Nonlinear Optical Characteristics of Crystal VioletDye Doped Polystyrene Films by Using Z-Scan Technique

Mahasin F. Hadi[1], Eman Mohi Alwaan[1], Wafaa Hameed Abass[2]
[1]Department of Physics, College of Science, Al–Mustansiriyah University, Baghdad, Iraq
[2]Ministry of Higher Education and Scientific Research, Baghdad, Iraq

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ABSTRACT
Z-scan technique was employed to study the nonlinear optical properties (nonlinear refractive index and nonlinear absorption coefficient) for crystal violet doped polystyrene films as a function of doping ratio in chloroform solvent. Samples exhibits in closed aperture Z-scan positive nonlinear refraction (self-focusing). While in the open aperture Z-scan gives reverse saturation absorption (RSA) (positive absorption) for all film with different doping ratio making samples candidates for optical limiting devices for protection of sensors and eyes from energetic laser light pulses under the experimental conditions.
Keywords: Crystal Violet, Dye Doped Polymer Films.

الخلاصة
استخدم في هذا البحث منظومة المسح على المحور الثالث لدراسة الخصائص البصرية اللاخطية والمتمثلة بمعامل الانكسار اللاخطي ومعامل الامتصاص اللاخطيللأغشية البولي ستايرين المطعمة بصبغة كرستل فايوليت والمحضرة بطريقة الصب كدالة لنسب التطعيم في مذيب الكلوروفورم باستخدام ليزر CW و بطول موجي 650 nm. أظهرت النتائج أن استخدام تقنية المسح على المحور الثالث عند االشق المغلق معامل انكسار لاخطي موجب بينما أظهر المسح عند استخدام الشق المفتوح امتصاص مشبع عكسي ولجميع الاغشية بنسب تطعيم مختلفة تجعل من هذه النماذج مرشحة ضمن أجهزة المحددات الضوئية لحماية الحواس والعين من طاقة ضوء الليزر عند الظروف التجريبية.

INTRODUCTION
Nonlinear optics in a material is a phenomenon in which intense light induces a nonlinear response in the medium; this phenomenon can be deduced due to electronic and non-electronic processes [1, 2]. Nonlinear optical materials required in a wide range of important applications such as optical limiting, optical computing and optical communication [3, 4].
Organic materials exhibiting nonlinear absorption are currently of interest because of their large third-order nonlinearities, instantaneous response time, high damage threshold, ease of processing, structural modification and their applicability over a wide range of wavelengths [5].
Let us consider a medium subjected to an optical electric field, the induced polarization P has nonlinear dependence on electric filed, and can be written [6]

$$P = \varepsilon_\circ(\overleftrightarrow{X^{(1)}.E} + \overleftrightarrow{X^{(2)}}:EE + \overleftrightarrow{X^{(3)}}:EEE + \cdots + \overleftrightarrow{X^{(i)}}:EEE) \quad (1)$$

Where $\varepsilon_\circ$ is the vacuum permittivity, $X^{(i)}$ is the electrical susceptibility of the order i, i.e. $X^{(1)}$ is the linear susceptibility (linear absorption and refraction), $X^{(2)}$ is the second order nonlinear responsible for sum and difference frequency mixing, optical rectification, $X^{(3)}$ is the third order nonlinear susceptibility related to the nonlinear index of refraction [7]. The real part of the third order optical susceptibility Re $\{X^{(3)}\}$ related to nonlinear refractive index n_2 through [9].

$$R_e\{X^{(3)}\}_{(esu)} = \frac{C\ n_o^2 n_2}{120\,\pi^2} \quad (2)$$

Where :
$n_\circ$ is the linear refractive index.
c the light velocity in vacuum .

And the imaginary part of the third order optical susceptibility $I_m\{ X^{(3)} \}$related to the nonlinear absorption coefficient *B* through [9].

$$I_m\{ X^{(3)} \}_{(esu)} = \frac{C^2 no^2 B}{240\, \pi^2 w} \quad (3)$$

B is nonlinear absorption coefficient.
W is the angular velocity.

