Optical Properties for Thin Film of Coumarin 334 Organic Laser Dye doped with PVA Polymer and Al_2O_3 Nanoparticles

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ABSTRACT

In this work,the optical properties for thin film of Coumarin 334 organic laser dye doped with PVA polymer and AL_2O_3 nanoparticles, dissolved in ethanol solvent at differents concentrations (1×10^{-5}, 3×10^{-5}, 5×10^{-5} and 7×10^{-5} M) at room temperature has been studied. Thin films tasts prepared from dyes solutions drop-casting method at (10^{-3} M). The recorded absorption and transmission spectra of all samples within the range of (328-530) nm .The quantum efficiency increased while life time decreased when increment ratio .The results presented that thin films have very large nonlinear refraction as compared with dyes as solutions. The measurements indicated that the nonlinear refractive index increased linearly with the nonlinear phase shift. The result suggest that it can be used as active laser medium and potential medium for several optoelectronic applications.

Keywords : *Organic Laser Dyes, Dye Lasers Linear Optical Properties.*

INTRODUCTION

A dye laser is a laser which uses an organic dye as the lasing medium, such as liquid solutions, gases and solid state. Organic dyes are characterized by a strong absorption band in the visible region of the electromagnetic spectrum. Such a property is found only in organic compounds which contain an extended system of conjugated bonds alternating single and double bonds [1]. In a dye laser, these molecules are dissolved in an organic solvent or incorporated in to a solid matrix. Although dyes have been demonstrated to laser in the solid, liquid, or gas phase ,it is in the liquid and solid phases that dyes have made a significant impact as laser media [2]. In this paper, the linear optical properties for thin film of Coumarin 334 organic laser dye doped with PVA polymer and Al_2O_3 nanoparticles dissolved in ethanol solvent have been study.

Theory

The linear absorption coefficient (α_o) was determined by the following formula [3]:

$$\alpha_o = \frac{\ln\left(\frac{1}{T}\right)}{t} \qquad (1)$$

Where (t) is the thickness of the sample, (T) is its transmittance, (n_o) its refractive index, which can be found from the transmittance spectrum of the film according to the following formula [3]:

$$n_o = \frac{1}{T} + \left(\frac{1}{T^2} - 1\right)^{\frac{1}{2}} \qquad (2)$$

Transmittance is the relative percent of light that passes through the solvent. Thus, if half the light is transmitted, it can be said that the solution has 50% transmittance [4].

$$T\% = \left(\frac{I}{I_0}\right) \times 100\% \qquad (3)$$

Where (I_o) is the intensity of the incident light beam, (I) is the intensity of the light coming out of the solvent. The relationship between transmittance (T) and absorbance (A) is expressed by the following equation [4]:

$$A = \log 10 \left(\frac{1}{T}\right) \qquad (4)$$

Materials and Chemicals

Coumarin and their derivatives represent a class of wellknown laser dyes in the blue-green spectral region, characterized by high-emission quantum yields and find many practical applications in the various fields of science and technology. Since they exhibit fluorescence in the UV-Vis region, they are used as colorants, dye lasers, and non-linear optical fluorophores [5]. Molecular formula $C_{17}H_{17}NO_3$ as shown in Figure (1).Solutions at concentration (10^{-4} M) from Coumarin 334 organic laser dye in ethanol solvent were prepared. The powder was weighted by using an electronic balance type (BL 210 S, Germany), having a sensitivity of four digits. Different concentrations from each dye (1×10^{-5}, 3×10^{-5}, 5×10^{-5}, and 7×10^{-5} M) were prepared according to the following equation [6]:

$$W = \frac{M_w \times V \times C}{1000} \qquad (5)$$

Where W is the weight of the dissolved material (g), M_w is the molecular weight of the material (g/mol), V is the volume of the solvent (ml), and C is the concentration (M).The prepared solutions were diluted according to the following equation [7]:

$$C_1 V_1 = C_2 V_2 \qquad (6)$$

Where C_1 and C_2 are the primary and new concentration, respectively, V_1 is the volume before dilution, and V_2 is the volume after dilution.

