Measurement of nonlinearity and spectral study of a laser dye

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ABSTRACT

The third order nonlinear optical properties of organic Polymers are used in high speed telecommunications, optical limiters and optical; computes. The purpose of study was to determine the spectral and third order nonlinear characteristics of the organic dye, victoria blue in liquid and in solid medium. The samples were prepared by dissolving the dye in n-butyl acetate (liquid medium) and a thin film of thickness 1mm was prepared by bulk polymerization method. The spectral characteristics of victoria blue dye doped poly(methylmethacrylate) modified with additive n-butyl acetate (nBA) are studied by recording its absorption and fluorescence spectra and the results are compared with the corresponding liquid mixture. The nonlinear refractive index of the dye in nBA and dye doped polymer film were measured using z-scan technique (Mansoor Sheik-Bahae et al.,1990), by exciting with He-Ne laser. The results obtained are intercompared. Both the samples of dye victoria blue in liquid and solid medium show a negative nonlinear refractive index. A negative nonlinear dye doped films can be used as optical limiters. The origin of optical nonlinearity in the dye may be attributed due to laser-heating induced nonlinear effect.

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Keywords: Victoria blue : solid dye laser; nBA; MMA; victoris bluet ; nonlinear refractive index
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INTRODUCTION:

Rapid technological developments in optics have placed great demand on the development of nonlinear optical (NLO) materials.The use of solid state dye lasers gets rid of many of the common problems associated with static or flowing liquid systems. The most frequently used polymeric material is polymethylmethacrylate (PMMA) (Somasundaram et al.,2000). The low solubility of dye in PMMA causes limitations, which is overcome by introducing modifying additives.

A review of literature showed that most of the work on dye-doped polymers has been done with Rhodamine dyes (Costela et al .,1997; .Dyanamaev et al., 1992) and pyromethane dyes. Some works are reported on coumarin dyes (.Somasundaram et al.,2000) The study of nonlinear refractive index on dye IR140(Umakanta Tripathy et al ., 2002) , has been reported. No work has been reported on the study of nonlinear refractive index of the dye victoria blue. The physical origin of nonlinear refraction can be electronic, molecular, electrostrictive or thermal. Historically , the first optical limiter was based on thermal mechanism

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with a cw laser (Leite et al., 1967). Recently, thermal effects have been shown to be efficient even with nanosecond pulses (Justus et al., 1993; Pascale Brochard et al ., 1997). In this paper, we have studied the spectral characteristics and nonlinear properties of the dye victoria blue in both the polymer and the corresponding monomer compositions in detail.

MATERIALS AND METHODS

The laser dye, Victoria blue obtained from Exciton Inc., USA was chosen for this study. Thin layer chromatography (TLC) test confirms the absence of any impurities in this dye. Methyl methacrylate (MMA) (Lancaster) was used as monomer. Initial MMA compositions were cleared of foreign inclusions. Spectroscopic grade n-butyl acetate (nBA) purchased from Merck. (India), was chosen as an additive because it combines good solubility for victoria blue dye.

2.1 Synthesis of dye-doped polymer rod and film
The dye-doped polymer rod of dye concentration 0.05×10^{-3}M was synthesized by thermal bulk free radical polymerization method (Costela et al., 1996). MMA and nBA were taken in the ratio 4:1(v /v). Known weight of dye was dissolved in this mixture. 3g of 2,2azobis (isobutyronitrile) per litre of MMA solution was used as an initiator for polymerization .The solution was put into a polymerization tube and kept in the nitrogen atmosphere. Bulk polymerization was carried out in a temperature controlled water bath and the temperature was maintained at 35°C for 2 days, at 40°C for another 2 days and at 50°C for 7 days . The polymerized rod was removed by breaking the glass tube. Rod (length 3cm: diameter 1cm) obtained, was cut, ground and polished to optical quality required. The internal optical qualities of polymer rod were checked by passing the He-Ne laser beam of 5mW through the rod. No dispersion or distortion of the He-Ne laser beam was observed. The dye doped polymer thin film of concentration 0.05×10^{-3}M was prepared by pouring the viscous dye solution with initiator mixture on to a glass slide placed inside a glass enclosure, kept at a temperature of 40°C in temperature controlled water bath.

