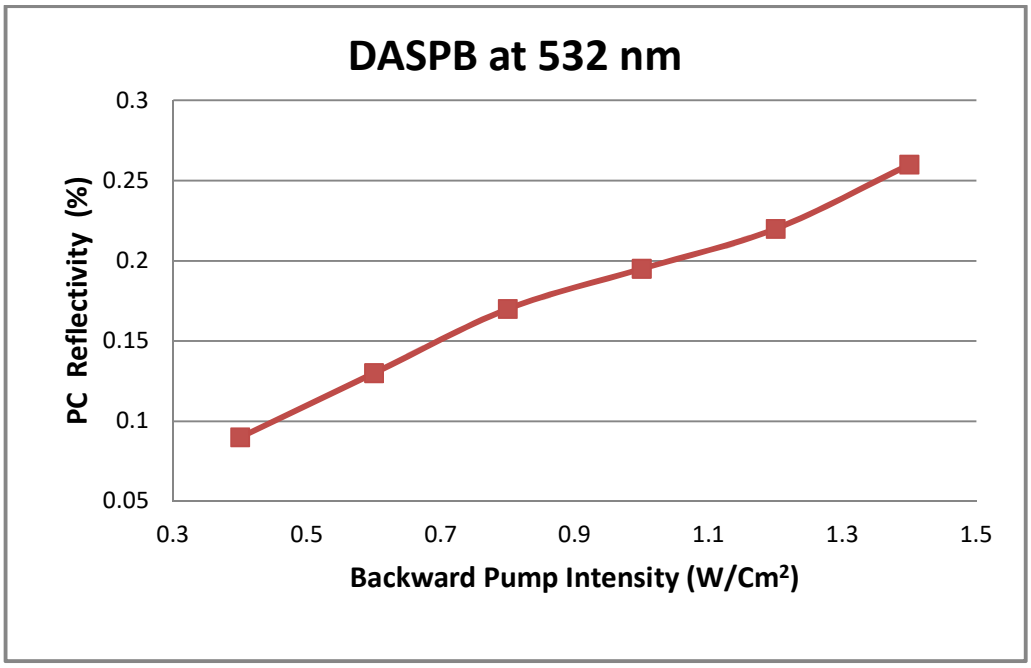

Fig. 6.5 (b) : Dependence of P.C. reflectivity on backward pump Intensity at 532 nm.

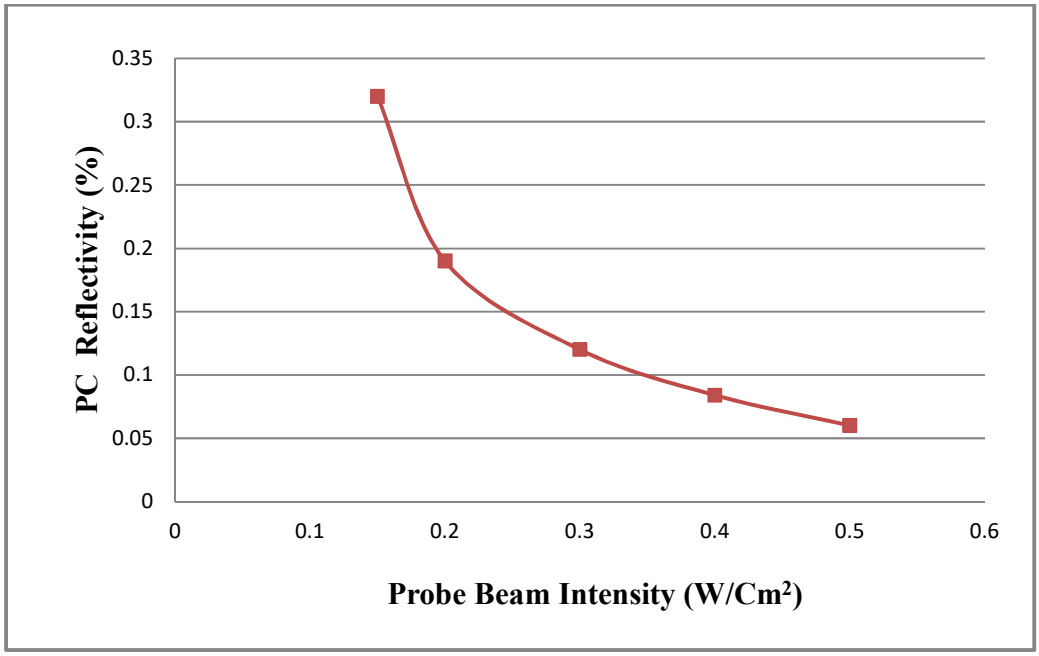

Fig. 6.6 (a) : Variation of P.C. reflectance with probe beam intensity at 633 nm.

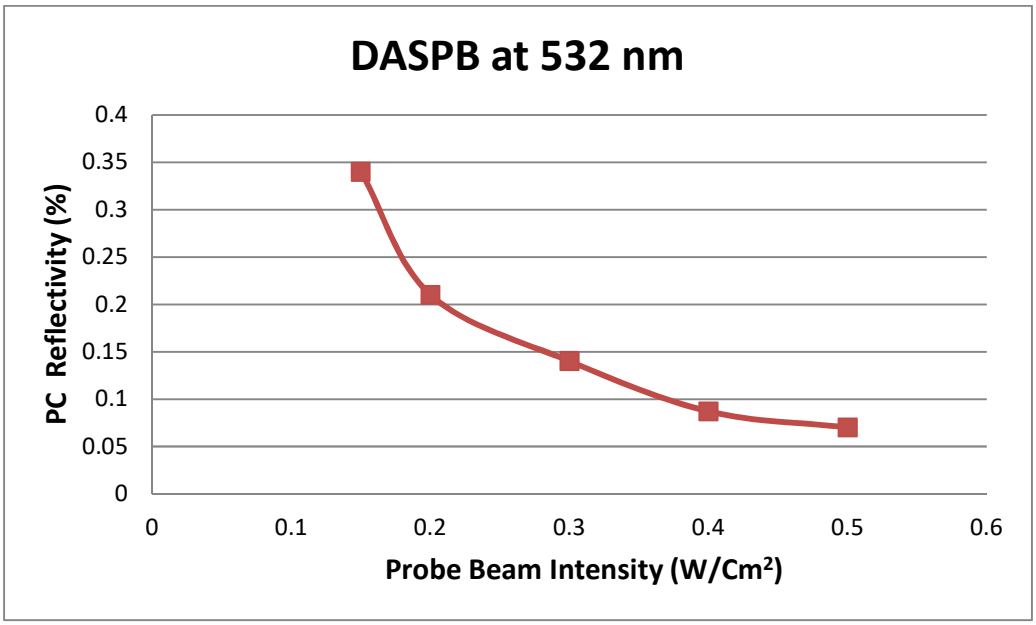

Fig. 6.6 (b) : Variation of P.C. reflectance with probe beam intensity at 532 nm.

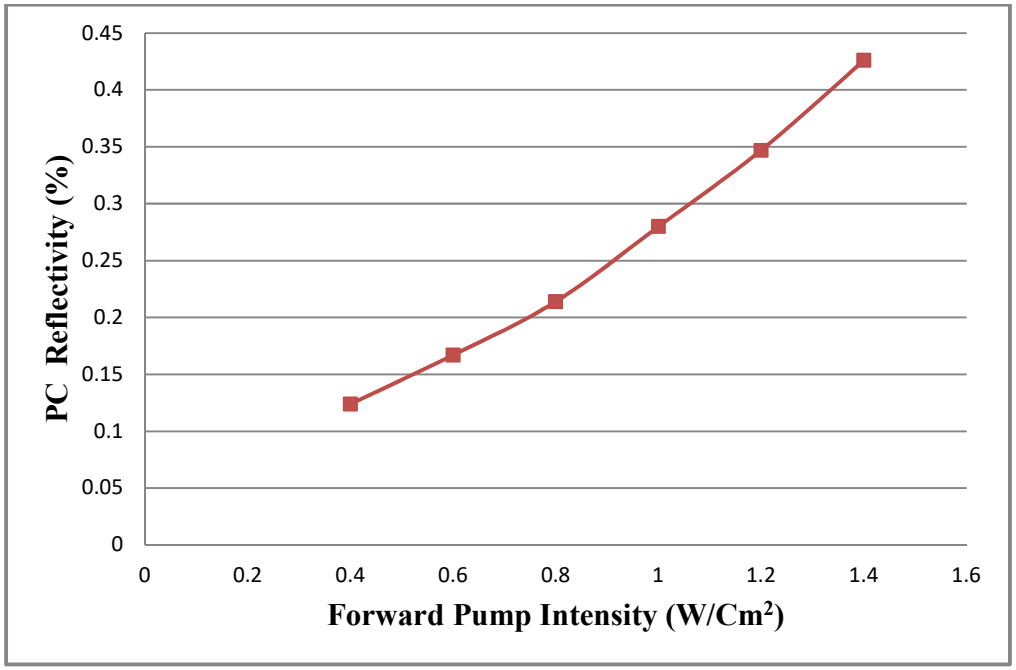

Fig. 6.7 (a) : Variation of P.C. reflectance on forward pump power at 633 nm.

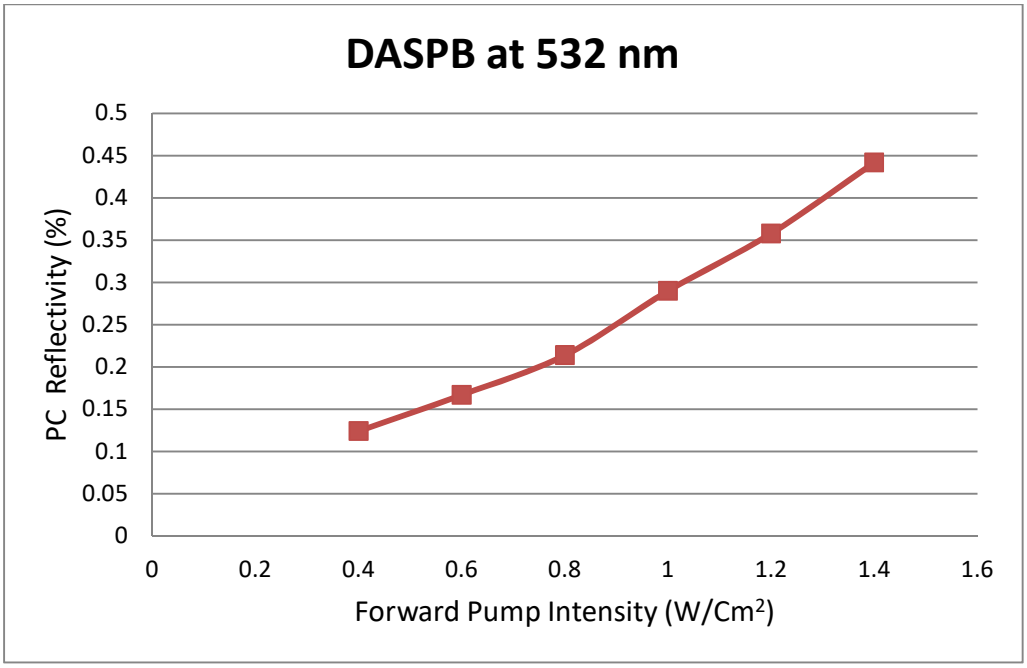

Fig. 6.7 (b) : Variation of P.C. reflectance with forward pump power at 532 nm.

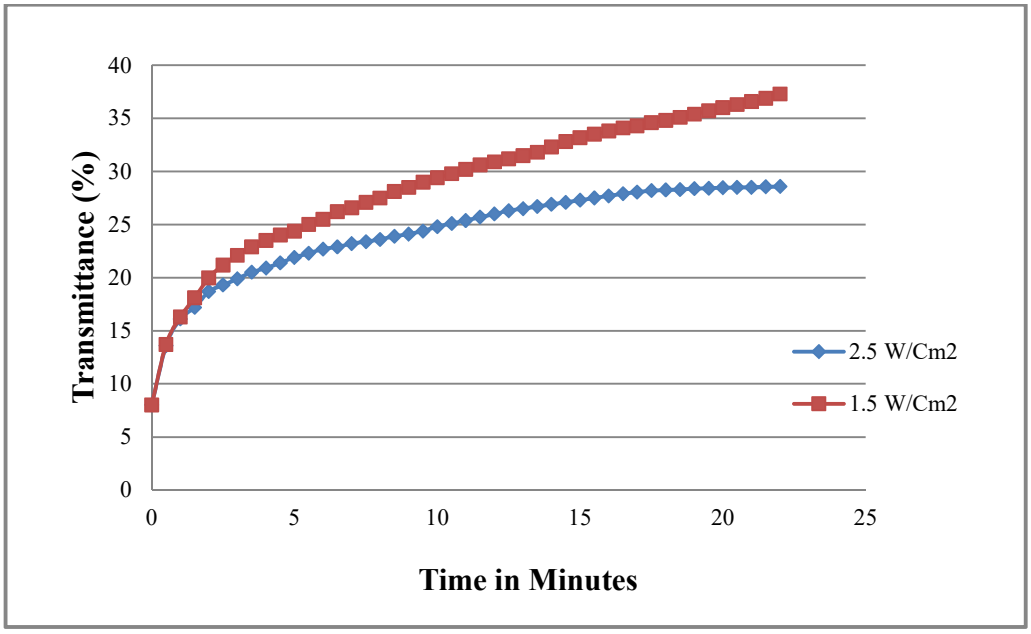

Fig. 6.8 (a). Transmittance as a function of time at 633 nm.

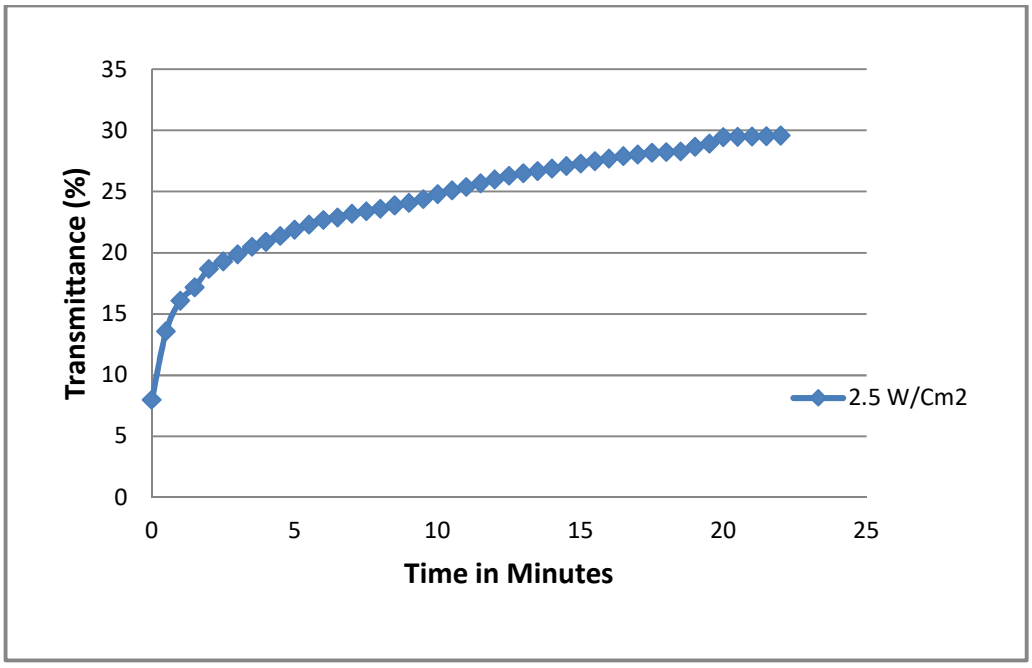

Fig. 6.8 (b). Transmittance as a function of time at 532 nm.