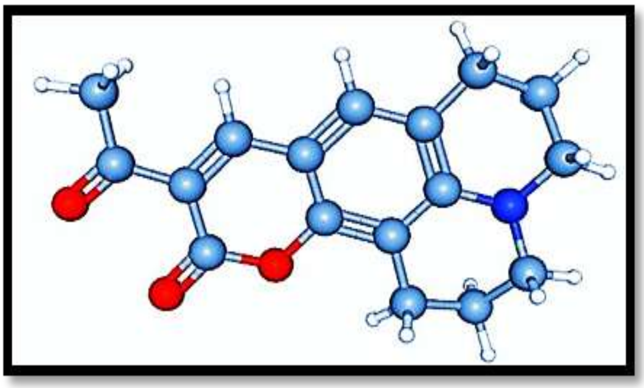


Figure (1): Molecular structure of Coumarin 334 and organic dye.

Result And Discussion

Figures (2) show 2-D and 3-D images of AFM for thin films Coumarin (334) doped with PVA polymer and (Al_2O_3) nanoparticles at (10^{-3}) M, a diagram of distribution of growth granular groups on the surfaces of the deposited films.Table (1) shows that the average diameters (grain size) of thin films .It is found that the grain size and the (r.m.s) of surface roughness increases when thickness increases for thin films Coumarin (334) doped with PVA polymer and (Al_2O_3) nanoparticles [3].

Absorbance spectra of coumarin organic laser dye at different concentrations (1×10^{-5}, 3×10^{-5}, 5×10^{-5} and 7×10^{-5} M) in ethanol solvent recorded for wavelengths (190 to 1100 nm) were tested using UV-VIS spectrometer model (Aquarius 7000, Optima, Japan), at room temperature. As shown in Figures (3). From these Figures we can observed that absorption spectrum of coumarin (334) solution has a wide spectral range at wavelength range between 328-530 nm. It has also increased the absorbance due to the increase in concentration which produces an increase in number of molecules in volumetric unit which effect in the energy state, as well as increasing of linear absorbance index and refractive index and decrease in transmittance. The results show good agreement with Beer-Lambert law [8].

The linear absorbance spectra of thin films of Coumarin (334) dye at concentration (10^{-3}) M doped with PVA and (Al_2O_3) nanoparticles are shown in Figure (4) .The present results show that the absorption peaks were shifted toward the longer wavelengths after addition (PVA) polymer and

(Al_2O_3 nanoparticles) to pure dyes. This shift obtain due to electronic and vibrational states of interfacial molecules, which is lead to increasing absorption for all samples of nanocomposites, this is suggested to take place because of the excitations of high occupation molecular orbital (HOMO) electrons to the lowest inoccupation molecular orbital (LUMO).

The nonlinear refractive coefficient (n_2) by closed-aperture Z-Scan measurements and nonlinear absorption coefficient (β) by open-aperture Z-Scan. The measurements were done at 457nm,84 mW. The normalized transmittances of Z-Scan measurements as a function of distance of Coumarin 344 organic laser dyes dissolved in ethanol solvent at concentrations (1×10^{-5}, 3×10^{-5}, 5×10^{-5} and 7×10^{-5} M) M shown in Figures (9 and 10), the nonlinear effect region is extended from (-2) mm to (2) mm. The peak followed by a valley transmittance curve obtained from the closed aperture Z-Scan data indicates that the sign of the refraction nonlinearity is positive ($n_2 > 0$), leading to self-focusing [10].The normalized transmittances of Z-Scan measurements as a function of distance of for thin films of Coumarin 344 organic laser dyes doped with PVA polymer and (Al_2O_3) NPs in Ethanol solvent in Figures (9). Self-focusing lensing is observed also.(Saturable Absorption) phenomenon were observed for open-aperture Z-Scan of thin films as shown in Figures (11). The nonlinear parameters are calculated ,as tabulated in Table (2) from this Table we show that the values of nonlinear parameters (n_2 and β) are increased with increasing the mixing ratios, as increasing the values of linear parameters (α_o and n_o). This is due to increasing number of molecules per volume unit at high mixing ratios .

