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## Nonlinear characterization of orcein solution and dye doped polymer film for application in optical limiting

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### Abstract

The single beam Z-scan technique was used to determine the nonlinear optical properties of the orcein dye in the solvent chloroform and a dye doped polymer film. The experiments were performed using cw SDL laser with a wavelength of 532 nm. This material exhibits negative optical nonlinearity. The dye exhibited a nonlinear refractive index ( $n_2 = 0.22 \times 10^{-7}$  and  $2.32 \times 10^{-7} \text{ cm}^2/\text{W}$  in dye solution and polymer film, respectively) and nonlinear absorption coefficient ( $\beta = 1.44 \times 10^{-3}$  and  $18.61 \times 10^{-3} \text{ cm/W}$  in dye solution and polymer film, respectively). Optical limiting characteristics of the dye solution and polymer film were studied. The result reveals that orcein dye can be a promising material for optical limiting applications.

**Key words:** Nonlinear optics, Nonlinear refractive index, Z-scan technique, Optical limiting, Dye

### 1- Introduction

The field of nonlinear optics (NLO) has been developing for a few decades as a promising field with important applications in the domain of photoelectronics and photonics [1,2]. NLO materials can be used to manipulate optical signals in telecommunication systems and other optical signal processing applications [3,4]. Organic materials are considered as one of the important classes of third-order NLO materials because they exhibit large and fast nonlinearities and are, in general, easy to process and

integrated into optical devices [5-7]. Moreover, a fine-tuning of the NLO properties of organic compounds can be achieved by rational modification of the chemical structure[8]. Various types of organic compounds have been studied to obtain materials with large third-order nonlinearity. On the other hand a wide range of techniques has been used to measure third-order nonlinearity: e.g. Z-scan [9,10], nonlinear interferometry [11], degenerate four-wave mixing [12], nearly degenerate three-wave mixing[13], ellipse rotation [14], beam

distortion measurements [15], optical third harmonic generation (THG) [16] and frequency resolved optical gating [17].

Among all these techniques Z-scan is a simple but effective tool for the measurement of the nonlinear refractive index and has been used widely in material characterization. It provides not only the magnitudes of the real and imaginary parts of the nonlinear susceptibility, but also the sign of the real part [18]. Both nonlinear refraction and nonlinear absorption in solid and liquid samples can be rapidly

## 2- Experiment

The chemical structure of orcein is shown in Fig.1. The solution sample of the dye orcein was dissolved in chloroform. The concentration of the dye solution is 0.5 mM. To prepare the solid films, PMMA was selected as the host material because it is hard, rigid and has a glass transition temperature of 125 °C. It also exhibits good linear optical transmittance, optical stability, thermal stability and moreover better compatibility with organics [18,19]. A known quantity of PMMA and orcein were dissolved in chloroform separately, the concentration of the orcein in chloroform is 0.5 mM, later both solutions were mixed and stirred for 2 hr using a magnetic stirrer. The ratio of PMMA solution and dye solution is 1:1. The film was prepared on a clean glass slide by the casting method and dried at 20 °C for 24 hrs. The film sample has a good purity and uniform thickness. The thickness of the film was measured using digital micrometer and is found to be 70.4 μ m.

The UV-Vis (Ultraviolet-visible) absorption spectra for orcein in solvent chloroform and orcein doped PMMA film are recorded using Cecil Reflected-

measured by the Z-Scan technique, which utilizes self-focusing or self-defocusing phenomena in optical nonlinear materials.

In this article, we report the results of experiments performed using the Z-scan technique to measure the magnitude and sign of the optical nonlinearity for orcein dye in the solvent chloroform and dye doped polymethyl methacrylate (PMMA) film. The optical limiting behavior of the dye solution and polymer film have been studied.

Scan CE 3055 reflectance spectrometer. The optical absorption for the orcein in the solvent chloroform and for orcein doped PMMA thin film with 0.5 mM concentration shows absorption peaks at 501 nm and 553 nm, respectively, as can be seen in Fig.2.

The spectrum of the optical absorption was computed from the absorbance data. The absorption coefficient ( $\alpha$ ) has been obtained directly from the absorbance against wavelength curves using the relation [ 20 ]

$$\alpha = 2.303A/d$$

where d is the sample thickness and A is the absorbance.