The phase conjugate signal measurements are carried out by varying certain parameters which affect the strength of P.C. signal during the DFWM process. Fig. 6.3 shows the P.C. signal versus the time for dye concentration of 1 mM and 2 mM doped polymer films. The strength of P.C. intensity increased linearly to certain maximum level and then started decreasing. To get maximum reflectance, it is essential that there must be a perfect synchronization/overlap of the probe and the pump beams in the DASPB dye-doped nonlinear medium. Fig. 6.4 shows the influence of the input probe beam intensity on the conjugate beam reflectance. From the figure, it is seen that the P.C. reflectance first increases and then decreases as the angle between the probe beam and the forward pump beam increases. This may be because as the angle between the pump and probe beams changes, the shape of probe beam modifies from circular to elliptical and only a part of the beam falls on the interaction area. Because of four-wave coupling, the maximum P.C. reflectance is obtained when the angle is 8 degrees.

The effect of the power of backward pump beam on the strength of P.C. reflectance by maintaining the power of the forward pump and probe beams constant and changing the power of backward pump beam is shown in Fig. 6.5. Fig. 6.6 shows the effect of the intensity of input probe beam on the P.C. beam reflectance. A maximum reflectance of 0.42% is observed at an intensity of probe beam is 2.5 W/cm^2, and as the probe beam intensity increased further, the P.C. reflectance decreased, which is in conjunction with other reported results on dyes doped in glass and polymers [453]. Fig. 6.7 shows the variation of P.C. reflectance with the angle between the probe beam and forward pump beam. It is found that the P.C. reflectance increases with the increase in forward pump beam power, linearly. The two main basic processes to be considered for the analysis of the origin of optical phase conjugation in dye-doped PMMA-PA films are : (1) the formation of thermal grating and (2) third-order nonlinear optical processes of molecules.

The DASPB dye-doped film irradiated with 633/532 nm radiation of a variable intensity and the transmitted beam from the samples are measured using photo detector power meter assembly. If the effect observed is of purely thermal in nature, bleaching of the dye films should have been observed. The obtained results for the sample dye of DASPB doped in PMMA-MA are shown in Fig. 6.8. It is clearly seen that the transmission of the samples dye increases with time. The experiment described above indicates that the third-order nonlinear processes like two photon

absorption and reverse saturation absorption are mainly responsible for OPC in DASPB doped in PMMA-MA polymer film.

Organic dyes doped in polymer matrices have the capability of generating a phase-conjugate wave by not only degenerate four-wave mixing (DFWM) but also by the holographic process [455]. To distinguish the phase-conjugate wave generated by DFWM in our experiment from that by the holographic process, the time response of the P.C. signal is studied. For this, the DASPB dye doped in PMMA – PA polymer matrix is first irradiated with three waves E_1, E_2, and E_3 for a specified duration, and afterward, E_1 and E_3 are successively switched off so that only E_2 is allowed to incident on the dye film. Here we call the duration for which all the three waves are incident on the dye film as the degenerate four-wave mixing duration. Figure 6.3 shows the observed strength of phase-conjugate signal as a function of time. The signal strength is initially increased slowly within few minutes to the level of peak value probably due to the reason of degenerate four-wave mixing and holographic mechanisms but suddenly decreased as shown in figure after switching off both the write beams E_1 and E_3. This proves that the phase conjugated signal is generated only by the contribution from the fast degenerate four-wave mixing process and not by holographic process. Therefore, it is inferred that the rapidly decaying component corresponds to the phase-conjugate wave which is generated by the degenerate four-wave mixing.

6.4.2 Degenerate Four Wave Mixing Property of DO -25 :

In the case of Disperse Orange dye-doped PMMA-MA films, the P.C. signal measurements are taken by varying the parameters which influence the strength of P.C. signal during the DFWM process. Fig. 6.9 shows the strength of the P.C. signal versus the time for different dye concentration of the DO-25 dye-doped polymer films. The strength of PC intensity rises linearly to a maximum value and then starts decreasing. To get maximum reflectance, it is essential that there must be a perfect synchronization/overlap of the probe and the pump beams in the DO-25 dye doped nonlinear medium. Fig. 6.10 shows the influence of the input probe beam intensity on the conjugate beam reflectance. From the figure, it is seen that the P.C. reflectance first increases and then decreases as the angle between the probe beam and the forward pump beam increases. This may be because as the angle between the pump and probe beams changes, the shape of probe beam modifies from circular to elliptical and only a part of the beam falls on the interaction area. Because of two-wave coupling, the maximum P.C. reflectance is obtained when

the angle is 7 degrees. The effect of the power of backward pump beam on the strength of P.C. reflectance by maintaining the power of the forward pump and probe beams constant and changing the power of backward pump beam is shown in Fig. 6.11. Fig. 6.12 shows the effect of the intensity of input probe beam on the P.C. beam reflectance. A maximum reflectance of 0.22% is observed at an intensity of probe beam is 0.11 W/cm^2, and as the probe beam intensity increased further, the P.C. reflectance decreased, which is in conjunction with other reported results on dyes doped in glass and polymers [453]. Fig. 6.13 shows the variation of P.C. reflectance with the angle between the probe beam and forward pump beam.

It is found that the P.C. reflectance increases with the increase in forward pump beam power, linearly. The two main basic processes to be considered for the analysis of the origin of optical phase conjugation in dye-doped PMMA-PA films are : (1) the formation of thermal grating and (2) third-order nonlinear optical processes of molecules.

The DO-25 film irradiated with 532 nm radiation of a variable intensity and the transmitted beam from the samples are measured using photo detector power meter assembly. If the effect observed is of purely thermal in nature, bleaching of the dye films should have been observed. The obtained results for the sample dye of DO-25 doped in PMMA-MA are shown in Fig. 6.14.

It is clearly seen that the transmission of the samples increases with time. The experiment demonstrated above shows that the third-order nonlinear process like reverse saturation absorption is mainly responsible for OPC in the sample of DO-25 under study.

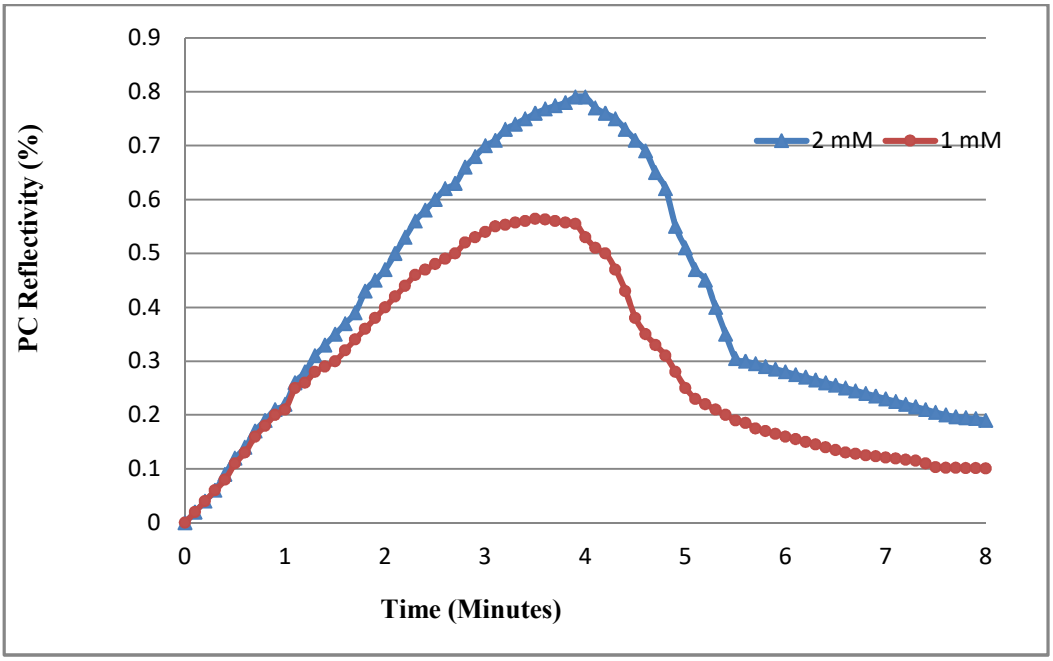

Fig. 6.9 : P.C. signal versus recording time for different concentration for DO-25 at 532 nm.

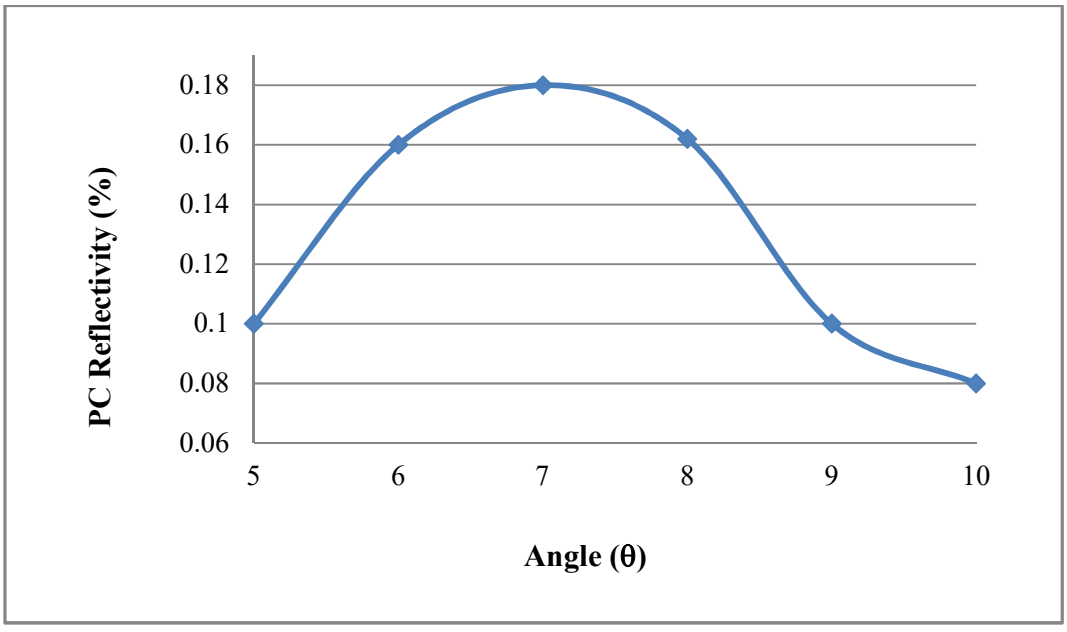

Fig. 6.10 : Variation of P.C. reflectance with the angle between the probe and forward pump beams for DO-25 at 532 nm.

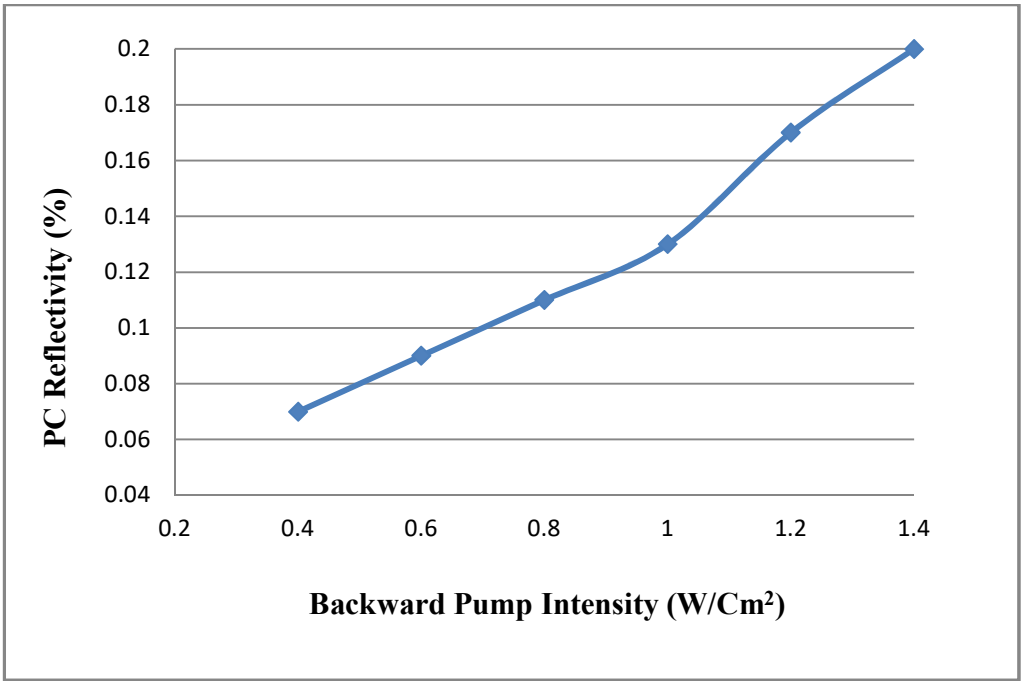

Fig. 6 .11 : Dependence of P.C. reflectance on backward pump Intensity for DO-25 at 532 nm.