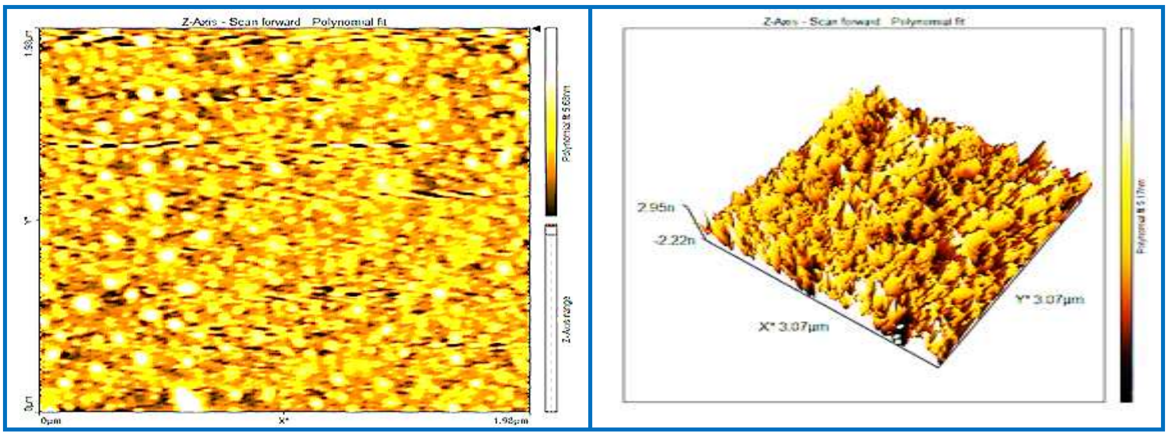


Figure (2): 2-D and 3-D AFM images for thin films of Coumarin (334) doped with PVA polymer and Al_2O_3 NPs.

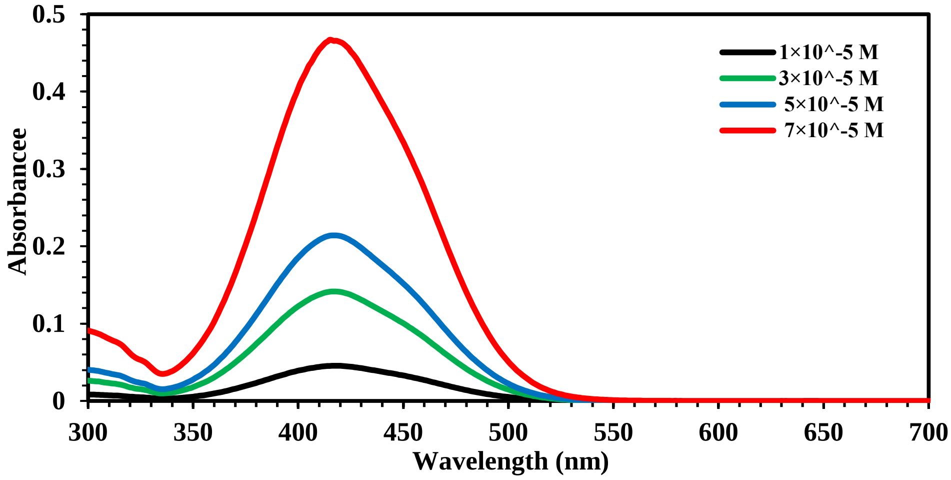


Figure (3):The absorbance spectra for Coumarin (334) organic laser dye at different concentrations.

