Chapter 3

Nonlinear Optical Studies on Samarium Phthalocyanine in Methyl Methacrylate using Z-Scan and Optical Limiting Techniques

Abstract

The effective nonlinear absorption coefficient $\beta_{\text{eff}}$ and the imaginary part of the nonlinear susceptibility $\text{Im}(\chi_{\text{eff}}^3)$ of Samarium Phthalocyanine are calculated from open aperture z-scan measurements. The sample is taken in Methyl Methacrylate, both in liquid (Methyl Methacrylate Monomer - MMA) and solid (Poly Methyl Methacrylate - PMMA) matrices. For sample excitation, nanosecond laser pulses at 532 nm have been employed. Nonlinear absorption is explained in terms of a five level model. Compared to the sample in solid matrix, sample in liquid medium is found to show better nonlinear behaviour and this is explained using bimolecular process taking place in these samples. Optical limiting efficiency of the samples is studied in both phases and the results are compared. The concentration dependence on the optical limiting nature is studied both in liquid as well as in solid medium and the role of RSA in the limiting behaviour is verified.
1. Introduction

In most of the materials the amount of light transmitted is a linear function of the intensity of light incident on these materials. In such cases, the absorption in these samples can be fully described by Beers-Lambert law [1].

\[
\frac{dI}{dz} = -\alpha I
\]

where \( \alpha \) is the absorption coefficient, \( I \) is the intensity of radiation and \( z' \) denotes the propagation depth inside the material. Obviously \( \alpha \) is independent of intensity and depends only on the wavelength of excitation. But there are some materials which show marked difference from this behaviour and they are called nonlinear absorbers. In recent year, the z-scan technique has been widely used to study the reverse saturable absorption (RSA) of various materials [1-2]. By RSA we mean the absorption coefficient \( \alpha \) in the Beer's equation increases with irradiance \( I \) (energy per area per time) or fluence \( F \) (energy per area). The z-scan technique involves measurements of the transmittance (transmitted energy/input energy) of tight focused laser beams (TEM\(_{00}\) mode, pulsed) of equal energy through the sample at various \( z \) positions relative to the focus. In the case of reverse saturable absorption (RSA), the sample experiences the strongest intensity and fluence at focus; therefore it absorbs the most energy and allows least transmittance. Away from the focus in the direction of both increasing and decreasing \( z \), transmittance increases evenly because the irradiance decreases symmetrically about the focus. RSA is the main topic of discussion in this chapter. In the case of saturable absorption (SA) the absorption coefficient \( \alpha \) decrease with intensity or fluence. But in the case of linear absorption \( \alpha \) remains constant irrespective of intensity or fluence of the incident radiation. Thus, it is evident that in the presence of nonlinear absorption, \( \alpha \) becomes a function of intensity also and hence it is usually written as \( \alpha(I, \lambda) \).
Materials showing saturable absorption become more transparent when the incident intensity is increased and this phenomenon is exploited for applications like passive mode locking in lasers [3]. Reverse saturable absorbers become more opaque on increasing the incident intensity and found applications in the design of passive optical power limiters to protect optical sensors, including human eye, from intense laser pulses [4-9]. Design and fabrication of devices based on the nonlinear optical (NLO) properties of materials is an exciting area of research in the field of optoelectronics and photonics. The measurement of nonlinear optical parameters of various materials has acquired great importance in this context. Useful data is now available in the literature on the NLO properties of materials like fullerenes, semiconductors, liquid crystals, conjugated polymers, dyes, organo-metalics [10-19] etc. Large non-resonant optical susceptibility, ultrafast response, thermal and chemical stability, ease of molecular structural engineering etc. are the most desired properties of a good NLO material. In general, it is not possible to simultaneously satisfy all these criteria in a single material. However, organic macromolecules with extensive π electron conjugation like porphyrins, phthalocyanines, napthalocyanines and their different derivatives form a class of compounds which satisfy many of such requirements [20]. The relatively low linear absorption and high ratios of excited state to ground state absorption cross section in the 400 – 600 nm region make the metallo-phthalocyanines ideal for the realization of design and fabrication of good quality optical limiters in the visible region. There are various reports in literature on the nonlinear optical properties of these materials in different solvents [21-22]. But when device applications are considered, the incorporation of these materials into solid matrices and the study of their behaviour in different host materials become important. Therefore we studied the NLO properties of Samarium Phthalocyanine in solid (PMMA) as well as in liquid (MMA) matrices.
Experimental