The third order optical susceptibility is given by [8]

$$|X^{(3)}| = [(R_e X^{(3)})^2 + (I_m X^{(3)})^2]^{1\backslash 2} \quad (4)$$

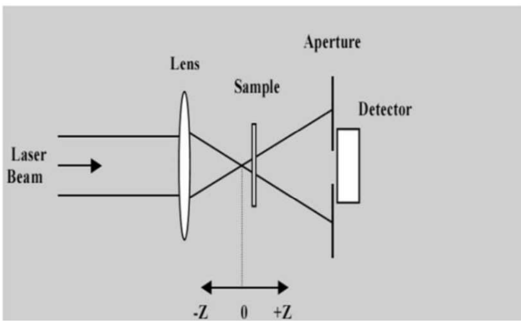

Figure 1:Experimental set-up for Z-scan

in nonlinear materials the change in the refractive index of a material proportional with the square of the applied field (Kerr effect) produces refractive index change with intensity (I) of the incident laser beam [6]. Researchers worked in nonlinear properties of dyes doped polymer such as; I.Dancus, V.I. Vland, A Petris [1] and P.GLouie Frobel, R.Sreeja, C.I Muneera [8]. In the present work nonlinear optical properties of crystal violet (CV) doped polystyrene (PS) films at different doping ratio [5, 10, 15, 25] ml will be studied.

MATERIALS AND METHODS

Crystal Violet (CV) is one of the important dyes that used in many applications such as; medical treatment, biology, chemistry [10]. The chemical formula of this dye is ($C_{24}H_{27}N_3HCl$). Polystyrene (PS) is a colorless and rigid plastic in solid form at room temperature. It is one of the most widely used plastic. The chemical formula $(C_8H_8)_n$ [11].
Purified chloroform is used as solvent with molecular formula $CHCl_3$. It is an organic compound clear colorless liquid with low viscosity and most polar solvent, and it is compatible solvent for both dye and polymer [11, 12].
Certain amount of polymer 0.5 g was dissolved in constant volume of solvent chloroform 10 ml. The crystal violet dye solution with concentration 0.5×10^{-4} mole/liter was prepared according to the method mentioned in [13].
The casting method was chosen to prepare dye doped polymer film [13]. Different doping ratio from crystal violet solution in chloroform was chosen (5, 10, 15, and 25) ml added to polymer solution. The mixture shake very well then poured into glass Petri dish with (10) cm diameter and left for 24hrs at room temperature (25- 30)$^\circ$C to get homogenous films.
The thicknesses of the films were measured with an electronic micrometer digital micrometer range of measure (0 – 150) (mm), and illustrated in Table (1).

Table 1: Thickness of CV-PS Films

Doping ratio CV (ml)	PS-Pure	PS-CV 5ml	PS-CV 10ml	PS-CV 15ml	PS-CV 25ml
Thickness (mm)	0.058	0.063	0.065	0.062	0.062

THE PRINCIPLE OF Z-SCAN TECHNIQUE

Z-Scan technique based on the principles of spatial beam distortion, it will be shown that for many practical cases nonlinear refraction index and it issign can be obtained from a simple linear relationship between the induced phase distortion without the need for performing detailed calculations [8]. There are two different
geometries in Z-scan technique (i) the geometry in which a finite aperture is kept before the detector is known as a closed – aperture (CA) Z-scan (ii) the geometry in which the aperture is removed referred to as an open – aperture (OA) Z-scan, hence all the transmitted light focus into detector [2].
In closed – aperture the sample is moved along the Z- direction and the transmitted intensity is measured as a function of the sample position Z, measured with respect to the focal plane. As the sample moves through the beam focus (at

