CHAPTER 5
NONLINEAR OPTICAL CHARACTERIZATION OF
DYES IN LIQUID AND SOLID MEDIA

5.1 INTRODUCTION

Nonlinear Optical (NLO) properties of various solid-state, inorganic and organic materials are being, extensively investigated for their use in photonic and opto-electronic applications. The study of nonlinear optical properties in organic and polymer systems has enjoyed rapid and sustained growth. Because of their large optical nonlinearities, organic nonlinear optical materials are the leading practical materials for fabricating optoelectronic devices. The potential use in optical information processing devices has been the driving force behind most of the research into characterization of nonlinear optical properties of materials (Carter et al 1987).

Large nonlinear optical susceptibility resulting from the nonlinear response of organic molecules has attracted much attention. Materials that possess third-order optical nonlinearities have been investigated extensively for applications such as Optical Phase Conjugation, Optical limiting, Image processing and Optical switching (Yin et al 2000). To assess a material for the above mentioned applications, one must characterize its index of nonlinear refraction (NLR). Nonlinear optical phenomena can be due to electronic and non-electronic processes. The former refers to those radiative interactions between the active electron and the optical electric field. Usually they are very
fast of the order of pico-second, and spatially localized. Non-electronic processes are non-radiative interactions such as temperature, density, cis–trans isomerism, phase transition, etc. These mechanisms usually do not involve generation of new frequency radiation. Several techniques were developed to measure the coefficient of nonlinear optical refractive index $n_2$. Nonlinear interferometry (Weber et al 1978, Moran et al 1975), degenerate four-wave mixing (Friberg et al 1987), nearly degenerate three-wave mixing (Adair et al 1987), ellipse rotation (Owyoung et al 1973) and beam-distortion are some of the sensitive techniques but usually require complex experimental apparatus. Beam-distortion measurements, on the other hand, require precise beam scans followed by detailed wave-propagation analysis. The single beam Z-scan technique, developed by Sheik Bahae et al (1989) is a simple and effective tool for determining the nonlinear properties and is used widely in material characterization. The Z-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for separately determining the nonlinear changes in index and changes in absorption. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the 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.

Said et al (1992) studied the real and imaginary parts of the third-order susceptibility (i.e., $n_2$ and $\beta$ respectively) in CdTe, GaAs and ZnTe using picosecond pulses by Z-scan. Cheung et al (1994) studied the magnitude of the third-order nonlinear susceptibility of black tea in water by using Z- scan and confirmed that the nonlinearity is due thermal origin. Krauss et al (1994) studied the nonlinear refraction of CdS, ZnSe, and ZnS using Z- scan technique with 100 femto second pulses at 610 nm, 780 nm and 1.27 $\mu$m and confirmed that the electronic nature of the observed non linearties and magnitude dispersion of non-linear response are in good

limiting and optical switching. This chapter is a study of optical nonlinearity of organic dyes taken from different families and measurement of third-order nonlinear optical susceptibility in both liquid and solid media using a pulsed Nd:YAG (532 nm) laser and a continuous wave He-Ne (632.8 nm) laser excitation depending on the absorption wavelength of the dye used.

5.2 NONLINEAR OPTICAL STUDIES OF ORGANIC DYES

The dyes whose spectral characteristic have been studied are used for nonlinear optical studies. The chemical structures of the dyes are shown in Table 2.1. The dye doped polymer films of thickness approximately 1 mm and dye concentration of 0.03 mM are synthesized as explained in section 2.7. The thickness of the film is measured using screw gauge with least count 0.01 mm. The optical quality of dye doped polymer films are checked by passing a 5 mW He-Ne laser beam through it. Films which are showing no distortion of laser beam are chosen for further studies. The Z-scan method proposed by Sheik Bahae et al (1990) is used for studying the nonlinear refractive index of these dyes in solvent and dye doped polymer films as explained in section 3.4. The digital photograph of the experimental set-up used is shown in Figure 5.1. A second harmonic nanosecond pulsed Nd: YAG laser (LAB-170-10; Quanta Ray Laser spectra) having 6 ns pulses at repetition rate of 10 Hz giving a second harmonic at 532 nm is used as the excitation source for the Z-scan technique. The Gaussian profiled laser beam is focused by lens of focal length 10 cm to produce a beam waist \( \omega_0 \) of 32 \( \mu \)m. In our experiment, the Rayleigh condition, diffraction length \( Z_R = K\omega_0^2 /2 > L \) is satisfied so that the sample can be considered as a thin medium, where \( L \) is the thickness of the sample and \( \omega_0 \) is the beam waist. The transmission of the beam through an aperture placed in the far field is measured using photo detector fed to the digital power meter (coherent). For an open aperture Z-scan, the aperture is removed.
and all the transmitted light from the sample is collected by the photodetector connected to the digital power meter.

Figure 5.1 Digital Photograph of the experimental set-up for Z-scan

5.3 NONLINEAR OPTICAL STUDIES OF XYLIDINE PONCEAU DYE

The Z-scan experiment was performed for the dye Xylidine Ponceau belonging to azo family. The solvent used was ethanol. The Xylidine Ponceau dye doped PMMA polymer film of concentration 0.03 mM were synthesized as explained in section 2.7. The optical quality of dye doped polymer film was checked by passing a 5mW He-Ne laser beam through it. Film which showed no distortion of laser beam was chosen for further studies.

