CHAPTER 1

INTRODUCTION

1.1 GENERAL

Third-order nonlinear optical effects are the basis for a number of applications in future high capacity communication networks in which ultrafast switching, optical power limiting, image manipulation, signal regeneration, and high-speed demultiplexing would be performed all optically. The nonlinear response of matter has been recognized as a powerful probe of the electronic and chemical nature of the illuminated material. Nonlinear optics has grown to include such diverse fields as optical chaos and bistability, optical rectification and Stimulated Raman Scattering.

Advancement of research in this field have placed great demand on the development of new nonlinear optical (NLO) materials with strong nonlinear optical effects has wide applications in optical limiting for sensor protection, all optical switching and optical signal processing. Materials that possess two-photon absorption (2PA), multi-photon absorption (MPA) and reverse saturable absorption (RSA) in which their transmittances reduce with the increase in optical intensity can be wildly used in two-photon microscopy and optical limiting.

Study of nonlinear optical properties in organic and polymer systems has enjoyed rapid and sustained growth over the last twenty years. Due to their large optical nonlinearities, mechanical, chemical, thermal and photo stabilities, organic nonlinear optical materials are found to be promising materials for fabricating optoelectronic devices (Kramer et al 1986). The most
important advantages of organic materials are the possibility of unique
diversity and the ability to be tailored with a variety of chromophores that
stimulate the photonic functions in a desirable manner. Organic dyes are
found to have attracted interest due to their low optical loss, high NLO
chromophore density and ultrafast response time (Mark & Ratner 1995).

They are molecular materials that represent an ensemble of
chemically bonded molecular units only weakly interacting with each other in
the bulk through vander Waals interactions. In such a case, the nonlinear
optical response of organic systems can be described primarily as derived
from a deformation of electron clouds within each molecule that arises from
the presence of the intense electric field of an applied optical energy. In other
words, the optical nonlinearity is primarily molecular in nature. In the case of
inorganic semiconductors or ionic crystals, the behavior is very different since
no single molecular unit in the bulk can be identified; consequently, the
nonlinearity in these inorganic systems is a bulk effect.

Conjugated structures involving alternate single and multiple bonds
are distinct class of organic materials is. In these structures, the \( \pi \)-electrons
are delocalized over an effective conjugation length. Even under non-resonant
conditions, these structures exhibit large optical nonlinearities (i.e., within the
optical transparency regions), the nonlinearity being primarily derived from
the delocalized \( \pi \)-electrons. The molecular materials, in addition to exhibiting
large non-resonant response, also offer tremendous flexibility for optimization
of nonlinear optical response, and necessary material fabrication both at
molecular and bulk levels.

In recent years, development of practical tunable solid-state laser
has found significant advances due to the synthesis of high performance dyes
and the implementation of new ways of incorporating the organic molecules
into the solid matrix. Because of their good compatibility with organic dyes,
this synthetic polymer host provides more advantages and is also amenable to inexpensive fabrication techniques.

Furthermore, laser radiation threshold of the newly modified dye doped polymers is comparable to or higher than that of laser damage resistant inorganic glasses and crystals. These polymers provide an opportunity for the production of polymer elements that can effectively control the characteristics of laser radiation. Due to the nonlinear characteristics of dyes in liquid and solid media, these dye doped polymers find many applications in the modern photonic technology apart from their use as active laser media (Welker & Kuzyk 1996). Hence, adequate knowledge of optical properties of dye doped polymers and greater understanding of the photo physical properties of the dye molecules in polymeric matrices is important in identifying suitable dyes in polymer media. Further studies on the optical nonlinear characteristics will lead to fabrication of new elements, which have potential applications in Optical limiting, bistability and in optical storage devices. In order to understand the lasing characteristics of these dyes, the general properties of organic dyes are to be studied.

1.2 PROPERTIES OF ORGANIC DYSES

Organic dyes are unsaturated hydrocarbons containing conjugated double bonds and have a high absorption in the ultraviolet and visible part of the spectrum. Organic dyes are found to be coloured due to the presence of special groups in the molecule namely chromophores and auxochromophores as perchromophore theory. The chromophores (colour-bearers) are groups capable of absorbing light of a definite wavelength. A characteristics structural feature of chromophores is the presence of unsaturated atoms and double bonds. The nitro group –NO₂, the nitrosyl group –N–O, and the azo group -N=N- are examples of strong chromophores. To turn a colored substance or a chromogen into dye, additional groups called auxochromes
(color intensifiers) are to be introduced into its molecule along with the chromophores. Typical auxochromes are the amino (–NH₂), hydroxyl (–OH) and N, N dimethyl (–N(CH₃)₂) groups.

In the dye molecule, bonds are formed by π electrons and σ electrons. The σ electrons are characterized by the rotational symmetric of their wave function with respect to the bond direction. i.e., the line connecting the two nuclei is linked by the bond. The π electrons are characterized by a wave function having a node at the nucleus and rotational symmetry along a line through the nucleus and normal to the plane subtended by the orbital of the 3σ electrons of the carbon or hetero atom.

A π bond is formed by the lateral overlap of the π electron orbitals which is maximal when the symmetry axes of the orbitals are parallel. The various possible electronic transitions of the dyes are π -π *, σ -σ * and n-π *. Of these transitions, π -π * transition occurs in the near UV or visible or in the near IR region and this transition is strong. Dyes generally have a strong absorption and emission transitions in the near UV or visible or in the IR region. This makes π -π * transition of the molecule more probable in laser processes. σ -σ * transitions occur in the wavelength region of about 200nm or less, the dye molecule tends to dissociate the photo chemically when excited to energies corresponding to this wavelength region. The n-π *transition occurs in the near UV or visible region. But this transition is very weak.

1.2.1 Energy Levels and Transition in Organic Dye Molecules

A dye molecule contains a large number of atoms and will have a number of possible energy states due to electronic, vibration and rotational motions making the complete energy level diagram more complicated. Using Jablonski diagram, the electronic transitions of large complex molecules can
be represented as shown in Figure 1.1 and it gives the configuration of the state in terms of one coordinate only. The energy levels of the organic molecules are named as singlet state when the total spin becomes zero and triplet states when the total spin is unity. In general, dye molecules have pairs of electrons in the ground state and the total spin is zero. And due to this, there exists only singlet ground states ($S_0$). When the molecule is excited, one of the electrons in the $\pi$ electrons cloud goes to the higher electronic state. In the excited state, the electrons may have its spin either parallel or anti-parallel to the ground state.

(Source: Laser Fundamentals by William T. Silfvast)

Figure 1.1 Energy level diagram of a dye molecule
Due to this, both the singlet and triplet states in the excited states are designated as $S_1, S_2... S_n$ and $T_1, T_2... T_n$ respectively. The triplet state is lower in energy than the corresponding singlet state Parker (1968). Each electronic state has many vibrational and rotational states, which are represented by horizontal lines in each electronic state. Electronic transition between the singlet-singlet or triplet-triplet states are allowed, but between singlet and triplet are forbidden. The energy gap between $S_1$-$S_2$ or $S_2$-$S_3$ or $T_1$-$T_2$ excited states is less. As a result, vibrational levels of one state ($S_1$) overlap with those of the other ($S_2$). This leads to a strong non-radiative decay to lower states by vibrational relaxation, when the molecules are excited to higher energy states such as $S_2$, $S_3$ etc. This takes place in time duration of the order in picoseconds. The non-radiative process between the singlet-singlet or triplet-triplet states is termed as internal conversion. For a dye molecule, the energy gap between $S_1$ and $S_2$ will be high compared to those between other higher states and internal conversion is weak. A radiative transition occurs between them. This emission is termed as fluorescence.

