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Third Order Optical Nonlinearity of Dye Doped Polymer

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Abstract: The conventional liquid dye solution are replaced by solid–state dye-doped polymer. In this paper the spectral characteristics and the nonlinear optical properties of the dye Congo red in polymethylmethacrylate is studied. The spectral characteristics are studied by recording steady state absorption and fluorescence spectra. Thermally induced nonlinearity of congo red dye in n-butyl Acetate is studied using cw He-Ne laser at 632.8 nm as source of excitation, both in solution and solid film. The property of dye in solid matrix is compared with that in liquid medium. The optical response is characterized by measuring the intensity dependent refractive index (n2) of the medium, using z- scan technique. The origin of optical nonlinearity in this dye may be attributed due to laser-heating induced nonlinear effect. The dye exhibited negative (defocusing) nonlinearity and it can be a promising material for optical limiting applications.
OCIS Codes:230.0230, 300.0300, 140.0140.
Keywords: Congo red; solid dye laser; nonlinear refractive index; nonlinear optics; polymer film; z scan.

1. Introduction:

The protection of sensitive optical equipment has been the focus of much attention in recent times. Of great importance is the protection of human eye from potentially harmful intense beams. A large number of compounds have been synthesized to realize nonlinear susceptibilities far larger than the inorganic optical material [1]. In this paper we report the synthesis, characterization and nonlinear optical properties of congo red dye doped polymer and compare it with dye doped monomer. Nonlinear optical properties of polymer solution were studied by means of a z-scan set-up. Nonlinear optical effects can be employed for the design and performance of optical limiter. It has been showed that optical limiting can be used for the protection of eyes and sensors from intense lasers[2].

The use of solid matrix for 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) [3].Review of literature showed most of the work on dye-doped polymers was done with rhodamine dyes [4-6] and pyromethane dyes [7, 8]. Some work were reported on coumarin dyes [3].The study of nonlinear refractive index on dye IR140 [9], the work on reverse saturable absorption and optical limiting properties of the dye cresyl violet [10] were reported. In this paper, the fabrication of dye congo red doped polymer rods and films, its spectral parameters and the study of nonlinear refractive index under the He-Ne laser excitation are reported. The properties of the dyes in liquid medium are compared with that in the solid matrix.

2. Experimental procedure:

2.1 Synthesis of dye-doped polymer rods and thin films

The Congo red dye, a triphenyl methane dye, supplied by Exciton, USA, is chosen for the study. The molecular structure of the dye is shown in figure.1. Thin layer choromatography (TLC) test confirms the absence of any impurities in the dye. Methyl methacrylate (MMA) is used as a monomer for synthesizing dye doped polymer film. Initial MMA compositions are cleared of foreign inclusions. Spectroscopic grade n-butyl acetate (nBA) is used as additive; because used as the initiator. The dye doped polymer film (DDP) is synthesized using thermal bulk free radical polymerization [11].

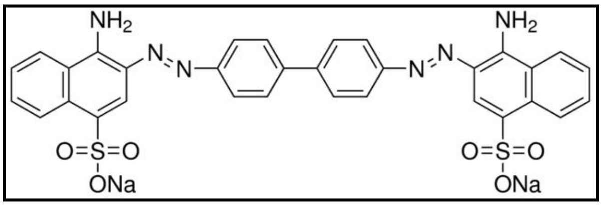

Figure.1 Molecular Structure of congo red

The DDP rods and polymer film of dye concentration 0.05× 10-3M are synthesized. The internal optical qualities of polymer rods and films are checked by passing the laser beam of 5mW He-Ne laser (632.8nm) through these rods. No dispersion or distortion of the He-Ne laser beam was observed.

