Chapter 5

Z-Scan Measurements of MB/PMMA and BTB/PMMA Matrices

The nonlinear optical properties of bromothymol blue/PMMA and methylene blue/PMMA were investigated by employing the open aperture Z-scan technique. The two nonlinear parameters, nonlinear absorption coefficient and imaginary part of third order susceptibility were determined from these measurements. The effect of input intensity and concentration of the dyes on these parameters were studied. The experimental results have been discussed by evoking the reverse saturable absorption (RSA) and excited state absorption (ESA) mechanisms using the six level energy model.
5.1 Introduction

Nonlinear optics (NLO) is concerned with the interaction of electromagnetic fields with materials to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. The invention of lasers paved the way to the development of a new field in optical phenomena called nonlinear optics. Nonlinear optics actually deals with the phenomena that occur as a result of the modification of the optical properties of a system in the presence of light. The laser light is sufficiently intense to change the refractive index of a material, which leads to phenomena like self focusing, phase modulation, frequency conversion etc. Nonlinear properties in optical region have been demonstrated by the harmonic generation of light observed for the first time by Franken and coworkers in 1961 [1]. They observed ultraviolet light at twice the frequency of a ruby laser light (λ=6943 Å), when the light was made to traverse a quartz crystal. This experiment attracted wide spread attention and marked the beginning of the experimental and theoretical investigations of nonlinear optical properties. Recent developments in the field of nonlinear optics hold promise for important applications in optical information processing, telecommunication, integrated optics etc.

To understand the nonlinear property, consider how the dipole moment per unit volume, the polarization of a material depends on the applied electric field. In the case of linear optics the polarization has a linear dependence on the electromagnetic field as given by,
where $\chi^{(1)}$ is the linear optical susceptibility and $\varepsilon$ is the permittivity. All the nonlinearity can be broadly classified into two groups, instantaneous and accumulative nonlinearities. For the first one, the polarization density resulting from an applied electric field occurs instantaneously. When the atoms are irradiated with high intense laser beams, for such interaction, polarization can be expressed as a power series of the local field by the equation

$$P(t) = \varepsilon \chi^{(1)} E(t)$$

5.1

where $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order susceptibilities. Since $P$ and $E$ are vector quantities $\chi^{(1)}, \chi^{(2)}, \chi^{(3)}$ etc., are tensors. $\chi^{(1)}$ is a second rank tensor and $\chi^{(2)}$ is a third rank tensor etc. The coefficients $\chi^{(1)}, \chi^{(2)}$ and $\chi^{(3)}$ are referred to as polarizability, first hyperpolarizability, and second hyperpolarizability, respectively. The hyperpolarizability terms are responsible for nonlinear response of the molecule to the impinging radiation. Here $P^{(2)}(t) = \chi^{(2)} E^2(t)$ is referred as the second order nonlinear polarization and $P^{(3)}(t) = \chi^{(3)} E^3(t)$ as third order nonlinear polarization. The nonlinear process involved here are sum and difference frequency mixing, optical rectification, electro-optic effect, two photon absorption (TPA), electronic Kerr effect etc. The electric field vector in the first term will have three components in the molecular co-ordinate system. Each
electric field component can contribute to polarization along each of the three directions in the molecular coordinate system. This triple contribution of electric field components leads to a total of nine elements to the second rank polarizability tensor. Similarly there are 27 components to the $\chi^{(2)}$ tensor and 81 components to $\chi^{(3)}$. Unless the molecular system lacks inversion symmetry, the form of odd-rank tensors such as $\chi^{(2)}$ will lead to zero induced polarization in this representation of optical nonlinearities. But third order nonlinear optical interaction can occur both in centrosymmetric and noncentrosymmetric media. The accumulative nonlinearities arise from interactions with memory, the polarization density generated by an applied fields either develops or decays on a time scale comparable to or longer than the excitation duration. These interactions are generally dissipative. The instantaneous nonlinearity depends on the instantaneous intensity within the medium, whereas the accumulative nonlinearities depend on the energy density deposited in the medium. This includes excited state absorption, free carrier absorption, free carrier generation and optically induced heating [2]. The medium which is described by a nonlinear relation of the type of Equation 5.2 is called a “nonlinear medium” [3]. The various nonlinear phenomena are,