2.2 Spectral characteristics, Quantum yield
The spectral properties of the dye are studied by recording the absorption and fluorescence spectra of dye in MMA, in nBA, in a mixture of MMA and nBA (liquid medium) and in the solid matrix (PMMA modified with nBA) using Hitachi U2000 spectrophotometer and Hitachi F2000 spectrofluorometer respectively. The fluorescence spectra were corrected using quinine sulphate in $0.1N\ H_2SO_4$ and fluorescein in 0.1N NaOH (Govindanunny et al., 1980). Care was taken to record all spectra under identical conditions. These spectra are shown in FIG.1, 2. Quantum yields (Demas et al., 1971) were calculated using Rhodamine 6G (Rh 6G) in ethanol as the fluorescence standard with refractive index and differential absorption correction. The absorbance of Rh 6G in ethanol at 500nm is 0.66 and the reported quantum yield of the dye Rh 6G is 0.95 (Kubin et al 1982). The spectral parameters such as absorption peak wavelength (peak λ), molar extinction coefficient (ϵ), bandwidth ($\Delta\mathrm{v}_{1/2}$), oscillator strength (F),fluorescence peak wavelength (peak λ), full width at half maximum (FWHM), fluorescence quantum yield ($\emptyset_f$), Stoke's shift of the dye were calculated and are shown in TABLE.1.

2.3 Nonlinear studies
The closed z-scan set up is shown in FIG 3. A He-Ne laser (632.8nm, power 10mW) was used as the light source. The dye doped polymer film was used as sample of thickness 1mm. The transmittance of the nonlinear medium through a finite aperture in the far field as a function of the sample position z was measured by using a positive lens having a focal length f = 4 cm. The results obtained are compared with the dye in nBA. The liquid was filled in the sample cell with a path length of 1mm.The beam waist (ω_0) of He-Ne laser was calculated using the formula $\omega_0 = 1.22\lambda$ f / d (d is the diameter of the aperture in front of the focal lens, f is the focal length of the convex lens used in the set up) and is found to be 75μm with a Rayleigh range of 27.91mm. The transmitted energy was measured using PMT (RCA 931) connected to an oscilloscope (OS768A) in a far field. Care was taken that PMT does not get saturated.

As the monomer (MMA) does not introduce any nonlinearity, the experiment was performed only for the dye in nBA. FIG.4, 5 show the z-scan of the dye victoria blue in nBA and thin polymer film respectively .

Fig.6 shows the optical limiting curves obtained with a He–Ne laser input of wavelength 632.8 nm for victoria blue

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in solvent nBA and polymer film.The samples show very good optical lim-iting behaviour arising from nonlinear refraction. The output power rises initially with 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 photodetector remained reasonably constant showing a plateau region.

RESULTS

The absorption and fluorescence spectral profiles of the dye in liquid and in solid media are identical. This indicates that at low concentrations, the dye exists only in its monomeric form inside a polymer matrix and that at such low concentration there is a given amount of free volume within the polymeric matrix in which the dye molecules distribute in a way to what happens in a diluted liquid solution of the dye (Amat-Guerri et al ., 1993).

