FOCUSING, DEFOCUSING AND OPTICAL LIMITING IN DODCI DOPED FILMS IN PMMA BY USING Z-SCAN TECHNIQUE [+]

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Abstract:

During this work a simplified and sensitive experimental technique named Z-scan (closed aperture) have been used, to study the optical nonlinearity and optical limiting of the organic dye DODCI doped with the polymer polymethylmethacrylate (PMMA) in the solvents Chloroform and THF with various concentrations (10^{-5} -10^{-3})M/L for dye doped polymer films. Samples were prepared by free casting method.

The results show that the investigated organic dye molecule exhibits negative refractive index (defocusing) and positive refractive index (focusing) as well as the behavior switch over from negative two positive refractive index for the film of concentration 10^{-3} M/L (as the thickness is increased). With closed aperture Z-scan the nonlinearity changed with changing the phase shift in the samples owing to the contribution of thermal effect .The measurements indicates that the nonlinear refractive index increased linearly with the nonlinear phase shift.

The results of this work shown too that only the doped film of DODCI in THF can be an optical limiter.

Keywords: DODCI Doped Films, Z-scan technique, nonlinear refractive index, nonlinear absorption coefficient, optical limiting.

التركيز البؤري الذاتي، عدم التركيز البؤري الذاتي، التحديد البصري في أفلام مطعمة في البوليمر لغشية رقيقة لصبغة DODCI باستخدام تقنية المسح على المحور الثالث

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المستخلص:

خلال هذا البحث استخدمت تقنية تجريبية سهلة ذات حساسية عالية تعرف بتقنية المسح على المحور الثالث (Z-Scan) لدراسة الخواص البصرية اللاخطية و التحديد البصري لأغشية الصبغة العضوية (DODCI) و المطعمة مع البوليمر (PMMA) بالمذيبين ((chloroform and Tetrahydrofloran (THF)) ،و بتراكيز مختلفة (10^{-5}-10^{-3}) مول /لتر للأفلام المطعمة بالبوليمر.حضرت الأغشية بطريقة تسمى تقنية الصب الحر (free casting technique) .

أظهرت التجارب إن جريئة الصبغة العضوية المدروسة تبدي معامل انكسار لاخطي سالب عدم تركيز بؤري(defocusing) ومعامل انكسار موجب (focusing) و ينقلب السلوك من معامل انكسار سالب إلى معامل انكسار موجب للغشاء الذي تركيزه 10^{-3} مول/لتر(كلما ازداد سمك الغشاء).عندما توضع فتحة أمام الكاشف يتغير السلوك اللاخطي مع تغير إزاحة الطور في النماذج و ذلك لإسهامات التأثيرات الحرارية (تأثير Kerr).أظهرت التجارب أن معامل الانكسار اللاخطي يزداد بصورة خطية مع إزاحة الطور اللاخطية.

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أظهرت النتائج أيضا إن الغشاء المطعم لDODCI في THF فقط هو الذي ممكن أن يكون محدد بصري.

Introduction

Nonlinear optics is the study of phenomena that occur as consequence of the modification of the optical properties of materials on interaction with intense light [1]. Nonlinear phenomena have since been studied extensively, leads to several technological advances such as, the design of high power solid state laser sources. On a fundamental level of bound, the origin of nonlinear response in an matter arises from a variety of basic mechanisms such as an harmonicity of bounded electrons, local polarization effects, molecular orientation, multiphoton transitions and variation of refractive index which are vary with the type of material and the parameters of laser used. For example; interaction with low power continuous wave lasers can cause local thermal variation in the refractive index and resulting beam profiles modification, this can be use to design of the efficient optical limiters which prevent optical damage to very sensitive sensors [2]. Excitation of nonlinear-optical (NLO) responses in materials generally requires radiation that has both high field strength and a high degree of phase coherence [3].