Self focusing
Optical bistability
Optical Kerr effect
Two photon absorption
Self phase modulation
Nonlinear light scattering
Optical phase conjugation
Excited state absorption
Optical parametric oscillation
Optical parametric amplification
Third order harmonic generation (THG)
Optical second harmonic generation (SHG)
Sum and difference frequency generation (SFG and DFG) etc.

5.2 Organic Molecules as Nonlinear materials

The nonlinear optical properties of organic and polymeric materials have been spawned in recent years by the recognition that these materials may have unique applications as active components in the rapidly expanding optical communication and optical information processing fields [4]. The interest in organic compounds has been stimulated by the ability of the organic synthetic chemist to provide molecules with structures designed to optimise properties of interest [5]. Organic materials that have been investigated for nonlinear optical phenomena can be summarised into several categories such as single crystals, Langmuir-Blodgett films, polar polymers, guest (NLO-dye) host (polymer matrix) systems, NLO chromophore functionalised polymers, self assembled systems and liquid crystals [6]. Certain classes of organic materials exhibit extremely large nonlinear optical and electro-optic effects. The electronic nonlinearities in these
materials are based on molecular units containing highly localized $\pi$ electrons and additional electron donor and electron acceptor groups in opposite sides of the molecule [7]. The effects of nonlinearity includes second harmonic generation (SHG), third harmonic generation (THG), optical bistability, degenerate four wave mixing, and phase conjugation. The nonlinear properties of many of the organic dyes are reported [8-12].

**5.3 Nonlinear Absorption.**

Nonlinear absorption refers to the change in transmittance of a material as a function of intensity or fluence. The amount of light absorbed in most of the absorbing materials increases linearly with input irradiance giving rise to constant transmittance. This is referred to as linear absorption and is independent of the intensity of the light. Here Beer-Lambert law can fully explain the absorption of the sample by,

$$I = I_0 e^{-\alpha l}$$  \hspace{1cm} 5.3

where $I_0$ is the transmitted intensity, $\alpha$ linear absorption coefficient and $l$ sample thickness. The deviation from the above equation is called nonlinear absorption. $\alpha$ can increase or decrease with respect to incident intensity so that it become a function of wavelength as well as $I$. The intensity dependent absorption arise due to third order optical nonlinearity in which the complete refractive index can be written as

$$n(I) = n_1 + n_2 I$$  \hspace{1cm} 5.4
both $n_1$ and $n_2$ are complex quantities. Then for a given wavelength if $\alpha(I)$, which is the absorption coefficient, increases with intensity, this effect is called reverse saturable absorption (RSA). If $\alpha(I)$ decreases with intensity, it is called saturable absorption (SA). In RSA sample becomes more and more opaque as intensity is increased due to the enhanced absorption at higher intensities. The first sign of recognition of the property of RSA was found in 1967 in vat dyes by Guiliano and Hess [13]. This phenomenon can be exploited in passive optical power limiting to protect optical sensors, including human eye from intense laser pulses. RSA based limiters and SA have been reported using organic compounds such as perylimide dyes [8] polymethene dyes [9, 10] and bis-phthalocyanine [11]. RSA can also occur when the absorption cross-section from the first excited level to the higher excited molecular state ($\sigma_{12}$) being greater than from the ground state to the first excited state ($\sigma_{01}$). As the optical excitation intensity increases more molecules are promoted to the excited state and gives higher absorption excited state absorption (ESA).