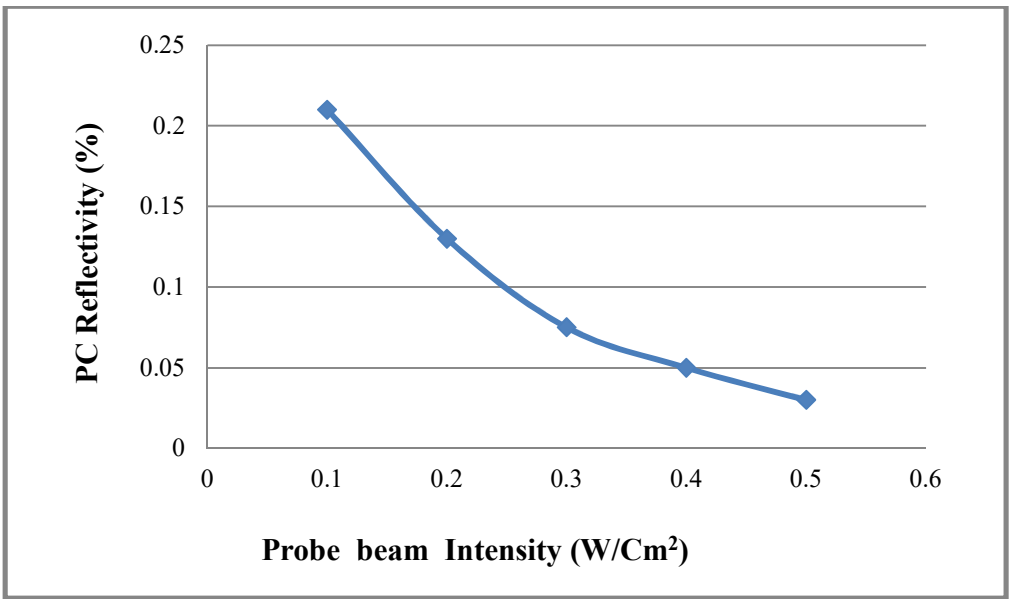

Fig 6.12 : Conjugate reflectance as a function of probe beam intensity for DO-25.

In the case of DO-25 dye-doped PMMA-MA film, by changing the input CW laser beam wavelength from 532 nm to 633 nm, we have not observed any drastic change in reflectivity. Hence such result is not shown in the form of graphs. Disperse Orange-25 dye doped in the polymer matrix has the capability of generating a phase-conjugate wave by not only by third-order nonlinear properties of DO-25 but also due to holographic process [456]. To distinguish the phase-conjugate wave generated by DFWM in our experiment from that by the holographic process, the time response of the PC signal is studied. For this, the DO-25 dye doped in PMMA-MA polymer matrix is first illuminated with three waves E_1, E_2, and E_3 for a specified time, and afterward, E_1 and E_3 were successively switched off, so that only E_2 is allowed to incident on the dye film. Fig. 6.9 shows the observed strength of phase-conjugate signal as a function of time. The signal strength is initially increased slowly within few minutes to the level of peak value probably due to the reason of degenerate four-wave mixing and holographic mechanisms, but suddenly decreased as shown in figure after switching off both the write beams E_1 and E_3. This proves that the phase conjugated signal is generated only by the contribution from the fast degenerate four-wave mixing process and not by holographic process. Therefore, it is inferred that the rapidly decaying component corresponds to the phase-conjugate wave which is generated by the degenerate four-wave mixing.

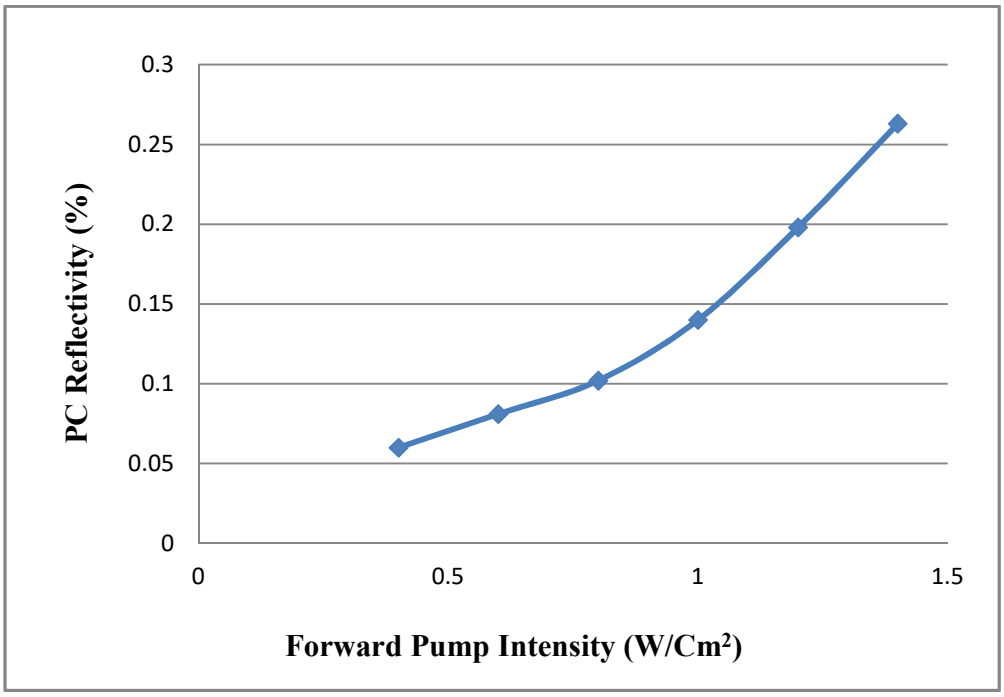

Fig. 6.13 : Dependence of P.C. reflectivity on forward pump power for DO-25.

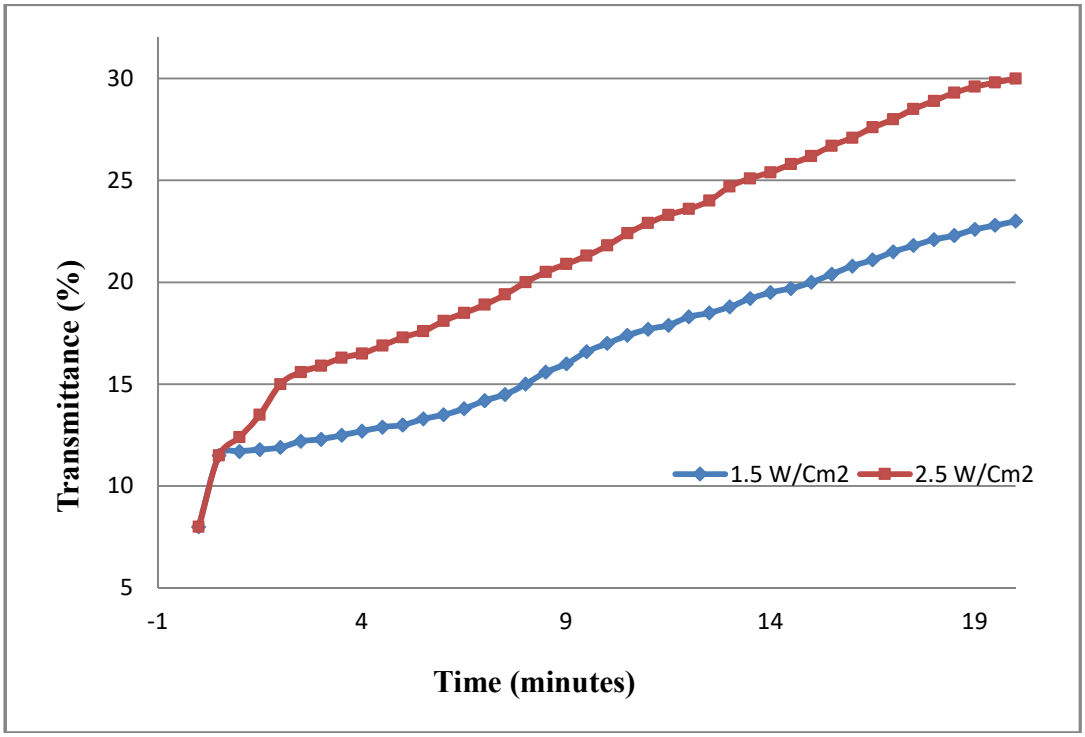

Fig. 6.14 : Transmission as a function of time for DO-25 at 532 nm

6.4.3 Degenerate Four Wave Mixing Property of DY-7 :

In the case of Disperse Yellow-7 dye-doped PMMA-MA films, the P.C. signal measurements are taken by varying the parameters which influence the strength of P.C. signal during the DFWM process. Fig. 6.15 shows the strength of P.C. signal versus the time for different dye concentrations of the doped polymer films. The strength of P.C. intensity rises linearly to a maximum value and then starts decreasing. To get maximum reflectance, it is essential that there must be a perfect synchronization/overlap of the probe and the pump beams in the DY-7 dye doped nonlinear medium. Fig. 6.17 shows the influence of the input probe beam intensity on the conjugate beam reflectance. A maximum reflectance of 0.16% is observed at an intensity of probe beam is 0.11 W/cm^2, and as the probe beam intensity increased further, the P.C. reflectance decreased, which is in conjunction with other reported results on dyes doped in glass and polymers [453]. Fig. 6.18 shows the variation of P.C. reflectance with the angle between the probe beam and forward pump beam. From the figure, it is seen that the P.C. reflectance first increases and then decreases as the angle between the probe beam and the forward pump beam increases. This may be because as the angle between the pump and probe beams changes, the shape of probe beam modifies from circular to elliptical and only a part of the beam falls on the

interaction area. Because of two-wave coupling, the maximum P.C. reflectance is obtained when the angle is 7 degrees. The effect of the power of backward pump beam on the strength of P.C. reflectance by maintaining the power of the forward pump and probe beams constant and changing the power of backward pump beam is shown in Fig. 6.19. Fig. 6.20 shows the effect of the intensity of input probe beam on the P.C. beam reflectance. It is found that the P.C. reflectance increases with the increase in forward pump beam power, linearly. The two main basic processes to be considered for the analysis of the origin of optical phase conjugation in dye-doped PMMA-PA films are : (1) the formation of thermal grating and (2) third-order nonlinear optical processes of molecules. The DY-7 film irradiated with 532 nm radiation of a variable intensity and the transmitted beam from the samples are measured using photo detector power meter assembly. If the effect observed is of purely thermal in nature, bleaching of the dye films should have been observed. The obtained results for the sample dye of DY-7 doped in PMMA-MA are shown in Fig. 6.16. It is clearly seen that the transmission of the samples increases with time. The experiment demonstrated above shows that the third-order nonlinear process like reverse saturation absorption is mainly responsible for OPC in the sample of DY-7 under study.

In the case of DY-7 dye-doped PMMA-MA film also by changing the input CW laser beam wavelength from 532 nm to 633 nm, we have not observed any drastic change in reflectivity. Hence such result is not shown in the form of graphs. It is found that any dye doped in the polymer matrix has the capability of generating a phase-conjugate wave by not only its third-order nonlinearity but also due to holographic process [456]. To distinguish the phase-conjugate wave generated by DFWM from that by the holographic process, the time response of the PC signal is studied. For this, the DY-7 dye-doped in PMMA–MA polymer matrix is first illuminated with three waves E_1, E_2 and E_3 for a fixed duration, and afterward, E_1 and E_3 are successively turned off, so that only E_2 is incident on the dye film. Fig. 6.15 shows the observed strength of phase-conjugate signal as a function of time. The signal strength is initially increased quickly within few minutes to the peak amplitude level may be due to both degenerate four-wave mixing and holographic mechanisms, but suddenly decreased as shown in figure after switching off both the write beams E_1 and E_3. This proves that the phase conjugated signal is generated only by the contribution from the fast degenerate four-wave mixing process and not by

holographic process. Therefore, it is inferred that the rapidly decaying component corresponds to the phase-conjugate wave which is generated by the degenerate four-wave mixing.

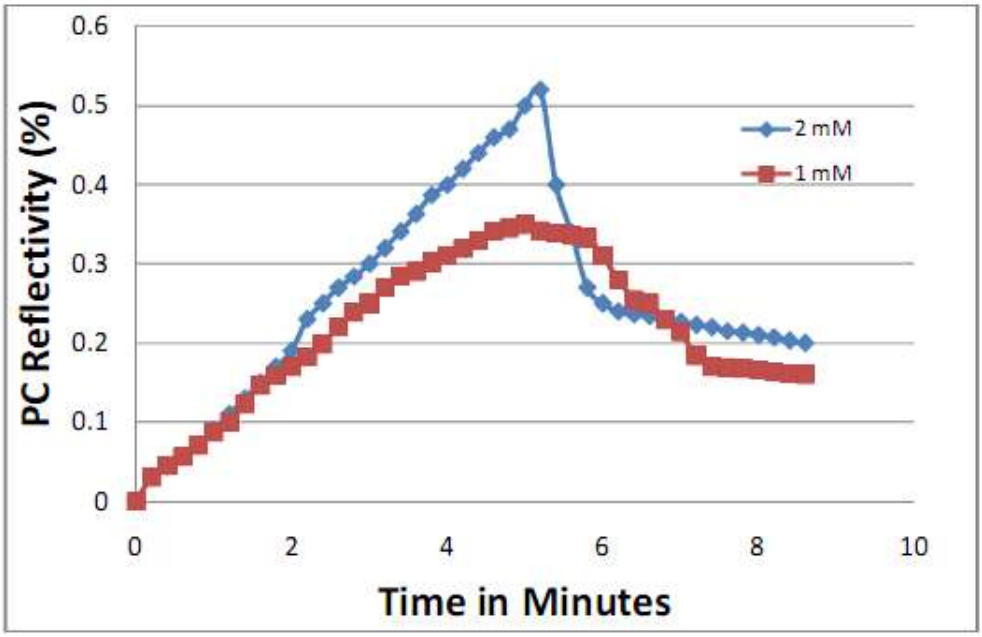

Fig. 6.15 : P.C. signal versus recording time for different concentration for DY-7 at 532 nm.

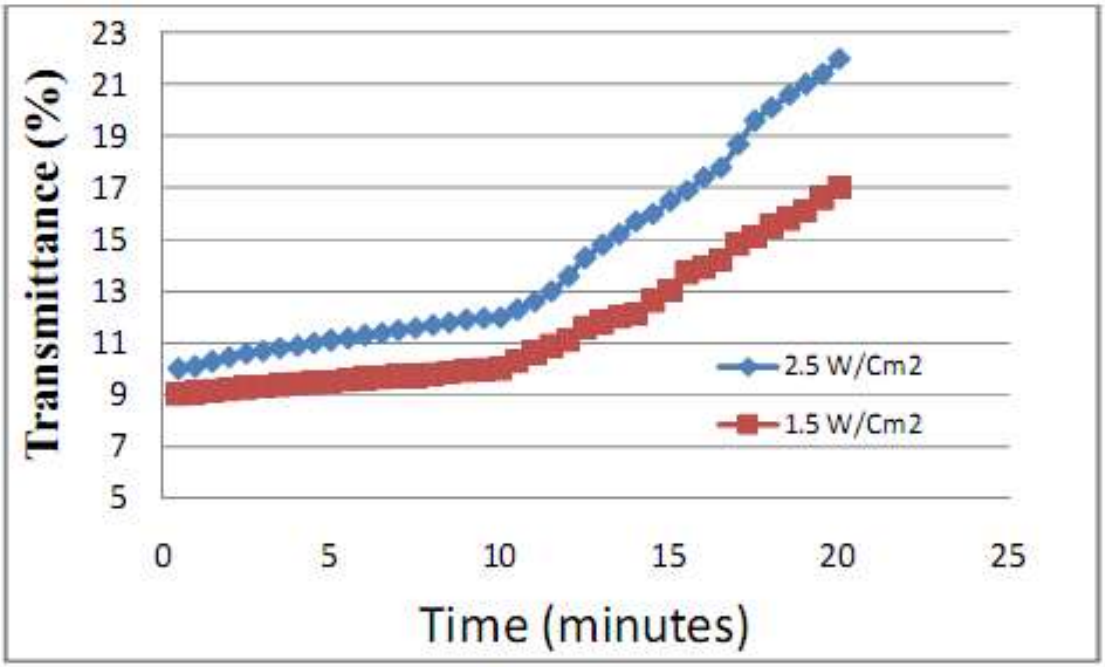

Fig. 6.16 : Variation of Transmission as a function of time for DY-7 at 532 nm.