As Xylidine Ponceau dye have absorption peak wavelength near to the 2nd harmonic wavelength of Nd:YAG laser, a pulsed Nd:YAG laser operated at wavelength 532 nm (LAB-170-10; Quanta Ray Laser spectra) having 6 ns pulses at repetition rate of 10 Hz was used as the excitation source. Z-scan experiments were performed for dye in ethanol solvent taken
in a 1mm quartz cuvette and then for the dye doped polymer film using a Gaussian beam from nanosecond Nd:YAG laser that was focused onto the sample by a convex lens of focal length 10 cm to produce a beam waist $\omega_0$ of 32 $\mu$m.

In order to study the contribution of the solvent to the nonlinear response, the Z-scan experiment was performed only with solvent ethanol (without dye). There was no variation in the transmittance to the nonlinear response.

5.3.1 Synthesis of Dye Doped Polymer Film

Xylidine Ponceau dye doped polymer film of concentration 0.03 mM was synthesized by thermal bulk free radical polymerization technique as explained in section 2.7. The thickness of the synthesized film was found out to be approximately 1mm. To study the contribution of PMMA matrix, the Z-scan experiment was performed with PMMA polymer film (without dye). There was no variation of transmittance intensity which indicates there is no nonlinear response due to PMMA matrix.

5.3.2 Closed Aperture Z-scan

Initially, the closed aperture Z-scan experiment was performed using dye solution of concentration 0.01mM in ethanol solvent. The peak intensity of the incident laser beam $I_0$ was found to be 0.77 MW/cm$^2$ and the diffraction length, $Z_R$ was calculated to be 6.04 mm. For closed Z-scan, the aperture linear transmittance $S$ was found to be 0.393. The same experiment was then repeated for the dye for different concentration namely 0.02mM and 0.03mM. The graph for closed aperture Z-scan for dye in the liquid medium for three different concentrations was shown in Figure 5.2 (a). The closed
aperture Z-scan experiment was repeated for dye doped polymer film of dye concentration 0.03 mM. The graph was as shown in Figure 5.2 (b).

Figure 5.2 Closed aperture Z-scan curve of Xylidine Ponceau dye in (a) solvent and (b) film

The closed aperture Z-scan experiment was then performed for 0.03 mM concentration of the dye for different input peak intensities namely 0.77, 1.67 and 2.43 MW/cm$^2$ and the graph was as shown in Figure 5.3.

Figure 5.3 Closed Aperture Z-scan curve of Xylidine Ponceau dye in the liquid medium at different input peak intensities
Experimental results for closed aperture Z-scan showed a peak followed by valley which suggested that the change in refractive index was negative exhibiting a self-defocusing effect.

5.3.3 Open Aperture Z-scan

The experiment was repeated for open aperture Z-scan (S=1). The graphs for open aperture Z-scan for the dye in liquid and solid (film) medium were shown in Figures 5.4 (a) and (b) respectively. Reverse saturable absorption was observed in the open aperture Z-scan trace for Xylidine Ponceau dye as it shows minimum transmittance. The nonlinear absorption coefficient ($\beta$) can be estimated from the open aperture Z-scan data.

![Graphs](a) and (b)

**Figure 5.4** Open Z-scan curve of Xylidine Ponceau dye in (a) solvent and (b) film

The graph for open aperture Z-scan experiment of the dye for different input peak intensities was as shown in Figure 5.5.
Generally, the measurements of normalized transmittance versus sample position, for the cases of closed and open aperture, allow determination of the nonlinear refractive index \( n_2 \) and the nonlinear absorption coefficient \( \beta \). Here, since the closed aperture transmittance is affected by the nonlinear refraction and absorption, the determination of \( n_2 \) is less straightforward from the closed aperture scans. It is necessary to separate the effect of nonlinear refraction from that of nonlinear absorption. A simple and approximate method to obtain pure nonlinear refraction is to divide the closed aperture transmittance by the corresponding open aperture Z-scans.

Figure 5.6(a) and (b) represents pure nonlinear refraction of Xylidine Ponceau dye in liquid (solvent) and solid (film) medium respectively. Figure 5.7 represents pure nonlinear refraction of the dye in the liquid medium at different input intensities.
Figure 5.6 Pure nonlinear refraction curve of Xylidine Ponceau dye in (a) solvent and (b) film

Figure 5.7 Pure nonlinear refraction curve of Xylidine Ponceau dye in the liquid medium at different input peak intensities

It was found that nanosecond pulse laser induced two kinds of possible contributions to nonlinear refractive index namely transient nonlinearity kerr effect and thermo-optical effect. The thermal effect of these dye molecules for a light of wavelength 532 nm can be nearly neglected since the absorption due to the material was too small.
Hence, it may be concluded that the nonlinearity originated in the dye was mainly due to electronic effect and was related with strong delocalization of $\pi$-electrons. Hence, the large refractive nonlinearity was mainly due to the electronic origin nonlinearity mechanism.

5.3.4 Third-order Nonlinear Optical Susceptibility

Experimentally determined nonlinear refractive index ($n_2$) and nonlinear absorption coefficient ($\beta$) can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) according to the equations (3.18) and (3.19) from chapter 3 (Cassano et al 2001). The nonlinear optical parameters such as normalised transmittance change ($\Delta T_{p-v}$), nonlinear refractive index ($n_2$), nonlinear absorption coefficient ($\beta$) and nonlinear susceptibility ($\chi^{(3)}$) were calculated as explained in section 3.4.2 for the dye in both liquid and solid media and were given in Table 5.1. Variation of (a) $\Delta T_{p-v}$, (b) $n_2$, (c) $\beta$ and (d) $\chi^{(3)}$ vs concentration of Xylidine Ponceau dye in liquid medium were as shown in Figures 5.8 (a) to (d) respectively.

