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Nonlinear characterization of Mercurochrome dye for potential application in optical limiting

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Thermally induced optical nonlinearity of Mercurochrome dye in methanol solution at four different concentrations and as solid films mixed with polymethylmethacrylate (PMMA) has been carried out using a CW Nd-YAG laser at 532 nm as the source of excitation. The optical response was characterized by measuring the intensity dependent refractive index n_2 of the medium using the *Z*-scan technique. The dye exhibited a negative (defocusing) nonlinearity and large nonlinear refractive index of the order of 10^{-7} cm^2/W. The nonlinear refractive index was found to vary with concentration. The third-order nonlinearity of the dye was dominated by nonlinear refraction, which leads to strong optical limiting of laser. Optical limiting characteristics of the dye at various concentrations in solution and film were studied. The result reveals that Mercurochrome dye can be a promising material for optical limiting applications.

Keywords: *Z*-scan, Mercurochrome dye, nonlinear optical (NLO) properties, optical limiting.

1. Introduction

Rapid technological advancements in optics have placed great demand on the development of nonlinear optical (NLO) materials with prominent applications in optical limiting and all optical switching [1–3]. Extremely large number of organic compounds with delocalized electron and conjugated double bond systems and a large dipole moment have been synthesized to realize the susceptibilities far larger than the inorganic optical materials [4].

Z-scan technique [5, 6], based on the spatial distortion of a laser beam passed through a NLO material, is widely used in material characterization because of its simplicity, high sensitivity and well-elaborated theory. The opportunity to conduct simultaneous measurements of various NLO parameters in one set of experiments also makes this technique attractive and applicable for different materials. This method yields both the sign and the magnitude of the nonlinearity, and the value of the nonlinear refractive index n_2 may be easily extracted from experimental data with

a minimum of analysis [7–9]. *Z*-scan studies also yield important information regarding the response time and the dynamics of the transient processes contributing to the nonlinear refractive index [10].

Xanthene dyes are of great interest because they have long phosphorescence lifetime and strong optical absorption at low intensity levels. These dyes were identified and characterized as materials suitable for optical phase conjugation (OPC) by degenerate four wave mixing (DFWM) and optical limiting applications in solid matrices of gelatin, polyvinyl alcohol (PVA), polymethylmethacrylate (PMMA), and boric acid glass [11]. In the present study, Mercurochrome dye from fluorone group which is a sub group from xanthene family is chosen, because the dyes cover the wavelength region from 500 to 700 nm and are generally very efficient.

Optical limiting is a nonlinear optical process in which the transmitted intensity of a material decreases with increased incident light intensity. Optical limiting performance will be enhanced by coupling two or more of the nonlinear optical mechanisms. Excited state absorption (ESA) and reverse saturable absorption (RSA) are the most common mechanisms for the nonlinear optical behavior of organic materials [12]. Nonlinear optical effects can be employed for the design and performance of optical limiter [13–15]. It has been demonstrated that optical limiting can be used for the protection of eyes and sensors from intense lasers [16]. In this paper, the optical nonlinearity and optical limiting action of dye in methanol solvent and thin film using PMMA at 50 mW CW Nd-YAG laser power at the wavelength of 532 nm was studied. The experiment was repeated for different dye concentration and the third order nonlinear refractive index was found to be linearly dependent on the dye concentration within the range studied.

2. Experiment

2.1. Materials

Mercurochrome dye obtained from S.D. Fine Chemicals, India, was chosen for the study. The molecular structure of the dye is shown in Fig. 1. Thin layer chromatography (TLC) test confirms the absence of any impurities in the dye. Methylmethacrylate (MMA) (Lancaster) was chosen as a monomer for synthesizing a dye doped polymer film. Spectroscopic grade methanol was chosen as additive; because it has good

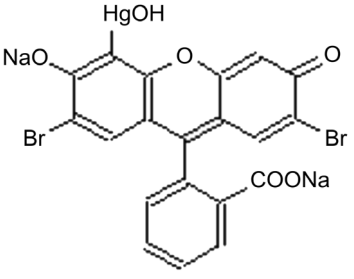

Fig. 1. Chemical structure and molecular formula of Mercurochrome dye ($C_{20}H_8Br_2HgNa_2O_6$).

solubility for the dye and enhances the laser damage threshold. Benzoyl peroxide was used as the initiator.