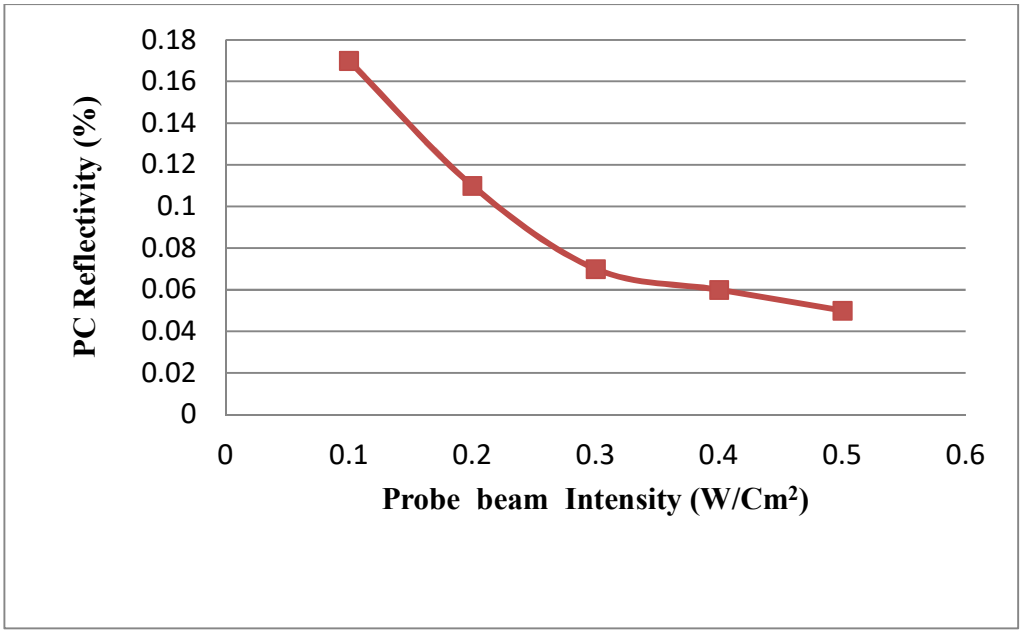

Fig. 6.17 : Variation of P.C. reflectance with probe beam intensity for DY-7 at 532 nm.

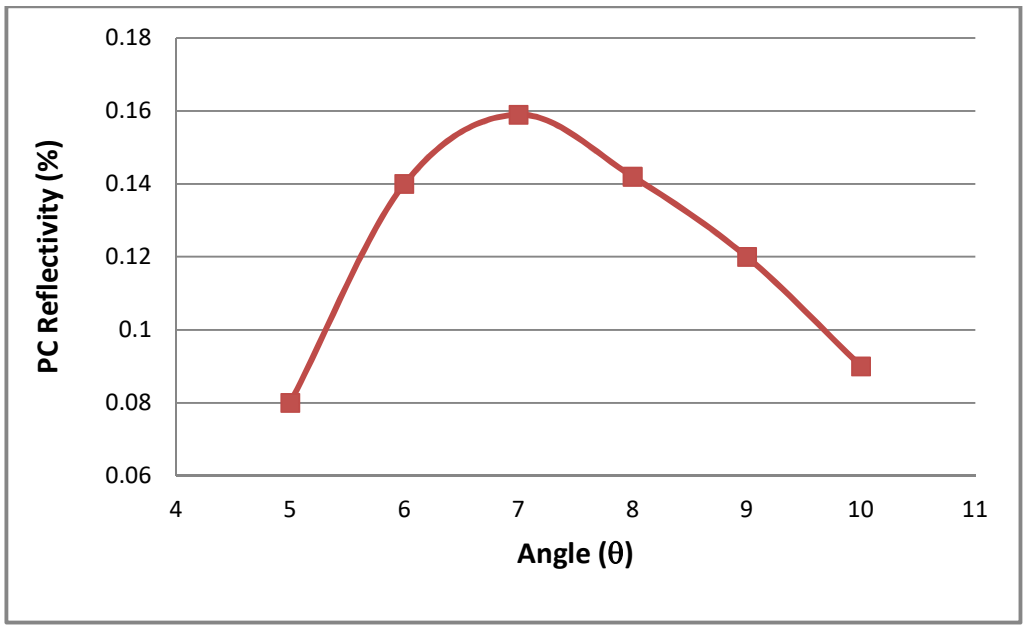

Fig. 6.18 Variation of P.C. Reflectance with angle between the probe and forward pump beams for DY-7 at 532 nm.

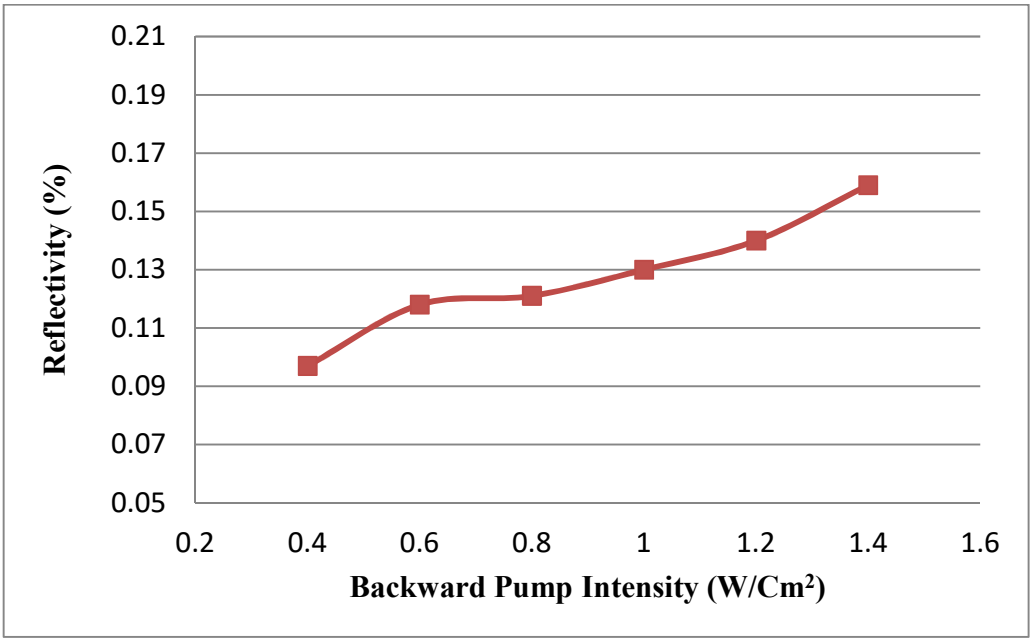

Fig. 6 .19 : Dependence of P.C. reflectivity on backward pump Intensity for DY-7 at 532 nm.

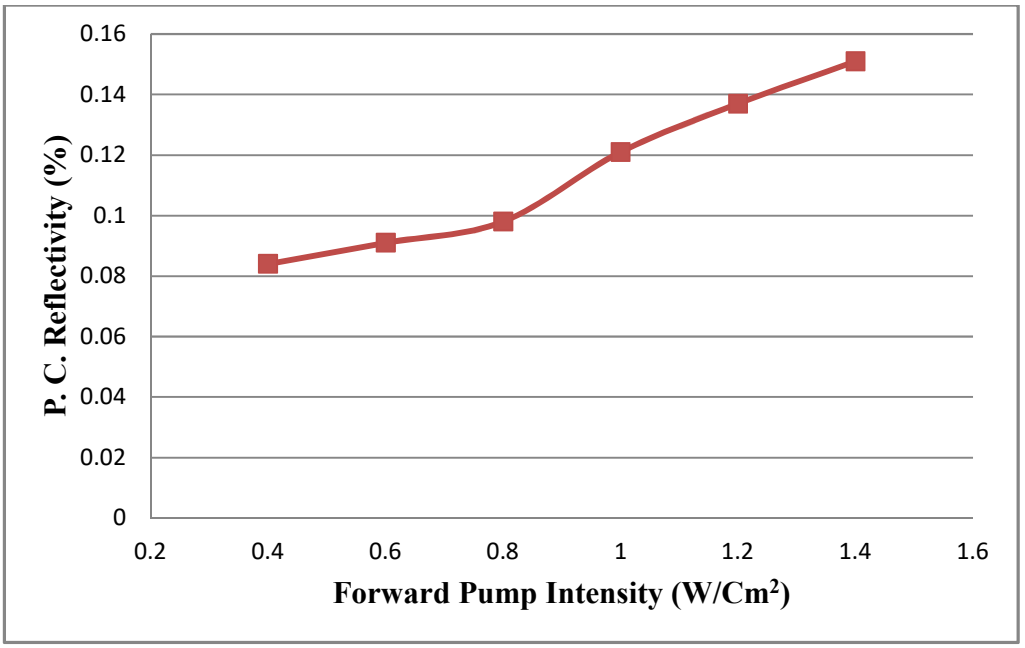

Fig.6.20 : Variation of P.C. reflectance on forward pump power for DY-7 at 532 nm.

6.4.4. Comparison of OPC property of DO-25 and DY-7 :

Fig. 6.21 shows the variation of P.C. reflectance with the angle between the probe beam and forward pump beam of DO-25 and DY-7 samples. From the figure, it is seen that the P.C. reflectance first increases and then decreases as the angle between the probe beam and the

forward pump beam increases. This may be because as the angle between the pump and probe beams changes, the shape of probe beam modifies from circular to elliptical and only a part of the beam falls on the interaction area. Because of two-wave coupling, the maximum P.C. reflectance is obtained when the angle is 7 degrees in the case of both DO-25 and DY-7 samples [457-458].

A maximum reflectance value of 0.18 % is obtained in the case of DO-25 and of 0.14 % is observed in the case of DY-7 for probe beam intensity at 0.15 W/cm^2, and by increasing the probe beam intensity further, resulted in a decrease of P.C. reflectance. The effect of the power of backward pump beam on the strength of P.C. reflectance of both the samples by maintaining the power of the forward pump and probe beams constant and changing the power of backward pump beam is shown in Fig. 6.22.

Fig. 6.23 shows the effect of the intensity of input probe beam on the P.C. beam reflectance. A maximum reflectance value of 0.22% is observed in the case of DO-25 and of 0.17% is observed the in the case of DY-7 for probe beam intensity at 0.11 W/cm^2 respectively, and by increasing in the probe beam intensity further resultant P.C. reflectance is decreased. Similar results have been obtained in other material like glasses doped with organic dyes [459]. Fig. 6.24 shows the variation of P.C. reflectance for the different power of forward pump beam for both the samples. It is found that the P.C. reflectance increases with the increase in forward pump beam power, linearly. The two main basic processes to be considered for the analysis of the origin of optical phase conjugation in dye-doped PMMA-PA films are : (1) the formation of thermal grating and (2) third-order nonlinear optical processes of molecules.

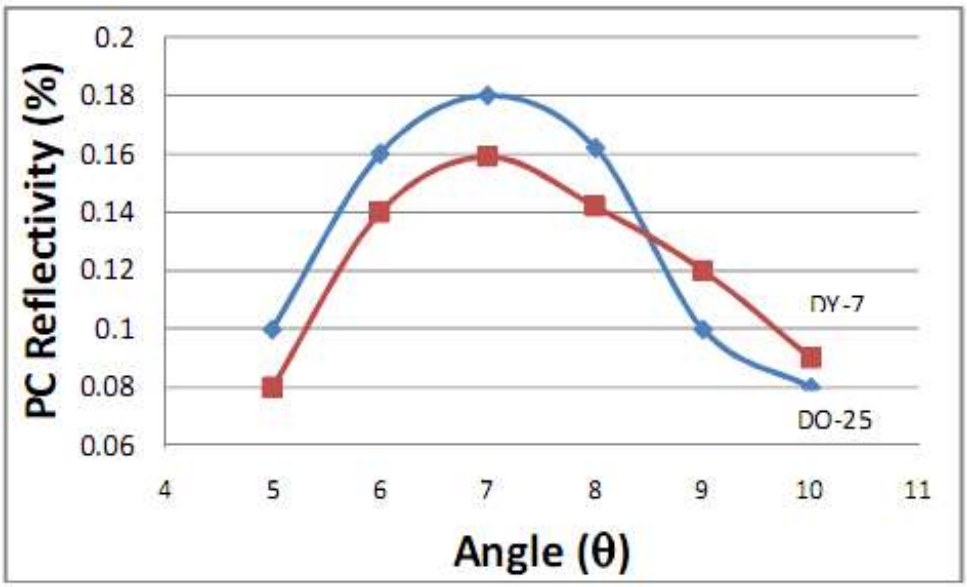

Fig. 6.21. P.C. Reflectivity as function of angle between the probe and forward pump beams at 532 nm.

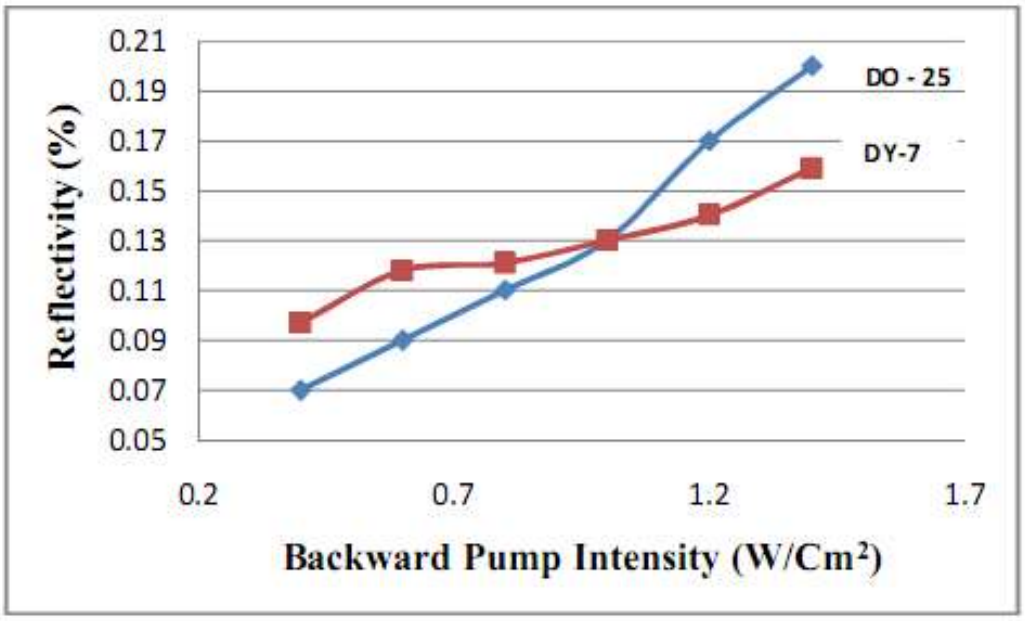

Fig. 6.22.: Dependence of P.C. reflectivity on backward pump Intensity at 532 nm.