The peak wavelength of absorption and fluorescence of victoria blue in the solid matrix shows a blue shift from that in the liquid media. These changes may be attributed to the structure of dye. The spectral changes of the dye in the solid matrix and liquid media may also be due to the changes in the dielectric constant of the respective media.
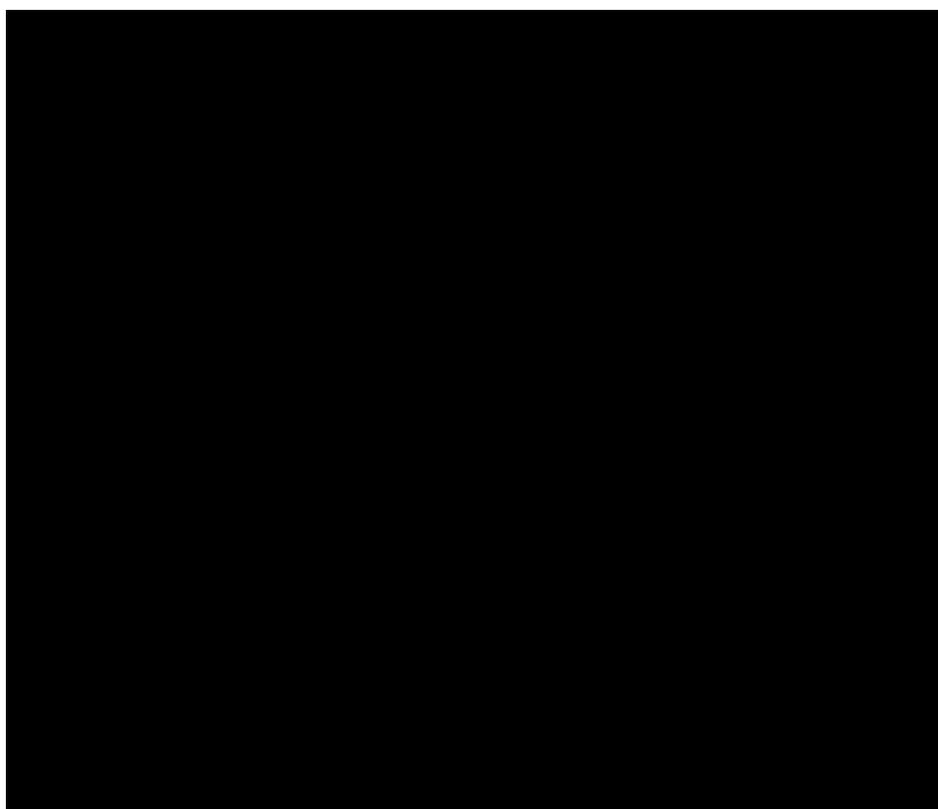

Figure.1 Absorption spectra of dye victoria blue in (a) MMA (b) MMA+ nBA (c) nBA (d) PMMA+nBA

The absorption bandwidth and the fluorescence bandwidth of the dye victoria blue are broader in solid matrix than in liquid medium. The spectral characteristics of the lasing dye in polymer depend on the intermolecular interaction between the dye molecule and macromolecules.