Table 5.1 Nonlinear Optical Parameters of Xylidine Ponceau dye in both liquid and solid media

| Concentration      | $\Delta T_{p-v}$ | $n_2 \times 10^{-10}$ (cm$^2$/W) | $\beta \times 10^{-6}$ (cm/W) | $|\chi^{(3)}| \times 10^{-9}$ (esu) |
|--------------------|------------------|---------------------------------|--------------------------------|----------------------------------|
| Liquid Medium      |                  |                                 |                                |                                  |
| 0.01mM             | 0.951            | -2.93                           | 3.64                           | 0.737                            |
| 0.02mM             | 1.299            | -4.02                           | 5.58                           | 1.123                            |
| 0.03mM             | 1.522            | -5.19                           | 7.73                           | 1.554                            |
| Polymer film       | 1.615            | -5.51                           | 8.67                           | 1.649                            |
From Table 5.1, it was found that the value of $\Delta T_{p-v}$ was more for polymer film when compared to the dyes in solvent. This showed that the change in refractive index in the solid media was higher compared to that liquid media. This may be attributed to the fact that due to poor thermal conductivity of the film, the rate of heat dissipation in solid was less than that in liquid leading to higher increase in temperature in solid medium compared to that in the liquid medium leading to higher nonlinear refractive index change. The concentration dependent nonlinear refractive index and nonlinear
absorption coefficient were measured and found that there was an increasing trend in values of \( n_2, \beta \) and \( \chi^{(3)} \) with increase of concentration. The intensity induced localised change in refractive index of the dye due to the nanosecond pulsed Nd:YAG laser excitation resulted in a lensing effect on the optical beam and was found to increase with increase of concentration. This may be attributed to the fact that as concentration was increased, the number of dye molecules interacting with the laser beam also increased and hence more particles were involved in the origin of nonlinearity resulting in an enhanced effect. The third-order nonlinear optical susceptibility of the dye calculated was found to be of the order of \( 10^{-9} \) esu.

**Table 5.2 Nonlinear Optical Parameters of Xylidine Ponceau dye in liquid medium at different input peak intensities**

<table>
<thead>
<tr>
<th>Input Peak Intensity (MW/cm(^2))</th>
<th>( \Delta T_{p-v} )</th>
<th>( \beta \times 10^{-6} ) (cm/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.77</td>
<td>1.52</td>
<td>7.73</td>
</tr>
<tr>
<td>1.67</td>
<td>1.59</td>
<td>5.41</td>
</tr>
<tr>
<td>2.43</td>
<td>1.65</td>
<td>4.96</td>
</tr>
</tbody>
</table>

**Figure 5.9** Variation of (a) \( \Delta T_{p-v} \) and (b) \( \beta \) vs input peak intensities for Xylidine Ponceau dye
Table 5.2 gives the values of the normalised transmittance change ($\Delta T_{p-v}$) and nonlinear absorption coefficient ($\beta$) of the dye at different input peak intensities. Variation of (a) $\Delta T_{p-v}$ and (b) $\beta$ vs input peak intensities for Xylidine Ponceau dye are as shown in Figures 5.9 (a) and (b) respectively. It was found that that the transmittance change increased with increase of input peak intensity but the nonlinear absorption coefficient decreased with increase of input peak intensity which indicated that the nonlinear absorption coefficient ($\beta$) was inversely proportional to the input energy. According to literature, such an effect occurs when there was an additional contribution from a higher order nonlinear process such as 3PA to the observed third-order nonlinearity of the dye molecules (Couris et al 1996). It has also been reported that under excitation with nanosecond laser pulses, a 3PA process can readily be realised in organic dyes (Auger et al 2003).

5.4 NONLINEAR OPTICAL STUDIES OF AZOPHLOXINE DYE

The Z-scan experiment was performed for the dye Azophloxine belonging to Azo family. The solvent used was ethanol. Azophloxine dye doped PMMA polymer film of concentration 0.03 mM were synthesized as explained in section 2.7. The optical quality of dye doped polymer film was checked by passing a 5mW He-Ne laser beam through it. Film which showed no distortion of laser beam was chosen for further studies.

Azophloxine dye have absorption peak wavelength near to the second harmonic wavelength of Nd:YAG laser. Hence pulsed Nd:YAG laser (LAB-170-10; Quanta Ray Laser spectra) having 6 ns pulses at repetition rate of 10 Hz giving a second harmonic at 532 nm was used as the excitation source. Z-scan experiments were performed for dye in ethanol solvent taken in a 1mm quartz cuvette and then for the dye doped polymer film using a Gaussian beam from nanosecond Nd:YAG laser that was focused onto the
sample by a convex lens of focal length 10 cm to produce a beam waist $\omega_0$ of 32 $\mu$m.

In order to study the contribution of the solvent to the nonlinear response, the Z-scan experiment was performed only with solvent ethanol (without dye). There was no variation in the transmittance to the nonlinear response.

5.4.1 Synthesis of Dye Doped Polymer Film

The dye doped polymer film of Azophloxine with dye concentration 0.03mM was synthesized by thermal bulk free radical polymerization technique as explained in section 2.7. The thickness of the synthesized film was found out to be approximately 1 mm. The Z-scan experiment was performed using a pulsed Nd:YAG laser beam. To study the contribution of PMMA matrix, the Z-scan experiment was performed with PMMA polymer film (without dye). There was no variation of transmittance intensity which indicates there was no nonlinear response due to PMMA matrix.