The Z scan technique is a simple, sensitive and popular experimental method to measure nonlinear optical prosperities (NLO) of materials. Closed aperture Z-scan helps to measure the sign and magnitude of real part of third order susceptibility ($\chi 3$) and nonlinear refractive index (n_2) [4].

Theory:

1- Closed – Aperture Z- Scan:

The standard "closed aperture" Z-scan (i.e. aperture is placed in the far field) for determining nonlinear refraction is shown in Fig. (1), where the sample is moved along the propagation direction z while keeping the input pulse energy fixed. The normalized transmittance of the sample through the aperture is monitored in the far field as a function of the position Z. The normalization is performed in such a way that the transmittance is unity for the sample far from focus where the nonlinearity is negligible [5]. An intensity dependent on the refractive index causes the beam radius of the transmitted beam to change while retaining the Gaussian profile.

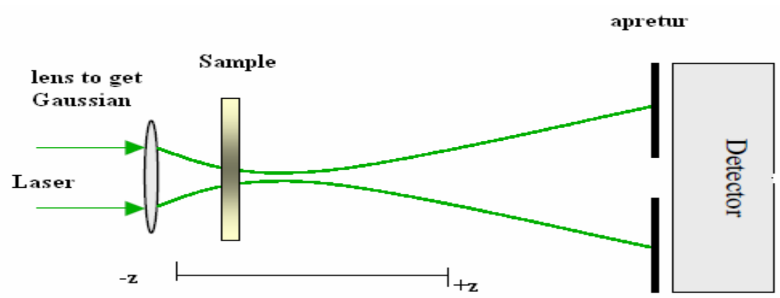

Figure (1): The scheme of the closed aperture z-scan [6]

The size of the aperture is signified by its transmittance (S), in the linear regime. In most reported experiments, 0.1<S<0.5 has been used for determining nonlinear refraction. [7].

The Z-scan technique is based on the transformation of phase distortions to amplitude distortions during beam propagation. A qualitative physical argument that explains the transmittance variations in the Z-scan experiment can be given as follows: Starting the scan from a distance far away from the focus (negative z), the beam irradiance is low and negligible nonlinear refraction occurs leading to linear transmittance. As the sample is brought closer to the focus, the beam irradiance increases leading to self-lensing in the sample. A negative self-lensing (self-defocusing) prior to focus tends to collimate the beam and reduce the diffraction leading to a smaller beam at the aperture and an increased transmittance. As the scan continues and the sample crosses the focal plane to the right (positive z), the same self-defocusing effect will tend to augment diffraction and reduce the aperture transmittance .A prefocal transmittance maximum (peak) and a post focal transmittance minimum (valley) will be, the z-scan signature of a negative nonlinearity as shown by the dote line figure. (2), while a positive one, following the same analogy, will give rise to an opposite valley-peak configuration,as shwon by Solid line fig. (2). [8].

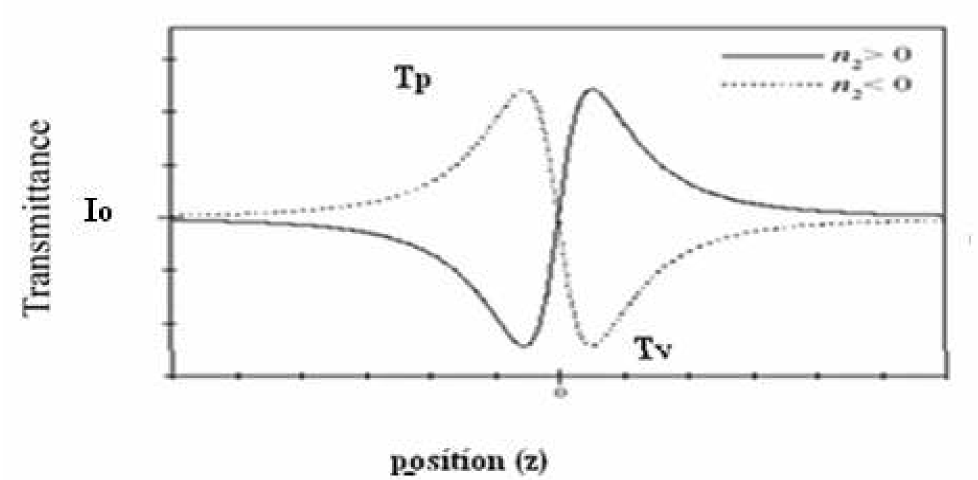

Figure (2): Calculated Z-scan transmittance curves for a third order nonlinearity [6].