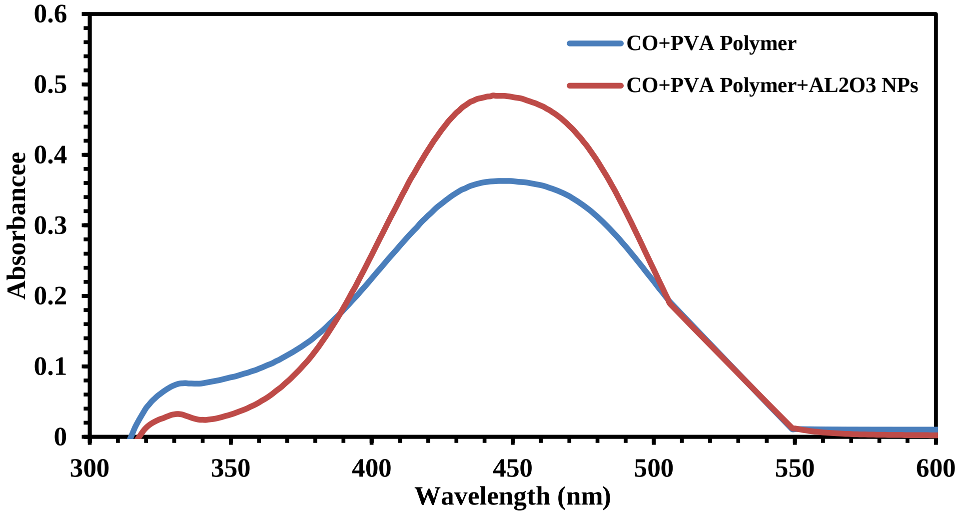


Figure (4): The Absorbance Spectrum For Thin Films of Coumarin (334) Organic Laser Dye Doped With PVA Polymer And Al_2O_3 Nps.

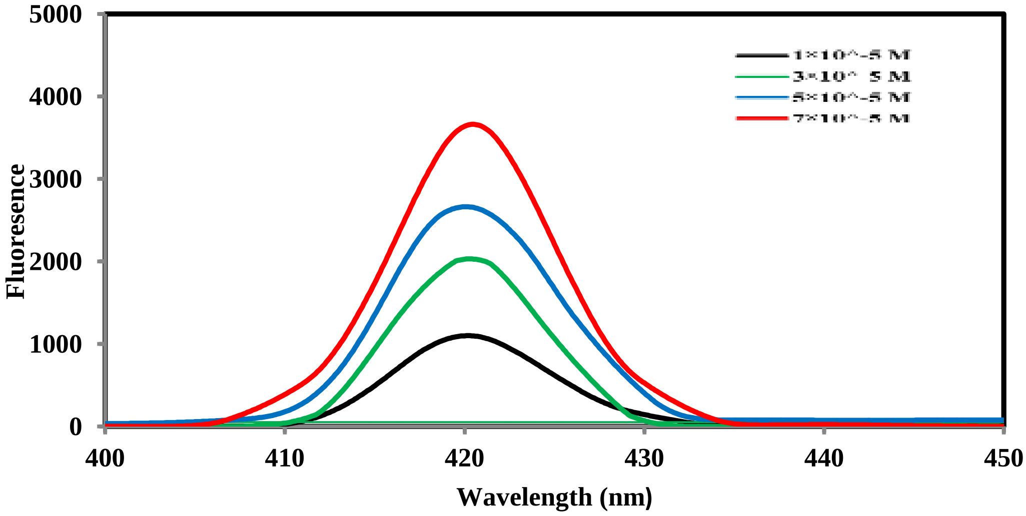


Figure (5): Fluorescence spectra for (Coumarin (334) organic laser dye at different concentrations.