5.4.2 Closed Aperture Z-scan

The closed aperture Z-scan experiment was performed using dye solution of concentration 0.01mM in ethanol. The peak intensity of the incident laser beam $I_0$ was found to be 1.36 MW/cm$^2$ and the diffraction length, $Z_R$ was calculated to be 6.04 mm. For closed Z-scan, the aperture linear transmittance $S$ was found to be 0.39. The same experiment was repeated for the dye in ethanol for two different concentrations namely 0.02mM and 0.03mM. The graph for closed aperture Z-scan for dye in ethanol solvent for three different dye concentrations was as shown in Figure 5.10 (a). The closed aperture Z-scan experiment was repeated for dye doped
polymer film of dye concentration 0.03 mM. The graph was as shown in Figure 5.10 (b).

![Graph of Z-scan curve with normalised transmittance vs Z position for different dye concentrations.](image)

**Figure 5.10** Closed aperture Z-scan curve of Azophloxine dye in (a) solvent and (b) film

The closed aperture Z-scan experiment was then performed for 0.03 mM concentration of the dye for different input peak intensities namely 1.36, 2.33 and 3.26 MW/cm² and the graph was as shown in Figure 5.11.

![Graph of Z-scan curve with normalised transmittance vs Z position for different input peak intensities.](image)

**Figure 5.11** Closed aperture Z-scan curve of Azophloxine dye in the liquid medium at different input peak intensities
Experimental results for closed aperture Z-scan showed a valley followed by peak which suggested that the change in refractive index was positive exhibiting a self-focusing effect

5.4.3 Open Aperture Z-scan

The experiment was repeated for open aperture Z-scan (S=1). The graphs for open aperture Z-scan for the dye in liquid and solid media were shown in Figures 5.12 (a) and (b) respectively. Reverse saturable absorption was observed in the open aperture Z-scan trace for Azophloxine dye as it showed minimum transmittance. The nonlinear absorption coefficient $\beta$ can be estimated from the open aperture Z-scan data.

![Graphs of open aperture Z-scan](image_url)

**Figure 5.12 Open Z-scan curve of Azophloxine dye in (a) solvent and (b) film**

The open aperture Z-scan experiment was then performed for 0.03mM concentration of the dye for different input peak intensities and the graph was as shown in Figure 5.13.
Figure 5.13 Open Z-scan curve of Azophloxine dye in the liquid medium at different input peak intensities

Figure 5.14 (a) represents pure nonlinear refraction for Azophloxine dye at different concentrations in liquid medium and Figure 5.14 (b) represents pure nonlinear refraction for the dye in solid medium.

Figure 5.14 Pure nonlinear refraction curve of Azophloxine dye insolvent and (b) film
Figure 5.15 represents pure nonlinear refraction for Azophloxine dye at different input peak intensities.

![Normalized Transmittance vs. Z position](image.png)

**Figure 5.15** Pure nonlinear refraction curve of Azophloxine dye in the liquid medium at different input peak intensities

It was found that the origin of large refractive nonlinearity in the dye was mainly due to electronic effect as the thermal effect of these dye molecules due to nanosecond laser excitation was found to be small. However, for nanopulsed laser light excitation of organic dye molecules embedded in a solid matrix, the effect of a possible thermal nonlinearity cannot be completely ignored; more detailed study is, therefore, required to assess thermal contribution to the observed refractive nonlinearity.

### 5.4.4 Third-order Nonlinear Optical Susceptibility

Experimentally determined nonlinear refractive index ($n_2$) and nonlinear absorption coefficient ($\beta$) can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) according to the equations (3.18) and (3.19) from chapter 3 (Cassano et al 2001).
The nonlinear optical parameters, such as nonlinear refractive index ($n_2$), nonlinear absorption coefficient ($\beta$) and third-order nonlinear susceptibility ($\chi^{(3)}$) were calculated as explained in section 3.4.2 for the dye in both liquid and solid media and were given in Table 5.3.

Variation of (a) $\Delta T_{p-v}$, (b) $n_2$, (c) $\beta$ and (d) $\chi^{(3)}$ vs concentration of Azophlozine dye in liquid medium were as shown in Figures 5.16 (a) to (d) respectively.

Table 5.3 Nonlinear Optical Parameters of Azophloxine dye in both liquid and solid media

| Concentration | $\Delta T_{p-v}$ | $n_2 \times 10^{-10}$ (cm$^2$/W) | $\beta \times 10^{-6}$ (cm/W) | $|\chi^{(3)}| \times 10^{-8}$ (esu) |
|---------------|------------------|---------------------------------|-------------------------------|----------------------------------|
| Liquid Medium | 0.01mM           | 0.437                           | 0.844                         | 2.269                            | 4.583                           |
|                | 0.02mM           | 0.549                           | 0.955                         | 2.852                            | 5.687                           |
|                | 0.03mM           | 0.693                           | 1.204                         | 3.453                            | 6.888                           |
| Polymer film   |                  | 0.768                           | 1.336                         | 3.872                            | 7.723                           |

Figure 5.16 (Continued)
Figure 5.16 Variation of (a) $\Delta T_{p-v}$, (b) $n_2$, (c) $\beta$ and (d) $\chi^{(3)}$ vs concentration of Azophloxine dye in liquid medium