The transition from singlet to triplet or vice-versa is termed as intersystem crossing. Some of the molecules in $S_1$ may decay non-radiatively to the triplet state $T_1$. This tripping of spin of the molecules in the excited states due to the perturbation arising out of spin-orbit coupling increases with the number of atoms in the molecule and also with the atomic number of the atoms constituting the molecule. The radiative transition between $T_1$ and $S_0$ states is termed as phosphorescence, which is forbidden and weak. Hence $T_1$ is usually a metastable state. The lifetime of the triplet state $T_1$ is in the range of milliseconds to seconds depending upon the environment of the molecule. However, in liquid media, the molecule in $T_1$ decays to $S_0$ non-radiatively in 100 ns due to collisions with solvent molecules at room temperature. The absorption and emission spectra of dyes are broad bands. The broadband characteristics are due to the vibrational structure and the change in their
internuclear distances on excitation. The minima of $S_1$ and $S_2$ states have different configuration coordinates. This causes the emission peak to be shifted to the longer wavelength side of the absorption peak. This shift is called the Stoke’s shift. A number of factors can influence the absorption & emission processes between $S_0$ and $S_1$ states by causing changes in the magnitude of the various competing processes Schafer (1975).

1.3 ORIGIN OF NONLINEAR OPTICS

Nonlinear optics is the study of phenomena that occurs as a result of modification in the optical properties of a material system by the presence of light. Only laser light is sufficiently intense to modify the optical properties of a material system. In linear optical response, the processes such as reflection, transmission, and absorption scale linearly with the intensity of the applied optical source but in the nonlinear optical response, this behavior is quite different. Nonlinear optical phenomena occur when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical field. For example, second harmonic generation occurs as a result of the part of the atomic response that scales quadratically with the strength of the applied optical field. The intensity of light generated at second harmonic frequency tends to increase as the square of the intensity of the applied laser light (Boyd 2003).

1.3.1 Concept of Nonlinearity

To describe the optical nonlinearity of a material system, dipole moment or polarization $P(t)$ of the material system dependence on the strength of the applied field $E(t)$ is to be considered. In linear optics, the induced polarization depends linearly upon the electric field strength that is given as,
\[ P(t) = \varepsilon_0 \chi^{(1)} E(t) \quad (1.1) \]

where \( \chi^{(1)} \) is the constant of proportionality and is known as the linear susceptibility and \( \varepsilon_0 \) is the permittivity of free space.

In nonlinear optics, the optical response can often be described by generalizing the above equation by expressing polarization \( P(t) \) as a power series in the field strength \( E(t) \) as

\[ P(t) = \varepsilon_0 [\chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t)] \quad (1.2) \]

\[ = P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) \]

Where \( P^{(1)}(t) = \varepsilon_0 \chi^{(1)} E(t) ; P^{(2)}(t) = \varepsilon_0 \chi^{(2)} E^2(t) \) and \( P^{(3)}(t) = \varepsilon_0 \chi^{(3)} E^3(t) \)

The quantities \( \chi^{(2)} \), \( \chi^{(3)} \) are known as the second and third-order nonlinear optical susceptibilities respectively and \( P^{(2)}(t) \) and \( P^{(3)}(t) \) are called as second-order and third-order nonlinear polarization respectively. The second-order nonlinear optical interactions can occur only in crystals that do not display inversion symmetry. In other words, it can occur only in non-centrosymmetric crystals. Since amorphous solids (such as glass), liquids, gases and many crystals display inversion symmetry, \( \chi^{(2)} \) vanishes for such media and consequently they cannot exhibit second-order nonlinear optical interactions. But the third-order nonlinear optical interactions can occur for both centrosymmetric and non-centrosymmetric media. These third-order nonlinear optical effects are the prerequisites for various optoelectronic applications.

1.3.2 Parametric and Nonparametric Processes

There are two types of nonlinear optical processes namely parametric process and nonparametric process. In parametric process, the
system has identical initial and the final quantum states of the system. Consequently, in parametric process population can be removed from the ground state only for short intervals of time when it resides in a virtual level. Population can reside in a virtual level for a time interval of the order of $\hbar/\delta E$, where $\delta E$ is the energy difference between the virtual level and the nearest real level as per uncertainty principle and can be described by a real susceptibility.

In nonparametric processes, there is no transfer of population from one real level to another and are described by a complex susceptibility. The photon energy is always conserved in parametric processes, but not conserved in nonparametric processes. The real part of the refractive index is a consequence of parametric processes whereas its imaginary part is due to the nonparametric processes, since the imaginary part of the refractive index describes the absorption of radiation from the ground state to an excited state. Second harmonic generation, third harmonic generation, sum frequency generation, difference frequency generation and optical parametric oscillation, intensity dependent refractive index are all examples of parametric processes whereas saturable absorption, two-photon absorption and stimulated Raman scattering are the examples for nonparametric processes.

1.3.3 Third-order Optical Nonlinearity

The third-order nonlinear polarization is given by

$$P^{(3)}(t) = \epsilon_0 \chi^{(3)} E^3(t)$$  \hspace{1cm} (1.3)

The field $E(t)$ is made up of different frequency components and the expression for $P(t)$ is very complicated. Consider the simplified case in which the applied field is monochromatic which is given by
Then, through use of the identity

\[ \cos^3 \omega t = \frac{1}{4} \cos 3\omega t + \frac{3}{4} \cos \omega t \]  

(1.5)

Applying in the third-order nonlinear polarization gives

\[ P^{(3)}(t) = \frac{1}{4} \varepsilon_0 \chi^{(3)} E^3 \cos 3\omega t + \frac{3}{4} \varepsilon_0 \chi^{(3)} E^3 \cos \omega t \]  

(1.6)

The first term in Equation (1.6) describes a response at frequency \(3\omega\) created by applied field at frequency \(\omega\). This leads to the process of third harmonic generation. The second term in Equation (1.6) describes a nonlinear contribution to the polarization at the frequency of the incident field. This term leads to a nonlinear contribution to the refractive index experienced by a wave at frequency \(\omega\). The refractive index in the presence of this type of nonlinearity can be represented as

\[ n = n_0 + n_2 I \]  

(1.7)

where \(I\) is the intensity of the incident wave, \(n_0\) is the linear index of refraction, \(n_2\) is the third-order nonlinear refractive index which characterizes the strength of the optical nonlinearity is given by

\[ n_2 = \frac{12 \pi^2}{n_0^2 c} 10^7 \chi^{(3)} \text{ (esu)} \]  

(1.8)

1.3.3.1 Self-focusing and Self-defocusing

The process that occurs as a result of intensity dependent refractive index of the medium is called as Self-focusing. It is also called self-action because the nonlinear polarization induced by the incident beam changes the
propagation or other properties of the same incident beam. It can occur when
a beam of light having a non-uniform transverse intensity distribution
propagates through a material for which \( n_2 \) is positive. The material will
effectively acts as a positive lens under such conditions and causes the rays to
curve towards each other as shown in Figure 1.2(a).