At sufficiently high intensities, enhanced absorption of radiation in normally transparent region of the spectrum is observed due to multiphoton absorption process. The probability of absorption of N photons by such a process at a given $\lambda$ is proportional to $\sigma N^I_n$, where $\sigma$ is the N photon absorption cross-section, I intensity of radiation and $n$ the number of photons absorbed in a single multiphoton absorption. When N is 2 it is a two photon absorption (Figure 5.1).
Nonlinear absorption plays a crucial role in limiting the transparency of optical window materials and in causing laser induced damage to optical components, particularly at shorter wavelengths. Multiphoton absorption (MPA) processes have been successfully used to produce population inversion in semiconducting laser materials. Multiphoton absorbers can also be used as negative-feedback elements in laser cavities. MPA is a powerful technique to study the properties and processes associated with ultrashort laser pulses.

The nonlinear spectroscopy has proved to be invaluable in determining the optical and electronic properties of materials, when one photon absorption is forbidden by selection rules, a higher-order MPA may be allowed under these conditions. MPA experiments can enable one to study the properties truly characteristic of the crystalline volume because of the smaller values of MPA coefficients [14].

Usually almost all the organic dyes possess a large number of π-conjugated bonds which cause large value of nonlinear susceptibilities. Kerr effect, reverse saturable absorption, multiphoton absorption,
excited state absorption and saturable absorption are main nonlinear optical processes during the propagation of high intense laser beams through such dyes.

5.4 Z-Scan

5.4.1 Experimental Setup

The experimental setup for Z-scan measurement is given in Figure 5.2.

Using a single laser beam in tight focus geometry, the transmittance of a nonlinear medium through a finite aperture in the far field as a function of the sample position $Z$ measured with respect to the focal plane. Starting scan from the far field (negative $Z$), the beam irradiance is low and negligible nonlinear refraction occurs. Hence the transmittance $(D2/D1)$ remains relatively constant. As the sample is brought closer to the focus, the beam irradiance increases leading self-lensing in the sample. A negative self-lensing prior to focus will tend to collimate the beam, causing a beam narrowing at the aperture which results in an increase in the measured transmittance. As the scan in $Z$
continues and the sample passes the focal plane to the right (positive Z),
the same self-defocussing increases the beam divergence leading to the
beam broadening at the aperture and thus decrease the transmittance. This
suggests that there is null as the sample crosses the focal plane [15]. A
prefocal transmittance (peak) followed by a post focal transmittance
(valley) is the Z-scan signature of a negative refractive nonlinearity.
Positive nonlinear refraction gives rise an opposite valley-peak
configuration. The multiphoton absorption suppresses the peak and
enhances the valley, while saturation absorption produces the opposite
effect. The removal of the aperture completely eliminates the effect and
the Z-scan is sensitive to nonlinear absorption which is termed as open
aperture Z-scan. Closed aperture Z-scan measurements gives
information about the nonlinear phase variations and hence the
resulting focusing and defocusing of the transmitted beam. Using open
aperture Z-scan nonlinear absorption coefficients can be extracted. The
three phenomena occur in an open aperture Z-scan is given below in
Figure 5.3.
In our study we are using an excitation wavelength of 532nm from a Quanta Ray MOPO (MOPO700) pumped by Q-switched Nd:YAG laser at 355 nm, which emits 7ns pulses. Spatially filtered input beam is focused using an achromatic lens of focal length, \( f = 20\text{cm} \). The lens produces a beam waist (\( \frac{1}{e^2} \) intensity level) radius of \( \omega_0 = 36.46\mu\text{m} \) at 532 nm. The Rayleigh range is \( z_0 = 7.42\text{mm} \).

**5.4.2 Theory of Open aperture Z-Scan**

The detailed theory of Z-scan measurements is given by Sheik Bahae *et al.* [15]. When the absorption coefficient of a medium has a nonlinear dependence on laser beam intensity, one can use the relation

\[
\alpha(I) = \alpha + \beta I
\]
where $\alpha$ is the linear absorption coefficient and $\beta$ is the two photon absorption coefficient of the medium. In the case of three photon absorption, the dependence of the absorption coefficient on the laser radiation intensity can be represented as

$$\alpha(I) = \alpha + \beta^{2\omega} I + \beta^{3\omega} I^2 = \alpha + \beta_{\text{eff}} I$$  \hspace{1cm} (5.6)$$