2.2. Synthesis of dye doped polymer films

Methylmethacrylate (MMA) is used as the monomer for the preparation of the dye doped polymer (DDP) films. MMA and methanol are taken in the ratio 4:1 (v/v). Known weight of the dye is dissolved in this mixture. 0.5 g of benzoyl peroxide, per 100 ml of MMA solution, is used as an initiator for polymerization. The solution taken in polymerizing tubes is deoxygenated in a nitrogen stream, and the glass containers are sealed. Thermal bulk free-radical polymerization [17, 18] is carried out in a temperature controlled water bath and the temperature is maintained at 35 °C for 2 days and at 40 °C for another 2 days till the solution becomes viscous. The DDP films of desired concentrations are synthesized by pouring the viscous dye solution with initiator mixture onto a Petri dish placed in a glass enclosure to prevent from dust, during natural drying. The optical quality of this film is checked by passing He-Ne laser beam of power 5 mW. Film which shows no distortion or dispersion of the laser beam alone is taken for further studies. The dye doped polymer films of concentration 0.03×10^{-3} M to 0.1×10^{-3} M and thickness of 0.93–0.98 mm were synthesized.

2.3. Absorption spectra

The UV-VIS absorption spectrum of the dye in methanol solvent was obtained using a spectrophotometer (Perkin–Elmer Lamda 35) and is shown in Fig. 2. The spectral parameters, such as absorption-peak wavelength, molar-extinction coefficient $\varepsilon(\lambda)$, oscillator strength f, bandwidth $\Delta\nu_{1/2}$, were calculated to be 516 nm, 5.936×10^4 L mol^{-1}cm^{-1}, 0.596×10^{-24} L mol^{-1}cm^{-2} and 2.32×10^3 cm^{-1}, respectively.

2.4. *Z*-scan technique for determining the nonlinear refractive index

A diode-pumped Nd:YAG laser of wavelength 532 nm (Coherent Compass TM 215M-50) is used as the excitation source for the *Z*-scan technique. The laser of Gaussian beam profile was focused by a convex lens, of focal length $f = 3.5$ cm,

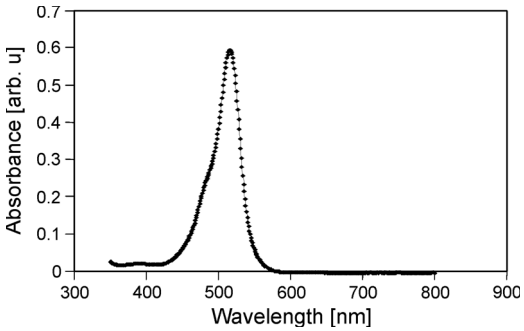

Fig. 2. UV-VIS absorption spectrum of Mercurochrome dye.

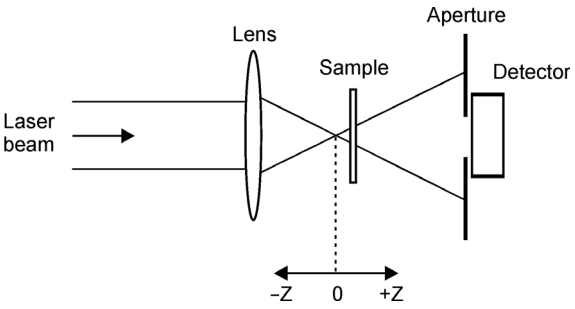

Fig. 3. Experimental set-up for *Z*-scan.

to produce a beam thickness ω_0 of 20 μm. The peak intensity of the incident laser beam is $I_0 = 4.11$ kW/cm^2. The diffraction length z_R was found to be 2.36 mm. The schematic diagram of the experimental set-up used is shown in Fig. 3. A 1 mm wide optical cell containing the dye in solvent is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The transmission of the beam through an aperture placed in the far field is measured using photo detector fed to the digital power meter (Field Master Gs-coherent). For an open aperture *Z*-scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture. The same was repeated for the polymer film.