From Table 5.3, it was found that the normalised transmittance change ($\Delta T_{p-v}$) was more for polymer film when compared to the dyes in solvent resulting in higher change in refractive index in the solid medium when compared to the liquid medium. This may be attributed to the fact that in solid medium, due to its poor thermal conductivity, the rate of heat dissipation was less than that in liquid leading to higher increase in temperature in solid media than that in liquid media. The concentration dependent nonlinear refractive index and nonlinear absorption coefficient observed in these dyes shows that there was an increasing trend in values of $n_2$, $\beta$ and $\chi^{(3)}$ with increase of temperature. The intensity induced localised change in refractive index of the dye due to the nanosecond pulsed Nd:YAG laser excitation resulted in a lensing effect on the optical beam and was found to increase with increase of concentration as more particles then interacted with the laser beam resulting in enhanced effect in the optical nonlinearity (Auger et al 2003). The third-order nonlinear optical susceptibility of the dye calculated was found to be of the order of $10^{-8}$ esu.
Table 5.4 Nonlinear Optical Parameters of Azophloxine dye in liquid medium at different input peak intensities

| Input Peak Intensity (MW/cm$^2$) | $\Delta T_{p-v}$ | $n_2 \times 10^{-10}$ (cm$^2$/W) | $\beta \times 10^{-6}$ (cm/W) | $|\chi^{(3)}| \times 10^{-8}$ (esu) |
|---------------------------------|----------------|---------------------------------|----------------------------|----------------------------------|
| 1.36                            | 0.693          | 1.204                           | 3.453                      | 6.888                            |
| 2.33                            | 0.983          | 0.997                           | 3.011                      | 6.004                            |
| 3.26                            | 1.238          | 0.93                            | 2.794                      | 5.563                            |

Figure 5.17 Variation of (a) $\Delta T_{p-v}$ and (b) $\beta$ vs input peak intensities for Azophloxine dye

Table 5.4 gives the values of the nonlinear refractive index ($n_2$), nonlinear absorption coefficient ($\beta$) and third-order nonlinear susceptibility ($\chi^{(3)}$) of the dye at different input peak intensities. Variation of (a) $\Delta T_{p-v}$ and (b) $\beta$ vs input peak intensities for Azophloxine dye are as shown in Figures 5.17 (a) and (b) respectively. It should be noted that under nanosecond laser pulse excitation, nonlinear absorption coefficient decreased with increase of input peak intensity indicating nonlinear absorption coefficient ($\beta$) was inversely proportional to the input energy. This may be
due to the additional contribution from a higher order nonlinear process such as 3PA to the observed third-order nonlinearity of the dye molecules.

5.5 NONLINEAR OPTICAL STUDIES OF PURPURIN DYE

Z-scan experiment was performed for the dye Purpurin belonging to Anthraquinon family. The solvent used was ethanol. The Purpurin dye doped PMMA polymer film of concentration 0.03 mM were synthesized as explained in section 2.7. The optical quality of dye doped polymer film was checked by passing a 5mW He-Ne laser beam through it. Film which showed no distortion of laser beam was chosen for further studies.

Purpurin dye have absorption peak wavelength close to the second harmonic wavelength of Nd:YAG laser, a pulsed Nd:YAG laser operated at wavelength 532 nm (LAB-170-10; Quanta Ray Laser spectra) having 6 ns pulses at repetition rate of 10 Hz was used as the excitation source. Z-scan experiments were performed for dye in ethanol solvent taken in a 1mm quartz cuvette and then for the dye doped polymer film using a Gaussian beam from nanosecond Nd:YAG laser that was focused onto the sample by a convex lens of focal length 10 cm to produce a beam waist $\omega_0$ of 32 $\mu$m.

In order to study the contribution of the solvent to the nonlinear response, the Z-scan experiment was performed only with solvent ethanol (without dye). There was no variation in the transmittance to the nonlinear response.

5.5.1 Synthesis of Dye Doped Polymer Film

Purpurin dye doped polymer film of concentration 0.03 mM was synthesized by thermal bulk free radical polymerization technique as explained in section 2.7. The thickness of the synthesized film was found out
to be approximately 1 mm. To study the contribution of PMMA matrix, the Z-scan experiment was performed with PMMA polymer film (without dye). There was no variation of transmittance intensity which indicates there was no nonlinear response due to PMMA matrix.

### 5.5.2 Closed Aperture Z-scan

The closed aperture Z-scan experiment was performed using dye solution of concentration 0.01mM in ethanol. The peak intensity of the incident laser beam $I_0$ was found to be 1.36 MW/cm$^2$ and the diffraction length, $Z_R$ was calculated to be 6.04 mm. For closed Z- scan, the aperture linear transmittance, $S$ was found to be 0.39. The same experiment was repeated for the dye in ethanol for two different concentrations namely 0.02mM and 0.03mM. The graph for closed aperture Z-scan for dye in ethanol for three different concentrations was as shown in Figure 5.18 (a). The closed aperture Z- scan experiment was repeated for dye doped polymer film of dye concentration 0.03 mM. The graph was as shown in Figure 5.18 (b).

![Figure 5.18](image_url)  
**Figure 5.18** Closed aperture Z- scan curve of Purpurin dye in (a) solvent and (b) film
The closed aperture Z-scan experiment was then performed for 0.03 mM concentration of the dye for different input peak intensities namely 1.36, 2.33 and 3.26 MW/cm$^2$ and the graph was as shown in Figure 5.19.