1- self Focusing and Defocusing:

Self-focusing (or Kerr-Lansing) is a consequence of the non-uniform spatial profile of the laser Gaussian beam. If the intensity of a transmitted light beam is sufficiently high, the refractive index change will modify the light propagation
not only with respect to the polarization but in its geometrical properties too [9].
For a Gaussian beam of radius ω_o (beam waist) the Kerr-lens focal length is:

$$F = a\, \omega_o^2 / 4 L n_2 I \qquad (1)$$

Where L is the thickness of the nonlinear medium (sample), I is the irradiance and a is a correction term.

When n_2 is negative, the above equation shows there will be a negative focal length and thus self de-focusing of the incident beam [6].

We define the change in transmittance between the peak and valley in a Z-scan as:

$$\Delta T_{pv} = T_p - T_V \qquad (2)$$

where T_p and T_v are the normalized peak and valley transmittances as seen in Figure (2) The empirically determined relation between the induced on axis phase shift, $\Delta\Phi_0$, and ΔT_{pv} for a third-order nonlinear refractive process in the absence of nonlinear absorption (NLA) is,

$$\Delta T_{pv\cong} \cong 0.406 (1-s)^{0.27} |\Delta \phi_o| \qquad (3)$$

S: the size of the aperture.
If the Z-scan aperture is closed to allow linear transmission of less than 10 percent or 0.1<S<0.5, then:

$$\Delta T_{pv} \cong 0.406 \left| \Delta \phi_o \right| \ldots\ldots\ldots \quad (4) \quad [10]$$

The nonlinear refractive index is calculated from the peak to valley difference of the normalized transmittance by the following formula: -

$$n_2 = \Delta \phi_o / I_o L_{eff}\, k \quad \ldots\ (5)$$

$$Io = {2P_{peak}} / {\pi \omega_o^2} \ldots\ldots\ldots\ldots \ (6)$$

I_o is on the axis irradiance,

P_{peak}: The peak power given by: $P_{peak} = E/\Delta t$………… (7)

E: the energy of the pulsed laser,

ΔT: the time duration.

ω_o : The beam radius at the focal point, λ, is the wavelength of the beam.

L_{eff} : The effective length of the sample (thickness), can determined from the following formula: [6]

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

Where,

L: the sample thickness, [6]

α_o : Linear absorption coefficient,

$$\alpha_o = \frac{1}{L \quad \ln(\frac{1}{T})} \ \ldots\ldots\ldots\ldots\ldots\ldots \qquad (9)$$

Where T: linear transmittance

2- <u>Optical Limiting:</u>

In a material with a strong nonlinear effect, the absorption of light increases with intensity such that beyond a certain input intensity the output intensity approaches a constant value. Such a material can be used to limit the amount of optical power entering a system. This can be used to protect expensive or sensitive equipment such as sensors, can be used in protective goggles, or can be used to control noise in laser beams. The ideal behavior of such a device is shown in Figure (3), [11].