The values of absorption coefficient ( $\alpha$ ) at wavelength 532 nm for 0.5 mM concentration of orcein dye in chloroform and polymer film are 6.09 cm<sup>-1</sup> and 83 cm<sup>-1</sup>, respectively.

The Z-scan technique was applied for the measurements of nonlinear optical characteristics of investigated samples. We used a SDL laser beam with 532 nm wavelength and power of 40 mw, which was focused by (+5 cm) focal length lens. The laser beam waist  $\omega_0$  at the focus measures

21.63  $\mu\text{m}$  and the Rayleigh length measured  $Z_R = 2.76$  mm. A 1 mm thickness optical cell containing the orcein in chloroform is translated across the region along the axial direction of the laser beam propagation. The transmission of the beam through an aperture placed in the far field was measured using a photo detector fed to a power meter.

For the open aperture Z-scan, a lens was used to collect the entire laser beam transmitted through the sample replaced the aperture.

The limiting effect of the samples was studied using the same

### 3- Results and Discussion

Fig. 4 shows the closed aperture Z-scan data for 0.5 mM concentration of orcein dye in chloroform and polymer film at incident intensity  $I_0 = 5.44$  kW/cm<sup>2</sup>. The scan of both the samples has peak-valley configuration, corresponding to negative nonlinear refraction index, i.e. self-defocusing occur. The defocusing effect is attributed to a thermal nonlinearity resulting from the absorption of a tightly focused beam traversing through the absorbing dye medium that produces spatial distribution of the temperature in the sample and, consequently, a spatial variation of the refractive index that acts as a thermal lens resulting in phase distortion of the propagating beam.

Let  $\Delta\phi_0$  be the on-axis phase shift at the focus of the lens which is related to the difference in the peak and valley transmission  $\Delta T_{p-v}$  as [10]:

$$\Delta T_{p-v} = 0.406 (1-S)^{0.25} \Delta\phi_0 \quad (1)$$

Where  $S = 1 - \exp(-2r_0^2/\omega_0^2)$  is the aperture linear transmittance with  $r_0$  denoting the aperture radius and  $\omega_0$  denoting the beam radius at the aperture in the linear regime.

laser in the Z-scan technique. The experimental set-up for the demonstration of Z-scan and optical limiting is shown in Fig. 3. A 1 mm quartz cell containing dye solution is kept at the position where the transmitted intensity shows a valley in closed aperture Z-scan curve. A variable beam splitter (VBS) was used to vary the input power. The input laser intensity is varied systematically and the corresponding output intensity values are measured by the photo-detector.

The nonlinear refractive index,  $n_2$ , is given by [10]

$$n_2 = \Delta\phi_0 \lambda / 2\pi I_0 L_{\text{eff}} \quad (2)$$

Where  $\lambda$  is the laser wavelength,  $I_0$  is the intensity of the laser beam at lens focus  $z = 0$ ,  $L_{\text{eff}} = [1 - \exp(-\alpha L)] / \alpha$  is the effective thickness of the samples,  $L$  is the thickness of the sample.

Fig. 5 shows the measured Z-scan data for open aperture set-up for the dye in solvent and polymer film at 0.5 mM concentration. The typical Z-scan data with fully open aperture is insensitive to nonlinear refraction, therefore the data is expected to be symmetric with respect to the focus, but the absorption in the sample enhances

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{\text{eff}}} \quad (3)$$

the valley and decreases the peak in the closed aperture Z-scan curve and results in distortions in the symmetry of the Z-scan curve about  $Z=0$ .

The nonlinear absorption coefficient  $\beta$  can be estimated from the open aperture Z-scan data [ 21 ]

Where  $\Delta T$  is one-valley transmission.

In general, the measurements of the normalized transmittance versus the sample position for the cases of the closed and open apertures allow for the determination of the nonlinear refractive index,  $n_2$ , and the nonlinear absorption coefficient  $\beta$ , since the closed aperture transmittance is an effected by the nonlinear refraction and absorption. The determination of  $n_2$  is less straight forward from the closed aperture scans. It is necessary to separate the effect of the nonlinear refraction from that of the nonlinear absorption. A method to obtain a purely effective  $n_2$  is to divide the closed aperture transmittance by the corresponding open aperture scans [10]. The data obtained in this way purely reflects the effects of the nonlinear refraction. The ratio of Figs 4 to 5 scans is shown in Fig. 6 The values of the

nonlinear refractive index and nonlinear absorption for dye in solvent and polymer film at 0.5 mM concentration are given in Table 1. The value of  $n_2$  in a dye doped film is found to have large value than in the case of solutions, this may be attributed to three reasons, firstly absorption coefficient ( $\alpha$ ) for the dye doped film is larger than in the case of dye solution, secondly the heat dissipation being faster in liquids as compared to that in a solid medium, thirdly it is due to Anderson localization of photons [22]. 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.