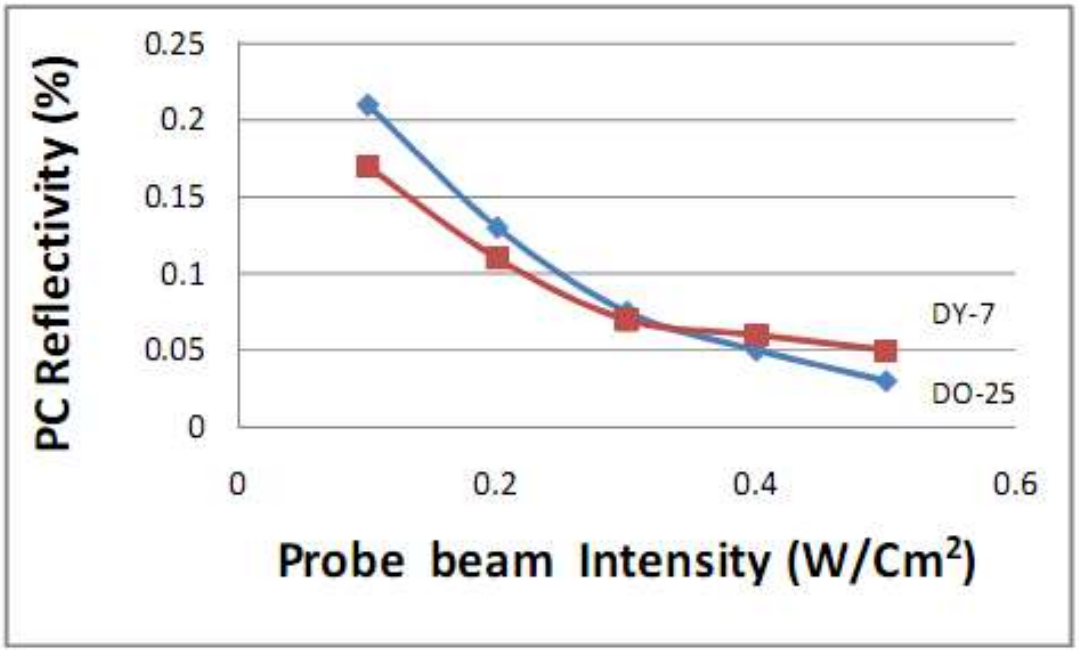

Fig 6.23 : P.C. reflectance as a function of probe beam intensity at 532 nm.

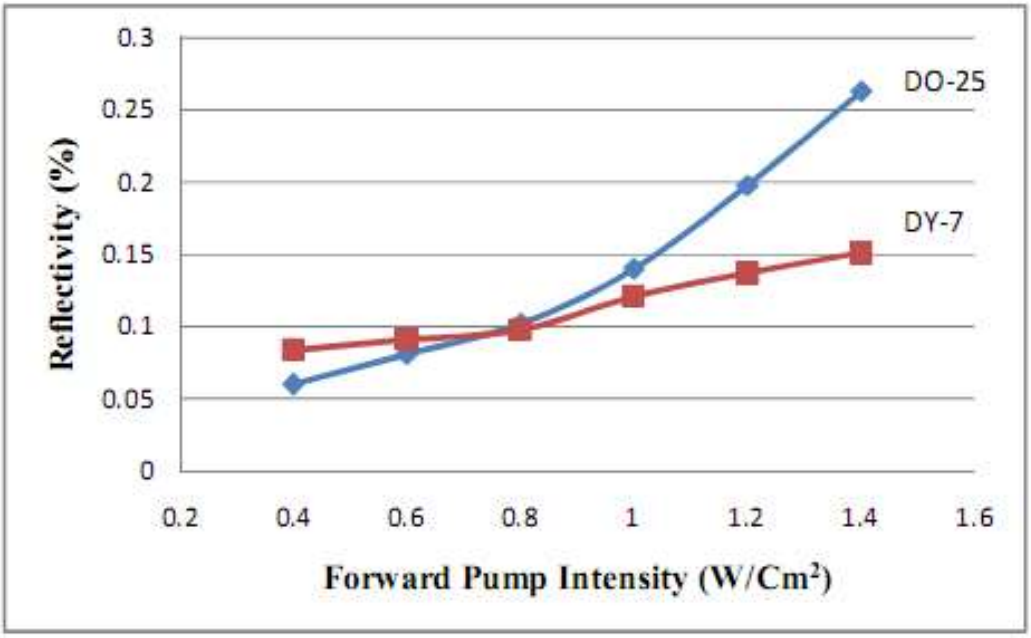

Fig.6.24 : Variation of P.C. reflectance on forward pump power at 532 nm.

The DO-25 and DY-7 films irradiated with 532 nm radiation of a variable intensity and the transmitted beam from the samples are measured using photo detector power meter assembly. If the effect observed is of purely thermal in nature, bleaching of the dye films should have been observed. The obtained results for the sample dyes are shown in Fig. 6.14 and Fig. 6.16 respectively. It is clearly seen that the transmission of the samples increases with time. The experiment demonstrated above shows that the third order nonlinear process like reverse saturation absorption is mainly responsible for OPC in the samples of DO-25 and DY-7 under study. The P.C. signal measurements are made by varying the affecting parameters which influence the strength of P.C. signal reflectivity during the DFWM process. Fig. 6.15 shows the P.C. signal strength versus the time for two dye concentration of the DY-7 doped polymer film. It is found that the P.C. intensity increases linearly to a maximum and then starts decreasing with inter-beam angle. To obtain maximum reflectivity, it is essential to have perfect synchronization between the probe and the pump beams in the nonlinear medium.

It is found that the dyes doped in polymer matrices have the capability of generating a phase-conjugate wave not only by DFWM but also due to holographic process [460]. To distinguish the phase-conjugate wave generated by DFWM from that by the holographic process, the transient characteristics of the P.C. signal reflectivity is studied. For this, the DO-25/DY-7 dyes doped in PMMA – MA polymer matrix are first irradiated with three waves E_1, E_2 and E_3 for a fixed duration, and afterward, E_1 and E_3 are successively switched off, so that only E_2 is incident on the dye film. Fig. 6.10 and Fig. 6.15 show the measured phase-conjugate signal reflectance as a function of time. In this case, the initial slow increase to a peak level within a few minutes is due to both DFWM and holographic processes, but the sudden drop in the intensity of the P.C. signal after switching off both the write beams E_1 and E_3 shows the contribution from the fast DFWM process. Due to the holographic process, the P.C. signal is present even after E_1 and E_3 are shut off, and it decays quite slowly. If the phase-conjugate wave is generated only by DFWM, the lack of only one of the three beams E_1, E_2 and E_3 would have stopped generation of the phase-conjugate wave. Therefore, it is inferred that the fast decaying component corresponds to the phase-conjugate wave which is generated by the DFWM [461].

6.5 RESULTS AND DISCUSSION OF OPC STUDY

The effects of various parameters like dye concentration, the intensity of backward pump beam, the intensity of forward pump beam and the angle between the probe and forward pump beam (inter-beam) on phase conjugation (P.C.) reflectivity on the phase conjugated signal reflectance are studied. The graphs of the different parameters in relation to optical phase conjugation study are depicted as shown below.

(1) Maximum P.C. Reflectance at different dye concentrations.

(2) P.C. signal recording time at different concentrations.

(3) P.C. reflectance as a function of the angle between the probe beam and forward pump beam.

(4) Dependence of P.C. reflectivity on backward pump intensity.

(5) Transmission as a function of Time.

(6) P.C. Reflectance as a function of the probe beam intensity.

(7) P.C. Reflectance as a function of forward pump beam intensity.

Table 6. 1 contains the results of the comparison of P.C. reflectivity at different pump beam, the probe beam and the angle between them at input wavelength 633 nm and Table 6.2 contains the results of the comparison of P.C. reflectance at different pump beam, probe beam and angle between them at the input wavelength 532 nm. The strength of nonlinear P.C. reflectance (R) which is the ratio of the incident beam intensity and the backward phase-conjugate beam intensity and determined for all the three dye-doped PMMA-MA samples. $R = I_1/I_2$. In the case of DASPB films, as the input wavelength of light is changed from 633 nm to 532 nm, there is a marginal change in reflectivity is observed. But in the case of both DO-25 and DY-7 films, by changing the input CW laser beam wavelength from 532 nm to 633 nm, we have not observed any change in the reflectivity. This is probably due to the fact that the observed nonlinearity in the case of DASPB is by two-photon absorption (TPA) and in the case of both DO-25 and DY-7 films is due to reverse saturation absorption (RSA).

Table 6.1 : Comparison of OPC properties of the three dyes in PMMA-MA matrix at 633 nm.

S. No.	OPC Parameter	DASPB	DO-25	DY-07
1	Maximum P.C. reflectance at pump beam intensity of 0.15 W/cm^2	0.325 %	0.18 %	0.14 %
2	Maximum P.C. reflectance at probe beam intensity 0.11 W/cm^2	0.42%	0.22%	0.16%
3	Optimum Dye Concentration	2 mM	1 mM	5 mM
4	Angle between probe &	8	7	7

	pump beam for maximum P.C. reflectance (in degrees)			
5	Nature of Nonlinearity	Two-Photon Absorption	Reverse Saturation Absorption	Reverse Saturation Absorption

Table 6.2 : Comparison of OPC properties of the three dyes in PMMA-MA matrix at 532 nm.

S. No.	OPC Parameter	DASPB	DO-25	DY-07
1	Maximum P.C. reflectance at pump beam intensity of 0.15 W/cm^2	0.30 %	0.18 %	0.14%
2	Maximum P.C. reflectance at probe beam intensity 0.11 W/cm^2	0.38 %	0.22%	0.16%
3	Optimum Dye Concentration	2 mM	1 mM	5 mM
4	Angle between probe & pump beam for maximum P.C. reflectance (in degrees)	8	7	7
5	Nature of Nonlinearity	Two-Photon Absorption	Reverse Saturation Absorption	Reverse Saturation Absorption

In azo dye-doped polymers, the chemical linking between the dye and the polymer is negligible and hence can be used as optical data storage media [462]. Another advantage of azo dye-doped polymers is their nonlinear optical behaviour at comparatively at low light intensity. Therefore, they can be used as optical frequency modulators or optical frequency doublers and optical switches while showing good mechanical characteristics and processability [463].

6.6 CONCLUSION

The optical phase conjugation property of these dye-doped polymer films are studied using degenerate four wave mixing method and the dependence of phase conjugated signal reflectivity on various parameters viz., dye concentration, intensity of backward, forward pump and inter-beam angle between probe and forward pump beam on phase conjugation reflectivity are studied and the results are depicted and compared. The low-intensity optical phase conjugation effect is observed in DASPB dye doped in PMMA – MA polymer matrix using a degenerate four-wave mixing set-up, employing 532 nm 633 light radiation from semiconductor lasers. The mechanism of the generation of phase conjugate wave in these dye-doped materials is discussed. In this case, the phase-conjugate signal is expected due to the DFWM and not from the holographic

processes. The highest phase conjugation beam reflectance observed in these dye-doped films is about 0.42%. The maximum P.C. reflectance is obtained when the angle between two beams (the probe beam and forward pump beam) is 8 degrees. The effects of various parameters like dye concentration, the intensity of backward pump beam, intensity of forward pump beam and the angle between the probe and forward pump beam (inter-beam) on phase conjugation (P.C.) reflectivity are also studied. It is found that the P.C. signal strength first increased and then decreased with increase in inter-beam angle. The strength of P.C. reflectance is enhanced by enhancing the intensity of the forward pump beam and the backward pump beam. The intensity and polarization properties are confirmed to be maintained in the conjugate light wave. The predominant phase conjugation signal is expected to be originated due to saturation absorption and two-photon induced fluorescence property of the dye molecules. The decay time of the recorded grating at fixed pump intensity also decreases with decreasing temperature. Since the DASPB dye in PMMA – MA polymer film is used at 633 nm and 532 nm and may become suitable candidate for low-power semiconductor lasers in the red and green wavelength region. Hence DASPB dye in PMMA – MA polymer films are optimum material for double-exposure, real-time phase conjugation interferometry.

Low-intensity optical phase conjugation signal is also observed in DO-25 dye doped in PMMA – MA polymer matrix and DY-7 dye doped in PMMA – MA polymer matrix using a degenerate four-wave mixing set-up, employing 532 nm light radiation from a CW Diode laser. In this case also it is expected that the phase-conjugate signal is obtained due to the mechanism of degenerate four-wave mixing and not from the holographic mechanism. The maximum amount of phase-conjugated beam reflectance is observed in these dye doped films and is about 0.22% in DO-25 doped PMMA-MA matrix and 0.17% in case of DY-7 doped PMMA-MA polymer matrix.

The maximum P.C. reflectivity is obtained when the angle between two beams (the probe beam and forward pump beam) is 7 degrees. The effects of various parameters like dye concentration, the intensity of backward pump beam, intensity of forward pump beam and the angle between the probe and forward pump beam (inter-beam) on phase conjugation (P.C.) reflectivity are also studied. It is found that the P.C. signal strength first increased and then decreased with increase in inter-beam angle. The strength of P.C. reflectivity is enhanced by enhancing the intensity of

the forward pump beam and the backward pump beam. The intensity and polarization properties are confirmed to be maintained in the conjugate light wave. The predominant phase conjugation signal is expected to be originated due to the reverse saturation absorption property and higher amount of third-order optical susceptibility of the doped dye molecules in polymer films. Since the DO-25 and DY-7 dyes in PMMA – MA polymer film are used at 532 nm and this may be suitable for low-power semiconductor lasers in the green wavelength region, DO-25/DY-7 dyes in PMMA – MA polymer films will be optimum materials for double-exposure real-time phase-conjugation interferometry [464-467].