![Closed aperture Z-scan curve of Purpurin dye in the liquid medium at different input peak intensities](image)

**Figure 5.19** Closed aperture Z-scan curve of Purpurin dye in the liquid medium at different input peak intensities

Experimental results for closed aperture Z-scan showed a peak followed by valley which suggested that the change in refractive index was negative exhibiting a self-defocusing effect

5.5.3 Open Aperture Z-scan

The experiment was repeated for open aperture Z-scan (S=1). The graphs for open aperture Z-scan for the dye in liquid and solid medium were shown in Figures 5.20 (a) and (b) respectively. Saturable absorption was observed in the open aperture Z-scan trace for Purpurin dye as it showed maximum transmittance. The nonlinear absorption coefficient $\beta$ can be estimated from the open aperture Z-scan data. The open aperture Z-scan experiment was then performed for 0.03 mM concentration of the dye for different input peak intensities namely 1.36, 2.33 and 3.26 MW/cm$^2$ and the graph was as shown in Figure 5.21.
Figure 5.20 Open Z- scan curve of Purpurin dye in (a) solvent and (b) film

Figure 5.21 Open Z- scan curve of Purpurin dye in the liquid medium at different input peak intensities

Figure 5.22 (a) represents pure nonlinear refraction curve for Purpurin dye at different concentrations in liquid medium and Figure 5.22 (b) represents pure nonlinear refraction curve of the dye in solid medium.
Figure 5.22 Pure nonlinear refraction curve of Purpurin dye in (a) solvent and (b) film.

Figure 5.23 Pure nonlinear refraction curve of Purpurin dye in the liquid medium at different input peak intensities.

Figure 5.23 represents pure nonlinear refraction curve for Purpurin dye at different input peak intensities. Nanosecond pulse Nd:YAG laser induces two kinds of possible contributions to nonlinear refractive index namely transient nonlinearity kerr effect and thermo-optical effect. The thermal effect of this dye molecules for a light of wavelength 532nm can be nearly neglected since the absorption due to the material is too small. Hence, it may be concluded that the nonlinearity originated in the dye is mainly due...
to electronic effect and is related with strong delocalization of \(\pi\)-electrons. However, for nanopulsed laser light excitation of organic dye molecules embedded in a solid matrix, the effect of a possible thermal nonlinearity cannot be completely ignored; more detailed study is, therefore, required to assess thermal contribution to the observed refractive nonlinearity.

### 5.5.4 Third-order Nonlinear Optical Susceptibility

Experimentally determined nonlinear refractive index \(n_2\) and nonlinear absorption coefficient \(\beta\) can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility \(\chi^{(3)}\) according to the Equations (3.18) and (3.19) from chapter 3 (Cassano et al 2001).

The nonlinear parameters, such as nonlinear refractive index \((n_2)\), nonlinear absorption coefficient \((\beta)\) and third-order nonlinear susceptibility \((\chi^{(3)})\) are calculated as explained in section 3.4.2 for the dye in both liquid and solid media and were given in Table 5.5. Variation of (a) \(\Delta T_{p-v}\), (b) \(n_2\), (c) \(\beta\) and (d) \(\chi^{(3)}\) vs concentration of Purpurin dye in liquid medium were as shown in Figures 5.24 (a) to (d) respectively.

| Concentration | \(\Delta T_{p-v}\) | \(n_2 \times 10^{-11}\) (cm\(^2\)/W) | \(\beta \times 10^{-5}\) (cm/W) | \(|\chi^{(3)}| \times 10^{-8}\) (esu) |
|---------------|-------------------|-----------------------------------|-------------------------------|----------------------------------|
| Liquid Medium | 0.01mM            | 0.241                             | -4.1937                       | -2.561                           | 1.726                           |
|               | 0.02mM            | 0.318                             | -5.53                         | -3.414                           | 2.462                           |
|               | 0.03mM            | 0.381                             | -6.624                        | -4.871                           | 3.446                           |
| Polymer film  | 0.424             | -7.357                            | -7.369                        | 4.9688                           |                                 |

Table 5.5 Nonlinear Optical Parameters of Purpurin dye in both solid and liquid media
It is found from Table 5.5 that the value of $\Delta T_{p,v}$ and nonlinear refractive index change was more for polymer film when compared to the dyes in solvent. This was due to the higher increase in temperature in solid media due to its poor conductivity. It was also seen that there was an increasing trend in values of $n_2$, $\beta$ and $\chi^{(3)}$ with increase of concentration. The intensity induced localised change in refractive index of the dye due to the nanosecond pulsed Nd:YAG laser excitation resulted in a lensing effect on the optical beam and was found to increase with increase of concentration. This may be attributed to the fact that as when the concentration is increased, the number of dye molecules also gets increased and hence more particles were involved in the origin of nonlinearity resulting in an enhanced effect (Auger
et al 2003). The third-order nonlinear optical susceptibility of the dye calculated was found to be of the order of $10^{-8}$ esu.