2.2 Spectral characteristics

The spectral properties of the dyes are studied by recording the absorption and fluorescence spectra of these dyes in MMA, nBA, MMA and nBA (liquid medium) and the solid matrix (PMMA+nBA) using Hitachi U2000 spectrophotometer and Hitachi F2000 spectrofluorometer respectively. These spectra are shown in figure.2, 3. The parameter calculated are tabulated in Table.1

Table.1 Spectral characteristics of the dye in liquid and solid medium

Solvent/Medium	Absorption spectra				Fluorescence spectra		
	Peak wavelength in nm	ε 10^4 L mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$ cm^{-1}	Oscillator Strength f 10^{-24} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}
MMA	493.75	1.28	6288	0.3485	537.25	78	1436.8
MMA and nBA	500	1.1778	6929	0.3533	532	80	1203
nBA	496.25	1.344	6362	0.3702	530	77.5	1283
PMMA modified with nBA	450	2.658	6004	0.6910	487	115	1688.3

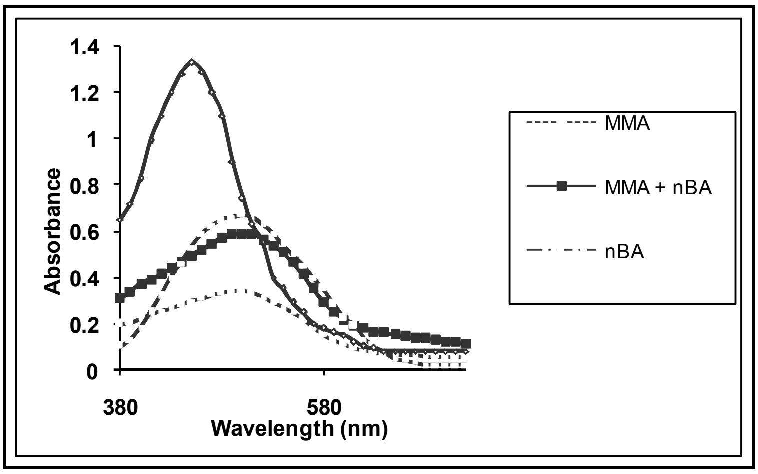

Figure.2 Absorption spectra of dye Congo red in (a) MMA (b) nBA (c) MMA+nBA(d) PMMA+nBA

2.3 Nonlinear studies

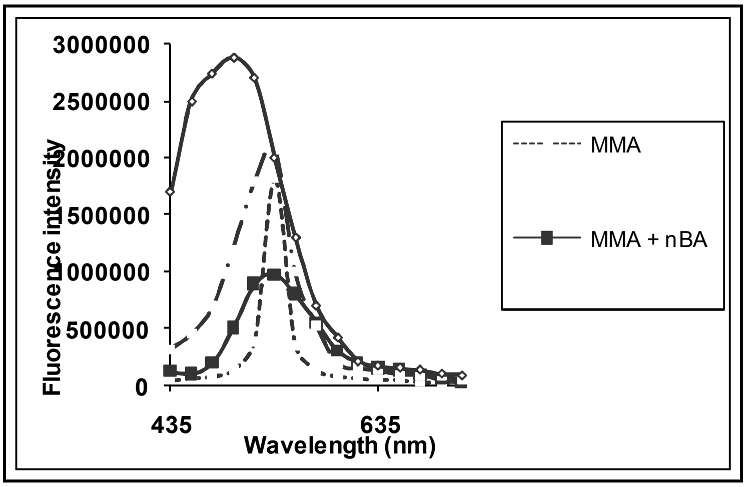

Figure.3 Fluorescence spectra of dye Congo red in (a) MMA (b) nBA (c) MMA+nBA (d) PMMA+nBA

The closed z-scan [15] set up is shown in figure 3. A He-Ne laser (632.8nm , power : 10mW) was used as the light source. The z-scan technique developed by Sheik Bahae et a is a simple technique for us to measure the nonlinear properties and has been used widely in material characterization. It provides not only the magnitude of real and imaginary parts of the nonlinear susceptibility, but also the sign of real part [15] . The transmittance of a nonlinear medium through a finite aperture in the far field as a function of the sample position z is measured with respect to the focal plane. Figure.4 shows the z-scan of the dye congo red. The radius of the beam waist (ωo) was 75μ m with a Rayleigh range of 27.91mm. The transmitted energy is measured using power/energy meter. Care is taken that the absorber is not saturated. The film is more valuable in application than the solution and the discrepancy between films and solutions will greatly affect the behavior of molecules, which will have an obvious influence on their nonlinear properties. Measured nonlinear parameters are shown in Table.2