Z=0), self-focusing or - defocusing modifies the wave front phase, there by modifying the detected beam intensity. The experimental set-up for Z-scan is shown in Figure (1).
The change in transmittance between the peak and valley in a Z-scan as

$$\Delta T_{pv} = T_p - T_V \quad (5)$$

Where T_p and T_v are the peak and valley transmittance. When the Z-scan aperture is closed linear transmission allow where 0.1<S< 0.5. The relation between the induced on axis phase shift at focus $\Delta\Phi$ and ΔT_{pv} for third – order nonlinear refractive process .

$$\Delta T_{pv} \cong 0.406|\Delta\varphi_o| \quad (6)$$

$$n_2 = \Delta\varphi_o / I_o L_{eff} K \quad (7)$$

Where K is the wave vector, I_o is the on- axis intensity at focus, L_{eff} is the effective length of the sample which can be determined from the following formula [14].

$$L_{eff} = (1 - e^{-\alpha_o L})/\alpha_o \quad (8)$$

Where L is the sample thickness and the linear absorption coefficient α_o is given by

$$\alpha_o = \frac{1}{L \ln\left(\frac{1}{T}\right)} \quad (9)$$

Where; T acts the linear transmittance.
While in the second geometry in which the aperture is removed to focus all the transmittance light into the detector. The absorption nonlinearity can be due to either saturable absorption (SA) in which the absorption coefficient decreases resulting in the transmittance increased with increase the input laser intensity, and reverse saturable absorption (RSA) when the absorption coefficient increases resulting in the transmittance decreases with increasing in the input laser intensity [15]. In open-aperture Z-scan very important to know the behavior of materials, materials that exhibited (RSA) can be used in optical limiting devices for protection of sensors and eyes against radiation induced damage [7], so this makes Z-scan a preferred technique when assessing materials for optical power limiting application [8].
The Z-scan experiment were performed using (CW) diode laser beam at (650 nm) to use as an excitation light source, the beam focused by a lens of 30 cm focal length, the transmission of the beam measured using photo detector attached to a digital power meter (Sanwa electric instrument co. LTD).

RESULTS AND DISCUSSIONS

Using single Gaussian laser beam in light focus as in Fig (1), the transmittance of a nonlinear medium (crystal violet doped polystyrene film) with different doping ratio through a finite aperture is measured as a function of the sample position with respect to the focal plane.
The close- aperture (CA) Z-scan curve 0.1<S< 0.5 for the crystal violt doped polystyrene; Figure (2) show the typical (CA) Z-scan profiles of the films for pure polystyrene and four doping different ratio (5, 10, 15, 25 ml). This Figure shows when the sample is moved from negative Z-position at the far field into focus, the transmittance remains relatively constant for all samples, as the sample is brought closer to the focal a valley followed by a pack in the transmittance obtained for all samples indicates to positive nonlinearity phase shift at 650 nm (i.e. self – focusing) which denotes that the nonlinear refractive index is positive. The parameters ΔT_{pv}, Equation (6), $\Delta\Phi$, Equation (7), L_{eff}, Equation (9), and n_2 from Equation (8) has been calculated and Tablet in Table (2).
The open-aperture (OA) Z-scan for the dye crystal violet doped polystyrene for pure (PS) and four doing different ratio has been shown in Figure (3). It shows (RSA) reverse saturation absorption when they moved to the locality of the focal plane, a symmetric valley is contributed to the positive nonlinear absorption coefficient B

Table 2: The calculated value of T_{PV}, $\Delta\Phi$, α_o, L_{eff}, and n_2 for pure PS and different doping ratio of CV-PS films