**Table 1: Linear and nonlinear optical parameters for orcein in chloroform solution and polymer film**

Concentration 0.5 mM	$n_2$ cm <sup>2</sup> /w	$\beta$ cm/w
Dye solution	$0.15 \times 10^{-7}$	$1.44 \times 10^{-3}$
Polymer film	$2.32 \times 10^{-7}$	$18.61 \times 10^{-3}$

The optical limiting curve for the dye in solvent and polymer film at 0.5 mM concentration is shown in Fig.7. The output power rises initially with an increase in input power for both samples, 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. The limiting behavior observed in both samples is attributed mainly to nonlinear refraction. Since the samples were pumped with cw laser beam the arising nonlinearities are predominantly thermal in nature. The experiment was repeated for the pure solvent chloroform to account for its contribution, but no limiting action was observed.

#### 4- Conclusion

We have measured the nonlinear refraction,  $n_2$ , and the nonlinear absorption coefficient,  $\beta$ , for orcein in solvent chloroform and polymer film at 0.5 mM concentration using the Z-scan technique with 532 nm of SDL laser. The results of Z-scan indicate that the samples have a large optical nonlinearity compared with other optical materials; nonlinear refraction

index  $n_2$  for the samples are of the order of  $10^{-7} \text{ cm}^2/\text{W}$  at 532 nm. The sample shows good optical limiting behavior at 532 nm. All these experimental results show that such material have potential applications in nonlinear optical devices.

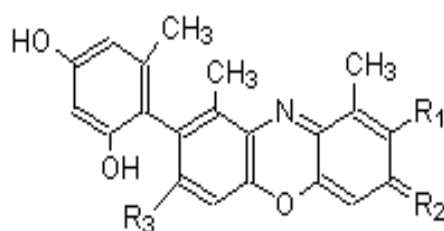


Fig. 1. Chemical structure of Orcein dye.