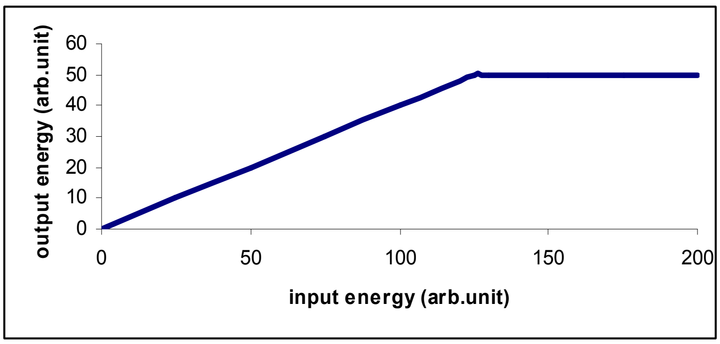

Fig. (3): An ideal optical limiter [3]

Experimental Section:

The chemical structure of DODCI (3,3'Diethyloxadicarbocyanine Iodide) (LC 6550), ($C_{23}H_{23}N_2O_{2I}$) shown in fig.(4). Polymethylmethacrylate (PMMA) is from ICI Company. The spectroscopic grade solvent THF is from (BDH) laboratory reagents (BDH Chemicals Ltd, Poole, England. Chloroform: From Lab-Scan Ltd. Analytical Sciences HPLC, Dublin Ireland.

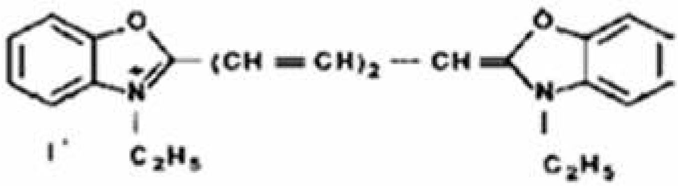

Fig. (4): The chemical structure of DODCI [12]

Solution of concentrations (10^{-5}, 10^{-4}, 10^{-3}) M/L in Chloroform and THF were prepared by weighting amount of the material by using a sensitive matter
balance having a sensitivity of 10^{-4} gm. Dye doped polymer films were fabricated by the free casting technique(FC). Polymer solution was prepared by dissolving the required amount of polymer (7 gm. in 100ml of the used solvent THF and Chloroform).

The free casting (FC), involves casting a polymer solution in a flat bottomed glass cup (Petri dish) without imposing hydrodynamic stress on the liquid .Solvent is allowed to evaporate under ambient conditions until the films harden.The thickness of the films produced by this method is dependent on concentration and the volume of the liquid in the dish. The liquid volume was (10) ml, yielding film of different thickness.

The thickness of the films was measured with an electrical device (Mini-test 3000 microprocessor coating thickness) from electro, phyisk, Germany (ERICHSEN).

The doping ratio was 1:2 dye to the polymer.

The CW laser system from Institute of Laser for Postgraduate Studies consists of: diode laser with such characteristics: (wavelength 650 nm, with maximum power 50 mwatt, beam diameter 1.5 mm, beam divergent, 1.5 mrad, Ac :220-240 volt, of 50-60 Hz, and 250 mA), collimated lens, and the detector which was used to measured the output power.

Results and Discussion:

Fig. 5 and 6 show the closed aperture Z-scan curves for dye doped polymer films in the two solvents.

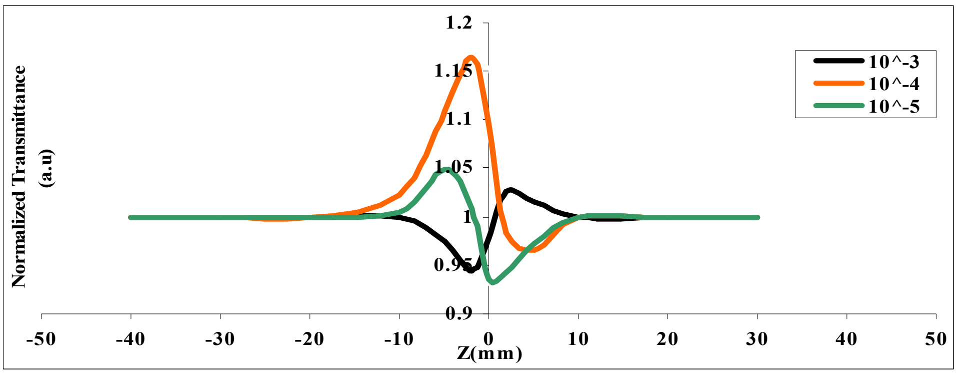

Figure (5): Closed aperture z- scan curve for DODCI doped polymer film in Chloroform

Figure (5) indicates to negative refractive index for films of concentration 10^{-5} and 10^{-4} M/L, positive refractive index for film of dye concentration 10^{-3} M/L.