**Table 5.6 Nonlinear Optical Parameters of Purpurin dye in liquid medium at different input peak intensities**

| Input Peak Intensity (MW/cm²) | $\Delta T_{p-v}$ | $n_2 \times 10^{-11}$ (cm²/W) | $\beta \times 10^{-5}$ (cm/W) | $|\chi^{(3)}| \times 10^{-8}$ (esu) |
|-------------------------------|------------------|-------------------------------|-------------------------------|---------------------------------|
| 1.36                          | 0.381            | -6.624                        | -4.871                        | 3.446                           |
| 2.15                          | 0.696            | -7.315                        | -3.922                        | 3.520                           |
| 3.21                          | 0.989            | -7.769                        | -2.191                        | 3.665                           |

**Figure 5.25** Variation of (a) $\Delta T_{p-v}$, (b) $n_2$, (c) $\beta$ and (d) $\chi^{(3)}$ vs input intensities for Purpurin dye
Table 5.6 gives the values of the nonlinear refractive index \( n_2 \), change in refractive index \( \Delta n \), nonlinear absorption coefficient \( \beta \) and third-order nonlinear susceptibility \( \chi^{(3)} \) of the dye at different input peak intensities. Variation of (a) \( \Delta T_{p-v} \), (b) \( n_2 \), (c) \( \beta \) and (d) \( \chi^{(3)} \) vs input peak intensities of Purpurin dye in liquid medium are as shown in Figures 5.25 (a) to (d) respectively. The magnitude of nonlinear absorption coefficient \( \beta \) decreased with increase of input peak intensity which means that the nonlinear absorption coefficient \( \beta \) was inversely proportional to the input energy (Rusal et al 2013). Such an effect occurs due to the additional contribution from the higher order nonlinear process such as 3PA to the observed third-order nonlinearity of the dye molecules.

### 5.6 NONLINEAR OPTICAL STUDIES OF METHYL BLUE DYE

The Z-scan experiment was performed for the dye Methyl Blue belonging to Triarylmethane family. The solvent used was ethanol. The Methyl Blue dye doped PMMA polymer film of concentration 0.3 mM were synthesized as explained in section 2.7.

Methyl Blue dye have absorption peak wavelength near to 632.8 nm which is the operating wavelength of He-Ne laser. Hence continuous wave He-Ne laser was used as the excitation source. Z-scan experiments were performed for dye in ethanol solvent taken in a 1mm quartz cuvette and then for the dye doped polymer film using the He-Ne laser beam that was focused onto the sample using a 10 cm focal length convex lens, leading to a measured beam waist \( \omega_0 \) of 21 \( \mu \)m to give the intensity at the focus 3.19 kW/cm\(^2\) and the Rayleigh length \( Z_R \) was calculated to be 2.25 mm.

In order to study the contribution of the solvent to the nonlinear response, the Z-scan experiment was performed only with solvent ethanol (without dye). There was no variation in the transmittance to the nonlinear response.
5.6.1 Synthesis of Dye Doped Polymer Film

Methyl Blue dye doped polymer film of concentration 0.3 mM was synthesized by thermal bulk free radical polymerization technique as explained in section 2.7. The thickness of the synthesized film was found out to be approximately 1 mm. To study the contribution of PMMA matrix, the Z-scan experiment was performed with PMMA polymer film (without dye). There was no variation of transmittance intensity which indicates there is no nonlinear response due to PMMA matrix.

5.6.2 Closed Aperture Z-scan

The closed aperture Z-scan experiment was performed using dye solution of concentration 0.1 mM in ethanol. For closed Z-scan the aperture linear transmittance $S$ was found to be 0.42. The same experiment was repeated for the dye in ethanol for two different concentrations of 0.2 mM and 0.3 mM. The graph for closed aperture Z-scan for dye in ethanol solvent for three different dye concentrations are shown in Figure 5.26 (a). The closed aperture Z-scan experiment was repeated for dye doped polymer film of dye concentration 0.3 mM. The graph was as shown in Figure 5.26 (b).

![Figure 5.26 Closed aperture Z-scan curve of Methyl Blue dye in (a) solvent and (b) film](image-url)
The peak followed by a valley-normalized transmittance obtained from the closed aperture Z-scan data, indicates that the sign of the refraction nonlinearity is negative i.e. self-defocusing.

5.6.3 Open Aperture Z-scan

The experiment was repeated for open aperture Z-scan (S=1). The graphs for open aperture Z-scan for the dye in liquid and solid medium are shown in Figures 5.27 (a) and (b) respectively. Saturable absorption was observed in the open aperture Z-scan trace for Methyl Blue dye as it showed maximum transmittance. The nonlinear absorption coefficient ($\beta$) can be estimated from the open aperture Z-scan data.

Figure 5.28 (a) represents pure nonlinear refraction curve obtained for Methyl Blue dye at different concentrations in liquid medium and Figure 5.28 (b) represents the same for the dye in solid medium.

Figure 5.27 Open Z-scan curve of Methyl Blue dye in (a) solvent and (b) film
The defocusing effect shown in the closed set-up was attributed to a thermal nonlinearity resulting from absorption of radiation at 632.8 nm. The linear absorption of Methyl Blue dye was found to be around 607 nm, which was very close to the wavelength of the light used for excitation. Therefore, with 632.8 nm cw laser irradiation, which was near the resonance absorption peak, light energy was absorbed significantly by the sample which leads to the increase in local temperature by optimizing the absorbed energy into heat in the sample. When the medium was irradiated by laser, a small portion of its energy was absorbed by the particles resulting in the defocusing effect.

5.6.4 Third-order Nonlinear Optical Susceptibility

Experimentally determined nonlinear refractive index ($n_2$) and nonlinear absorption coefficient ($\beta$) can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) according to the Equations (3.18) and (3.19) from chapter 3 (Cassano et al 2001). The nonlinear parameters, such as nonlinear refractive index ($n_2$), nonlinear absorption coefficient ($\beta$) and nonlinear susceptibility ($\chi^{(3)}$) were
calculated as explained in section 3.4.2 for the dye in both liquid and solid media and are given in Table 5.7. Variation of (a) $\Delta T_{p-v}$, (b) $n_2$, (c) $\beta$ and (d) $\chi^{(3)}$ vs concentration of Methyl blue in liquid medium are as shown in Figures 5.29 (a) to (d) respectively.