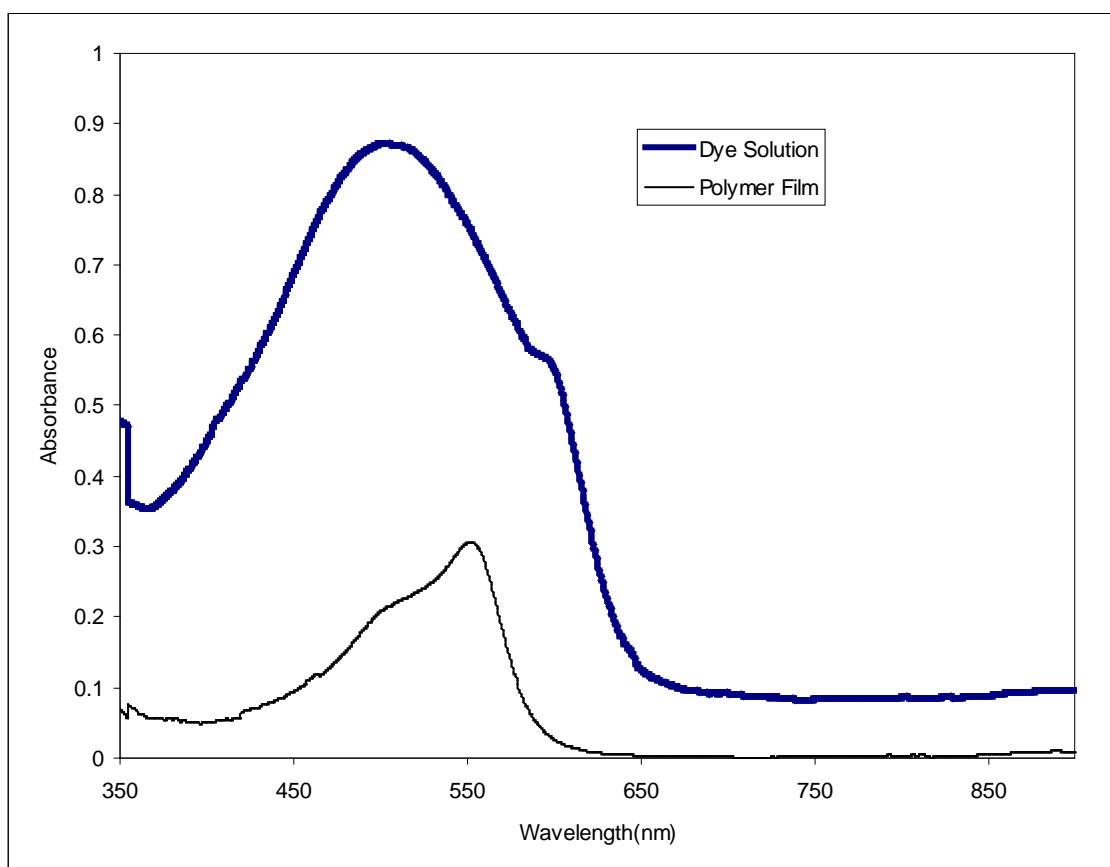
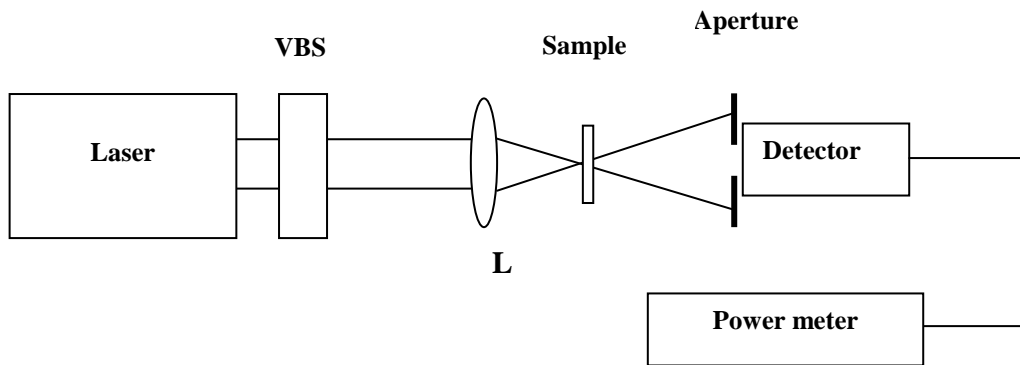
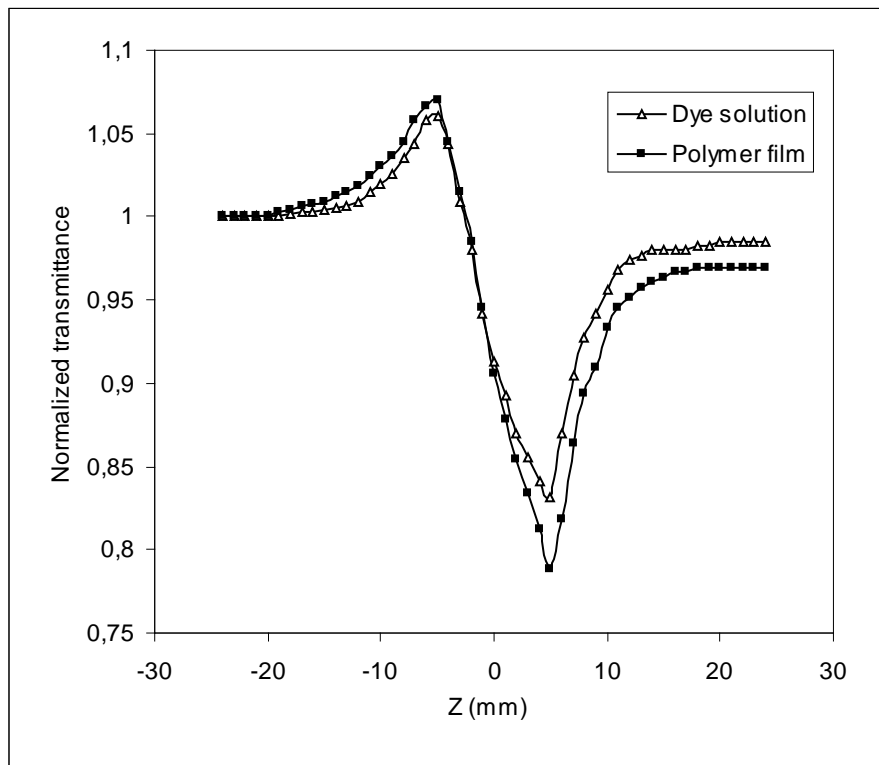


Fig. 2. UV-vis absorption spectrum of orcein solution and dye doped polymer film.