The Stoke's shift of the dye in solid matrix is more than that in the liquid medium. The Stoke's shift of the dye molecule in the solid matrix depends on the difference in the dipole moments between the ground state and the excited state of the dye molecules . The Stoke's shift also depends on the size, polarity and relaxation time of the additive molecules.
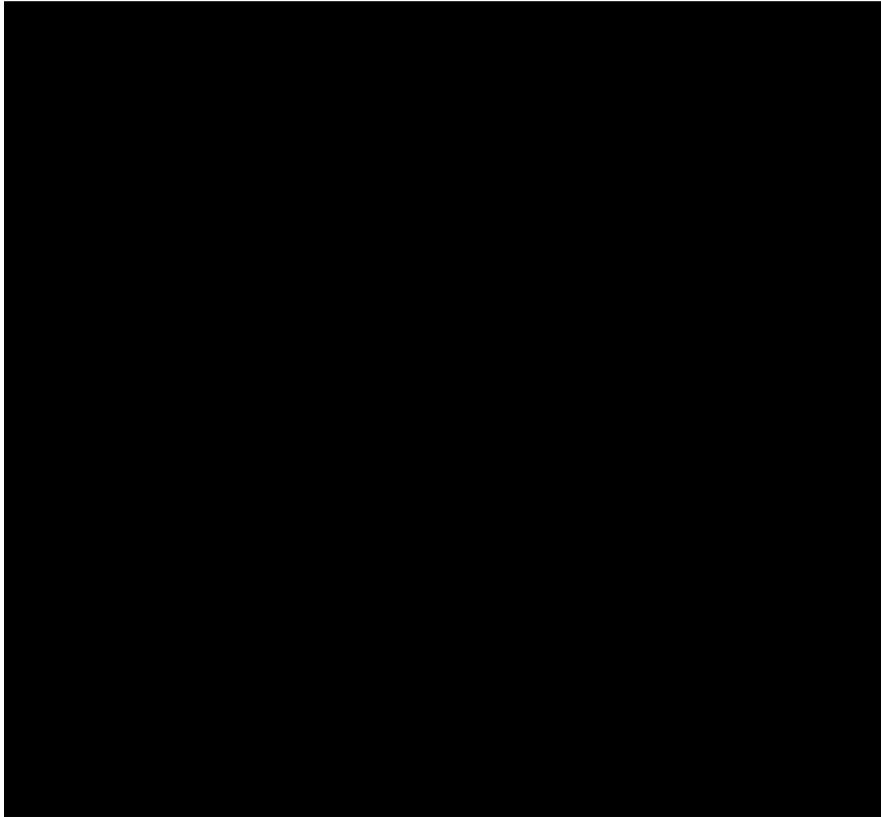
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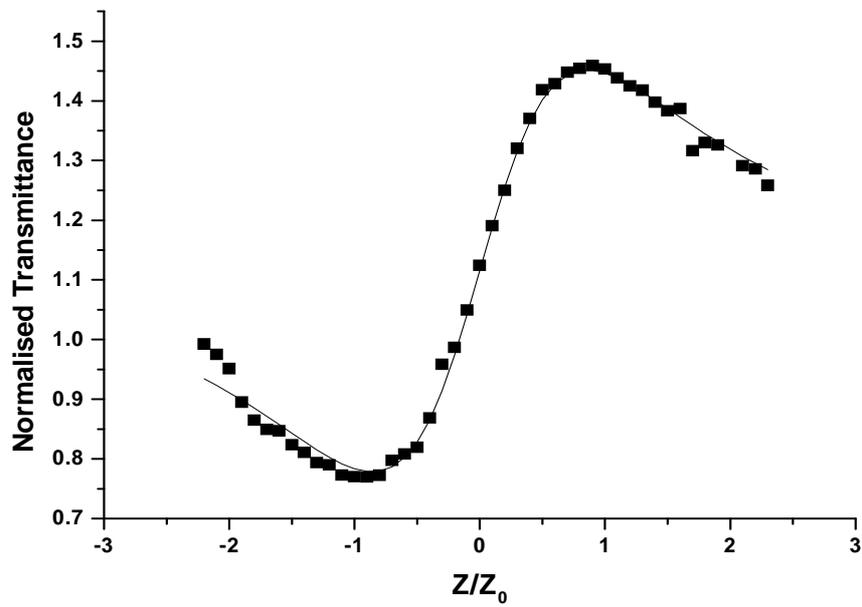**Figure.2 Fluorescence spectra of dye victoria blue in (a) MMA (b) MMA+ nBA (c) nBA (d) PMMA+nBA**