**Table 5.7  Nonlinear Optical Parameters of Methyl Blue dye in both solid and liquid media**

| Concentration | $\Delta T_{p-v}$ | $n_2 \times 10^{-8} (\text{cm}^2/\text{W})$ | $\beta \times 10^{-4} (\text{cm/W})$ | $|\chi^{(3)}| \times 10^{-6} (\text{esu})$ |
|---------------|------------------|------------------------------------------|-------------------------------------|------------------------------------------|
| Liquid Medium |                  |                                          |                                     |                                          |
| 0.1mM         | 0.7              | -1.40                                    | -3.42                               | 0.665                                    |
| 0.2mM         | 0.83             | -1.66                                    | -3.86                               | 0.783                                    |
| 0.3mM         | 1.01             | -2.03                                    | -4.47                               | 0.958                                    |
| Polymer film  | 1.02             | -2.04                                    | -4.78                               | 0.964                                    |

![Graph](image-url)  
**Figure 5.29 (Continued)**
The value of $\Delta T_{p-v}$ has increased for dye doped polymer film when compared to the dyes in solvent. Hence the nonlinear refractive index change was more in solid media than liquid media due to the increase in temperature of the solid media due to its lesser rate of heat dissipation. The concentration dependent nonlinear refractive index and nonlinear absorption coefficient observed in these dyes indicated that there was an increasing trend in values of $n_2$, $\beta$ and $\chi^{(3)}$ with increase of concentration. This may be attributed to the fact that with increase of concentration, more number of particles are thermally agitated due to the local heating of the absorbed medium resulting in temperature variation of the sample medium (Henari & Cassidy 2012). The nonlinearity was temperature dependent and resulted in increase in third-order optical nonlinearity. The third-order nonlinear optical susceptibility of the dye calculated was found to be of the order of $10^{-6}$ esu.

5.7 RESULTS AND DISCUSSION

The Z-scan experiment for a closed and open aperture was performed for studying the nonlinear refraction and nonlinear absorption of dyes in solvent and dye doped polymer (PMMA) films. The graphs were
plotted by taking the position of the sample (Z mm) along x axis and normalized transmittance along y axis.

The dyes (Xylidine Ponceau, Purpurin and Methyl Blue) studied show a negative nonlinear refractive index, characterized by a pre-focal transmittance maximum (peak) followed by post-focal transmittance minimum (valley) while Azophloxine dye exhibited a positive nonlinear refractive index characterized by pre-focal transmittance minimum (valley) followed by a post-focal transmittance maximum (peak) for the closed Z-scan trace.

The reason for the nonlinearity observed in the closed aperture Z scan of the Xylidine Ponceau, Azophloxine and Purpurin dye due to pulsed Nd:YAG laser excitation was attributed to the electronic nonlinearity and was related with strong delocalization of \( \pi \)-electrons. Hence, the large refractive nonlinearity was mainly due to the electronic origin nonlinearity mechanism. However, for nanopulsed laser light excitation of organic dye molecules embedded in a solid matrix, the effect of a possible thermal nonlinearity cannot be completely ignored; more detailed study is, therefore, required to assess thermal contribution to the observed refractive nonlinearity.

The defocusing effect observed in the closed aperture Z-scan due to continuous wave He-Ne laser excitation on the dye is attributed to a thermal nonlinearity resulting from absorption of radiation at the excitation wavelength. The localized absorption of a tightly focused beam propagating through an absorbing dye medium produces a spatial distribution of temperature in the dye solution or polymer film and consequently, a spatial variation of the refractive index and that acting as a thermal lens resulting in severe phase distortion of the propagating beam.
Z-scan with an open aperture is insensitive to nonlinear refraction (thin sample approximation). Reverse Saturable absorption is observed in the open aperture Z-scan for the dyes Xylidine Ponceau and Azophloxine while the dyes Purpurin and Methyl Blue exhibited Saturable absorption.

The value of $\Delta T_{p-v}$ of all these dyes has increased for solid medium when compared to liquid medium. This shows that the change in refractive index in the solid media was higher for all the dyes when compared to that liquid media. The concentration dependent nonlinear refractive index and nonlinear absorption coefficient were calculated for all these dyes and was found that there was an increasing trend in values of $n_2$, $\beta$ and $\chi^{(3)}$ as the concentration increases. The intensity induced localised change in refractive index of the dye due to the nanosecond pulsed Nd:YAG laser excitation results in a enhanced lensing effect on the optical beam with increase of concentration. As with continuous wave laser, with increase of concentration, more number of particles are thermally agitated due to the local heating of the absorbed medium resulting in temperature variation of the sample medium.

It is also found that under nanosecond laser excitation, the magnitude of $\beta$ is found to decrease with the increase in input fluence, which indicates that the nonlinear absorption coefficient ($\beta$) is inversely proportional to the input energy. According to literature, such an effect occurs when there is an additional contribution from a higher order nonlinear process such as 3PA to the observed third-order nonlinearity of the dye molecules.

From the Z-scan measurements, it is found that all these dyes exhibited large nonlinear optical properties and the third-order nonlinear optical susceptibility calculated for all these dyes are found to be larger than some representative third-order nonlinear optical materials such as chalcone and its derivatives which are of the order of $10^{-14}$ esu (Ganeev et al 2003).
The UV-Visible absorption spectra of the samples recorded before and after the laser irradiation shows that the pattern and intensity of the spectra have no change. This indicates that the all these dye samples possesses good photo stability.