2.5. Optical limiting technique

The limiting effect of the Mercurochrome dye was studied by using a 50 mW Nd-YAG CW laser at 532 nm. The experimental set-up for the demonstration of optical limiting is shown in Fig. 4. A 1-mm quartz cuvette containing nonlinear material (sample

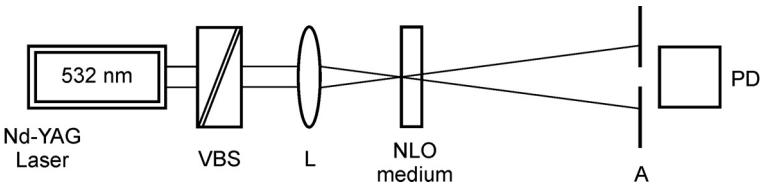

Fig. 4. Experimental set-up for measuring limiting effect.

solution) is kept at the position where the transmitted intensity shows a valley in closed aperture *Z*-scan curve [19]. A variable beam splitter (VBS) was used to vary the input power. An aperture A of variable diameter is used to control the cross-section of the beam coming out of the sample cuvette. This beam is then made to fall on the photo detector (PD). The input laser intensity is varied systematically and the corresponding output intensity values were measured by the photo detector. At very high peak intensities (closer to the focus) we could observe diffraction type pattern with concentric ring structures probably due to self-phase modulation. However, in limiting

experiments we have ensured that there is no ring pattern formation by placing the sample away from focus.

3. Results and discussion

The Mercurochrome dye in methanol and polymer films at various concentrations for the incident intensity $I_0 = 4.11$ kW/cm^2 were evaluated by the measurements of *Z*-scan. The saturation absorption for the dye in solvent and polymer film is shown by the open *Z*-scan curve in Fig. 5. The transmission at the focus decreases with increasing sample concentration. At higher concentration, the sample gives better NLO properties. Absorption saturation in the sample enhances the peak and decreases the valley in the closed aperture *Z*-scan and results in distortions in the symmetry of the *Z*-scan about $z = 0$. The peak followed by a valley-normalized transmittance curve obtained from the closed aperture *Z*-scan data, indicates that the sign of the refraction nonlinearity is negative, *i.e.*, self-defocusing. The self-defocusing effect is due to the local variation of the refractive index with temperature.

The defocusing effect for the dye in solvent and polymer film shown in Fig. 6 are attributed to a thermal nonlinearity resulting from the absorption of radiation at

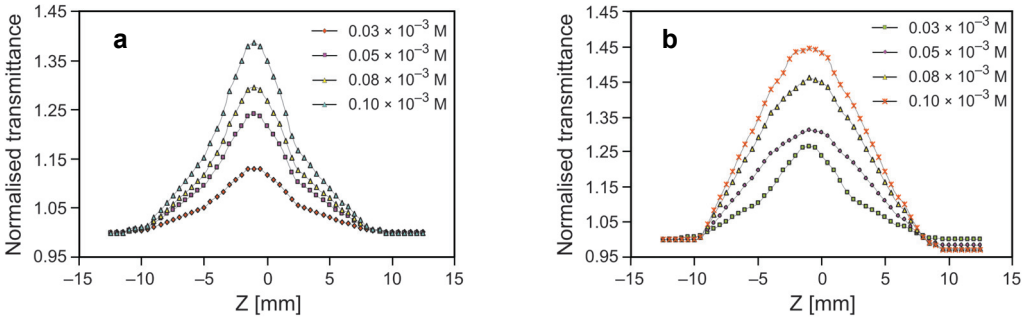

Fig. 5. Open *Z*-scan curve at various concentration. Dye in solvent (**a**), polymer film (**b**).

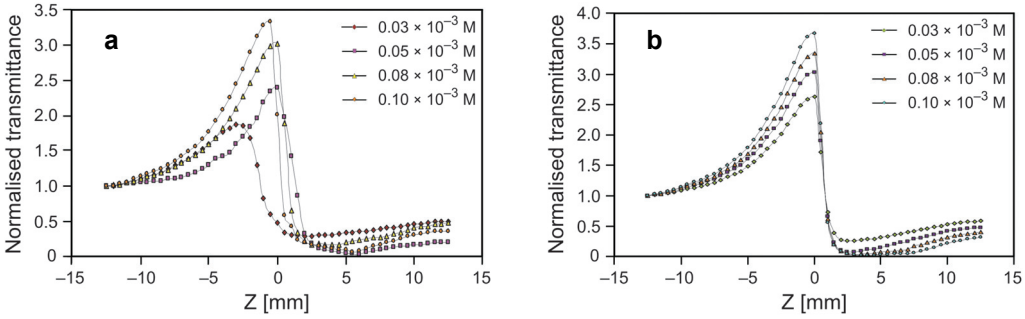

Fig. 6. Closed *Z*-scan curve at various concentration. Dye in solvent (**a**), polymer film (**b**).