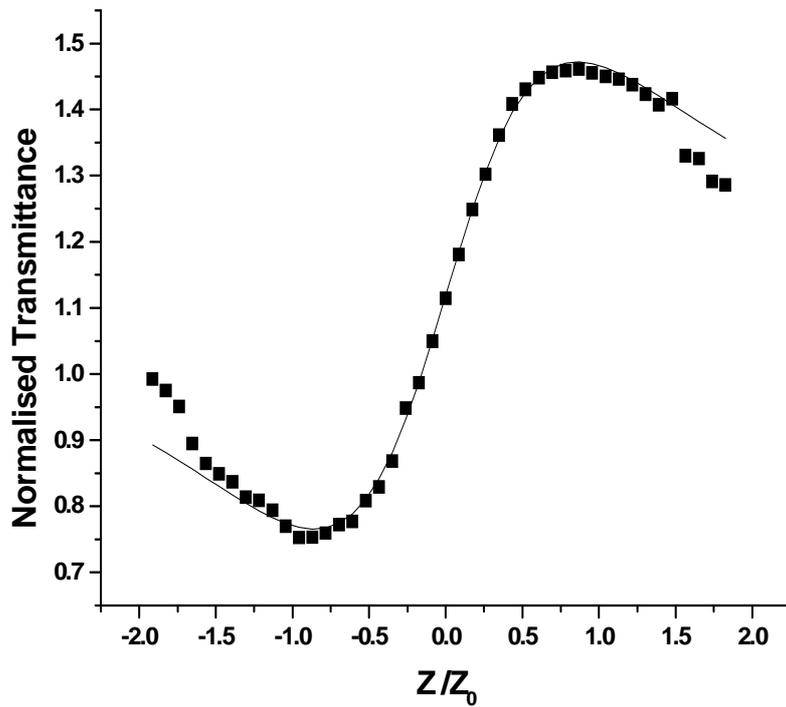**Figure.4 Measured z-scan of the dye victoria blue in nBA. The solid line is the calculated result with $\Delta\emptyset_o$ =1.72**

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Figure.5 Measured z-scan of the dye victoria blue doped polymer film . The solid line is the calculated result with ΔØₒ =1.77.
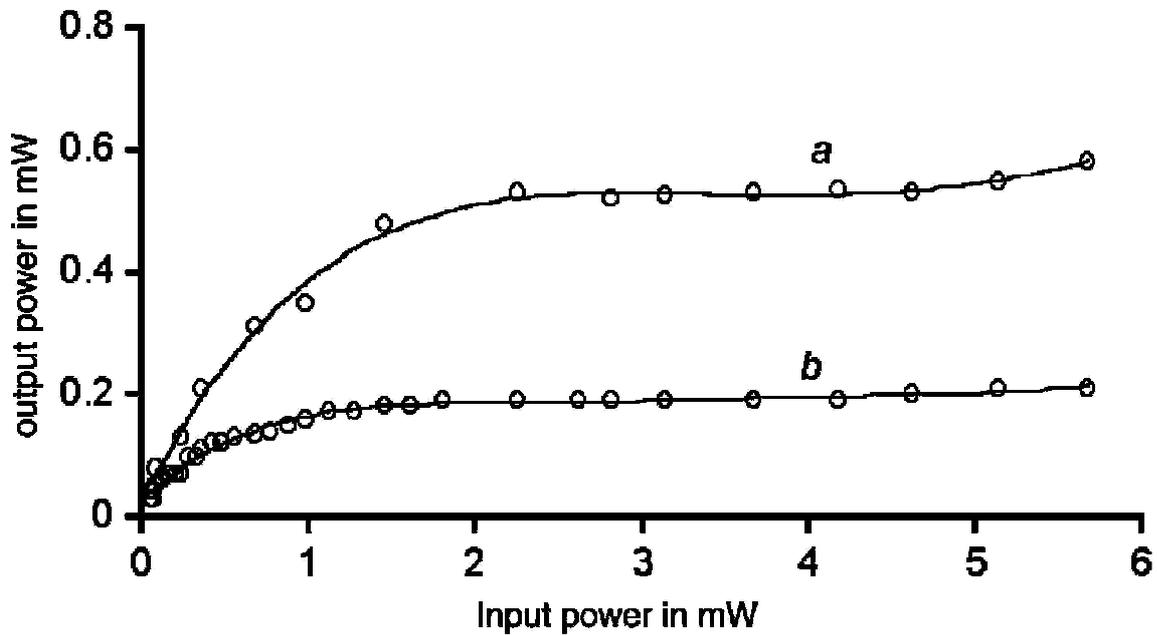