This process is of significant importance because the intensity at
the focal spot of the self focused beam is usually sufficiently large to lead to
optical damage of the material. Self defocusing occurs when a beam of light
having non-uniform transverse distribution propagates through a material in
which \( n_2 \) is negative and the material start behaving like a negative lens and
tend to diverge as shown in Figure 1.2 (b).

![Figure 1.2 Self-focusing and Self-defocusing of light beam in a
nonlinear medium](image)

1.3.3.2 Saturable absorption

Saturable absorption is a nonparametric nonlinear optical process in
which the absorption coefficient of the material decreases when a very high
intensity laser beam propagates through it. The absorption coefficient \( \alpha \)
depends on the intensity \( I \) of the incident laser radiation and is given by the
expression,
\[ \alpha = \frac{\alpha_0}{1 + \frac{I}{I_s}} \]  

(1.9)

where \( \alpha_0 \) is low intensity absorption coefficient and \( I_s \) is known as the saturation intensity.

### 1.3.3.3 Two-photon absorption

The transition of an atom from its ground state to an excited state by the simultaneous absorption of two laser photons is called as two photon absorption. The absorption cross-section \( \sigma \) describing this process increases linearly with laser intensity according to the relation

\[ \sigma = \sigma^{(2)} I \]  

(1.10)

where \( \sigma^{(2)} \) is a coefficient and it describes the strength of two-photon absorption process. The atomic transition rate \( R \) due to two-photon absorption depends on the square of the laser intensity, i.e.

\[ R = \frac{\sigma^{(2)} I^2}{\hbar \omega} \]  

(1.11)

where \( \omega \) is the frequency and \( \hbar \) is reduced Planck constant.

Two-photon absorption is an effective tool to determine the positions of energy levels that are not connected to the atomic ground by a one-photon transition. Two-photon absorption was first observed experimentally by Kaiser & Garret (1961).

Suppose a single input beam is incident on a nonlinear material that displays linear absorption. Then, the nonlinear phase shift \( (\Phi_{NL}) \) is given by,

\[ \Phi_{NL} = n_2 \left( \frac{\omega}{c} \right) I_0 L_{eff} \]  

(1.12)
where \( L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha} \) is the effective length of the material, \( L \) is the path length and \( c \) is the velocity of light.

For a strongly absorbing nonlinear optical material, the effective interaction length can be much shorter than the physical length of the nonlinear medium. When the optical material exhibits two-photon absorption as well as linear absorption, the absorption coefficient in the Equation (1.9) should be replaced by

\[
\alpha = \alpha_0 + \beta I
\]  

(1.13)

where \( \beta \) is the two-photon absorption coefficient. Two-photon absorption is often a significant problem in the design of all optical switching devices because it occurs at the same order of nonlinearity as the intensity dependent refractive index \( n_2 \) (because these processes are proportional to the imaginary and real parts of \( \chi^{(3)} \) respectively).

### 1.4 METHODS OF MEASURING OPTICAL NONLINEARITY

There are several techniques such as interferometry, degenerate four-wave mixing and Z-scan technique to measure the nonlinear optical response. But it is very difficult to compare the nonlinear optical response of organic systems examined with different techniques. The third-order susceptibility is strongly frequency (wavelength) dependent and resonance enhancement occurs close to the absorption band. The repetition frequency and the pulse duration of the laser used for material characterization are of equal importance. It is practically impossible for any single technique to unambiguously separate the different nonlinear responses. Experiments are generally sensitive to several different nonlinearities at a time. Different measurements are usually required to explore the underlying physics by varying parameters such as irradiance and pulse width. Near instantaneous
nonlinearities such as two-photon absorption and the optical Kerr effect are independent of pulse width. Slower nonlinear responses change as the pulse width approaches the response time. Faster and slower nonlinearities are often present simultaneously in the measurements made with different experimental techniques, thus hindering their experimental isolation. Here some of the few commonly used experimental methods for exploring the optical nonlinearities are discussed.

1.4.1 Interferometry

Interferometric methods can be used to measure nonlinearly induced phase distortion (Weber et al 1978; Moran et al 1975). One implementation of this approach places a sample in one path (e.g. arm) of an interferometer and the interference fringes are monitored as a function of irradiance. If the interferometer is set-up to give a series of straight-line interference fringes for low input irradiance (linear regime), the fringes become curved near the region of high irradiance, such as the center of a Gaussian beam. The addition of a streak camera can add time resolution (Diels & Rudolph 1996). Alternatively, a third beam can be added to the experiment. The sample is in the path of one weak beam and the strong third beam. The fringe pattern of the two weak beams is monitored as a function of sample irradiance provided by the strong beam. The relative fringe shift observed in the presence and absence of the beam gives the optical path length change. The nonlinear phase shift can thus be determined. Interferometric experiments require excellent stability and precise alignment. When these conditions are met, sensitivities of better than $\lambda/10^4$ in induced optical path length change can be measured.
1.4.2 Degenerate Four Wave Mixing (DFWM)

DFWM predicted by Hellwarth (1977) in its most popular geometry (the phase conjugate configuration) is essentially a real-time holography in which a phase or amplitude grating is written in a nonlinear optical medium by two strong pumping beams, and detected by the diffraction of a third weak probe beam. DFWM is especially favored for thin film studies owing to its high sensitivity and relatively large resonant enhancement (when performed at visible wavelength). In this process, three coherent waves are incident on a nonlinear medium, and a fourth wave (the phase conjugate) is generated. The strength of this phase conjugate wave is dependent on a coupling coefficient that is proportional to the effective $\chi^{(3)}$ for the interaction. Hence measurements of the phase conjugate intensity can yield the $\chi^{(3)}$ tensor components of the medium. This is a popular method for characterizing third-order nonlinear materials and has been used extensively. Both backward and forward DFWM geometries can be employed, with the choice depending on experimental conditions. Using various combinations of polarizations for the four beams employed in the experiment, it is possible to measure all of the independent $\chi^{(3)}$ tensor components of an isotropic material.

The objective of the experiment is to measure the intensity of the phase conjugate beam or equivalently the phase conjugate reflectance. The phase conjugate beam is readily distinguishable by its spatial separation from the other interacting beams. Under reasonable experimental conditions, the detected signal has a characteristic dependence on the laser intensity ($I \propto I^3$ or $R \propto I^2$), which can easily be verified experimentally. Samples can be in a variety of forms and all the independent $\chi^{(3)}$ can be measured in a single experimental set-up (for isotropic materials). The beams employed in the experiment need not necessarily be true TEM$_{00}$ Gaussian modes as long as they are well characterized. Moreover, the time dependence of the
nonlinearity can be readily studied, and other material parameters besides $\chi^{(3)}$ can sometimes be measured. The disadvantages of this technique include the fact that only the modulus of $\chi^{(3)}$ (i.e., $|\chi^{(3)}|$) can generally be measured. The technique must in general be supplemented with another measurement to extract the real and imaginary parts of $\chi^{(3)}$. Another disadvantage is the alignment sensitivity of the three incident beams on the sample. The angles of the beams and their overlap within the sample must be carefully controlled. This is especially true for time resolved measurements where the time of arrival of the pulse in one beam is varied with respect to the other two incident pulses. Finally, the backward DFWM geometry, that most commonly used, employs counter propagating pump beams with inevitable feedback of optical energy into the laser cavity. Steps must be taken to ensure that this feedback does not disturb the stability of the laser.