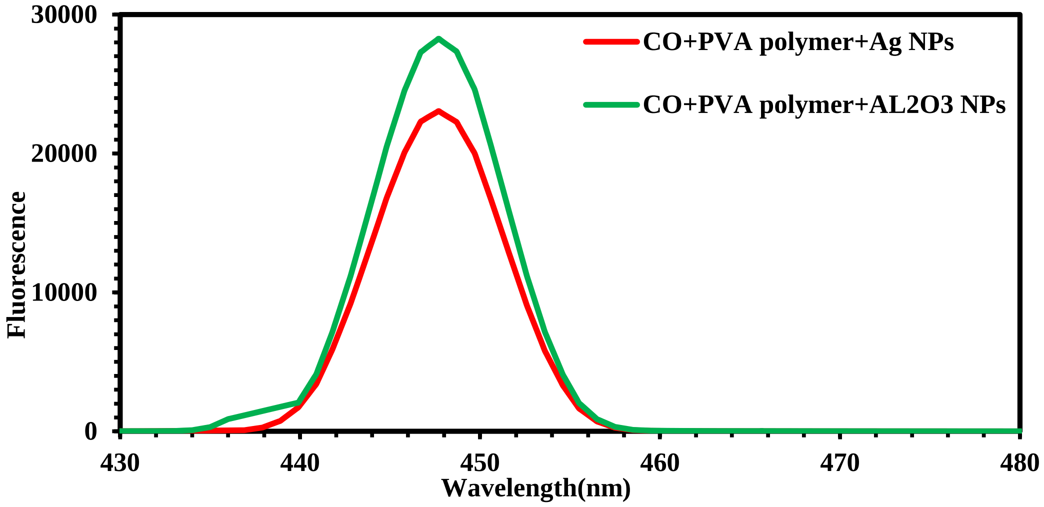


Figure (6): Fluorescence spectrum for thin film for Coumarin (334) organic laser dye doped with PVA polymer and (Al_2O_3) NPs.

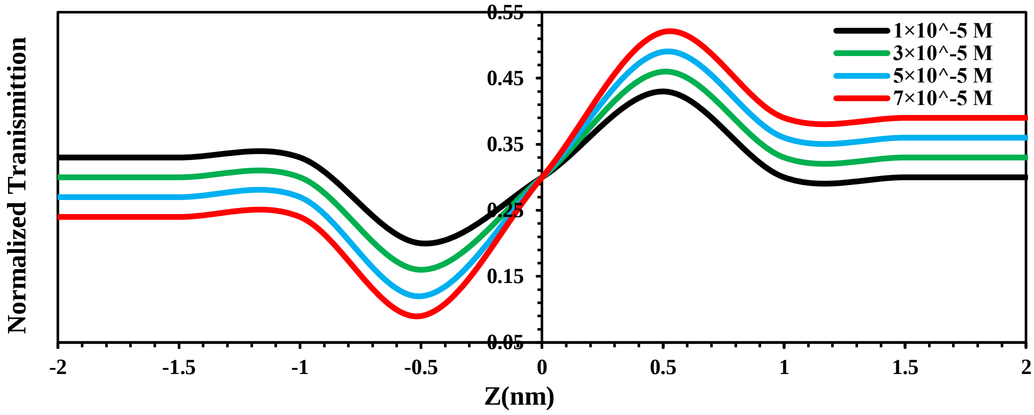


Figure (7): Closed-aperture Z-Scan data for different concentrations of (Coumarin (334)) organic laser dye in (Ethanol) solvent.