**Fig. 3.** Experimental set-up for Z-scan and limiting effect.



**Fig. 4.** Closed Z-scan curve of the dye in solvent and polymer film.

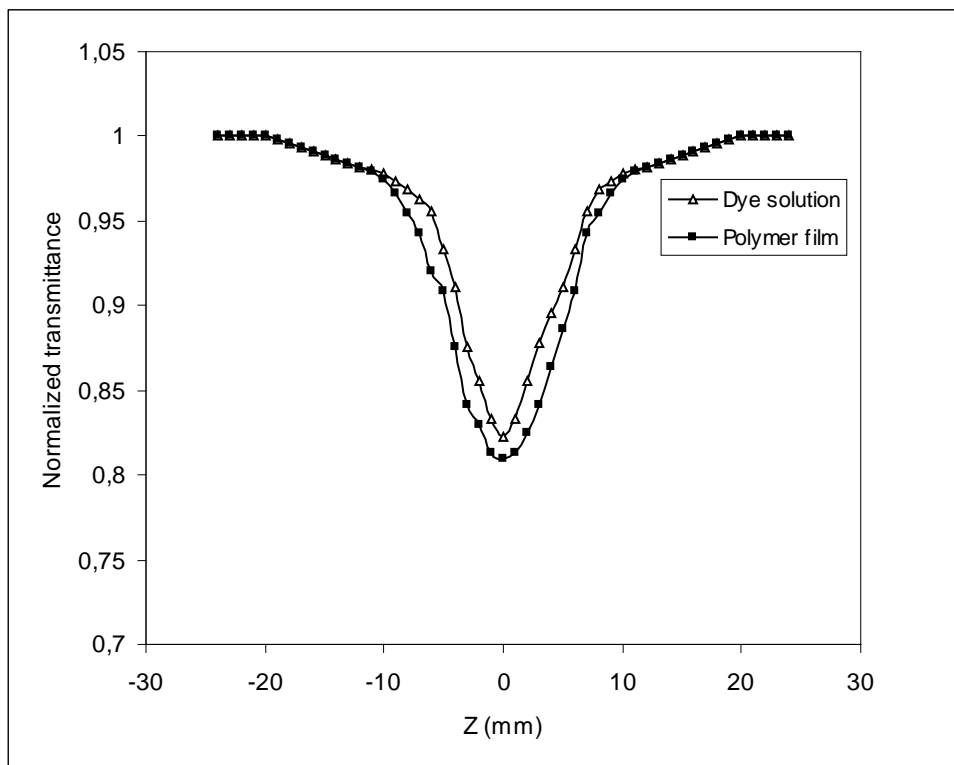


Fig. 5. Open Z-scan curve of the dye in solvent and polymer film.

