Spectroscopic Properties Study of Coumarine -47 Dye doped Poly Methyl Methacrylate

*Mohammad T. Hussian** *Rafah A. H. Omar***
*Lamia K.Khlaif***

Received 3, January, 2011
Accepted 20, May, 2011

Abstract:

A thin film of Coumarine -47 has been prepared in a chloroform solvent mixed with the same ratio of Poly Methyl Meth Acrylate (PMMA) at different concentrations ($1x10^{-4}$, $5x10^{-4}$ and $1x10^{-3}$) M . This film has been prepared by using thermal oven with temperature about (333 K) and pressure at 10^{-2} torr for 1 hour. The prepared thin film thickness measured using Michelson interferometer is around 0.2mm.

The quantum efficiency decreased as follows (80%, 74% and 59%) respectively.

The radiative life time and fluorescent life time has been investigated as a function of dye concentration and it can be shown that they both decreased (8.57, 3.35 and 2.5) ns and (6.85, 1.97 and 1.85) ns respectively.

It has been determined that the resulting overlap between the absorption spectrum and fluorescence spectrum for thin film is less than that shown for the solution, therefore stock shift will be more . From the morphological studying of the thin film it has been shown that with the increasing the concentration the defects and inhomogenity of the film increase.

Key words: Coumarin dye, Dye solutions, Spectroscopic properties.

Introduction:

In a solid – state dye laser the organic dye molecules are uniformly distributed in a highly homogenous polymer matrix. An example of such polymer is a highly pure form of (Poly Methyl Mehta Acrylate) (PMMA). Solid state dye lasers that span from the ultraviolet to the near Infrared regions have been successfully demonstrated photo stability of laser dyes in solid matrices remain an issue for continuous study [1].AN Important feature of the dye laser is easily tunable over a wide range of a wavelengths. Fluorescent dyes play an important role for staining and censoring in analytical chemistry, environmental science, biology and medicine [2]. Some fluorescence dyes are used in dye lasers as active media [3]. To under stand the behavior of the prepared laser dye – doped polymer thin film a spectral properties (absorption and fluorescence) have been studied.

Theory

Once a molecule has absorbed a photon it can emit a photon upon returning to the electronic ground state from the electronic excited state. As with absorbance, the strength of the transition is governed by the transition moment. The related peaks in turn will be the dominant peaks in the resulting spectrum. Two processes that emit light from a dye molecule are fluorescence, where the emitted photon is from the decay of excited state S_1 to the ground state S_0, and

---

*University of Baghdad . college of scince – physics department
**University of Baghdad . college of scince for women – physics department

phosphorescence, which is a transition from the triplet state T_1 to the electronic ground state S_0. Most ground states are singlet due to the total spin being zero, cancelled out by pairs of electrons with opposite spin. The direct transition from S_0 to T_1 is forbidden since the value of the spin quantum number S would have to change. Similarly a transition from $T_1$to S_0 is slow due to the same reason, resulting in a slow process called phosphorescence. Triplet-triplet absorption bands tend to heavily overlap the fluorescence region. The triplet state has a long lifetime leading to a buildup of population inversion.

However since the transition from S_0 to T_1 is forbidden, it would require very high dye concentrations for lasing. Fluorescence can be used at relatively low dye concentrations for laser applications. If the triplet state is at a lower energy thanS_1, it then competes with the buildup of the excited $S1$ state, lowering the quantum yield of the fluorescence.

Decay to the lowest level of S_1 is very quick provided that the temperature is low enough to prevent thermal excitation to a higher vibronic level within S_1. The number of excited atoms N where k is the Boltzmann's constant is $N_{excited} = N_0$ exp [$\Delta E=kT$]. At room temperature $kT = 2.15x10^{-2} eV$ so the population density of the excited state will be low.

The longevity of different excited states is important to the usefulness of a dye as a laser medium. The typical time scales for these processes are: 1ps from S_2 to S_1 (non-raditative transition), 10ns from S_1 to T_1 (non-raditative transition), 1µs from T_1 to S_0 (phosphorescence) and 1ns from $S_1$to S_0 (fluorescence) (Figure 1) [4].

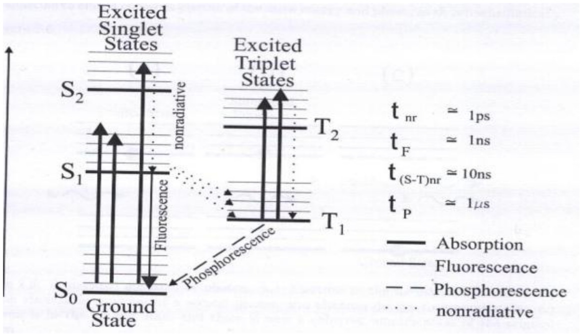


Fig (1) Dye molecule energy state [4].