Although azo dye-doped polymers present a considerable field of organic compounds for contemporary applications, there is a constant demand for further improvement and research, especially to optimize the technological, sustainability, and environmental consciousness. For example, there are various applications in which the uses of dye-doped polymers have reasonable advantages including eco-friendly and cheaper while showing improved properties. The technological issues like organic light-emitting diodes using dye-doped polymers represent a crucial topic of further research.

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CHAPTER SEVEN

Summary of Results, ABCD Analysis, Conclusion, & Suggestions

CONTENTS PAGE No.

7. 1 INTRODUCTION

The invention of new materials with superior quality and characteristics is often responsible for major advances in new technologies. The high speed, high degree of parallelism of optics will lead gradually to optoelectronic systems to be converted into photonic systems where an increasing number of functions or all functions will be implemented optically. The development of photonic technology is expected to be largely rely on the progress achieved in fabricating new optical materials with optimum performance. In this chapter, the results present studies on linear absorption, nonlinear absorption, nonlinear refraction, optical limiting, and optical phase conjugation using degenerate four wave mixing are depicted and discussed. Nonlinear absorption coefficients of the samples films are calculated using DFWM and Z-scan techniques and the results are compared. The optical limiting and optical phase conjugation (P.C.) behavior of these dye-doped polymer samples are analyzed. The causes for observed experimental results are explained in terms of the two-photon absorption, saturation and reverse saturation absorption properties of the molecules. The use of these dye-doped polymer films in photonic device and applications are analysed using a recently developed system/concept/technology/strategy analysis technique called ABCD analysis framework. Further research possibility and usage of these materials in Photonic devices are also discussed in this concluding chapter and many suggestions are provided for future research directions.

Using optimum structural design of organic dye molecules for better nonlinear properties we have prepared three types of dye-doped polymer film samples with variable dye concentration and variable film thickness using the hot-press technique. Based on the molecular structural patterns three dyes namely 4-(4-(Dimethylamino)styryl)-1-docosyl pyridinium bromide [DASPB], 3-(N-ethyl-4-(4-nitrophenylazo) phynyl-amino)propionitrile (Disperse Orange, DO-25), and 4-(4-(Phenylazo)phenylazo)-o-cresol [Disperse Yellow, DY-7)] are chosen for further study.

7. 2 SUMMARY OF RESULTS OF LINEAR ABSORPTION STUDY

The linear absorption property of prepared films of these three dyes doped in Polymethyl methacrylate methacrylic acid (PMMA-MA) are studied using molecular absorption spectroscopy and the results are discussed. The results of the physical parameters and linear optical properties are summarized in Table 7.1.

Table 7.1 : Comparison of Physical parameters and Linear Absorption properties of dye-doped samples.

S. No.	Parameter/Property	DASPB in PMMA-MA	DO-25 in PMMA-MA	DY-7 in PMMA-MA
1	Linear absorption range (bandwidth)	100 nm	100 nm	80 nm
2	Linear absorption peak (nm)	479 nm	468 nm	468 nm
3	Linear Transmission Range (nm)	480 – 1,600	530 – 1,600	528 – 1,600
4	Transmittance (T) at 532 nm	0.7	0.6	0.58
5	Linear absorption coefficient (α_0) at 532 nm	-0.03567	-0.0510786	-0.05447226
6	Linear Refractive index (n_0) at 532 nm	2.4488	2.999	3.12864
7	Dye concentrations in prepared films	1 mM, 2mM, & 5 mM	1 mM, 2mM, & 5 mM	1 mM, 2mM, & 5 mM
8	Film Thickness	10 µm	10 µm	10 µm

7. 3 SUMMARY OF RESULTS OF NONLINEAR REFRACTION STUDY

In Z-scan setup, if the transmitted beam is maximum/ minimum it is referred to as peak/valley. The peak to valley configuration of the closed aperture curves of the samples shows that the refractive change is positive or negative, exhibiting a self-focussing or self-defocusing effect respectively. Based on nonlinear refraction studies using Z-scan technique, it is found that the DASPB dye-doped PMMA-MA sample shows self-focusing characteristics and the Azo-dye, Disperse Orange-25 has also shown self-focusing characteristics, whereas, the Azo-dye, Disperse Yellow-7 has shown self-defocusing characteristics.

7. 4 SUMMARY OF RESULTS OF NONLINEAR ABSORPTION STUDY

It is found that DASPB shows two-photon absorption property whereas DO-25 and DY-7 show Reverse Saturation Absorption at high intensity laser beam irradiation. The results of nonlinear absorption study on all the three dyes doped in PMMA-MA polymer films are depicted in Table 7.2. It is found that DASPB has shown positive nonlinearity due to its self focusing property. Both DO-25 and DY-7 dyes have shown negative nonlinearity due to their self defocusing properties. The nonlinear parameters for these dye-doped samples at 532 nm wavelength are listed in table 7.3.

Table 7.2: Nature of Nonlinearity of dye samples doped in PMMA-MA polymer films

S. No.	Dye	Medium	Nature of Nonlinearity
1	DASPB	PMMA-MA polymer film	Positive Nonlinearity Focusing effect
2	Disperse Orange DO-25	PMMA-MA polymer film	Negative Nonlinearity Defocusing effect
3	Disperse Yellow DY-7	PMMA-MA polymer film	Negative Nonlinearity Defocusing effect

Table 7.3 : Nonlinear parameters for dye-doped samples at 532 nm.

S. No.	Parameter	Dye concentration	DASPB	DO-25	DY-7
1	β (× 10^{-3}) (cm/W)	1 mM	0.64	-0.74	- 0.97
		2 mM	0.81	-0.88	-2.10
		5 mM	1.13	-1.13	-2.75
2	n_2 (× 10^{-7}) (cm^2/W)	1 mM	0.69	-0.325	-0.248
		2 mM	0.87	-0.557	-0.471
		5 mM	1.09	-0.836	-0.702
3	$\Delta n = n_2 I_0$ (× 10^{-4})	1 mM	2.415	-1.138	-0.868
		2 mM	3.045	-1.950	-1.649
		5 mM	3.815	-2.926	-2.457
8	$\|\chi^3\|$ × 10^{-6} |esu|	1 mM	9.149	5.69	5.12
		2 mM	10.998	7.45	6.82
		5 mM	13.349	9.73	8.52

7. 5 SUMMARY OF RESULTS OF OPTICAL LIMITING STUDY

Optical limiting behavior for three dye-doped PMMA-MA polymer films under low power cw laser excitation for different dye concentrations are studied. In case of DASPB doped PMMA-MA films, the mechanism responsible for type 1 optical limiting is mainly attributed to the combined effect of reverse saturation absorption and two-photon absorption which further increased with thermally induced nonlinear refraction. The focusing effect observed in DASPB 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 behave as good type 1 optical limiters even at low powers. Table 7.4 contains the concentration dependence of limiting threshold values of three dye-doped in PMMA-MA films and Table 7.5 lists the concentration dependence of saturated output power in these dye-doped PMMA-MA films.

Table 7.4 : Concentration dependence of limiting threshold of dye-doped in PMMA-MA films.

S. No.	Sample	Dye Concentration (mM)	Type 1 Optical Limiting Threshold (mW)	Type 2 Optical Limiting 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
2	DO-25 in PMMA-MA	1 mM	22	15
		2 mM	25	12
		5 mM	27	10
3	DY-7 in PMMA-MA	1 mM	23	18
		2 mM	25	15
		5 mM	26	09

Table 7.5 : Concentration dependence of saturated output power in dye-doped PMMA-MA films.

S. No.	Sample	Dye Concentration (mM)	Type 1 Optical Limiting Saturated Output Power (mW)	Type 2 Optical Limiting Saturated Output Power (mW)
1	DASPB in PMMA-MA	1 mM	11	10.5
		2 mM	8.0	8.06
		5 mM	4.0	6.10
2	DO-25 in PMMA-MA	1 mM	5.10	4.0
		2 mM	4.0	3.10
		5 mM	2.92	1.99
3	DY-7 in PMMA-MA	1 mM	4.3	3.50
		2 mM	3.5	2.10
		5 mM	2.2	0.95

7.6 SUMMARY OF RESULTS OF OPTICAL PHASE CONJUGATION STUDY

In this work, we have studied the low-intensity optical phase-conjugation phenomenon in DASPB dye in PMMA – PA polymer matrix using a degenerate four-wave mixing set-up, employing 633 nm and 532 nm light radiation from a semiconductor laser. The mechanism of P.C. wave generation involved with this dye-doped system is analysed. The phase-conjugate signal is found to have maximum contribution from the DFWM process. The maximum phase-conjugate beam reflectance observed in these dye films is about 0.42%. The maximum P.C. reflectance is found when the angle between the forward pump beam and the probe beam is 8º. Effects of various parameters like dye concentration in the films, intensity of backward pump

beam, intensity of forward pump beam, and inter-beam angle between probe beam and forward pump beam on phase conjugation reflectance are also studied. The strength of P.C. signal is first increased and then decreased with inter beam angle. P.C. reflectance is increased by increasing the intensity of the backward beam and forward pump beam. The polarization and intensity profiles of the conjugate signal are verified and found to be preserved. The predominant phase conjugation signal can be explained due to the fact of reverse saturation absorption and two-photon induced florescence property of the dye molecules. The decay time of the recorded grating at fixed pump intensity also decreases with decreasing temperature. Since the DASPB dye in PMMA – PA polymer film is used at 633 nm and this may be suitable for low-power semiconductor lasers in the red wavelength region, DASPB dye in PMMA – PA polymer film may be a potential organic material for double-exposure real-time P.C. interferometry.

We have also studied low-intensity optical phase-conjugation signal in DO-25 dye-doped in PMMA–MA polymer matrix using a degenerate four-wave mixing set-up, employing 532 nm laser light from a low power semiconductor laser. It is also proved that the P.C. signal observed has major contribution from the DFWM process and not from the holographic process. The maximum phase-conjugate beam reflectivity observed in these dye films is about 0.22%. The maximum P.C. reflectance is observed when the angle between the probe beam and forward pump beam is at 7º. Effects of various parameters like, dye concentration in the films, intensity of backward pump beam, intensity of forward pump beam, and inter-beam angle between probe beam and forward pump beam on phase conjugation reflectance are also studied. The strength of P.C. signal is first increased and then decreased with inter beam angle. P.C. reflectance is increased by increasing the intensity of the backward and forward pump beam.

The polarization and intensity profiles of the conjugate signal are verified and found to be preserved.

The predominant P.C. signal can be explained due to the fact of reverse saturation absorption and large third-order susceptibility of the dye molecules. Since the DO-25 dye in PMMA – MA polymer film is used at 532/633 nm and this may be suitable for low-power semiconductor lasers in the green and red wavelength region. Thus DO-25 dye in PMMA – MA polymer film may be potential material for double-exposure real-time P.C. interferometry.

Table 7.6 : Comparison of OPC properties of the three dyes in PMMA-MA matrix at 633 nm.

S. No.	OPC Parameter	DASPB	DO-25	DY-07
1	Maximum PC reflectivity at pump beam intensity of 0.15 W/cm^2	0.325 %	0.18 %	0.14 %
2	Maximum PC reflectivity at probe beam intensity 0.11 W/cm^2	0.42%	0.22%	0.16%
3	Optimum Dye Concentration	2 mM	1 mM	5 mM
4	Angle between probe & pump beam for maximum PC reflectivity (in degrees)	8	7	7
5	Nature of Nonlinearity	Two-Photon Absorption	Reverse Saturation Absorption	Reverse Saturation Absorption

Table 7.7 : Comparison of OPC properties of the three dyes in PMMA-MA matrix at 532 nm.

S. No.	OPC Parameter	DASPB	DO-25	DY-07
1	Maximum PC reflectivity at pump beam intensity of 0.15 W/cm^2	0.30 %	0.18 %	0.14%
2	Maximum PC reflectivity at probe beam intensity 0.11 W/cm^2	0.38 %	0.22%	0.16%
3	Optimum Dye Concentration	2 mM	1 mM	5 mM
4	Angle between probe & pump beam for maximum PC reflectivity (in degrees)	8	7	7
5	Nature of Nonlinearity	Two-Photon Absorption	Reverse Saturation Absorption	Reverse Saturation Absorption

Therefore, the above dye-doped PMMA-MA polymer films can be used in optical power limiter, Two-Photon Absorption (TPA) microscopy, Photonic (both positive and negative nonlinearity) devices, broad band optical windows, all optical switching devices, and holographic applications (negative refractive index). These dye-doped polymer films do not exhibit any SHG due to centrosymmetric nature of the materials.

7.7 FACTORS & ELEMENTAL ANALYSIS USING ABCD FRAMEWORK

7.7.1 Ideal Properties of Nonlinear Optical Materials

It is well known that one can improve the performance of any system by comparing it with a hypothetical, predicted system of that kind called "Ideal system" [468]. Ideal properties of a device or a system can be used to upgrade or improve its properties towards reaching 100% efficiency. 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 [469]. Many systems like an ideal gas, ideal fuel, ideal solution, ideal fluid, ideal engine, ideal switch, ideal voltage source, ideal current source, ideal diode, ideal transistor, and ideal amplifier are familiar to everybody since school days. Recently, ideal business system [469-470], ideal education system [471-473], ideal technology system [468], ideal strategy [474], ideal energy source [475], ideal banking system [476], and ideal library system [477] are studied and their input, system, output and environmental characteristics are discussed. The properties of the ideal nonlinear material are interesting to know. In table 7.8, we have summarized the ideal properties of the nonlinear optical material.

Table 7.8. Ideal Properties of optical nonlinear material

S. No	Property	Value
1	Nonlinear Susceptibility	Infinity (High)
2	Refractive index	Low & constant value
3	Dielectric property	Low
4	Material property	optimum
5	Material Processing	Easy
6	Colour	Transparent and colourless
7	Transmission range	Infinite
8	Durability	Life time without degradation
9	Laser damage threshold	High
10	Transmission range	Infinite
11	Material state	Solid (Film & Fiber)
12	Electro-optic Coefficient	Infinity (High)
13	Photoconductivity	Infinity (High)
14	Photorefractive co-efficient	Infinity (High)
15	Degradation with time	No
16	Cost	Zero
17	Availability	Abundant
18	Environmental degradation	Zero
19	Weight	Zero (Low)
20	Angular Bandwidth	Infinite

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) Bio-derived and bio-inspired materials. Organic nonlinear materials are currently finding importance due to their advantages and benefits for photonics device fabrication. 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 4,32,000 20-nanosecond pulses at 20 Hz without any evidence of damage to the organic material, making it ideal for use in photonic applications.

In this section, we made an attempt to analyse nonlinear dye-doped polymer films for nonlinear and photonic applications using recently developed analysis framework called ABCD analysis framework. The acronym ABCD stands for Advantages, Benefits, Constraints, and Disadvantages.