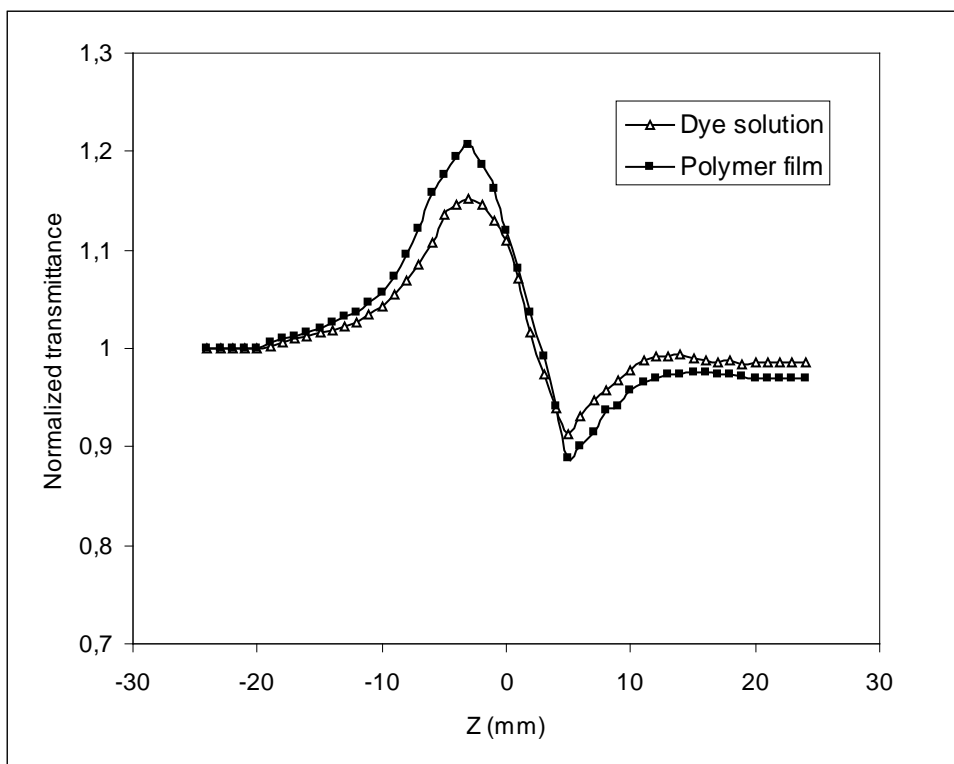


Fig. 6. Z-scan data obtained by dividing the closed aperture data by open aperture data for dye in solvent and polymer film.

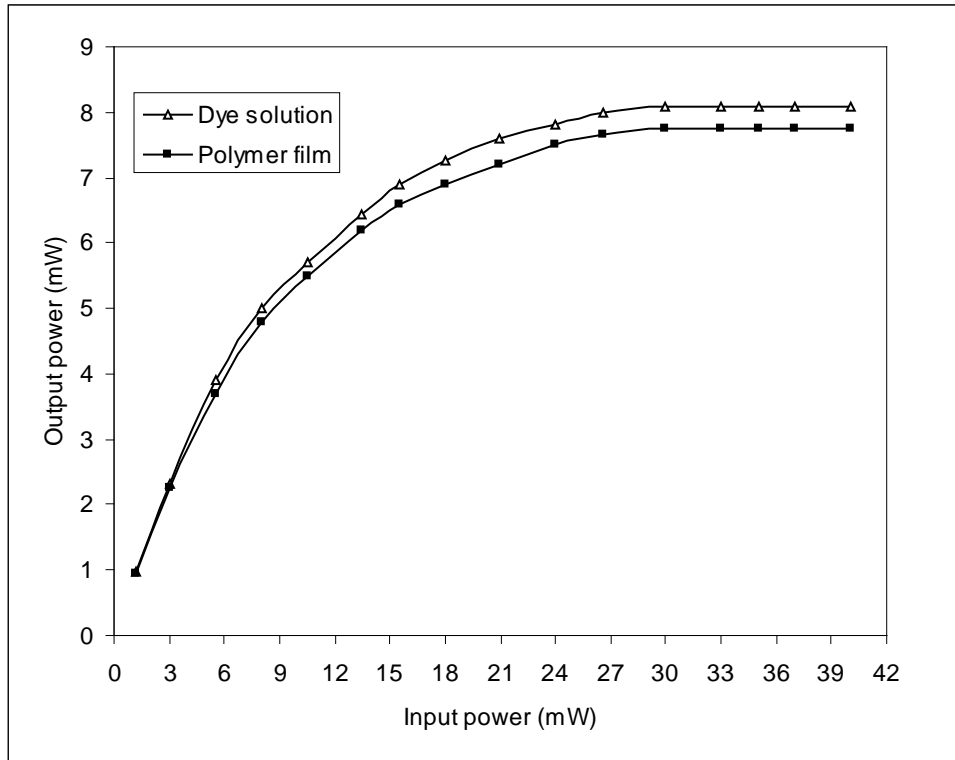


Fig. 7. Optical limiting effects of the dye in solvent and polymer film.