In this technique the fundamental laser beam is split into a forward pump beam and a probe beam. When a nonlinear sample to be studied is placed in front of a mirror, the backward pump beam is created by reflection of the forward pump beam on this mirror. The probe beam is directed on the sample under a small angle with these pump beams. This method is called the back-reflection method. In the counter-propagating mode, the backward pump beam is not created by reflection of the forward pump beam, but by splitting the pump beam in two with a beam splitter and directing these beams with mirrors in a counter-propagating way. The intensity of the phase conjugate signal is measured and compared with a reference (usually Carbon disulphide (CS$_2$)). The $\chi^{(3)}$ value is obtained by using the following equation in the case of a non-absorbing sample (Bredas et al 1994).

\[
\frac{\chi^{(3)}_{\text{Sample}}}{\chi^{(3)}_{\text{Reference}}} = \left(\frac{n_{\text{Sample}}}{n_{\text{Reference}}}\right)^2 \frac{l_{\text{Reference}}}{l_{\text{Sample}}} \left(\frac{l_{\text{Sample}}}{l_{\text{Reference}}}\right)^{1/2}
\]  

(1.14)
where \( n \) is the refractive index, \( I \) is the intensity of the conjugate beam and \( L \) is the path length in medium. For an absorbing sample, one has to include an exponential factor accounting for the loss.

### 1.4.3 Z-scan Technique

The Z-scan method is found to be a standard technique for determining the changes in both nonlinear refractive index and absorption. It is due to the simplicity of the technique and its interpretation. In most experiments, the index change (\( \Delta n \)) and absorption change (\( \beta \)) can be determined directly from the data without resorting to computer fitting. This method is sensitive to all nonlinear optical mechanisms. Sheik-Bahae et al (1989) developed a sensitive self-focusing measurement technique that involves focusing a laser beam through a thin sample and detecting the light transmitted by a small aperture in the far field. This simple method is illustrated in Figure 1.3.

![Figure 1.3 Schematic illustration of the Z-scan method](Source : Sheik-Bahae et al (1989))

**Figure 1.3 Schematic illustration of the Z-scan method**
The far-field aperture transmittance is measured for a constant laser input as the sample is scanned along the z-direction through the focus of the lens and is referred to as Z-scan technique. The medium acts like an intensity dependent lens. As it is scanned along the beam path, as the incident intensity is changing, its effective focal length also changes. This change is reflected in the intensity distribution at the aperture in the far field. The amount of energy transmitted through the aperture depends on the sample location on the z-axis and on the sign of \( n_2 \). Consider, for example, a material with a positive \( n_2 \). When the sample is far from the focus, the intensity in the sample is small, and since the sample is thin, the energy transmitted through the aperture remains approximately constant.

![Figure 1.4 Characteristic curves depicting (a) positive and (b) negative nonlinear refraction using Z-scan method](image)

As the sample gets nearer the focus, the intensity is high enough to produce a positive lensing effect. For \( z < 0 \), this lensing causes the beam to come to focus earlier, so that it diverges more rapidly in the far field. The result is that the aperture transmittance decreases. On the other hand, for \( z > 0 \), the positive lensing causes the beam divergence to decrease, resulting in an increased aperture transmittance. At \( z >> 0 \), again the sample is far from
the focus and the intensity in the sample is small. The aperture transmittance returns to its starting value. The net Z-scan yields a dispersion shaped transmittance curve, as illustrated in Figure 1.4 (a). Obviously, a negative $n_2$ material will produce a similar curve, but with the peak and valley reversed about $z = 0$ as illustrated in Figure 1.4 (b).

The aperture transmittance as a function of sample position depends on the magnitude and the sign of $n_2$. This is the basis of the Z-scan technique. The nonlinear medium impresses a phase distortion on the electric field of the transmitted light. The objective of the Z-scan technique is to measure this transmittance and extract $n_2$ by inversion of the formula for the aperture transmittance. The Z-scan has several advantages. Among these is its simplicity. As a single-beam technique, it has no difficulty in alignment other than keeping the beam centered on the aperture. As stated above, it can be used to determine both the magnitude and the sign of nonlinear refractive index. The sign is obvious from the shape of the transmittance curve. The data analysis is also quick and simple, making it a good method for screening new nonlinear materials. Under certain conditions, it is possible to isolate the nonlinear refractive and nonlinear absorption contributions to the far-field transmittance. Thus, unlike most DFWM methods, Z-scan can determine both the real and the imaginary parts of $\chi^{(3)}$. The technique is also highly sensitive, capable of resolving a phase distortion of $\lambda/300$ in samples of high optical quality. Z-scan technique can also be modified to study nonlinearity on different time scales as well as higher order contributions. Limitation of the technique is that it requires a high quality Gaussian TEM$_{00}$ beam for absolute measurements. Different analysis should be done for non-Gaussian beam.

Although several experimental techniques have been used to determine the nonlinear optical properties of materials, it is difficult to measure the nonlinear optical parameters accurately. In that aspect, the Z-scan
technique has been evolved as a versatile technique to measure the nonlinearity because of its high sensitivity and simplicity. Open aperture (OA) and Closed aperture (CA) Z-scan techniques invented by Sheik Bahae et al (1990) has been extensively used as an effective and convenient tool for exploring the nonlinear absorption and nonlinear refraction properties of various materials respectively.

This dissertation presents nonlinear optical studies carried out on dyes in solvent (liquid medium) and dyes doped in polymer (solid medium). Steady state absorption and fluorescence measurements are also made in this present investigation which provides additional data for understanding the spectral behavior of dyes in both solid and liquid media. During the investigation, nonlinear optical techniques such as Z-scan analysis and optical limiting studies using transmittance technique are used.

1.5 REVIEW OF PRECEEDING WORK

To plan and execute the proposed work, review of literature in the relevant field is very much essential. In this present work, three studies have been carried out. As a first part, material characterization and spectral characteristics of the dyes are studied. In the second part of the study, the optical nonlinearity of organic dyes is studied using Z-scan technique. In the third part of the study, as an application of the nonlinear optical study, the optical limiting ability of organic dyes are studied.

1.5.1 Review of Z-scan Technique

Sheik-Bahae et al (1990) have invented a single-beam method called as Z-scan technique for measuring the sign and magnitude of nonlinear refraction ($n_2$). They found the nonlinearity for Carbon disulphide (CS$_2$) liquid filled in 1 mm thick cuvette with NaCl windows. They used 300 ns TEA CO$_2$
laser pulse having energy of 0.85 mJ. This technique was based on the spatial beam distortion. Later, this technique was also used to find the nonlinearity of organic materials, semiconductors, nanoparticles etc by many others. Since the present study is on the organic materials, the following review stresses mainly on the exploration of optical nonlinearity of different organic materials as determined by Z-scan technique.

Gall et al (1994) have incorporated a number of dyes into sol-gels for DFWM studies and found that the nonlinear response did not change from the solution values. They also reported Z-scan measurements on chloroaluminium - phthalocyanine (CAP) in a xerogel using 15ns, 532 nm laser pulses with beam waist, $\omega_o$ of 7 $\mu$m.

Kim et al (1994) investigated the optical switching behaviour of poly [2,4-hexdiyne-1,6-diol-bis-p-toluene-sulfonate] (PTS) at an wavelength of 1.3 $\mu$m. They also measured $n_2$ and $\beta$ using 100 ps laser pulses in a sample of PTS of thickness 210 $\mu$m. They observed higher order effects reducing the value of nonlinear refraction and increasing the value of nonlinear absorption as the input irradiance is increased. However, they found the figures of merit were within the range necessary for all-optical switching.