In a typical open aperture z-scan experiment the transmittance of the sample is measured as the sample is moved along the propagation direction (z) of a focused Gaussian laser beam. In the present experiment the beam is focused with a lens of focal length 30 cm producing a spot size \( \omega_0 \) of \( 2 \times 10^{-5} \) m and Rayleigh range \( z_0 \) of \( 2.3 \times 10^{-3} \) m. The z-scan measurements in liquid phase are done by dissolving the samples directly in Methyl methacrylate monomer and the samples are taken in a 1.5 mm cuvette. Doped PMMA samples are prepared by directly dissolving the sample in MMA containing suitable initiators and keeping the solution at a constant temperature (50°C) waterbath for a period of 48 hours. Fine polished solid samples of suitable dimensions (1.5 mm) are prepared from the polymer thus obtained. The damage thresholds of the samples thus obtained were measure and it is found to be 1.9 J/cm\(^2\) for the doped PMMA samples and 2.2 J/cm\(^2\) for the undoped PMMA. The damage threshold of the undoped PMMA is in agreement with the value already reported in the literature [23]. The decrease of the laser damage threshold in the doped polymer samples is due to the defects in the microstructure of the polymer as well as the presence of foreign bodies within the polymer. Incident energy as well as the transmitted energy from the sample is measured using a dual channel energy ratio meter (Rj-7620, Laser probe inc.) and averaged over hundred pulses.

3.3 Effective nonlinear absorption coefficient

Though the original theory of Z-scan was derived for pure TPA, it has been shown that the same theory can also be used for ESA. However, in this case we have to properly redefine the nonlinear absorption coefficient \( \beta \) as \( \beta_{\text{eff}} \). The present measurements have been taken using nanoseconds pulses and therefore, two assumptions can be made: (1) intersystem crossing [from \( S_1(\nu = 0) \) to \( T_1(\nu = 0) \)] is fast compared to the laser pulse width and (2) intersystem crossing yield \( \Phi_{\text{isc}} \) is nearly one i.e. virtually all the atoms excited from \( S_0 \) reach the first excited triplet state \( T_1 \).
As mentioned previously, atoms then get excited from $T_1$ to $T_2$ as a result of ESA. Under these assumptions, intensity variation through the sample and population in the first excited triplet state $T_1$ are respectively given by following equations [24]

\[
\frac{dI}{dz} = -\sigma_0 n_0 I - \sigma_1 n_I I
\]

\[
n_I = \sigma_0 n_0 I \Phi_{isc} \quad (\Phi_{isc}=1)
\]

Here $\sigma_0$, $\sigma_1$, $n_0$ and $n_I$ are ground state absorption cross-section, first excited triplet state absorption cross-section, number of molecules in the ground state per ml, and number of molecules in the first excited triplet state per ml respectively. ($z$ corresponds to sample length). From equations (3.2) and (3.3), the intensity dependent absorption coefficient $\alpha(I)$ and $\beta_{eff}$ are given respectively by

\[
\alpha(I) = \sigma_0 n_0 + \sigma_1 \sigma_0 n_0 I
\]

\[
\beta_{eff} = n_0 \sigma_0 \sigma_1
\]

It is clear that $\beta_{eff}$ is intensity dependant for STPA through the factor $n_0$, whereas $\beta$ is independent of intensity for pure TPA. $\beta_{eff}$ is a measure of the overall absorptive nonlinearity present in the sample [24].

**3.4 Rate equations**

Dynamics of ESA can be described using rate equations. Under nanosecond excitation, amongst singlet states, populations at $S_1$ alone is important. This is because of the fact that higher excited singlet states have a lifetime of the order of picosecond, which is much less than the laser pulse width. Therefore, only the ground state ($S_0$), first excited singlet state ($S_1$) and first excited triplet state ($T_1$) are considered. If $\sigma_g$,
\( \sigma_0 \) and \( \sigma_1 \) represent the absorption cross sections of \( S_0 \), \( S_1 \) and \( T_1 \) respectively, the rate equations for the population in these energy levels may be written as [4]

\[
\frac{dn_0}{dt} = -\frac{\sigma_0 I}{h \nu} n_0 + \frac{1}{\tau_{10}} n_1 + \frac{1}{\tau_{20}} n_2
\] (3.6)

\[
\frac{dn_1}{dt} = \frac{\sigma_0 I}{h \nu} n_0 - \left( \frac{1}{\tau_{10}} + \frac{1}{\tau_{12}} \right) n_1
\] (3.7)

\[
\frac{dn_2}{dt} = \frac{1}{\tau_{12}} n_1 - \frac{1}{\tau_{20}} n_2
\] (3.8)