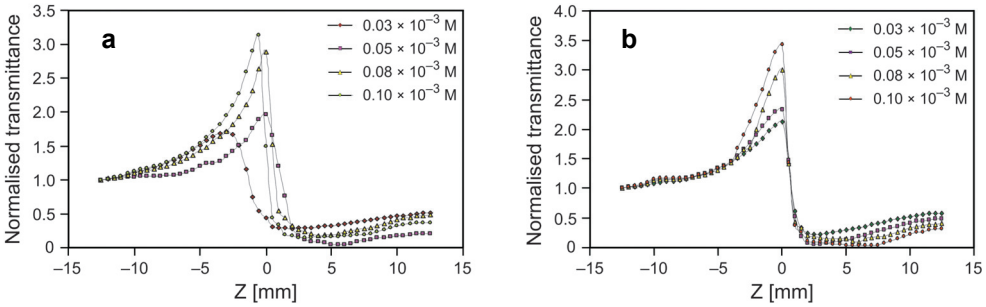

Fig. 7. Pure nonlinear refraction curve at various concentration. Dye in solvent (**a**), polymer film (**b**).

532 nm. The measurable quantity ΔT_{p-v} can be defined as the difference between the normalized peak and valley transmittances. The pure nonlinear refractive index n_2 was obtained by dividing the closed aperture data by the open aperture data [6]. The pure nonlinear refraction *Z*-scan curves are shown in Fig. 7 for the dye in solvent and polymer film. Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in finding the absolute value of the third-order nonlinear optical susceptibility. In order to know the contribution from the solvent to the observed nonlinear response, the *Z*-scan was performed on pure solvent. Neither nonlinear absorption nor nonlinear refraction was observed. The value of ΔT_{p-v} has increased for the dye doped polymer film when compared to the dye in methanol. This may be due to the heat dissipation being faster in liquids as compared to that in a solid medium. The experimentally determined values of ΔT_{p-v}, n_2, β, Δn and χ^3 are given in the Table. The values of n_2 in a dye doped film is found to have larger values than in the case of solutions [20], as it is due to Anderson localization of photons. This is because of the strong scattering regime as the scattering mean free path of photons is less than in the case of liquids, so the localization of strong electromagnetic field inside the solid is responsible for the increase in nonlinearity in optical materials.

T a b l e. Nonlinear parameters of Mercurochrome dye in methanol.

Concentration		ΔT_{p-v}	$n_2\times10^{-7}$ [cm^2/W]	$\beta\times10^{-3}$ [cm/W]	$\Delta n\times10^{-4}$	$\lvert\chi^3\rvert\times10^{-6}$ (e.s.u.)
0.03×10^{-3} M	Solvent	1.55	–1.00	–1.10	–4.00	4.38
	Polymer film	2.37	–1.89	2.31	–7.55	8.30
0.05×10^{-3} M	Solvent	2.36	–1.52	–1.88	–6.08	6.67
	Polymer film	2.95	–2.34	–2.80	–9.40	10.3
0.08×10^{-3} M	Solvent	2.85	–1.84	–2.31	–7.36	8.07
	Polymer film	3.31	–2.631	–4.05	–10.5	11.6
0.10×10^{-3} M	Solvent	3.23	–2.08	–2.98	–8.35	9.16
	Polymer film	3.66	–2.92	–4.81	–11.7	12.8

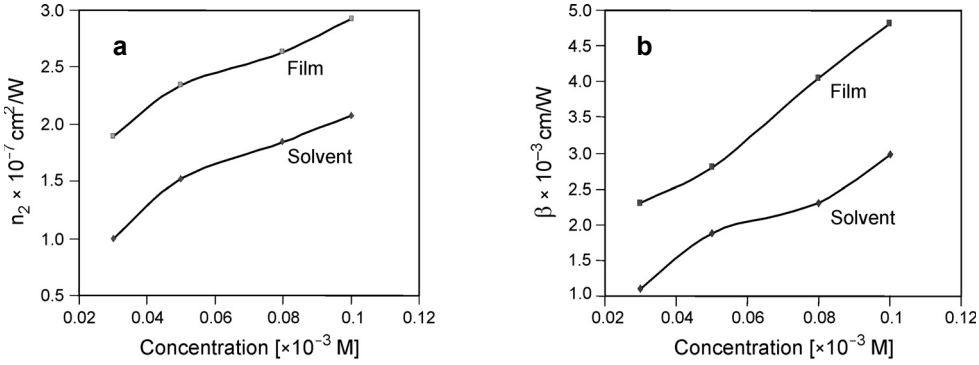

Fig. 8. Concentration dependence n_2 (**a**) and β (**b**) of Mercurochrome dye in methanol and polymer film.