7.7.2. About ABCD Analysis

Various techniques are used to analyze the individual characteristics, system characteristics, effectiveness of a concept or idea, effectiveness of a strategy while studying the business value in the society. The individual characteristics or organizational effectiveness & strategies in a given environment can be studied using SWOT analysis, SWOC analysis, PEST analysis, McKinsey

7S framework, ICDT model, Porter's five force model etc. Recently introduced business analysis framework called ABCD analysis framework [478] is suitable for analysing business concepts, business systems, technology, business models or business idea in terms of determining various factors for chosen determinant issues under four constructs called advantages, benefits, constraints, and disadvantages. In the qualitative analysis using ABCD framework, the concept/system/strategy/technology/model/idea is further analysed by identifying constitutional critical factors. In the quantitative analysis using ABCD framework [479], the appropriate score/weightage is given to each constituent critical factor under each construct, through empirical research, the total score is calculated for each construct and by evaluating the scores, the concept/idea/system/technology/strategy can be accepted or rejected. Thus, ABCD analysis framework can be used as a research tool in these areas and is a simple but systematic analyzing technique for business models/systems/concepts/ideas/technology/strategy analysis.

In 2015, Aithal P. S. et. al. [478] developed ABCD analyzing framework to analyze any business model/strategy/concept/system and to study its effectiveness in providing value to its stakeholders and sustainable profit through expected revenue generation. Application of ABCD analysis results in an organized list of business advantages, benefits, constraints, and disadvantages in a systematic matrix. The entire framework is divided into various issues/area of focus and various business deployment factors affecting the business/concept can be identified and analyzed under each issue by identifying the suitable critical effective element. This analyzing technique being simple, gives he guideline to identify and analyze the effectiveness of any business model, business strategy, business concept/idea, and business system. Reshma et. al. [480], have analyzed the characteristics of "Working from Home" e-business model using 'ABCD Analysis Technique'. Based on numerous factors which decide the Working from Home system, a model of various factors and their constituent critical elements affecting under organizational objectives, employers point of view, employees point of view, customers/students point of view, environmental/societal point of view and system requirements are derived from a qualitative data collection instrument namely focus group method. It is found that the factors supporting advantages and benefits are more effective compared to constraints and disadvantages of this model so that working from the home model may become more popular from the perspective of employers and employees in the organization in the future.

ABCD analysis framework is used for analysing Black Ocean Strategy (BOS) concept [481]. The numerous factors & their constituent critical factors affecting the BOS concept adopted in some of the business organizations for quick relief from the problems are identified for organizational point of view, administrative point of view, employee point of view, operational point of view, business point of view and external issues point of view are determined under the four constructs - advantages, benefits, constraints, and disadvantages. ABCD analysis framework has been used for analysis of a concept "Higher Education Stage Model". The characteristics of the concept are evaluated based on identifying and analyzing the advantages, benefits, constraints, and disadvantages. The result supported the logic of using ABCD analyzing technique in any concept/idea performance evaluation [482]. ABCD analysis framework is also used for analysing National Assessment and Accreditation Council (NAAC) accreditation process on higher education institutions [483]. The various features of the NAAC accreditation system is evaluated based on identifying and analyzing the advantages, benefits, constraints, and disadvantages of some of the chosen issues like organizational issues, Faculty performance issues, student development/progression issues, social/environmental/community engagement issues, Infrastructure And Learning resources, and Issues on Innovations Creativity and Best Practices. The affecting factors under these issues found out using focus group method and the constituent critical elements under each factor are identified. The result supported the logic of using ABCD analyzing technique in any System/concept performance evaluation. In another paper on “Study on ABCD Analysis Technique for Business Models, business strategies, Operating Concepts & Business Systems”, the author discussed the detailed ABCD framework for quantitative studies and explained how this framework can be used for four specific instances namely Business model, Business strategy, Operational concept and Functional system are outlined here. Finally, ABCD analysing framework is compared with other known analyzing techniques like SWOC, Competitive Profile Matrix (CPM) analysis, EFE & IFE Matrices, BCG analysing frameworks, Porter's Five Forces Model, and PESTLE Analysis [479]. Application of ABCD Analysis Framework on Private University System in India is another paper published using this model in which for six determinant issues related to the functioning of a University has been chosen. These are Organizational aspects, Students Progression, Faculty development, Societal & other stakeholders issues, Governance, Leadership, and Issues on Innovations and Best Practices. Four key issues were identified under each of these and critical constituent

elements under these factors are worked out. Through this analysis, 192 critical constituent elements which satisfy the success of a private university have been explored [484]. Recently, another paper on "Study of New National Institutional Ranking Framework (NIRF) System using ABCD Framework, is published in which the ranking system is evaluated using four constructs Advantages, Benefits, Constraints, and Disadvantages, this system consider all determinant issues in key areas through analyzing the major issues and identifying the critical constituent elements and concluded that NIRF provides a comprehensive ranking suitable for higher educational institutions and it takes care of many small and subtle aspects comparable to quality assessment criterion of National Assessment and Accreditation Council. [485]. Apart from using ABCD framework for Qualitative analysis, in several research studies, ABCD analysis is limited and simplified to only listing of various advantages, benefits, constraints, and disadvantages of either concept, models, systems, strategies, technology, or ideas [486-492]. These studies on ABCD listing can be analysed in detail using ABCD framework either qualitatively or quantitatively for further research.

7. 7. 3. ABCD Factors Analysis on Dye-doped Polymers

Advantages, Benefits, Constraints and Disadvantages (ABCD) of a System can be used to analyze and understand the model/system in an effective way. As per this analysis technique, the effectiveness of a material system can be studied by identifying and analyzing the advantages, benefits, constraints, and disadvantages by considering various determinant issues related to the use of dye-doped polymers for photonic applications as shown in the block diagram (fig. 7.1). As per the ABCD framework, the various determinant issues related to the success of dye-doped polymer films in photonic applications identified using focus group method [493] are : (1) Material Issues, (2) Application Issues, (3) Commercialization Issues, (4) Production/Service providers Issues, (5) Customer Issues, and (6) Environmental/Social Issues.

(1) Material Issues :

The affecting factors under key properties like Processing for device fabrication, Third order susceptibility, Laser damage threshold, Electro-optic coefficient value, and Dielectric constant value are determinant factors under the constructs Advantages, Benefits, Constraints, and Disadvantages of the System.

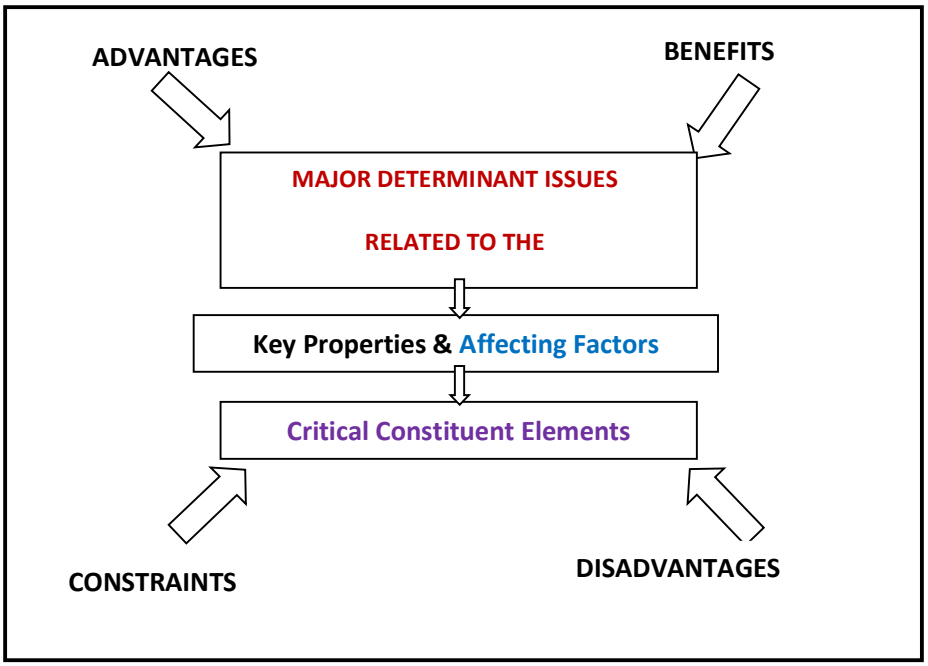

Fig. 7.1. Block diagram of issues affecting the dye-doped polymer films for photonic applications as per ABCD framework.

(2) Application Issues :

The affecting factors under key properties like Optical limiting, Electro-optic modulators, Photorefractive memories, Optical switches, and Optical computer components are determined under the constructs Advantages, Benefits, Constraints, and Disadvantages of the System.

(3) Commercialization Issues :

The affecting factors under key properties like Easy to process, Low cost, High reliability, and Long life are determined under the constructs Advantages, Benefits, Constraints, and Disadvantages of the System.

(4) Production/Service providers Issues :

The affecting factors under key properties like Production cost, Performance, Durability, and Raw materials availability are determined under the constructs Advantages, Benefits, Constraints, and Disadvantages of the System.

(5) Customer Issues :

The affecting factors under key properties like Quality, Durability, Cost, and Availability are determined under the constructs Advantages, Benefits, Constraints, and Disadvantages of the System.

(6) Environmental/Society Issues :

The affecting factors under key properties like Environmental degradation, Social perception, Future scope, and Recycling are determined under the constructs Advantages, Benefits, Constraints, and Disadvantages of the System.

Each determinant issue has sub-issues called key properties used for analyzing the advantages, benefits, constraints and disadvantages, the four constructs of the framework. The factors affecting the various determinant issues of private university system for each key issue under four constructs are derived by a qualitative data collection instrument namely, focus group method [493-500], and are listed in table 7.9.

Table 7.9 : Factor Analysis of the dye-doped polymer films for photonic applications using ABCD framework.

Determinant Issues	Key Properties	Advantages	Benefits	Constraints	Disadvantages
Material Properties Issues	Processing for device fabrication	Easy to fabricate as thin films	Microfilm component for device fabrication	Maintaining uniform thickness and surface	Low physico-chemical stability.
	Third order susceptibility	High third order susceptibility	Enhanced efficiency	Depending on film thickness	Bleaching of dye for long time
	Laser damage threshold	Effective performance at Low power laser	Suitable for low power devices	Sample may burn at high intensity laser beam	Low damage thresh old
	Electro-optic coefficient value	High at low applied electric field	High breakdown voltage	Applying external dc electric field is difficult	E-O coefficient varies with wavelength of laser beam
	Dielectric constant value	Low dielectric constant	No poling voltage required	Applying external dc electric field is difficult	Dielectric constant varies with wavelength of laser beam
Application Issues	Optical limiting	Limiting of High intensity laser light	Eye protection when working with laser beams	Limiter at all wavelengths	Nonlinear refraction property of dye
	Electro-optic	High electro-	Fast	High	Low physico-

	modulators	optic coefficient	response	voltage requirement for modulation	chemical stability
	Photorefractive memories	High PR coefficient	High density storage at high retrieval speed	Doping is required to increase trapping centers	Temperature dependent properties
	Optical switches	Fast optical response	High figure of merit	Doping is required to increase charge centers	Slow time response
	Optical computer components	Easy to fabricate thin film & fibers	High speed response	Doping is required to increase charge centers	Low physico-chemical stability
Commercialization Issues	Easy to process	Easy to fabricate as thin films and fibers	Less expensive equipment required	Tedious process	Colour of dye decreases the transparency range
	Low cost	Less expensive	Easily available in the market	Low profit due to low cost	More competitors
	High reliability	Stable nonlinear properties	Used for longer period	Degradation of performance for longer period	Low phisico-chemical stability
	Long life	Stable nonlinear properties for long time	High laser damage threshold	Delicate for replacement	Not withstands at higher laser intensity
Production/Service providers Issues	Production cost	Low	Less expensive	Assembling	Periodical Replacement
	Performance	Higher susceptibility	Fast response	Anti-reflection coating	Degrades with time
	Durability	Long time	Less after sales service	Periodic service	Less life with 100 % efficiency
	Raw	Easily	Cheap	Uniform	Environmental

	materials availability	available		doping	degradation of dyes
Customer Issues	Quality	High nonlinear properties	Easy processing	Soft material	Bleaching of dye after several years
	Durability	Long life with expected performance	Worth investment	Maintaining outer surface of thin sample	Bleaching of dye after several years
	Cost	Low cost device	Low price	Periodic up gradation	Periodic replacement
	Availability	Easily available	Anywhere usage	Simple component	Supply of components
Environmental/Society Issues	Environmental degradation	No green gas emission	Low environmental effect	Careful handling	Dyes are poisonous
	Social perception	Advanced device for society	High speed device	Environmental effect	Low phisico-chemical stability
	Future scope	High performance devices	Advanced technology usage	Availability of dyes	Threat of better components based on nanotechnology
	Recycling	Possible	No degradation	Dye stability	Dye may degrade drinking water

7.7.4. Critical Constituent Elements as per ABCD Framework

The critical constituent elements of these factors are listed under the four constructs - advantages, benefits, constraints and disadvantages of the ABCD technique and tabulated in tables 7.10 to 7.13.