### References

- [1] R. W. Boyd, *Nonlinear Optics*, Academic Press, San Diego, CA, 1992.
- [2] J. Zyss (Ed), *Molecular Nonlinear Optics: Materials, Physics and Devices*, Academic Press, New York, 1994.
- [3] S. P. Karna, A. T. Yeates, *Nonlinear Optics Material*, American Chemical Society, Washington, DC, 1996.
- [4] K. Ogawa, T. Zhang, K. Yoshihara and Y. Kobuke, *J. Am. Chem. Soc.*, 124,22, (2002).
- [5] J. L. Bredas, C. Andant, P. Tackx, A. Petersoons and B. M. Pierce, *Chem. Rev.*, 94, 243,(1994).
- [6] R. R. Tykwinski, U. Gubler, R. E. Martin, F. Diederich, C. Bosshard and P. Gunter, *J. Phys. Chem.*, B 102, 4451, (1998).
- [7] U. Gubler, C. Bosshard, K. S. Lee, *Polymers in Photonics Applications*, Springer Berlin, 2002.
- [8] G. Dela Torre, P. Vazquez, F. Agullo-Lopez and T. Torresm, *Chem. Rev.*, 104, 3723,(2004).
- [9] M. Sheik-bahae, A.A. Said and E.W. Van Stryland, *Opt. Lett.*, 14,955, (1989).
- [10] M. Sheik-Bahae, A.A.Said, T. Wei, D.J.Hagan and E.W. Van Stryland *IEEE J Quant Electron.*, QE-26,760, (1990).
- [11] M.J. Moran, C.Y. She and R.L. Carman, *IEEE J. Quant Electron.*, 11,259, (1975).
- [12] S.R. Friberg and P.W. Smith, *IEEE J. Quant Electron.*, 11,259, (1975).



- [13] R. Adair, L.L. Chase and S.A. Payne, J. Opt. Soc. Am., B 4,875, (1987).
- [14] A. Owyong, IEEE J. Quant Electron., 9,1064, (1973).
- [15] W.E. Williams, M.J. Soileau and E.W. Van Stryland, Opt. Commun., 50,256, (1984)
- [16] P. D. Maker and R. W. Terhune, Phys. Rev., 137,801, (1965).
- [17] J. K. Wang, T. L. Chin, C. H. Chi and C. K. Sun, J. Opt. Soc. Am., B16,651, (1999).
- [18] X. T. Tao, Watanabe T, Kono K, Deguchi T, Nakayama M, Miyata S., Chem Mater., 8, 1326, (1996).
- [19] H.M. Zidan,. Appl. Polym. Sci., 88, 104, (2003).
- [20] F. Yakuphanoglu, S. Ilcan, M. Caglar and Y. Caglar, J. of Optoelectro and Adv. Mater., 9, 218, (2007).
- [21] G. Vinitha and A. Ramalingam, Las Phy., 18, 37, (2008).
- [22] R. R. Krishnamurthy and A. Ramalingam, Opt Applicata, XL, 187, (210).

### دراسة الخواص اللاخطية لمحلول صبغة الاورسين ولبوليمر مشوب بالاورسين وتطبيقاتها في مجال المحددات البصريه

رضاب خلف منشد و قصي محمد علي حسن

#### الخلاصة

يتناول هذا البحث استخدام تقنيه المسح باتجاه z للحزمة المفردة لحساب المعاملات البصرية اللاخطية لصبغه منحلة بالكورفورم ولبوليمر مشوب بصبغه الاورسين. حيث استخدم ليزر ذي موجه مستمرة له طول موجي 532nm. أبدت هذه المادة خواصا بصرية لاخطية سالبة. قيم معامل الانكسار اللاخطي هي  $cm^2/W$   $0.15 \times 10^{-7}$  و  $2.32 \times 10^{-7}$  لمحلول الصبغه ولبوليمر مشوب بصبغه الاورسين على التوالي وقيم معامل الامتصاص اللاخطي هي  $cm/w$   $1.44 \times 10^{-3}$  و  $18.61 \times 10^{-3}$  على التوالي. كذلك درست خواص التحديد البصري لمحلول الصبغه ولبوليمر المشوب بصبغه الاورسين. فأظهرت النتائج بأن هذه المادة تعتبر مادة واعده في مجال التطبيقات البصرية الحديثة.

**الكلمات مفتاحيه:** بصريات لاخطيه، معامل انكسار لاخطي، تقنيه المسح باتجاه Z، المحدد البصري، اصباغ