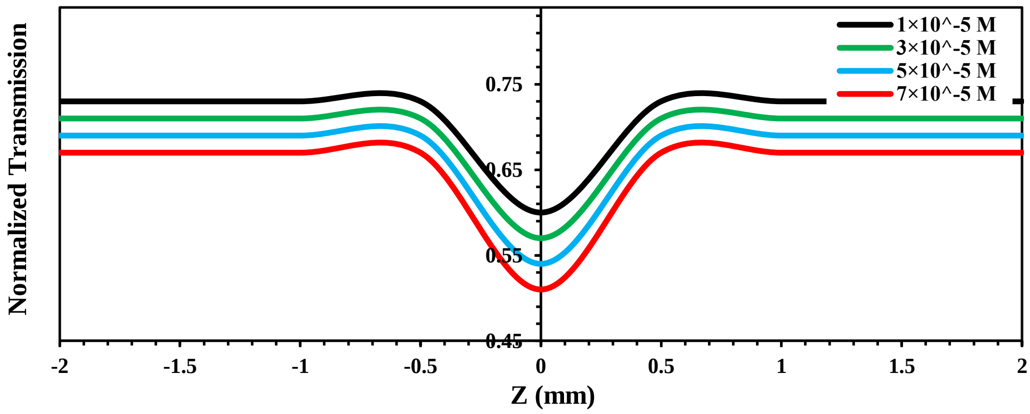


Figure (8): Open-aperture Z-Scan data for different concentrations of (Coumarin (334)) organic laser dye in ethanol solvent.

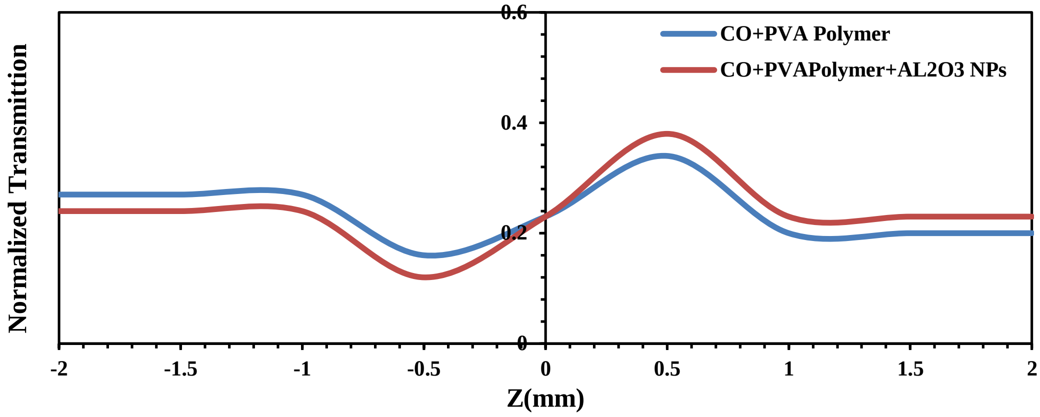
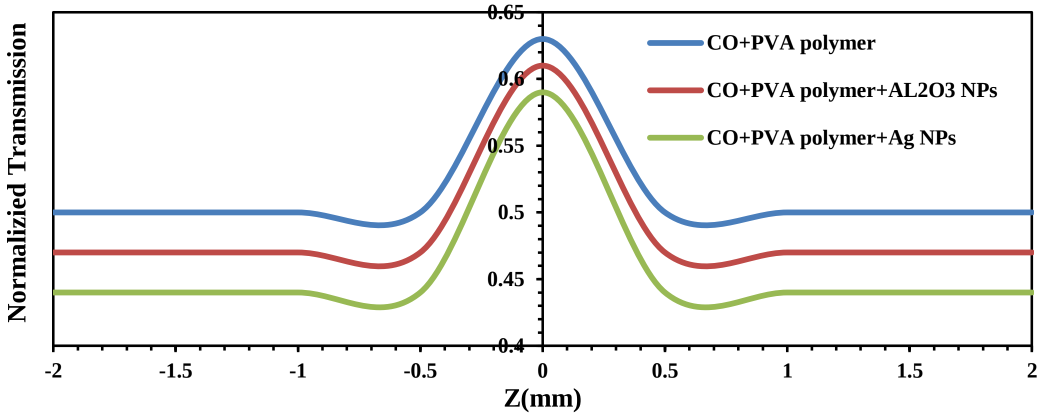


Figure (9): Closed-aperture Z-Scan data for thin films of (Coumarin (334)) organic laser dye doped with PVA polymer and (Al_2O_3) NPs.