Ravindra Kumar et al (1995) studied the optical nonlinearity of a mode-locking dye (Kodak 9740) using the Z-scan technique using picosecond laser pulses operated at a wavelength of 532 nm. Theoretical fits to the data give a value of 3.2 GW/cm for the two-photon absorption coefficient ($\beta$) and -2.1 GW/cm$^2$ for the real part of the nonlinearity. Using two-photon absorption as well as self-defocusing, they also demonstrated optical limiting effect for the dye.

Fei et al (1995) used a continuous wave He-Ne laser at wavelength of 633 nm to measure DFWM and Z-scan signals and determined the
nonlinear refractive index and third-order nonlinear optical susceptibility ($n_2 = 6 \times 10^{-4}$ esu and $\chi^{(3)} = 10^{-4}$ esu respectively) and reported that the nonlinearity is due to the slow realignment of the long chain molecules of azobenzene-compound-doped poly(methyl methacrylate) with a push group -NH-C$_{16}$H$_{23}$ and pull group -NO$_2$ attached. The sample was in the form of a 0.01 cm thick film.

Nonlinear responses in thin films of Fluorescein-doped boric acid glass were investigated by Deshpande et al (1996) using Ar$^+$ laser at different wavelengths. The reverse saturation and defocusing effect at 476.5 nm were observed. By modeling the fluorescein molecule as four level system model, they analyzed the Z-scan results.

Tadashi Kawazoe et al (1998) determined the third-order nonlinear optical response of thin films containing conjugated polymers of a regioregular (head to tail) and irregular poly (3-(4-dodecylphenyl)-thiophene) using a mode-locked Ti:sapphire laser as a pump source with pulse duration 150 fs and repetition rate of 80 MHz at wavelength of 755 nm by. They determined the value of third-order susceptibility by both FWHM and Z-scan technique.

Venugopal Rao et al (1998) reported both theoretical and experimental results for dispersion studies of nonlinear absorption in C$_{60}$ solution. They reported that the excited state absorption dominates in the shorter wavelength region (440–560) nm whereas the two-photon absorption dominates in the longer-wavelength region (580–660) nm. They interpret their results by using 5 level model taking into account both the excited state absorption and two-photon absorption processes.

Hernandez et al (1998) investigated the third-order nonlinearities of a new organometallic compound by Z-scan technique performed with
nanosecond pulsed Nd:YAG laser at wavelength of a 532 nm. They determined nonlinear refractive index \(n_2\) in the order of \(10^{-11}\) W/cm\(^2\) and two photon absorption coefficient in order of \(10^8\) W/cm. They reported that the material shows a good figure of merit. They attributed the origin of the nonlinearity to the electronic nature.

Tadashi Kawazoe et al (1998) measured the relaxation time of the nonlinear refractive index in CS\(_2\) and head-to-tail-poly (3-alkylthiophene) using time resolved Z-scan technique with mode-locked femto second laser pulses and orthogonal polarization at a wavelength of 775 nm. They found that there are two decay components, slow and fast, which ascribes the origin of these two components to the thermal and dielectric effects.

Mauro Falconieri (1999) reported the thermo optical nonlinearities due to cumulative heating of CS\(_2\) by using Z-scan technique. He developed a generalized theory to calculate closed aperture Z-scan curves due to diffusive thermo optical nonlinearities caused by absorption process of arbitrary order. He found a very good agreement between the experimental and theoretical data.

Unikrishnan et al (2000) studied the nonlinear absorption in solution of rare earth substituted phthalocyanines by using open aperture Z-scan technique with nanosecond pulse excitation operated at 532 nm and attributed it to the sequential two photon absorption (STPA) process.

Measurement of nonlinear refractive index in Rhodamine-B (Rh-B) organic dye solution at 510.6 nm was carried out by Sinha et al (2000) using the Z-scan technique with 40 ns laser pulses from a copper vapor laser. They found that the nonlinear refraction was of thermal origin resulting from nonradiative energy transfer from the dye molecules to the solvent molecules and thereby strongly dependent on the thermal properties of the solvent.
Cassano et al (2001) studied the relationship existing between the third-order nonlinear optical properties and the chemical structure of some poly (2,5-dialkoxy-1,4-phenylenevinylene) polymers. They measured nonlinear refractive index and two-photon absorption coefficient using the picosecond Z-scan technique. They found that all the organic molecules which they investigated exhibit a small Im $\chi^{(3)}$ and a large, negative Re $\chi^{(3)}$ at $\lambda = 1064$ nm.

Rao et al (2002) reported the experimental results of the nonlinear absorption and excited state dynamics in Rhodamine B in methanol at 532 nm and 600 nm using the standard Z-scan and degenerate four wave mixing techniques. They observed saturable absorption at 532 nm and a transition from saturable absorption to reverse saturable absorption at 600 nm with increase in either intensity or concentration.

Yu Shi-Rui et al (2003) studied the nonlinear absorption of the organic material Zn-tetrabenzoporphin-crotonicacid-phenoxy resin (ZnTBP-CA-PhR) in the donor-acceptor energy-transfer (DA-ET) system by the irradiation of Ar$^+$ laser on its solid film. A reverse saturable absorption is observed in a visible wavelength range.

Yavrian et al (2004) used a continuous wave illumination of 514.5 nm on azo dye doped PMMA films to demonstrate the photo induced absorption and refraction by Z-scan technique.

The third-order nonlinear optical response of carbondisulfide(CS$_2$) was determined by using Z-scan technique with (femto, pico and nano second) pulse duration at 532, 795 and 1054 nm of Nd-YAG laser by Ganeev et al (2004). They observed a growth of a nonlinear refractive index values with the increasing of the laser pulse duration. They attribute the nature of nonlinear optical behavior in CS$_2$ to molecular reorientation nature. In
addition to the measurement of third-order optical nonlinearity, fifth order nonlinearity was also measured using Z-scan technique by Ganeev et al (2004). They studied the third and fifth order nonlinearities in aqueous solution of pseudoisocyanine (PIC) solution, using 529 nm. The third and fifth order nonlinear refractive indices of PIC solution were measured to be \(-8 \times 10^{-14} \text{ cm}^2/\text{W}\) and \(4 \times 10^{-24} \text{ cm}^4/\text{W}^2\). The imaginary part of third-order nonlinear susceptibility was measured to be \(-2 \times 10^{-12} \text{ esu}\).

Vanessa Rosso et al (2004) have used continuous wave illumination at wavelength of 514.5 nm to study Third-order nonlinear optical effect and the optical Kerr effect in azo dye named disperse red 1 dye doped sol-gel by using Z-scan technique. Saturation phenomena is due to the reduction of absorption from the fundamental state which is depopulated generated by an intense irradiance.

Del Nero et al (2005) described experimental and theoretical studies of the third-order nonlinear optical coefficients of methyl orange solutions under different PH conditions using the Z-scan technique. They determined the nonlinear refractive index and nonlinear absorption coefficient under picosecond excitation in the visible spectral region.