Here \( n_0, n_1 \) and \( n_2 \) are the populations in \( S_0, S_1 \) and \( S_2 \) levels respectively. \( \tau_{10}, \tau_{12} \) and \( \tau_{20} \) are the life times of \( S_0 \rightarrow S_1, T_1 \rightarrow S_1 \) and \( S_0 \rightarrow T_1 \) transitions respectively.

Transmitted light intensity may be written in terms of total absorption coefficient, which is also a function of time. The equations (3.9) and (3.10) give total absorption coefficient and transmitted intensity respectively.

\[
\alpha(t) = \sigma_0 n_0(t) + \sigma_1 n_1(t) + \sigma_2 n_2(t)
\] (3.9)

\[
\frac{dI}{dz} = -\left( \sigma_0 n_0 + \sigma_1 n_1 + \sigma_2 n_2 \right) I
\] (3.10)

The equations (3.9) and (3.10) can be numerically solved using the initial conditions, \( n_0(t = -\infty, z) = N = n_0 + n_1 + n_2, \ n_1(t = -\infty, z) = n_2(t = -\infty, z) = 0. \sigma_1 \) and \( \sigma_2 \) are kept as adjustable parameters. In macromolecules the vibrational levels of excited singlet states (\( S_1 \ & S_2 \)) and triplet states (\( T_1 \ & T_2 \)) overlap in most cases. Intersystem crossing occurs in nanosecond time scales. Hence under picosecond excitation, \( S_2 \) level is considered instead of \( T_1 \). In the steady state conditions, the nonlinear absorption coefficient is written as [4]

\[
\alpha = \alpha_0 \left[ \frac{1 + K_I}{1 + I} \right]
\] (3.11)
Investigations of nonlinear ..........

Here $I' = I/I_s$ where $I_s$ is the saturation intensity and $K = \sigma_T/\sigma_0$. If $K$ is greater than one, we get RSA and a value of $K$ less than one, yields SA. In this chapter, $\beta_{\text{eff}}$ is measured using two-photon absorption theory introduced by Sheik Bahae et. al [1].

3.5 Results and discussion
The structure of the sample used in the present study, Samarium Phthalocyanine [Sm(Pc)], Bis-Phthalocyanine, and a typical absorption spectrum in MMA and PMMA are given in figures 3.1 and 3.2 respectively. Bis-Pc's have a sandwich structure in which the metal ion lies in between the two Pc planes [25]. Phthalocyanine has a characteristic low energy absorption band in the 600-800 nm region and it is generally called the Q-band. They also have a high energy absorption band in the 300-400 nm region called Soret or B band and an absorption valley around 532 nm in the visible region. In the valley of the linear absorption spectrum, reverse saturable absorption could occur because in this wavelength region the absorption cross section of the excited state is larger than that of the ground state [4].

The advantages of polymer matrices over solution phase such as their compactness, ease of handling etc. are obvious in a wide range of applications. However, the extent to which the optical properties of the sample may differ in different matrices is an important aspect to be considered. We did not observe any marked differences between the absorption spectra obtained for the sample, Samarium Phthalocyanine, in methyl methacrylate monomer (MMA) and poly methyl methacrylate (PMMA) matrices. The spectra obtained are also identical with those reported in literature [26]. This clearly shows that the solid matrix (PMMA) does not modify the sample properties appreciably.
From the open aperture z-scan experimental data, nonlinear absorption coefficient $\beta$ is calculated using the model suggested by Sheik Bhahe et al. [1]. Nonlinear absorption coefficient $\beta$ is calculated by fitting the experimental data to the normalized transmittance given by the equation
Chapter 3: Nonlinear optical ......

\[ T(z) = \frac{C}{q_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \ln\left(1 + q_0 e^{-\alpha t}\right) dt \] (3.12)