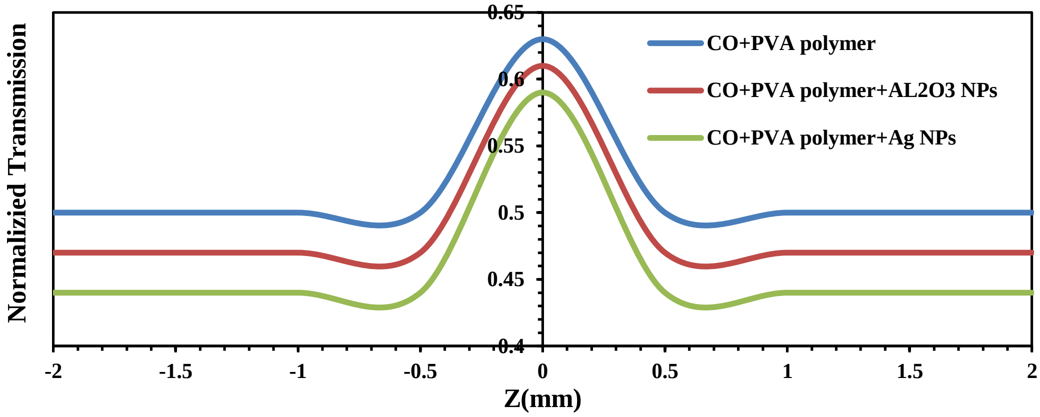


Figure (10): Open-aperture Z-Scan data for thin films of (Coumarin 344) organic laser dye doped with PVA polymer and(Al_2O_3) NPs.

Table (2): Linear and nonlinear optical parameters for different concentrations of Coumarin (344) and its thin films at λ=457nm.

Material	Concentration (Mol/L)	T	$(\alpha_\circ)$ cm^{-1}	$n_\circ$	ΔT_{P-V}	n_2 (cm^2/mW)	β (cm/mW)
Coumarin (344) (Solutions)	1×10^{-5}	0.9353	0.0667	1.1470	0.011	2.1188×10^{-11}	0.8392×10^{-3}
	3×10^{-5}	0.8170	0.20208	1.4296	0.024	4.2731×10^{-11}	1.0786×10^{-3}
	5×10^{-5}	0.7361	0.3062	1.6777	0.031	6.3839×10^{-11}	1.3073×10^{-3}
	7×10^{-5}	0.5086	0.6759	2.0583	0.043	6.9855×10^{-11}	1.4265×10^{-3}
CO+PVA polymer (Thin films)	1×10^{-3}	0.6018	5374.2	1.158	0.110	1.7310^{-7}	1.245
CO+PVA polymer + Al_2O_3 NPs (Thin films)	1×10^{-3}	0.5717	5971.44	1.1623	0.123	2.3410^{-7}	2.673

Conclusions

. The results showed when the concentrations increased the absorbance also increased for the same wavelength. It is concluded from this study that the absorption spectra of mixing of two dyes has increased with increasing the mixing ratios. As it can be seen that the fluorescence spectra also increased with increasing ratios.Absorbance and Fluorescence spectra of thin films, they have narrower band width than dyes as solution also the emission peaks are higher intensity than as solution. By using Gaussian beam from CW pulsed laser at 457 nm, we studied the nonlinear optical properties using Z-scan techniche. The nonlinearity of thin film is larger than those for pure dyes as solutions. As well as thin films possess very large nonlinearity as compared with pure of dyes as solution. The relation between the nonlinear refractive index and the nonlinear phase shift is a linear increasing relation.

The peak followed by a valley transmittance curve obtained from the closed aperture Z-Scan data indicates that the sign of the refraction nonlinearity is positive ($n_2 > 0$), leading to self-focusing, on the other hand all thin films exhibited (Saturable Absorption) behavior. The result imply that it can be used as active laser medium and potential medium for various optoelectronic applications.

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