Pure PMMA matrix showed no *Z*-scan signal. From Fig. 8, there is an increasing trend for the values of n_2 and β as the concentration increases. This may be attributed to the fact that the number of dye molecules increases as the concentration increases, and more particles are thermally agitated resulting in an enhanced effect. With increasing dye concentration there is an increase in dimmer concentration. These dimmers have shorter wavelength than monomers and are weakly fluorescent. Thus, for the incident radiation, the fraction absorbed by non-fluorescent dimmers eventually raises the temperature of the medium.

The source used to probe the nonlinear material is a continuous wave laser; the optical nonlinearity of the dye, observed here is likely to be of thermal origin arising from the temperature dependence of the refractive index of a sample which acts as a lens. The phase of the propagating beam will be distorted due to the presence of this thermal lens. The peak–valley separation of more than 1.7 times of Rayleigh range of –0.24 cm also suggests the presence of thermal component. It is well established that the separation of $1.7Z_0$ indicates Kerr type of nonlinearity [21].

The optical limiting curves obtained with a 50 mW Nd:YAG laser of wavelength 532 nm for the dye in solution at different concentrations and dye doped polymer film are shown in Fig. 9. The output power rises initially with an increase in input power, but after a certain threshold value the samples start defocusing the beam, resulting in a greater part of the beam cross-section being cut off by the aperture. Thus the transmittance recorded by the photo detector remained reasonably constant showing a plateau region. At incident power above 20 mW, the output power tends to be constant, because its nonlinear absorption coefficient increases with an increase in the incident irradiance. In liquids, where the thermal expansion is large, high absorbance of the nonlinear material at the corresponding wavelength leads to an increase in temperature and density of the sample. Heating due to laser absorption is responsible for changing the absorption coefficient and optical limiting effect [22].

Separate optical limiting experiment was performed on pure methanol and it is found to have no contribution to optical limiting in the power range of the laser used.

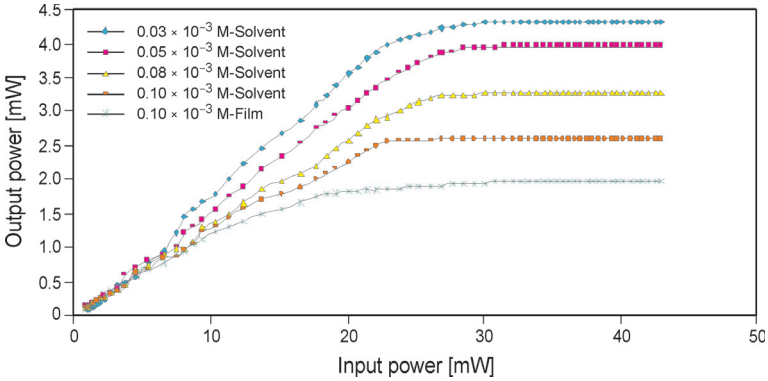

Fig. 9. Optical limiting effects of the dye in solvent and polymer film.

The UV-VIS absorption spectrum of the samples before and after the laser irradiation shows that the pattern and intensity of the spectrum do not show any change, indicating that the samples possess good photo stability. The dye investigated here is very weakly fluorescent and is non fluorescent at the wavelength studied, optimizing the conversion of the absorption energy into heat [22]. The optical limiting effect shows an increase with increasing the concentration of the dye solution. The results were comparable to some of the reports of low power optical limiting [23]. So the sample possesses limiting effect for the light of 532 nm.

4. Conclusions

The third order nonlinear optical properties and optical limiting behavior of Mercurochrome dye have been studied. Both nonlinear absorption (NLA) and nonlinear refraction (NLR) contribute to the large third-order nonlinearity of the dye. It is worth noting that the value of χ^3 for the dye studied is larger than those of some representative third-order nonlinear optical materials, such as chalcone and its derivatives and organic dyes like croconium [24, 25]. The origin of optical nonlinearity observed in the CW regime is attributed to the thermal variation of refractive index in the medium. The aperture limited designs based on thermo-optic nonlinearity, such as the one studied here, can be used as efficient limiters in the CW regime.

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