In equation 3.12, \( C \) is the normalization constant, \( \alpha = \left(\beta I_0 t_{\text{eff}}\right)/(1 + x^2) \) where \( I_0 \) is the irradiance at focus, \( x = z/z_0 \) and \( t_{\text{eff}} = (1 - e^{-\alpha l})/\alpha \) is the effective length of the sample, \( \alpha \) is the linear absorption coefficient and \( l \) is the sample length. It is well known that in Porphyrins like Pc’s, nonlinear absorption at 532nm is not due to pure two photon absorption but due to sequential two photon absorption, also known as excited state absorption or reverse saturable absorption (RSA) [27-28]. Therefore to distinguish this from the essentially non-resonant two-photon absorption, the nonlinear absorption coefficient in RSA media is usually referred to as \( \beta_{\text{eff}} \) [29]. The imaginary part of the nonlinear susceptibility (\( \text{Im}\chi_{\text{eff}}^3 \)) can be calculated from \( \beta_{\text{eff}} \) using the expression

\[ \text{Im}(\chi_{\text{eff}}^3) = \frac{\lambda \varepsilon_0 n^2 c \beta_{\text{eff}}}{4\pi} \] (3.13)

To explain nonlinear absorption under nanosecond excitation, a five level model involving the states \( S_0, S_1, S_2, T_1 \) and \( T_2 \) as shown in figure 3.3 [30] can be used. Here \( S_n \) and \( T_n \) are the singlet and triplet states respectively where \( n = 0, 1 \) or \( 2 \) and every electronic energy level involves many vibronic sublevels. Also \( \sigma \)'s represent absorption cross sections and \( \tau \)'s represent relaxation times of atoms in different energy levels. When interacting with a laser pulse at 532 nm, atoms get excited from the \( S_0(v=0) \) to the upper vibrational level of \( S_1 \). Here \( v \) corresponds to the vibrational quantum number. Through the nonradiative decay within picoseconds they can relax to the lowest vibrational level of \( S_1(v=0) \). Since Pc’s have very low fluorescence [4] the transition from \( S_1(v=0) \) to \( S_0 \) can be neglected. The occurrence of the \( S_2 \stackrel{\leftarrow}{\leftrightarrow} S_1 \) transition does not appreciably deplete the \( S_1 \) state, as the \( S_1 \stackrel{\leftarrow}{\leftrightarrow} S_2 \) decay also takes place within picoseconds. However the \( T_1(v=0) \stackrel{\leftarrow}{\leftrightarrow} S_1(v=0) \) intersystem crossing
cross section is large, leading to a strong triplet–triplet absorption $T_2 \leftarrow T_1$. Here we assume that the intersystem crossing [31] is fast compared with the laser pulse width (9 ns) and virtually all the atoms excited from $S_0$ reach first excited triplet state $T_1$. In fact the intersystem crossing is higher for heavy atom substituted Pc’s due to large spin orbit coupling of the metal orbital and their mixing with the orbitals of the conjugated ring [26]. Therefore under nanosecond pulse excitation, the nonlinear absorption observed here is a consequence of $T_2 \leftarrow T_1$ absorption [$T_2 \leftarrow T_1(v=0)$]

Fig 3. 3 Five level energy diagram for Phthalocyanine. $S_n (n = 0,1,2)$: Singlet levels; $T_n (n = 1, 2)$: Triplet levels $\sigma$: Absorption cross section $\tau$: Relaxation times. Solid lines are radiative and curved lines are non-radiative.
Fig 3.4 Z-Scan of Samarium Phthalocyanine in
(a) Methyl Methacrylate monomer (MMA) [LT 39%]
(b) Poly methyl methacrylate (PMMA) [46%]

Fig 3.5 Z-Scan of Samarium Phthalocyanine in
(a) Methyl Methacrylate monomer (MMA) [LT 74%]
(b) Poly methyl methacrylate (PMMA) [74%]
Chapter 3: Nonlinear optical ……