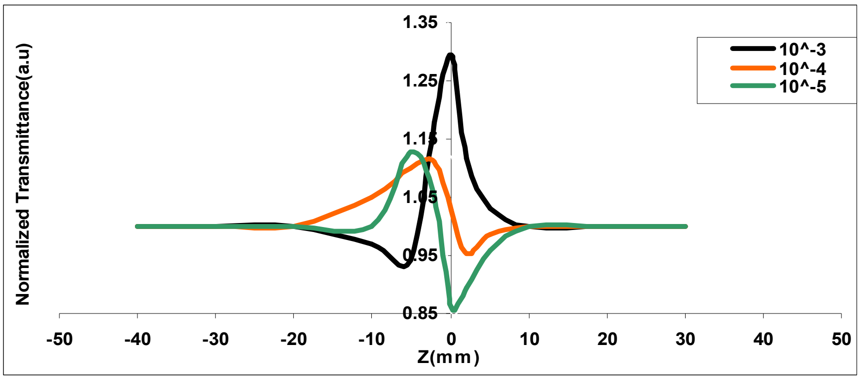

Figure (6): Cclosed aperture z- scan curve for dye doped polymer film in THF

Figure (6) indicates to negative refractive index for films of concentration 10^{-5} and 10^{-4} M/L, and positive refractive index for film of dye concentration 10^{-3} M/L. Films of concentration 10^{-3} M/L exhibited positive refractive index due to the increasing the film's thickness which mean increasing the optical path which lead to switch over the behavior from negative refractive index to positive refractive index.

ΔT_{pv}, $\Delta\phi o$, n_2, $L_{eff.}$ were calculated from equations :(2), (4), (5), and (8) respectively. The real part of the third order nonlinear susceptibility was calculated from this equation:

$$R\,\chi^{(3)} = 10^{-4}\,\epsilon_o\, n_o^2\, C^2\, n_2 / \pi \quad \ldots\ldots\ldots\ldots\ldots(10)$$

Linear refractive index n_o was calculated from equation:

$$n_o = 1/T + [(1/T^2) - 1]^{0.5} \quad \ldots\ldots\ldots\ldots (11)$$

Where T is the linear transmittance of the films.

Table (1) indicates to the nonlinear parameter of the doped films in the two solvents.

Table (1): Nonlinear parameters for DODCI Doped in PMMA Films with the two solvents with various Concentrations of the dye.

C M/L	Leff. cm	Tmax.	Tmin.	ΔT	$\Delta\phi o$	$ReX^{(3)}$ cm^2/watt	n_2 type	n2 cm^2/ watt (CW)
DODCI Doped Films in Chloroform								
10^{-5}	0.011	1.34	0.8362	0.5038	1.241	2.175 x10^{-9}	-ve	3.480 x10^{-6}
10^{-4}	0.017	1.14778	0.89	0.2583	0.636	1.31 x10^{-9}	-ve	1.6695 x10^{-6}
10^{-3}	0.011	1.1871	0.3613	0.8258	2.034	4.855 x10^{-8}	+ve	7.51049 x10^{-6}
DODCI Doped Films in THF								
10^{-5}	0.013	1.2553	0.8511	0.404	0.996	1.854x10^{-9}	-ve	3.11087x10^{-6}
10^{-4}	0.014	1.1193	0.9358	0.183	0.452	6.84x10^{-10}	-ve	1.36x10^{-6}
10^{-3}	0.016	1.4118	0.9412	0.471	1.159	2.215x10^{-9}	+ve	3.0122x-6

Figures (7): represent the variation of the nonlinear refractive index with the nonlinear phase shift of the laser beam.