where $\beta^{3\omega}$ is the three photon absorption coefficient and $\beta_{\text{eff}}$ is the effective nonlinear absorption coefficient. For the measurement of nonlinear absorption coefficient, an open aperture Z-scan configuration is used. In the closed aperture Z-scan measurements the sensitivity of the experiment to refractive nonlinearities is entirely due to the aperture. When the aperture is removed and the entire transmitted light is collected by the detector, it is sensitive only to the absorptive nonlinearities. The transmitted light is not sensitive to the phase variations. The intensity dependent nonlinear absorption coefficient $\alpha(I)$ can be written in terms of the linear absorption coefficient $\alpha$ and the effective nonlinear absorption coefficient $\beta_{\text{eff}}$ due to TPA or ESA or both.

$$\alpha(I) = \alpha + \beta_{\text{eff}} I$$  \hspace{1cm} (5.7)$$

The irradiance at the exit surface of the sample can be written as

$$I_r(z,r,t) = \frac{I(z,r,t)e^{-\alpha_0 l}}{1 + q(z,r,t)}$$  \hspace{1cm} (5.8)$$
where
\[ q(z, r, t) = \beta_{\text{eff}} I(z, r, t) L_{\text{eff}} \quad 5.9 \]

$L_{\text{eff}}$ is the effective length and is given in terms of sample length $l$ and $\alpha_0$ by the relation
\[ L_{\text{eff}} = \frac{1 - e^{-\alpha l}}{\alpha} \quad 5.10 \]

The total power transmitted $P(z, t)$ is obtained by integrating equation 5.8 over $z$ and $r$ and is given by
\[ P(z, t) = R(t) e^{-\alpha t} \ln\left[ 1 + q_0(z, t) \right] \quad 5.11 \]

$P_1(t)$ and $q_0(t)$ are given by the equations
\[ P_1(t) = \frac{\pi \alpha_0^2 I_0(t)}{2} \quad 5.12 \]
\[ q_0(z, t) = \frac{\beta_{\text{eff}} I_0(t) L_{\text{eff}}}{1 + \left( \frac{z}{z_0^2} \right)} \quad 5.13 \]

For a pulse of Gaussian temporal profile, equation 5.11 can be integrated to give the transmission as
\[ T(z) = \frac{C}{q_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \ln\left( 1 + q_0 e^{-t^2} \right) dt \quad 5.14 \]

For $q_0 < 1$ this transmittance can be expressed in terms of peak irradiance in a summation form as,
The nonlinear absorption coefficient is obtained by fitting the experimental data to Equation 16. The magnitude of absorption coefficient is a measure of the size of the RSA, which is used to calculate the imaginary part of the nonlinear susceptibility $\chi^{(3)}$,

$$\text{Im} \chi^{(3)} = \frac{n^2 \varepsilon_0 c \lambda \beta}{2\pi}$$  

In electrostatic units (esu),

$$\text{Im} \chi^{(3)} = \frac{10^{-7} c^2 n^2 \beta}{96\pi^2 \omega}$$

Where $n$ is the refractive index, $\varepsilon_0$ is the permittivity of the free space and $c$ the speed of light in vacuum, $\lambda$ is the wavelength of laser used.

5.5 Sample Preparation and Analysis

PMMA doped with methylene blue and bromothymol blue were prepared using the procedure discussed in chapter 4. Two concentrations of both dyes were prepared using bulk polymerisation. BTB/PMMA was prepared for $1 \times 10^{-3} \text{M}$ and $3 \times 10^{-3} \text{M}$, MB/PMMA was for $2 \times 10^{-4} \text{M}$ and $1 \times 10^{-3} \text{M}$. The samples were cut and polished well for the Z-scan measurements. The thickness of the samples used were varied from 0.50-0.75mm.
5.6 Results and Discussions

Polymethyl methacrylate is a hard transparent material with excellent ultraviolet stability. It has a glass transition temperature of around 108°C. The dye bromothymol blue is used as an absorption-based sensor in many of the planar waveguide and optical fiber systems [16]. It is a neutral dye. Methylene blue is a cationic dye. Methylene blue sensitized PMMA matrix was used for simple and fast formation of holographic films [17].