Figs. 3.4 and 3.5 show the open aperture z-scan curves obtained for the samples investigated. Solid curves are numerical fits to the experimental data. The nonlinear absorption seen in both solid (PMMA) and liquid (MMA) matrices is found to be similar. Sample thickness is 1.5 mm in both cases and the reduction in transmittance around the focal region reveals the nonlinearity. The experiments have been repeated in the pure host materials MMA and PMMA in identical conditions but no measurable nonlinearity could be observed. The calculated values of $\beta_{\text{eff}}$ and $\text{Im}(\chi_{\text{eff}}^{3})$ along with the linear absorption coefficient are given in table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Host Matrix</th>
<th>Absorption Coefficient $\alpha$ (cm$^{-1}$)</th>
<th>Linear Transmittance (LT)%</th>
<th>$\beta_{\text{eff}}$ cm/GW</th>
<th>$\text{Im}(\chi_{\text{eff}}^{3}) \times 10^{-11}$ m$^2$V$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SmPc</td>
<td>MMA</td>
<td>0.086</td>
<td>74</td>
<td>47.83</td>
<td>1.075</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.475</td>
<td>39</td>
<td>198.45</td>
<td>4.460</td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>0.119</td>
<td>74</td>
<td>20.49</td>
<td>0.511</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.328</td>
<td>46</td>
<td>69.66</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Table 1: Measured values of nonlinear absorption coefficient and imaginary part of susceptibility tensor of Samarium Phthalocyanine in PMMA and MMA

The nonlinear absorption seen in these samples reveal that they can be used as potential optical limiters. For being used as a good optical limiter, a number of important requirements should be met by the nonlinear material. Fast response, high damage threshold and an excited state absorption cross-section larger than the ground state absorption cross-section are the most important among them [32]. At 532nm the excited state absorption cross section of phthalocyanine is higher than the ground
Investigations of nonlinear 

state absorption cross section [26]. Moreover, this class of materials responds to both fast and slow laser pulses via the \((S_2 \leftrightarrow S_1)\) and \((T_2 \leftrightarrow T_1)\) transitions respectively. Consequently, these molecules can be used for passive optical power limiting. Figures 3.6 and 3.7 show the normalized transmittance of the present samples as a function of the input fluence, plotted using data extracted from the z-scan curves. From the curves and the \(\beta_{\text{eff}}\) values we can conclude that limiting in the liquid samples is somewhat better as compared to that in the solid matrix.

Fig 3. 6 Optical limiting response of Samarium Phthalocyanine in 
(a) Methyl Methacrylate monomer (MMA) [LT 46%]
(b) Poly methyl methacrylate (PMMA) [39%]
Chapter 3: Nonlinear optical ….

Fig 3. 7 Optical limiting response of Samarium Phthalocyanine in
(a) Methyl Methacrylate monomer (MMA) [LT 74%]
(b) Poly methyl methacrylate (PMMA) [74%]

The observed better optical limiting behaviour of the sample in liquid phase as compared to the same in solid can be explained on the basis of the bimolecular process suggested by Jason et. al. [33]. Diffusion of molecules in solutions will provide an extra contribution towards the optical limiting property through bimolecular process of excitation and de-excitation mechanism. The energy level diagram corresponding to bimolecular process is given below (Fig. 3.8). Where S’s and T’s represent singlet and triplet transitions and σ’s represent relation time. The excited state energy of one molecule will be transferred to another one and this will result in the enhancement in optical limiting property of the sample. However in the case of solids such diffusion process is not possible in the time scale (ns) of the laser pulse used in the present experiment. Hence the optical limiting in solids can arise from excited state absorption process through the phenomenon of reverse saturable absorption. This argument supports the present observation that at low concentration
Investigations of nonlinear nonlinearity.

(as indicated by high linear transmittance) the optical limiting efficiency (as indicated by $\beta_{\text{eff}}$) does not differ much as in the case of higher concentration for both liquid and solid matrices [Fig. 3.7]. At this level of concentration there may not be sufficient amount of diffusion so as to support bimolecular processes.

Fig 3. 8 Reverse saturable absorption mechanism for phthalocyanine that includes both unimolecular and bimolecular excited state processes

As concentration is increased, the additional contribution through bimolecular process results in the higher optical limiting efficiency in liquids as compared to solids. Enhancements in the $\beta_{\text{eff}}$ at higher concentration in both solid and liquid media are due to the availability of more number of molecules to take part in the light-matter interaction. In liquids, over and above this, extra contributions to the optical limiting efficiency come from diffusion processes.
4.6 Concentration Dependence

In order to understand the effect of thickness and concentration of the material on the RSA the optical limiting responses were measured in a series of doped PMMA and MMA samples. To keep the linear transmittance constant same sample with different path length were used [4]. Figure 3.9 and 3.10 shows the optical limiting graphs thus obtained with Samarium Phthalocyanine in PMMA and MMA medium.