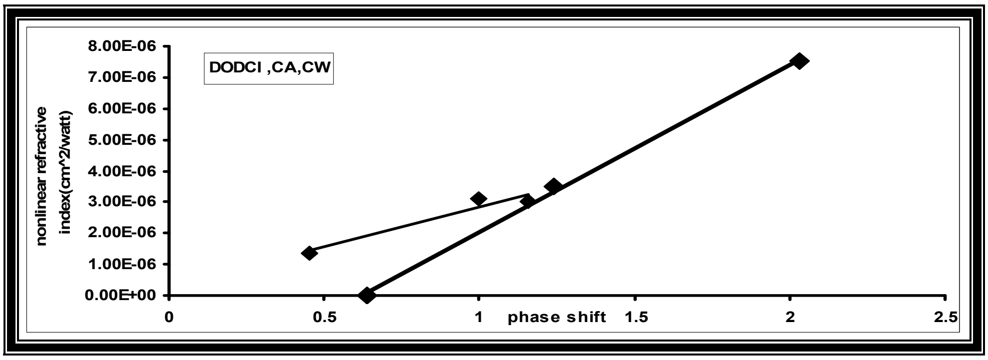

Figure (7): Variation of the nonlinear refractive index as a function of the phase shift which happened in the laser beam for the dye DODCI in PMMA doped films in the solvents Chloroform and THF

Fig. (7): show that there was a linear increasing relation between the nonlinear refractive index and the nonlinear phase shift.

The optical limiting behavior for DODCI doped films in the two solvents were performed by a closed-aperture Z-scan, where the output intensity was plotted versus the input intensity at various distances of-Z-. The limiting behavior was investigated have shown in Fig.8 and Fig.9.

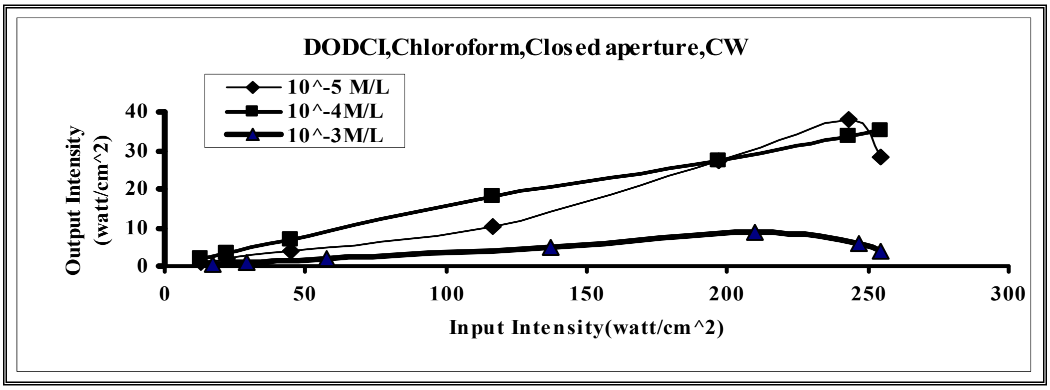

Figure8 :Optical Limiting for DODCI Doped films in Chloroform.

Figure (8) indicates that: no samples of the three concentrations can be an optical limiter.