The third-order nonlinear optical properties of Basic green 1 dye were reported by Qusay Mohammed Ali & Palanisamy (2005). Their experimental results showed that the Basic green 1 dye exhibited large nonlinear refractive index \((n_2 = -1.63 \times 10^{-7} \text{ cm}^2/\text{W})\) and the absorption coefficient \((\beta = -1.7 \times 10^{-3} \text{ cm/W})\) at the wavelength 632.8 nm of He–Ne laser.

Wei Feng et al (2005) have reported the measurements of third-order nonlinear susceptibility \(\chi^{(3)}\) and second hyperpolarizability \(\gamma\) of poly
{[3-octylthiophene-2,5-diyl]-[p-aminobenzylidenequinomethane]}-bonded multiwalled carbon nanotubes by using degenerate four wave mixing and Z-scan techniques with nanosecond pulses laser at wavelength of a 532 nm. They attributed the observed nonlinear absorption to a strong reverse saturable absorption (RSA) according to five level model under nanosecond excitation. They ascribed the nonlinear refractive index to the thermal excitation of the medium.

Sun Xiang-Bing et al (2006) demonstrated the Z-scan technique for solution of [(CH$_3$)$_4$N]Au(dmit)$_2$ (dmit = 4,5-dithiolate-1,3-dithiole-2-thione) at 532 nm and 1064 nm with pulses of picosecond duration. They found that Z-scan spectra reveal a strong nonlinear absorption (reverse saturable absorption) and a negative nonlinear refraction at 532 nm. No nonlinear absorption was observed at 1064 nm.

Measurements of third-order nonlinear refractive index n$_2$ of Phatholocyanine dye in solution and thin film of PMMA were described by Mathews et al (2007) at a wavelength of 632.8 nm using continuous wave laser pulses. They reported that the major contribution to the observed nonlinearities is due to thermal origin.

Shengwen et al (2007) used continuous wave illumination of 632.8 nm on ethyl red dye solution and film to demonstrate self-defocusing and saturable absorption. They also reported that such nonlinearity is thermal in nature (thermal self–defocusing).

Sree Kumar et al (2007) measured nonlinear refraction index n$_2$ of solid films of the organic dye amido black 10. They found that the sample exhibited negative nonlinearity and large nonlinear refractive index of the order $10^{-7}$ cm$^2$/W. They attributed the observed nonlinearity to thermally induced variation in the refractive index of the medium.
Henari & Ahmed (2008) investigated the nonlinear refractive index and nonlinear absorption coefficient of tri(acetylacetonato) manganese III solution by Z-scan technique with low power continuous wave laser at a wavelength of 514 nm. They demonstrated that the light–induced nonlinear refractive index variation led to strong self-focusing and self defocusing. They analyzed their results in term of thermal lensing and attributed the nonlinearity to be thermal in origin.

Measurements of third-order nonlinear refraction ($n_2$) and nonlinear absorption in organic dye, natural red were described by Mathew George et al (2008) by Z-scan technique with nanosecond laser pulse at 532 nm. They studied the nonlinear response of the material in both solution and solid film. They found that the observed nonlinear absorption was caused by a two photon absorption process.

With nanosecond pulses at a wavelength of 532 nm, John Kiran et al (2008) measured the nonlinear response of a bis-chalcone derivative P-(N,Ndimethylamino) doped by poly methacrylate matrix by single beam Z-scan and degenerate four wave mixing techniques. They found the nonlinear refractive index to be negative, and its magnitude was of the order $10^{-10}$ esu and the $\chi^{(3)}$ value was of the order $10^{-12}$ esu.

Gul Yaglioglu et al (2008) measured nonlinear refractive index and nonlinear absorption and the optical limiting performance of 4-(4,6-diaminopyrimidin-2-ylthio) substituted double–decker Lu(III) phthalocyanines(4) using 4 ns pulsed laser at 532 nm where Z-scan study have been conducted between 0.24 and 2.39 GW/cm$^2$ peak intensities for 10 Hz repetition rate.

With a frequency doubled Nd-YAG laser system, Wang Zhang et al (2008) investigated the nonlinear optical properties of the planar cluster
[MoS$_4$Cu$_4$I$_2$(py)$_6$] doped in PMMA using Z-scan technique at the wavelength of 532 nm and the pulse width of 8 ns. The sample demonstrated self defocusing effect with characteristic thermal effect.

Dongwang et al (2008) reported the measurement of the third-order nonlinear optical susceptibility of a novel hyperbranched poly(aryl ether keton) and functionalized with nickel phthalocyanine, using Z-scan technique at wavelength of 532 nm with very low repetition rate of 1Hz laser system. They found that the third–order nonlinear optical susceptibility of the polymer reached $\approx 10^{-11}$ esu.

Rashidian et al (2009) demonstrated the Z-scan technique for aqueous solution of Violet 16 dye with continuous wave laser at a wavelength of 532 nm. They have studied the effect of thickness, concentrations and the effect of the applied intensity.

The third–order optical nonlinearities of MeCu ([(CH$_3$)$_4$N]$_2$[Cu(dimt)$_2$]) were investigated by Jing et al (2009) using open aperture Z-scan technique with pico and nano second laser pulse in the near – infrared region. Two-photon absorption was found when they irradiated the sample with 40 ps pulse width at 1064 nm and strong reverse saturable absorption with 15 ns pulse width at 1053 nm.

Dhinaa et al (2010) studied nonlinear optical properties of total protein and albumin in blood serum samples using 532 nm Nd:YAG laser and 633 nm He-Ne laser by Z scan technique. They also found that the comparative analysis of these values is found to be in good agreement with that of standard conventional calorimetric method. They have reported that Z-scan technique can be used for the measurement of bioanalytes in serum.
Dong Shu-Guang (2011) measured the temperature change in nonlinear optical materials by using Z-scan technique. They studied the spatial and temporal changes of temperature in a novel polymer under ns laser pulse excitation.

Nastaran Faraji et al (2012) used a blue continuous wave laser beam to study the nonlinear optical properties of silver/PVA nanocomposites. The silver nanocomposites are nearly spherical in shape and their size is found to be from 10 to 25 nm. They found that the nonlinear refractive index of nanocomposites was found to increase from \(-0.913 \times 10^{-8} \text{ cm}^2 \text{ W}^{-1}\) to \(-3.369 \times 10^{-8} \text{ cm}^2 \text{ W}^{-1}\) with increase of reducing agent of 1ml to 15ml.

Pramodini et al (2013) reported the synthesis and measurement of \(\chi^{(3)}\) and optical power limiting of Polyaniline and its derivative Poly(o-toluidine) under continuous wave regime. They found the third-order optical susceptibility of the polyaniline and its derivate to be of the order of \(10^{-7}\) esu.

Nagaraja et al (2013) studied the effect of annealing on the structural and nonlinear optical properties of ZnO thin films deposited on quartz substrates by the RF magnetron sputtering technique under continuous wave regime. They observed multiple diffraction rings when the samples were exposed to the laser beam and found that the appearance of rings was due to the refractive index change and thermal lensing.

Nonlinear optical properties of Brilliant Green dye were demonstrated using Z-scan technique using He–Ne laser by Choubey et al (2014). It was found that the material exhibited multiphoton absorption type optical nonlinearity. They also found that the photoluminescence intensity of the dye was found to decrease due to quenching effect with increase of concentration.
Hussain Badran et al (2014) reported the third-order optical nonlinearity of Ethidium Bromide using a diode laser beam operated at 473 nm wavelength. They have studied the effect of concentration on the third-order nonlinear optical susceptibility.