Fig 3. 9 Variation of transmitted fluence with respect to incident fluence for Samarium Phthalocyanine doped PMMA of 50% linear transmittance (a) Path length 1.5 mm (b) Path length 3.0 mm (c) Path length 5.0 mm
From the results shown in Fig.3.9 and 3.10 it is obvious that the limiting shows clear concentration dependence. This result is in good agreement with the report on copper phthalocyanine by Li et.al. [4]. The sample with larger path length (lower concentration) shows a better optical limiting property, and its saturation threshold is rather low. It may be noted here that the ratio of the effective excited state to ground state absorption cross section $\sigma_{\text{exc}}/\sigma_g$ can be used as a figure of merit for RSA based optical limiters. This can be defined as $\sigma_{\text{exc}}/\sigma_g = \ln(T_{\text{sat}})/\ln(T_{\text{lin}})$ where $T_{\text{lin}}$ is the linear transmittance at very low excitation energy and $T_{\text{sat}}$ is the saturated transmittance at high excitation energies [26]. The saturation thresholds of output fluence are 0.18, 0.06 and 0.026 J/cm² corresponding to sample lengths of 1.5 mm, 3.0 mm and 5.0 mm respectively. The figure of merit calculated is 1.86. While the reported values of figure of merit are about 3 for $C_{60}$ and more than 10 for Phthalocyanine complexes, that of the rare-earth metallo-phthalocyanine doped
PMMA samples have been found to be lower [34], and this agrees with the present measurements. The linear transmittance of the sample in liquid medium used for the present study is very low (LT = 22%). Therefore the saturation threshold is further smaller in this case. The measured values are 0.10 J/cm² and 0.035 J/cm² corresponding to sample length 1.5 mm and 3.0 mm respectively.

Kojima et. al. [35] while explaining the optical limiting property of a polyacene based oligomer using a five level energy diagram, have shown that, in the case of reverse saturable absorption due to excited state absorption the incident laser intensity \( I_0 \) and the transmitted laser intensity \( I \) obey the relation

\[
\ln\left(\frac{I_0}{I}\right) = k(I_0 - I) + A_g \tag{3.14}
\]

where \( k \) is a constant that depends on the absorption cross sections and lifetimes of the ground, excited singlet and excited triplet states and \( A_g \) is the ground state absorbance. Equation (3.14) says that the plot of \( \ln(I_0/I) \) versus \( (I_0 - I) \) should be a straight line with slope \( k \) ad intercept \( A_g \).

Fig 3.11 Plot of \( \ln(I_0/I) \) verses \( (I_0 - I) \) of \( \text{Sm(Pc)}_2 \) doped in PMMA
Investigations of nonlinear …………..

Figure 3.11 and 3.12 shows the plot of $\ln(I_0/I)$ verses $(I_0 - I)$ for samarium Phthalocyanine doped PMMA and MMA respectively. The straight-line nature of the graph is a clear indication that RSA is the main mechanism causing optical limiting in these samples.

3.7 Conclusion

Using the open aperture z-scan technique, the effective nonlinear absorption coefficient $\beta_{\text{eff}}$ and imaginary part of the nonlinear susceptibility ($\text{Im}\chi^{3}_{\text{eff}}$) of Samarium Phthalocyanine in Methyl Methacrylate at 532 nm has been calculated, in both liquid and solid media. The optical limiting behaviour of the samples is also studied. The nonlinearity originates from the large excited state absorption cross section, the characteristic property of Phthalocyanines. Enhancement in optical
limiting property of samples in liquid phase over the solid phase is attributed to the bimolecular processes taking place in liquid media. The measured \( \beta_{\text{eff}} \) values as well as the optical limiting curves show that samples in liquid phase are moderately better in their optical limiting efficiency. However, the solid matrix gives rigidity to the nonlinear medium and the handling is more convenient. Therefore for a device application the polymeric solid matrix may be preferred over the monomeric solution phase. The concentration dependence on the optical limiting nature is studied both in liquid as well as in solid medium and the role of RSA in the limiting behaviour is verified.
3.8 References

Chapter 3: Nonlinear optical