Doping ratio (ml)	T_{max}	T_{min}	ΔT_{Pv}	$\Delta\Phi$	α_o cm^{-1}	L_{eff} Cm $\times10^{-3}$	n_2 $\times10^{-7}$	Type of n_2	Behavior
PS-pure	0.310	0.330	0.02	-------	--------	----------	--------	---------	----------
5	0.282	0.306	0.024	0.05911	143	6.992	3.44	+Ve	TPA or RSA
10	0.211	0.240	0.029	0.07142	132	7.574	3.84	+Ve	TPA
15	0.160	0.202	0.042	0.10344	161	6.208	6.8	+Ve	TPA
25	0.125	0.164	0.039	0.09605	272	3.676	10.6	+Ve	TPA

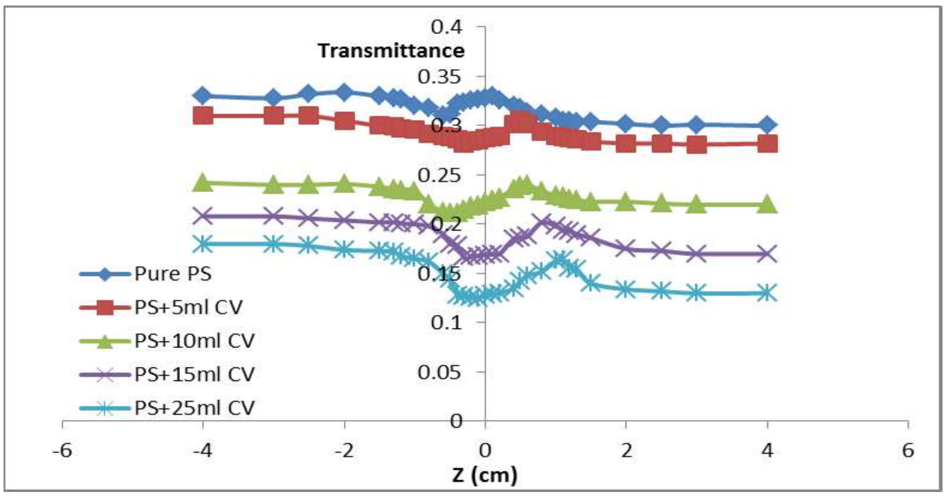

Figure 2: Closed aperture Z-Scan for different doping ratio of CV-PS films

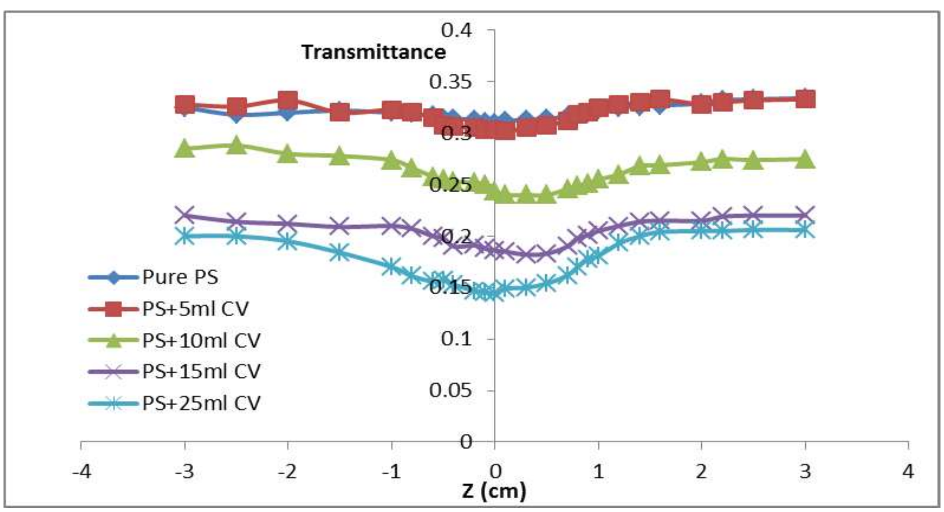

Figure 3: Open aperture Z-Scan for different doping ratio of CV-PS films

CONCLUSIONS

In this work we have obtain the following results

1. The nonlinear optical properties (nonlinear refractive index, nonlinear absorption coefficient) for the dye crystal violet doped polymer (polystyrene) for the samples changed with the doping ratio of the dye .
2. The observed nonlinearities were positive refractive index (self – focusing) $n_2>0$ as show in a valley- peak structure of the transmittance curve and positive absorption coefficient (reveres saturation absorption) (RSA) due to two photon absorption (TPA).
3. The value of T_{p-v} increases as increasing doping ratio that is because different of dye doping ratio in each film caused change in the nonlinear phase shift which is caused change in the value of the nonlinearities .
4. The result show the films of (CV) doped polystyrene possess both nonlinear absorption and nonlinear refraction properties attributed to the possible simultaneous occurrence of several nonlinear processes which high lights their potential for use in various optoelectronics device applications including the optical limiting one.

REFERENCES

[1] I.Dancusv, V.I. Vlad, A.Petris ,S. Fruivz, T. Beica, I. Zgura, F. Anicolesc U. V.V. Jerca, D. M. Vuluga, Low Power Laser Induced Optical Nonlinear Ties In Organic Molecules Romanian Report in Physics, 62(3), 567-580, 2010.

[2] I. C. Khoo, Liquid Crystals, Physical Properties and Nonlinear Optical Phenomena, Wiley, New-York 1995.