Zongo et al (2015) used Nd:YAG laser pulses to investigate the nonlinear optical properties of natural laccaic dye using Z-scan technique. They found that the observed nonlinear absorption was caused by a two photon absorption process. They reported that the optical limiting behavior in the laccaic acid dye is likely to be originated from the RSA and nonlinear refraction.

1.5.2 Review of Optical limiting

Mansoor Sheik-Bahae et al (1991) investigated experimentally and theoretically optical beam propagation in nonlinear refractive materials having a thickness greater than the depth of focus of the input beam (i.e., internal self-action). They made a simple model based on the constant shape approximation, inadequate for analyzing the propagation of laser beams within such media under most conditions. In tight focus geometry, they found that the position of the sample, z with respect to the focal plane is an important parameter that influences limiting characteristics of the output. The investigation was on CS$_2$ sample with picosecond CO$_2$ laser pulses to optimize the limiting behavior of devices based on a self action.

James et al (1993) described the performance of an optical limiter based on Pb-tetrakis (cumylphenoxy) phthalocyanine, a robust organic material with a large $\chi^{(3)}$ and figure of merit, $\chi^{(3)}/\alpha_0$ at 532 nm with 8 nsec laser pulses.
Justus et al (1993) reported the limiting behavior of nigrosin dye dissolved in carbon disulfide in an f/5 defocusing geometry using 6 ns pulse at 532 nm laser excitation. They found that maximum transmittance energy was only $\approx 40$ nJ for input energies of 20 $\mu$J representing a net transmission of only 2%.

Cha et al (1995) studied the nonlinear optical absorption of poly(3-octylthiophene) P$_3$OT sensitized with methanofullerene for wavelengths from 620 - 960 nm. They attributed the large nonlinearity result to the efficient photo-induced intermolecular charge transfer from P$_3$OT to methanofullerene followed by absorption in the charge separated excited state. They found that the damage threshold was 15 $\mu$J /pulse.

Shekhar Guha et al (1996) evaluated nonlinear optical behavior of carbon 60 (C$_{60}$), platinum polyyne and tetrabenzporphyrin (TBP) using laser with $\mu$s and ns pulse width at the wavelength of 750 nm in an f/5 optical set-up. They reported fluence limiting in all three materials and attributed it to the nonlinear absorption and nonlinear refraction and both pulse width and thermal lensing being the dominant contributor to the nonlinear refraction effect and arises from both linear and nonlinear absorption of light in materials.

Chunfeili Li et al (2000) demonstrated and proposed a novel optical limiting device by sandwiching a nonlinear liquid between two specially designed diffraction gratings. They found that under low intensity of light, the device has a high transmittance because of index matching between the liquid and grating materials. Strong light beam can induce the nonlinear effect such as reverse saturable absorption, nonlinear scattering and self-defocusing to reduce the transmittance of device. On the other hand, the strong light beam can also change the index of the liquid to induce index mismatch and reactivate the gratings to diffract the output light away from the
observed direction to protect eyes. They reported their device to be suitable to use in protection of human eyes in visible region under ns pulse laser.

Ya-Ping Sun et al (2000) have summarized and compared the optical limiting properties of carbon nanoparticles, fullerenes, suspended and solubilized carbon nanotubes. They discussed their results in term of the comparison between nonlinear scattering versus nonlinear absorption as the dominating optical limiting mechanism.

Mironova et al (2001) reported that the light-induced scattering makes a considerable contribution to the optical limitation of radiation by fullerene-containing solutions. Radiation is scattered by small-scale (1–10 mm) inhomogeneities of density, and the corresponding increments are rather large. Because of this, scattering can be initiated by small-scale inhomogeneities of the input beam. They found that the light scattering by induced density inhomogeneities can lead to a noticeable attenuation of axial intensity in the transmitted beam and an additional (along with reverse saturable absorption) limitation of the output power.

Gryaznova et al (2002) demonstrated the possibility of using liquid crystal micro lenses for solving the problems of optical limiting. They suggested a compact optical system based on micro lenses (liquid crystal). They reported that the major mechanism of optical limiting in their system (extrinsic nematic composition of liquid crystal) is related to two-photon absorption.

Vivien et al (2003) reported that suspensions of single wall carbon nanotubes are good candidates for optical limiting. They compared their performances with those of other carbonaceous materials. Z-scan and pump probe experiments were used to identify and investigate nonlinear scattering as the main origin of optical limiting. Also they predicted that nonlinear...
scattering is due to both heat transfer from particles to solvent (leading to solvent bubble formation) and sublimation of carbon nanotubes.


Danilo Dini et al (2003) reported the optical limiting performance exhibited by phthalocyanines substituted with electron withdrawing atoms such as F. Results considerably enhanced with respect to the optical limiting effect produced by unsubstituted or differently substituted phthalocyanines. This enhancement is verified by comparing under analogous conditions the nonlinear optical transmission of hexadecafluorophthalocyaninato complexes (containing TiIV, VIV, ZrIII, and InIII as coordination central atoms, and tetra or octa alkyl substituted phthalocyaninato complexes) with the same central atoms by means of the Z-scan technique. The remarkable variations of the nonlinear transmittance of perfluorinated phthalocyanines in solution 49 indicates the strong influence that electron-withdrawing groups exhibit upon the variations of the transition dipole moments involved in the electronic transition, which effectively limits the intense radiation.

Sheng-li Guo et al (2003) observed optical limiting of C$_{60}$ containing polyurethane-urea films on a nanosecond scale at a 532 nm and they reported that the optical limiting behavior in C$_{60}$ containing polyurethane-urea material were consistent with excited-state absorption (reverse saturable absorption) as a mechanism.

Jason et al (2004) have reported the study of optical limiting by investigating the dependence of optical limiting on concentration and the
medium of the organic dyes. They concluded that the optical power limiting properties of the organic dyes in different classes were apparently different with respect to the solution concentration and medium dependencies. They found that the solution concentration dependent optical limiting was common in organic dyes, and the most concentrated solution had the best limiting performance and the dilute solution had poor limiting response.

Guang et al (2005) have investigated the optical power limiting performance of novel liquid dye system named (ASEPT) by excitation source Nd-YAG laser at wavelength of 1064 nm with pulse duration 10 nanosecond. They found a good limiting performance in this dye solution based on two and three photon absorption mechanism.

Kaladevi et al (2006) studied the optical limiting behavior of zinctetraphnyle prophyrin by using continuous wave laser at 633 nm low power laser. They reported that the limiters with optimized parameters were decided by a proper combination of aperture size and experimental geometry to expunge the periphery of the defocusing beam cross section where most of the energy was concentrated.

Chen et al (2007) reported optical limiting properties of carbon nanoparticles, which were made in liquids by laser ablation of a bulk carbon target. The carbon nanoparticles were analyzed with micro-Raman spectroscopy, UV-Vis spectroscopy and Electron microscopy. Optical limiting responses towards 532nm wavelength were measured with a 7ns Nd:YAG laser. They have studied nanoparticle size and laser pulse repetition rate effects on optical limiting behavior.

Mathews et al (2007) studied the nonlinear optical properties and optical limiting of phthalocyanines in solution and PMMA thin films by using
continuous wave laser at wavelength of 633 nm. They observed a good optical power limiting performance with limiting threshold ~7 mW.