Figure.6   Optical Limiting of Victoria Blue in (a)nBA (b) in polymer thin film
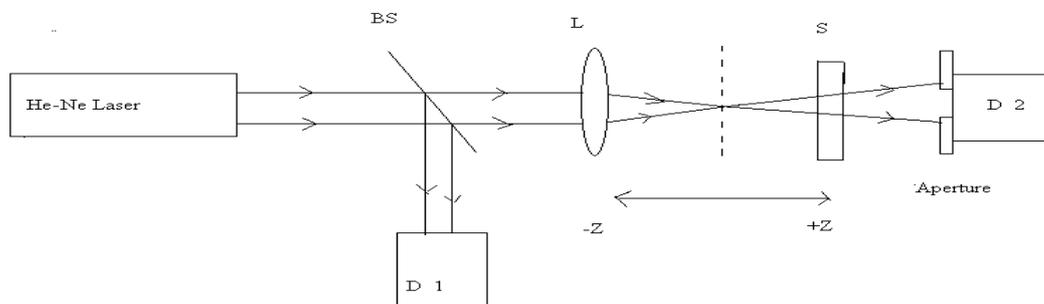
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Figure.3 The closed z-scan set up. D1,D2 – detectors, BS beam splitter, L – convex lens, S- sample

Analysis of nonlinearity in the   dye victoria blue shows   that the dye has a negative (self-defocusing) nonlinearity. Self-defocusing effect is due to   local variation of   refractive index with temperature. A pre-focal   transmittance minimum(valley) followed by a post-focal transmittance maximum (peak) in the z-scan experiment is a signature of positive nonlinearity. The z-scan signature for the dye victoria blue in nBA gives the value of the transmission from peak to valley (ΔT_{p-v}) is 0.19, which shows   an index change of $\langle\Delta n_o\rangle$= - 5.067×10^{-6} , calculated using the   formula, $\Delta\emptyset_o$ = k Δn_o L_{eff} , where k is the wave vector, L_{eff} = (1 - $e^{-\alpha\ L}$) / α , with   L the sample length and α the linear absorption coefficient. This value of $\langle\Delta n_o\rangle$ corresponds to the value   of nonlinear coefficient of refractive index γ = - 4.47×10^{-12}m^2/W, found using Δn_o = γ I_0 with I_0 being the on-axis irradiance at focus of the lens. The results are compared with dye doped polymer film which shows the value of transmission from peak to valley (ΔT_{p-v}) as 0.201 giving an index change of $\langle\Delta n_o\rangle$= - 5.22 $\times$ 10^{-6}. This value of $\langle\Delta n_o\rangle$ corresponds to the value of γ = - 4.61×10^{-12}m^2/W. The optical nonlinearity   in this dye   may be due to laser heating induced nonlinear effect. A laser beam, while passing   through an absorbing media, induces temperature and density   gradients   that change the refractive index profile. This intensity-induced localized change in the refractive index results in a lensing effect on the optical beam . The value of (ΔT_{p-v}) has increased for the dye doped polymer film when compared to the dye in nBA . This may be due to the heat dissipation in liquid is fast when compared to the polymer film. And it is this heat inducing a hike in (ΔT_{p-v}) value in   polymer   film.

Table . 1 Spectral characteristics, quantum yield, of the dye Victoria blue

Solvent/Medium	Absorption spectra				Fluorescence spectra		
	Peak wavelength in nm	ε 10^4 L mol^{-1} cm^{-1}	$(\Delta v)_{1/2}$ cm^{-1}	Oscillator Strength f 10^{-24} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}
MMA	550	2.934	4430.3	0.5628	585	96.25	1087.8
MMA and nBA	560	1.908	5615.2	0.4639	628	105	1933.5
nBA	480	1.318	5267.9	0.3	555	116.25	2815.3
PMMA modified with nBA	500	1.6386	5429.8	0.397	552	115	1884.05

CONCLUSION

The spectral characteristics of dye victoria blue in liquid and solid environments have been studied in detail. Nonlinear studies show that the Victoria blue show a negative nonlinear refractive index. This dye doped polymer can be utilized in optical limiting, low-power degenerate four wave mixing, data storage and gating applications. Nonlinear refraction in the membrane is used to obtain optical limiting behaviour in an aperture-limited geometry. The origin of optical nonlinearity ob-served in the CW regime is attributed to the thermal variation of local refractive index in the medium.

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