[3] M. Bass, J.M. Enoch, E. W. V. Stryland, W.L. Wolfe : Handbook of Optics IV, Fiber Optics and Nonlinear Optics ,2nd ed. MC Graw -Hill, New York 2001.

[4] S. Moorthy, PhD Thesis, Indian Institute of Technology Madras India 2007.

[5] A.Y. Nooraldeen, M. Palanichant, P.K. Palanisan, Influence of Solvent Polarity on NLO Properties of Fluorine Dye, International Journal of Nonlinear Science, 7(3), (2009), 290-300.

[6] Y.R. Shen, The Principles of Nonlinear Optics, Wiley, New York, 1984.

[7] M. Sheik – Bahae, M. P. Hassaibeak, “Handbook of Optics”, Vol. IV, Chapter 17, (2000).

[8] P.G Louie Frobel, R. Sreeja, C.I Maneera and M.K Jayaraj, “Nonlinear Optical Characterization of Biebrih Scarlet dye-PVA Solid Film under 532nm Nanopulsed laser light excitation ICOP International Conference on Optics and Photonics CSIO, Chadigarh, India, 30 Oct-1 Nov,(2009).

[9] U. Tripathy and P.B Bisht, J.optsoc. Am. B 24, 2147-2156 2007.

[10] R.W., Horbin and J.A Kieman, “Conn's Biological stains. A Handbook of Dyes Stains and FlyorochrmesFor Use in Biology and Medicine 10th ed. Oxford Bios 2002.

[11] M.R. Fraih, “Study of Thermal Aging Effect on Optical Properties of Some Polymer Blends ", MSC Thesis University of Technology, Department of Applied Sciences, 2010.

[12] P. Nightingale, G. Malin, P. Liss, Production of Chloroform and Other Low – Molecular – Weight – of Macroalgae, Limnology and Oceanography (American Society of limnology and Oceanography) 40 (4), 680, 1995.

[13] M.F. Al-Kadhemy “Optical Properties of Organic Dyes Using As Active Medium

in Dye Laser "MSC, Thesis in Baghdad University , College of Science, 1995.

[14] K. Sendhil, C. Vigayan, M.P. Kithira, Low-Threshold Optical Power Limiting of CW Laser Illumination Based on Nonlinear Refraction in Zinc Tetraphenyl Porphyrin "Optics & Laser Technology " No. 38, 512, 2006.

[15] M.Sheik – Bahae, Characterization Techniques and Tabulations For Organic Nonlinear Materials, M.G. Kuzyk and C-W Dirk, Eds., pp. 655-692 ,Marcel Dekker, INC.1998.