Table 7.10 : Advantages of dye-doped polymers for photonic applications

Sl. No.	Issue	Factors affecting	Critical Constituent Elements
1.	Material Issues	Easy to fabricate as thin films & fibers	Easy for spin coating
			Easy for hot press method
		High third order susceptibility	Non-centrosymmetric molecular structure
			Do not require electric poling

		Effective performance at Low power laser	Active for CW laser beam & pulsed laser beam
			Active for low power UV, visible, and IR region
		High at low applied electric field	Effective polarization
			High breakdown voltage
		Low dielectric constant	Polarization ability
			Electric field strength
2.	Application Issues	Limiting of High intensity laser light	High nonlinear absorption
			Wide transparency range
		High electro-optic coefficient	Variation of transmission amplitude
			High modulation index
		High Photorefractive coefficient	Refractive index variation with light intensity
			Charge transfer properties
		Fast optical response	Free carriers
			Optical bistability
		Easy to fabricate thin film & fibbers	Surface tension
			Strength of fibres
3.	Commercialization Issues	Easy to fabricate as thin films and fibers	Material property
			Tensile strength
		Less expensive	Easy availability
			Simple processes
		Stable nonlinear properties	Non-centrosymmetry
			Non-bleaching
		Stable nonlinear properties for long time	Material type
			Stable dye & polymer used
4.	Production/Service providers Issues	Low production cost	Easy component processing
			Availability of raw materials at low price
		Higher susceptibility	Quality of raw materials
			Organic nonlinear materials
		Long time	Functioning
			Same conversion efficiency
		Easily available	Abundant
			Low cost
5.	Customer Issues	High nonlinear properties	Non-centrosymmetry
			Efficiency
		Long life with expected performance	Faithfull operation
			Expected performance
		Low cost device	Low price
			Easy replacement
		Easily available	Abundant
			Continuous supply
6.	Environmental	No green gas emission	Clean operation

	/Society Issues		Clean environment
		Advanced device for society	Latest technology
			Environmental sustainability
		High performance devices	Efficiency
			Best output
		Recycling Possible	Low degradation
			Sustainability

Table 7.11 : Benefits of the dye-doped polymers for photonic applications

Sl. No.	Issue	Factors affecting	Critical Constituent Elements
1.	Material Issues	Microfilm component for device fabrication	Small device
			Simple device
		Enhanced efficiency	Best performance
			Better output
		Suitable for low power devices	Low cost
			Low input energy
		High breakdown voltage	Sustaining strong electric field
			High polarizability
		No poling voltage required	Natural nonlinearity
			Low cost
2.	Application Issues	Eye protection when working with laser beams	Low transmission at high intensity
			High laser damage threshold
		Fast response	Effective at nano and femto second regime
			High modulation index
		High density storage at high retrieval speed	High space charge field
			Refractive Index grating
		High figure of merit	High optical bistability
			Low noise for amplification
		High speed response	High speed grating
			High speed storage & retrieval
3.	Commercialization Issues	Less expensive equipments required	Simple and easy process
			Less and cheaper raw materials
		Easily available in the market	Abundant supply of raw materials
			Minimum raw materials requirement
		Used for longer period	Trouble free operations
			Minimum energy consumption
		High laser damage threshold	Durability
			No periodic material replacement
4.	Production/Service providers Issues	Less expensive	Low investment
			Small component size
		Fast response	Material property
			Amount of doping

		Less after sales service	No frequent breakdown
			Easy repairing/replacement
		Cheap	Simple raw materials
			Component in the form of thin film.
5.	Customer Issues	Easy processing	Simple process
			No special care needed
		Worth investment	No periodic replacement
			Return on investment
		Low price	Affordability
			High demand
		Anywhere usage	Simple operations
			Easy procurement
6.	Environmental/Society Issues	Low environmental effect	Emission
			Recycling
		High speed device	Technology
			Speed
		Advanced technology usage	Comfortability
			Better facilities
		No degradation	Poisonous gas
			Green house effect

Table 7.12 : Constraints of the dye-doped polymers for photonic applications

Sl. No.	Issue	Factors affecting	Critical Constituent Elements
1.	Material Issues	Maintaining thickness and surface	Viscosity
			Surface Tension
		Depending on film thickness	Noncentrosymmetry
			Doping concentration
		Sample may burn at high intensity laser beam	Phisico-chemical stability
			Power of input light
		Applying external dc electric field is difficult	Electric field intensity
			Film thickness
		High AC electric field is required for modulation	Material property
			Modulation index
2.	Application Issues	Limiter at all wavelengths	Material transmission range
			Nonlinear refractive index
		High voltage requirement for modulation	Electro-optic coefficient
			Modulating voltage strength
		Doping is required to increase trapping centers	Space charge
			Dye concentration
		Doping is required to	Nature of Dye

		increase charge centers	Intensity variation of external light
3	Commercialization Issues	Tedious process	Thickness monitoring
			Uniform doping
		Low profit due to low cost	Less investment
			Low price
		Degradation of performance for longer period	Dye bleaching
			Film cracking
		Delicate for replacement	Thin film
			Trouble free performance
4.	Production/Service providers Issues	Assembling	Delicate
			Simple processes
		Anti-reflection coating	Enhanced interaction of light
			Avoid reflection of light
		Periodic service	Film replacement
			Easy service
		Uniform doping	Proper solvent
			Uniform drying
5.	Customer Issues	Soft material	Polymer as backbone
			Film between glass plates
		Maintaining outer surface of thin sample	Antireflection coating
			Film between thin glass plates
		Periodic up gradation	Increases performance
			Easy
		Simple component	Susceptibility for damage
			Easy replacement
6.	Environmental/Society Issues	Careful handling	Fragile
			Complete replacement & recycling
		Environmental effect	Dyes are poisonous
			Degradability of dyes
		Availability of dyes	Nature of dye
			Supply of dye
		Dye stability	Component replacement
			Easy recycling

Table 7.13 : Disadvantages of the dye-doped polymers for photonic applications

Sl. No.	Issue	Factors affecting	Critical Constituent Elements
1.	Material Issues	Low physico-chemical stability.	Softness of film
			Fragileness/brittleness
		Bleaching of dye for long time	Reaction with atmosphere
			Reaction of dye with light beam
		Low damage threshold	Intensity of pulsed laser beam
			Choice of polymer base

			Dye concentration
		E-O coefficient varies with wavelength of laser beam	Material property with laser wavelength
			Nature of dye
		Dielectric constant varies with wavelength of laser beam	Polarizability
			Bandwidth
2	Application Issues	Nonlinear refraction property of dye	Material property
			Wavelength of light
		Low physico-chemical stability	Instability in electro-optic property
		Temperature dependent properties	Thermal stability
			Working temperature range
		Slow time response	Optical bistability
			Effective intensity & wavelength range
		Low physico-chemical stability	Durability of components
			Assembling of components
3.	Commercialization Issues	Colour of dye decreases the transparency range	Transmission range of dye
		More competitors	Demand
			Profit
		Low phisico-chemical stability	Durability of device
			After sales support
		Not withstands at higher laser intensity	Dye bleaching
			Threshold intensity
4.	Production/Service providers Issues	Periodical Replacement	Durability
			Warranty
		Degrades with time	Aging of components
			Safe input intensity range
		Less life with 100 % efficiency	Warranty period
		Environmental degradation of dyes	Production easiness
			Demand for dye
5.	Customer Issues	Bleaching of dye after several years	Nature of dye used
			Operating light intensity range
		Bleaching of dye after several years	Dye property
			Faithful operation of device
		Periodic replacement	Cost of replacement
			Troubleless working time
		Supply of components	Demand
			Importance of component
6.	Environmental/Society Issues	Dyes are poisonous	Recycling the component
			Air tight system
		Low phisico-chemical	Optimum ingredients

		stability	Softness & bleaching
		Threat of better components based on nanotechnology	Dye sensitized nanomaterials
			Nano-composites
		Dye may degrade drinking water	Recycling
			Usage of selective dyes

7. 8. SUMMARY & CONCLUSION OF ABCD ANALYSIS

We have studied the application of dye-doped polymer films for nonlinear and photonics processes using ABCD analysis framework. The various determinant issues of related to the use of dye-doped polymer films in photonic applications identified using focus group method are : (1) Material Issues, (2) Application Issues, (3) Commercialization Issues, (4) Production/Service providers Issues, (5) Customer Issues, and (6) Environmental/Social Issues. The analysis identified the affecting factors for various determinant issues under four constructs advantages, benefits, constraints, and disadvantages. The analysis has brought about 204 critical constituent elements which satisfy the success of this analysis methodology.

7. 9 GENERAL DISCUSSION & CONCLUSION

In our experiment, it is observed that DASPB is an optimum candidate for optical limiting due to its two-photon absorption induced fluorescence property and high cross section on excited state absorption. Both DASPB and Disperse Orange – 25 have shown stronger Optical Phase Conjugation signal when they are doped in PMMA-MA polymer matrix compared to, Disperse Yellow – 7 due to its low third harmonic susceptibility.

The research work on dye-doped polymer matrix is carried out with the following objective :

(1) To find an easy alternative for inorganic composites, organic and inorganic crystals for optical limiting, all-optical components, and optical storage devices.

(2) To make the fabrication process easy by using commonly available materials in the market so that complex preparation and processing of initial chemical can be avoided.

(3) To make the sample preparation process simple we prepared the dye-doped polymer films on glass-slide as well as in the form of thin sheets.

(4) To avoid the complex process of controlled growth of samples in the form crystals where the researcher spend a lot of time and effort for cutting and polishing the grown crystals, dye-doped polymer films are used in this study.

(5) To study the possibility of using these samples in simple and low-cost equipment, we studied the nonlinear limiting properties as well as optical phase conjugation properties using low power CW laser.

(6) The organic dyes in the organic polymer were used to en-cash potential advantages of organic materials over inorganic counterparts. The experiments were carried in a simple set-up by taking care of all possible errors.

(7) ABCD analysis technique is used to analyze the application of dye-doped polymer films for nonlinear and photonics processes. The various determinant issues of related to the use of dye-doped polymer films in photonic applications identified using focus group method are : (1) Material Issues, (2) Application Issues, (3) Commercialization Issues, (4) Production/Service providers Issues, (5) Customer Issues, and (6) Environmental/Social Issues. The analysis identified the affecting factors for various determinant issues under four constructs advantages, benefits, constraints, and disadvantages. The analysis has brought about 204 critical constituent elements which satisfy the success of this analysis methodology.

7.10 SUGGESTION FOR FUTURE RESEARCH

The major challenge seems to be the collective effort required to solve many issues related to collaborative physical, chemical, and optical-device related issues necessary to fabricate an organic all-optical switch device from any chosen materials. Such efforts and skills may not be available in a single institution. The collaborative effort by several institutions and researchers supports further developments in the field and the emergence of reliable photonic devices for practical applications. Based on the opportunities for further research and support for commercialization of the inventions, the following new areas & possibilities for further research are suggested.

(a) Suggestion for developing all-optical device :

An all-optical device allows one optical signal to control by another optical signal, i.e. control of light by light. These devices are used in ultra-fast communication systems based on all-optical signal processing and in also used in the fabrication of all-optical computers to eliminate the need for optical-electrical-optical (OEO) conversions. Dye-doped polymer films can be effectively used for this purpose. The major types of all optical ultra-fast communication devices are light sources, all-optical gates, and wavelength converters [501-517]. All optical devices

including optical switches can be constructed with optimum switching properties using nanoparticles sensitized dye-doped polymer films [518-525].

(b) Suggestion towards improving the efficiency :

Nanoparticles based dye sensitization may improve the charge carriers and polarization property of the dye-doped polymer films so that one can improve the efficiency of nonlinear optical properties [526–537]. Following research results have supported such predictions :

(1) Wenqiang Zou1et. al. [538] showed that the overall up-conversion by the dye-sensitized nanoparticles is comparatively enhanced (by a factor of ∼3,300) due to increased absorptivity and overall broadening of the absorption spectrum of the upconverter. The proposed concept can be extended to wide band of the solar spectrum by using a set of organic dye molecules with overlapping absorption spectra acting as an extremely broadband antenna system, connected to suitable upconverters [538].

(2) It is also found that the mobile quantum dots (QDs) functionalized with thiol ligands in the electrolyte are used to fabricate dye–sensitized solar cells. The QDs works as mediators to receive and re–transmit signal to sensitized dyes, thus amplifying photon collection of sensitizing dyes in the visible energy range and enabling frequency up–conversion of low-energy photons to higher-energy photons for dye absorption [539].

(3) It is also found that the sensitization by dye molecules on gold nanoparticles caused six-fold enhancement of the anti-Stokes emission of gold nanoparticles [540].

(4) In another investigation, plasmonic aluminium (Al) nanoparticles (NPs) were used to enhance the optical absorption of dye-sensitized solar cells. The Al nanoparticles not only increase the light absorption in solar cells with localized surface plasmon (LSP) effect but also the chemical stability to iodide/triiodide electrolyte [541].

(5) Dye-sensitized solar cells (DSSCs) have attracted tremendous research interest during the past several decades and their efficiency has recently been raised up to ∼ 15% [542].

(6) Solution-Processed Silver Nanoparticles are used in Dye-Sensitized Solar Cells to improve the efficiency of the photon to electron conversion process [543].

(c) Suggestion towards improving laser damage threshold :

Even through organic materials have better laser damage threshold compared to the inorganic counterpart, while working with high power pulsed lasers, there is always a possibility of material damage or dye bleaching for a long time exposure. Researchers have the opportunity to study the possibility of improving laser damage threshold of dye-doped polymer films. Again, by using suitable methods including embedding nanoparticles in the dye-doped polymer film, one can study the possibility of improving the laser damage threshold of these samples. It is also found that irradiation of high frequency light on the sample improves laser damage threshold properties [544].

(d) Suggestions towards improving physical and chemical properties which are favorable for material property :

The physical properties and chemical properties of dye-doped polymers can be improved by means gamma ray irradiation [545]. Similarly one can study the effect of electron beam irradiation and heavy ion irradiation on dye-doped polymer films and its impact on the optical performance behavior of the doped films.

(e) Study of electron beam irradiation and ion irradiation on nonlinear optical properties as well as other material properties of dye-doped polymer films :

It is well known that the process of systematic and controlled irradiation of energetic electrons and lighter ions modifies and improves dielectric and optical processes in nonlinear optical materials [546-548]. As a continuation of the effort of improving the third harmonic efficiency of dye-doped polymer films, one can study detailed process of modifying the physio-chemical properties further by means of systematic research on electron/ion beam irradiation study on nonlinear optical properties of dye-doped polymers.

(f) Suggestion for Fabrication of Dye-Doped Polymer Optical Flber :

Dye-doped polymer waveguide structures and devices have been found to be suitable for optical integrated circuits and short distance communications. Although optical flber networks are mainly made up of silica optical flbers (SOFs), dye-doped polymer-optical-fiber (POF) -based systems are seriously being considered for short-distance communication. This is due to the competitive ability of POF in device handling, flexibility of usage, and cost-effectiveness with respect to silica fibers [549-550]. Even though a higher loss factor is a major handicap for POF, recently developed techniques for decreasing losses in poly(methyl methacrylate) (PMMA) – based POF have raised much interest in this field [551-555]. The availability of inexpensive

sources in the visible region has increased the use of POF in data communication over local area network systems [556]. The implementation of short distance optical communication in the visible region demands the development of suitable optical amplifiers working in this region. [557-566]. Good quality dye-doped polymer optical fibers can be used for this purpose. It is shown that the performance and stability can be improved in case of Rhodamine 6G doped polymer optical fiber as an amplifying medium [567].

(g) Exploring the possibility of improving the performance of all optical devices using nanophotonics.

Nanophotonics is an emerging area where nanotechnology is used to change the physical and chemical properties of photonic materials or the effectiveness of photonic processes. Even though it is a multi-disciplinary integrated effort, future photonic components and devices will be different in terms principle, look, size, functions, features, and performance leading to optimum systems to support the major application areas like optical communication, optical computation, and Optical medical equipment. Nanotechnology is already proven as general-purpose technology and its advantages in tailoring the physio-chemical properties both at fundamental and applied areas are already established a new field of technology nanophotonics. This new area has further hope to scientists and engineers to miniaturize and optimize the speed-bandwidth problems in all-optical photonic devices [568]. Hence by using nanotechnology and discovering an effective way of tailoring the properties of dye-doped polymer films, one can further continue and take the present research to the next stage.

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