The absorption spectra of both dyes in PMMA matrix is shown in Figure 5.4 The methylene blue has a strong absorption band in the visible region at around 620 nm in the polymer matrix. The bromothymol shows absorption below 400 nm in PMMA. The green region in the absorption spectra is characterized by low absorption for both the dyes. Therefore the region is probed for nonlinear absorption using 532nm from an Nd-YAG laser.
The open aperture Z-scan measurements for the two dyes are performed for different input energies. The normalized transmission as a function of distance along the axis of the lens is given in Figures 5.5-5.8 for both the dyes. The fit of the experimental data with Equation 5.15 is also shown in the figures. The plot shows valley at the focus and this minimum transmittance at the focal point is an indication of reverse saturable absorption (RSA). The RSA phenomenon is predominant whenever the quantity $\beta_{\text{eff}}$ is larger than $\alpha$, the linear absorption coefficient [8]. This condition is satisfied in the present case. The value of the constant $q_0$ is obtained from the theoretical fit and knowing the values of $I_0$ and $L_{\text{eff}}$, the nonlinear absorption coefficient $\beta_{\text{eff}}$ can be calculated. The imaginary part of third order nonlinear susceptibility can be evaluated by using the relation 5.17.
Figure 5.5 Z-scan and theoretical fit for BTB (1x10^{-3}M) at (a) 20\mu J (b) 45\mu J and (c) 70\mu J
Figure 5.6 Z-scan curves and theoretical fit for BTB-3x10^{-3}M at (a) 20μJ (b) 45μJ and (c) 70μJ.
Figure 5.7 Z-scan traces of MB-2x10^{-4} M at (a) 20\mu J (b) 30\mu J and (c) 45 \mu J
Figure 5.8 Z-scan curve and theoretical fit for MB-1x10^{-3}M at (a) 16\mu J (b) 30\mu J (c) 45\mu J
The measured values of $\beta_{\text{eff}}$ and $\Im \chi^{(3)}$ for BTB/PMMA and MB/PMMA are tabulated in Table 5.1 and Table 5.2 respectively. From the tables it is clear that the value of $\beta_{\text{eff}}$ decreased with increasing input irradiance. This type of behaviour is usually seen in samples, which exhibit ESA [11, 18]. With increasing intensity the total absorption of the PMMA system approaches asymptotically the value of the absorbance of the triplet state.

**Table 5.1** Values of $\beta_{\text{eff}}$ and $\Im \chi^{(3)}$ for BTB/PMMA

<table>
<thead>
<tr>
<th>Concentration</th>
<th>1x$10^{-3}$M</th>
<th>3x$10^{-3}$M</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ (cm$^{-1}$)</td>
<td>2.94</td>
<td>6.30</td>
</tr>
<tr>
<td>Energy</td>
<td>20 $\mu$J</td>
<td>45 $\mu$J</td>
</tr>
<tr>
<td>$\beta_{\text{eff}}I_0$ (cm$^{-1}$)</td>
<td>12.07</td>
<td>13.51</td>
</tr>
<tr>
<td>$\beta_{\text{eff}}$ (cm/GW)</td>
<td>167</td>
<td>83</td>
</tr>
<tr>
<td>$\Im \chi^{(3)}$ (10$^{-12}$ esu)</td>
<td>9.95</td>
<td>4.95</td>
</tr>
</tbody>
</table>

The mechanism of RSA can be explained with the help of six level model shown in Figure 5.9 [8]. The photons excite the dye molecules from ground state $S_0$ to the upper vibronic energy levels.