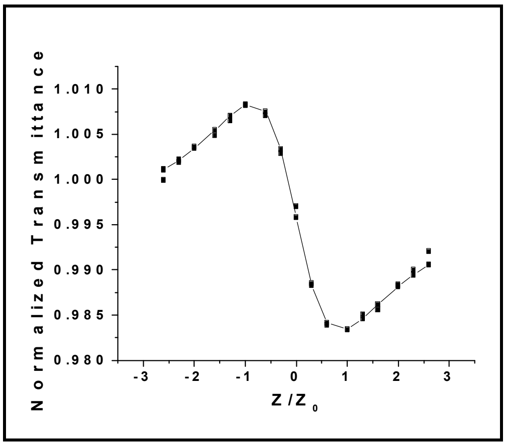

Figure.4 Measured z-scan of the dye Congo red in monomer. The solid line is the calculated result with Øo = -0.0548

Table.2 Non-linear parameters of the dye congo red

Solvent/ Media	ΔT_{p-v}	$\lvert\Delta\varphi_0\rvert$	$< \Delta n_0 >$	γ
NBA	0.0218	- 0.0548	- 5.73 x 10^{-7}	- 5.06 x 10^{-13}
Dye doped polymer film	0.0248	- 0.622	- 6.483 x 10^{-7}	- 5.725 x 10^{-13}

3. Results

Analysis of nonlinearity of the dye congo red showed a negative (self-defocusing) nonlinearity .A pre-focal transmittance maximum (peak) followed by a post-focal transmittance minimum (valley) in the z-scan experiment is a signature of negative nonlinearity. The z-scan signature for the dye Congo red in liquid medium gives the value of the transmission from peak to valley (Tp-v) as 0.0218, The Figure.4 gives ΔT_{p-v} to be 0.0248 Here, the solid line is the calculated result for congo red doped polymer film with $\Delta\varphi_0$ as -0.0622. By knowing the linear absorption coefficient of congo red doped polymer film as 0.074 mm^{-1}, L_{eff} is calculated and obtained as 0.963. The index change $<\Delta n_0>$ is found to be -6.483 x 10^{-7}, from which the nonlinear refractive index is calculated as -5.72 x 10^{-13} m^2/W.

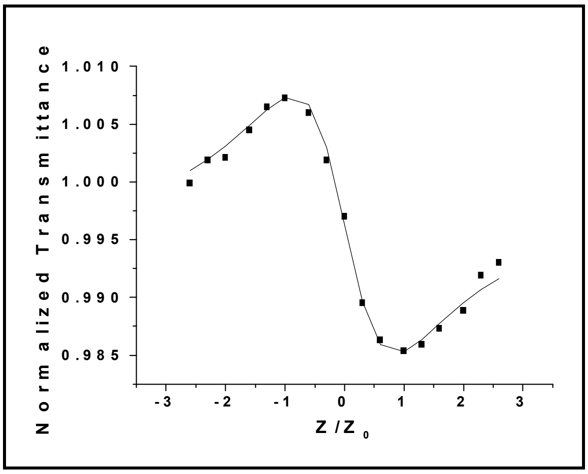

Figure.5 Measured z-scan of the polymer dye Congo red. The solid line is the calculated result with Øo = -0.622.

The difference between the peak-to-valley normalized transmittance obtained from Figure.5 is 0.0218. The solid line in the graph is the calculated result with $\Delta\varphi_0$= -0.0548. The value of α of dye in nBA is 0.067 mm^{-1}, from which L_{eff} is calculated to be 0.9671. The $<\Delta n_0>$ is -5.73 x 10^{-7} which gives value of γ to be -5.72 x 10^{-13} m^2/W.

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