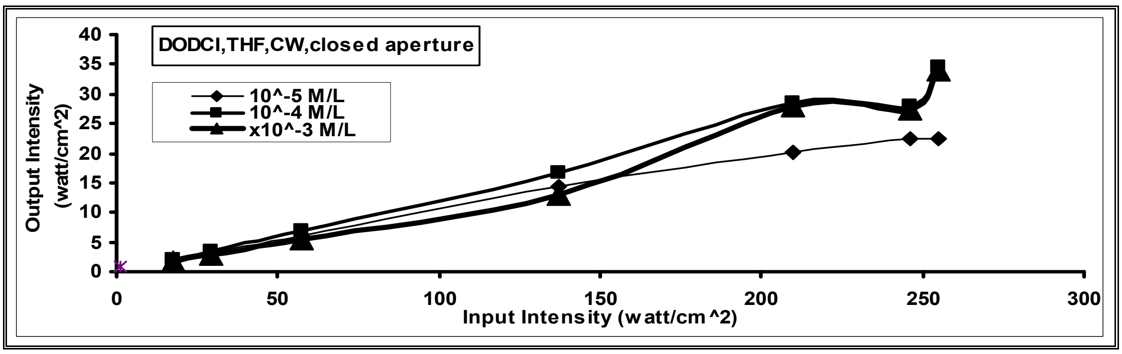

Fig.9: Optical Limiting for DODCI Doped films in THF.

Figure 9 indicates that only the film of the dye concentration 10^{-5} M/L with closed aperture z- scan can be a good optical limiter. The output intensity is found to vary linearly with input intensity only for small values of initial intensity. A threshold is reached at a low value of the input intensity (246.329wat/cm^2) with little change in the output intensity for larger values of the input intensities. Thus the output gets clamped and stabilizes at a low threshold size.

Table (2): Represents DODCI doped film which exhibited an optical limiting behavior for closed aperture z-scan by using CW laser.

C M/L	Z (cm)	input intensity Watt/cm^2	output intensity Watt/cm^2
10^{-5}	4	17.311	1.8081
	3	29.231	3.0529
	2	57.520	6.0077
	1	137.173	14.3269
	0.5	209.808	20.0
	0.2	246.329	22.4433
	0	254.777	22.4269

By comparing the results of this work with works of other researchers its found that the values of the nonlinear refractive index and its sign, the value of nonlinear susceptibility and the optical limiting behavior were changed with the kind of the nonlinear medium , used solvents, dye concentrations,and that a good agreement with the works of K.Milanchian and Krishnamurthy [13,14].

Conclusion:

By using Gaussian beam from CW pulsed laser at 650 nm, we studied the characteristics of DODCI doped films by using Z-scan with a various concentrations in chloroform and THF. It has been verified that the values of n_2 with closed aperture Z-scan is changed with the change of the phase shift due to the change of the films thickness.The relation between the nonlinear refractive index and the nonlinear phase shift is a linear increasing relation. The sample of dye concentration 10^{-5} M/L has an optical limiting behavior so it can be available for the applications used in handling the laser output to protect human eye and the sensors, because this film has the largest nonlinear refractive index in its grope**.**

List of Abbreviations

List of Abbreviations	
CA	Closed aperture
DODCI	3,3'Diethyloxadicarbocyanine Iodide
NLA	Nonlinear absorption
NLO	Nonlinear Optics
NLR	Nonlinear refraction
OA	Open aperture
PMMA	polymethyl methacrylate polymer
RSA	Reverse Saturable Absorption
SA	Absorption saturation
TPA	Two Photon Absorption

The symbols

symbol	Symbol's Name
A	Absorbance
c	Speed of light
E_{ref}	The reference energy of the laser pulse
f	The focal length of the lens
h	Planck Constant
I	Transmitted intensity
I_o	Peak intensity at the focus
K	Wave number
L	The thickness of the dye doped films
n_2	Nonlinear refractive index
P_{peak}	The peak power of the laser pulse
T	Transmittance
T_{peak}	The maximum transmittance of laser pulse
T_{valley}	The minimum transmittance of laser pulse
Z	Travel distance along the Gaussian beam
α	Linear absorption coefficient
ß	Nonlinear absorption coefficient
$_o\epsilon$	Permittivity in vacuum
σ_o	Ground state cross section
$\sigma_{Exc.}$	Excited state cross section
$\Delta\Phi_o$	The maximum nonlinear - induced phase shift
ω_o	The radius of waist beam

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