**Table 5.2** Values of $\beta_{\text{eff}}$ and $\Im \chi^{(3)}$ for MB/PMMA

<table>
<thead>
<tr>
<th>Concentration</th>
<th>2x$10^{-4}$M</th>
<th>1x$10^{-3}$M</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ (cm$^{-1}$)</td>
<td>4.93</td>
<td>9.49</td>
</tr>
<tr>
<td>Energy</td>
<td>20 $\mu$J</td>
<td>30 $\mu$J</td>
</tr>
<tr>
<td>$\beta_{\text{eff}}I_0$ (cm$^{-1}$)</td>
<td>19.96</td>
<td>15.08</td>
</tr>
<tr>
<td>$\beta_{\text{eff}}$ (cm/GW)</td>
<td>276</td>
<td>138</td>
</tr>
<tr>
<td>$\Im \chi^{(3)}$ (10$^{-12}$ esu)</td>
<td>16.45</td>
<td>8.23</td>
</tr>
</tbody>
</table>
The absorption is followed by a rapid relaxation in to lowest vibrational sublevel of the emitting level $S_1$. Excited state absorption can occur from $S_1$ to higher singlet excited state and the RSA phenomenon is produced. Radiation to a lower triplet state may also happen and ESA between two triplet states can occur and participate in the nonlinear phenomena. The nonlinear optical phenomenon like ESA can be used for passive optical limiting. Such optical limiters have importance in the protection of eye and sensors in optical systems such as direct viewing devices (telescopes), focal plane arrays, night vision systems etc. Using an appropriate limiter we can operate the devices even above the damage threshold intensity conditions.

For a fixed input intensity $I_0$, the sample with higher concentration of the dye shows larger nonlinear absorption coefficient.
The linear increase with concentration is already reported in the case of Phthalocyanine and C$_{60}$ [11, 18]. It shows that there is no aggregation of the molecules at these concentrations and it also indicates that the ground state of the dyes is optically thin. In the case of MB/PMMA system single photon is sufficient to lift the molecule from the ground state to the excited state. At high intensities ESA becomes dominant and hence one observes a decreasing tendency with laser intensity. However in the case of BTB/PMMA system at high intensities it is quite possible to observe ESA from a two photon pumped state. Such an accumulative nonlinear effect is responsible for the decrease of $\beta_{\text{eff}}$ with intensity. Comparing to bromothymol blue, methylene blue possesses stronger nonlinear absorption Table 5.3. The reason for this behavior may be due to the difference in their spectral absorption. It was previously reported that the charge condition of dyes have negligible influence on their optical nonlinearities [9]. A complete consideration of various kinetic processes and the rate equation analysis is necessary to find out the contribution of each nonlinear phenomena involved when an intense laser light is passed through such systems.
Table 5.3 Comparison of $\beta_{\text{eff}}$ and $\text{Im}\chi^{(3)}$ BTB/PMMA and MB/PMMA

<table>
<thead>
<tr>
<th>Samples</th>
<th>BTB/PMMA (1x10^{-3}M)</th>
<th>MB/PMMA (1x10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (µJ)</td>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td>$\beta_{\text{eff}}$ (cm/GW)</td>
<td>83</td>
<td>77</td>
</tr>
<tr>
<td>$\text{Im}\chi^{(3)} \ (10^{-12} \text{ esu})$</td>
<td>4.95</td>
<td>4.62</td>
</tr>
</tbody>
</table>

5.7 Conclusion

The nonlinear properties of the two dyes, bromothymol blue and methylene blue are studied using open aperture Z-scan experimental technique. The reverse saturable absorption phenomenon is observed in all the samples at 532nm. The nonlinear absorption coefficient, $\beta_{\text{eff}}$, imaginary part of third order susceptibility, $\text{Im}\chi^{(3)}$ are calculated for the two dyes at different input intensities. The value is found to decrease with intensity, which shows the presence of excited state absorption, (ESA) in both the samples. The concentration dependence on the nonlinear absorption coefficient is also studied. For both the samples there is linear increase of the nonlinear absorption coefficient, as seen in many of the dye systems, which shows no aggregation of the molecules at these concentrations.
References