Shengwen et al (2007) have demonstrated the nonlinear optical properties of ethyl red (ER) dye with continuous wave illumination at wavelength of 441.6 and 535 nm by studying the self–diffraction of solution of ER dye. They obtained threshold power for optical limiting property as 2.8 mW for 441.6 nm and 3.6 mW for 535 nm.

Qi Wang et al (2008) measured the optical limiting performance of nitric-sulfuric processed multi-walled carbon nanotubes and surfactant-assisted multi-walled carbon nanotubes in water. They found that multiwalled carbon nanotubols showed much better optical limiting performance than (C_{60}) fullerols and C_{60}. They attributed the optical limiting property to the hydrogen bond interactions between MWNTols (multi-walled carbon nanotubols) and water play an important role in the nonlinear scattering process. However, C_{60}-OH showed unsatisfactory optical limiting due to the disturbance of conjugated structure.

Xinyan Su et al (2008) studied optical limiting performance of a polyhedral oligomeric silsesquioxane (POSS)-containing organic-inorganic hybrid nanocomposite by a Q-switched Nd-YAG laser system with a wavelength of 532 nm and 4 nanosecond pulse width. They found that the POSS-containing organic-inorganic hybrid nano composition exhibited novel optical limiting properties, good photo and thermal stability. They also found that the limiting effect was affected by the concentration owing to higher concentration solution having more molecular per unit volume to absorb the energy of the laser more efficiently.

Sathiyamorthy et al (2008) studied optical power limiting properties of chloroaluminiumphthalocyanine (ClAlPc) in ethanol solution
with low power laser regime by using a continuous wave He-Ne laser as a source of excitation. They found that the C1A1Pc exhibited optical power limiting properties and the threshold value for saturation for all concentrations which had been used was around 3 mW. They ascribed the optical limiting properties to the thermal defocusing and self diffraction phenomena.

Xinyan Su et al (2008) investigated Optical limiting properties in soluble functional polyacetylenes through studying the relationship between optical limiting properties and molecular structure. They found that Optical limiting mechanism originated from reverse saturable absorption mechanism. Also they found that the optical limiting thresholds were affected by the concentration and the molecular structure of the material.

Optical limiting property in a series of incorporated fulleropyrrolidines with nano scale cavities of nafion were described by Junxin Li et al (2008) at wavelength of 532 nm of Q-switched frequency-doubled Nd:YAG laser. They obtained threshold optical limiting value between 120–160mJ/cm². They attributed the optical limiting mechanism of solid state C₆₀ material to reverse saturation absorption which involves the formation of the excited state with absorption cross section area larger than the ground state absorption cross section area under photo excitation, therefore leading to nonlinear absorption.

Ying et al (2008) studied the optical limiting properties with nanosecond laser. They found that PMMA polymer host led to considerable decrease in the saturation energy density when compared to the same phthalocyanine molecules in solution.

Ying Qion et al (2009) investigated optical limiting properties of triphenylamine multipolar derivative at the service of different number of chromophore with nanosecond laser pulses at wavelength of 800 nm. They
suggested that this type of power limiters were suitable for optical peak power limiting and stabilization.

Poornesh (2010) studied the nonlinear optical and optical power limiting studies on a new thiophene-based conjugated polymer in solution and solid PMMA matrix. It is found that the new polymer exhibits good optical power limiting properties in the nanosecond regime in solution as well as in solid PMMA matrix.

Zidan et al (2011) studied the optical limiting behavior of disperse red 1 dye doped polymer using 532 nm wavelength, 10ns pulses from a frequency doubled Nd:YAG laser. The results revealed that the dye exhibit strong Optical limiting effect.

Soma Venugopal et al (2011) investigated the ultrafast nonlinear optical and optical limiting properties of Phthalocyanine thin films using Z-scan technique. They evaluated the figure of merit for these films and suggested that they can be utilised for multiphoton imaging and Optical limiting applications.

Manshad et al (2012) measured the optical limiting properties of magneta doped PMMA films using continuous wave laser beam at 532 nm wavelength. They found that the absence of photochemical or photothermal destruction processes in the studied materials enhanced their perspective application as a stable optical limiter in photonic devices.

Qusay Ali Hassan et al (2012) investigated the third-order optical nonlinearities and optical limiting properties of Phloxine B dye doped PMMA films using Z scan technique. They demonstrated self-diffraction of the dye under continuous wave Nd:YAG laser illumination. They found that both the number of rings and the size of the outermost ring are intensity dependent.
They also found that the optical limiting thresholds were affected by the concentration.

Investigation of optical power limiting properties of terphenyl derivatives were done by Laxminarayana Kamath (2013) using Nd:YAG laser. The Z-scan experiments revealed that the compounds exhibit strong nonlinear refraction coefficient of the order $10^{-11}$ esu and the molecular two photon absorption cross section is $10^{-46}$ cm$^4$ s/ photon. The results showed that the structure of the compounds have great impact on NLO properties. They found that the compound exhibited optical power limiting behavior due to two-photon absorption (TPA).

Hussain et al (2015) studied the large third order optical nonlinearity and optical limiting properties of a 3,4-diaminopyridine with different MgCl$_2$ concentrations using 473 nm continuous wave laser. They investigated that the nonlinear refractive index, nonlinear absorption coefficient and efficiency of limiting are found to increase with increase in the concentration of MgCl$_2$. They observed a good optical power limiting performance in this compound.

1.6 SCOPE OF THE PRESENT WORK

Need for optical limiters due to the advent of high power laser sources operating over a wide range of wavelengths and pulse durations has placed a great demand on the necessity for protection of sensors and eye. Owing to their high polarizability and ultrafast nonlinear response, organic materials with strong nonlinear optical effects may be utilized in such potential optical devices. Organic dyes and polymers has attracted much attention compared to other nonlinear optical materials due to their lower dielectric constant, greater processing, flexibility, lower optical loss, and potentially greater NLO properties. But the challenge is the preparation and
characterization of these materials. The last two decades of work has resulted in a broad range of new materials whose optical and nonlinear optical properties have been characterized, many of these new materials being organic materials and include crystals, polymers, composites, liquids and liquid crystals. The present work aims at exploring the nonlinear optical properties of different organic dyes in both liquid and solid media.

In the present proposed study, the nonlinear absorption coefficient and nonlinear refractive index for different dye samples namely Xyolidline Ponceau, Azophloxine and Purpurin are measured by using open aperture and closed aperture Z-scan techniques respectively with the help of pulsed Nd:YAG laser in both solid and liquid media. Similarly, the nonlinear optical characterization of Methyl Blue dye sample is also studied by Z-scan technique using continuous wave He-Ne laser in both solid and liquid media. The optical limiting behavior of these dyes and the applicability of these dyes for fabrication of optoelectronic device are also discussed.

The dissertation is presented in the following sequence

I. Spectral analysis of the dye by recording the absorption and fluorescence spectra.

II. Synthesis of dye doped polymer films using thermal bulk free radical polymerization technique

III. Nonlinear optical characterization of the chosen dyes using Z-scan technique.
   - Open and closed aperture Z-scan studies in liquid medium.
   - Open and closed aperture Z-scan studies in solid medium.
- Measurement of third-order nonlinear parameters such as nonlinear refractive index \( n_2 \), nonlinear absorption coefficient \( \beta \) and third-order susceptibility \( \chi^{(3)} \) using Z-scan technique in both liquid and solid media.

IV. Study on optical limiting behavior of organic dyes using transmittance technique.