1. Fluorescence

Excitation of a molecule from absorption of a photon or thermal energy promotes the molecule to an excited energy state, setting up the possibility of emission of a photon. The excited molecules may lose energy through a non-radiative process to reach the lowest vibrational level of the excited state. Fluorescence is then the radiative loss of energy as a photon is emitted from a molecule in the excited state returning to the ground state. Since a non-radiative loss of energy occurs between the absorption and subsequent fluorescence, the emitted photon is of lower frequency than the absorbed photon producing a red shift between the absorbance and fluorescence spectra. The fluorescence from the excited state dye molecule is reabsorbed by the ground state molecule which shifts the fluorescence peak to lower energy [5].

2. Quantum Efficiency

The fluorescence efficiency Φ_{fm}, also known as the quantum yield, indicates the fraction of pump photons that are converted to fluorescence photons per dye molecule, where the maximum value is unity. Fluorescence quantum yield is one of the key photophysical quantities that are amenable to direct experimental determination. The quantum yield of fluorescence is a measure of the rate of non-radiative transitions that compete with the emission of light. The knowledge of fluorescence quantum efficiency of organic dyes and its concentration dependence are essential for selecting efficient laser media [6]. The fluorescence efficiency for different concentrations of C_{47} in chloroform solvent was determined and their values are listed in table (1).

The spectrum of the molecular fluorescence F(ύ) gives the relative fluorescence intensity at wave-number (ύ), this is related to the quantum efficiency by the following equation [7,8]

$$q_{fm} = \int_{0}^{\infty} F(\upsilon')d\upsilon' \quad ------ \quad (1)$$

In order to evaluate absolute quantum efficiency, we have to consider both the radiative and non-radiative processes taking place in the medium, therefore

$$q_{fm} = \frac{K_{fm}}{K_{fm} + \Sigma K_{d}} = \frac{K_{fm}}{K_{fm} + K_{IC} + K_{ISC}} \quad ----- \quad (2)$$

Since $K_{fm} = 1/\ \tau_{fm}$ and $\tau_f = 1 / K_{fm} + \Sigma K_d$

Therefore

$$q_{fm} = \frac{\tau_{f}}{\tau_{fm}} = \int_{0}^{\infty} F(\upsilon') \quad d\upsilon' \quad ------ \quad (3)$$

Where τ_f is the fluorescence lifetime and τ_{fm} is the radiative lifetime of the excited state to circumscribe the possible reasons for q_{fm} variations. The radiative lifetime being a function of the absorption strength, it is invariant for any molecule unless its absorption spectrum changes. As this, to first order, is not the case in concentration quenching, the mechanism for q_{fm} variations must be changes in τ_f, caused, for example, by changes in the nonradiative lifetime of the excited state [9].

Material and Method:

A- Solutions preparation

Solutions of concentration $1x10^{-4}$ M for C_{47} in chloroform solvent were prepared. The powder is weighting using an electronic balance type (mettler AE 166) German – mode having a sensitivity four digits. Different concentration was prepared according to the following equation:

$$\mathbf{W} = \frac{\mathbf{M_W \ x \ V \ x \ C}}{\mathbf{1000}} \quad \ldots\ldots (4)$$

Where

where W weight of the dissolved dye (gm)

$\mathbf{M}_W$ molecular weight of the dye (gm/mol)

V the volume of the solvent (ml)

C the dye concentration (mol/l)

The prepared solution were diluted according to the following equation

$C_1 V_1 = C_2 V_2$ …….. (5)

Where

C_1 Primary concentration

C_2 New concentration

V_1 the volume before dilution

V_2 the volume after dilution

There concentration was prepared for C_{47} are $1x10^{-4}$, $5x10^{-5}$and $1x10^{-5}$ molary.

B – preparation of thin – film

Dye doped polymer films were fabricated by dry method. The solution of the polymer is prepared by dissolving the required amount of polymer. A required amount of dye solution was added to polymer solution, on a glass Petri dish, put in oven and up at 333 K

Process of solution mixing and their ratios were performed for each concentration of dye – doped as the following.

C_{47} (two ml) + PMMA (two ml)

The vacuum Galleukamp kind of German – made and equipped with a vacuum pump rotary.

The steps of preparation of the thin film dye laser as shown in fig 2.

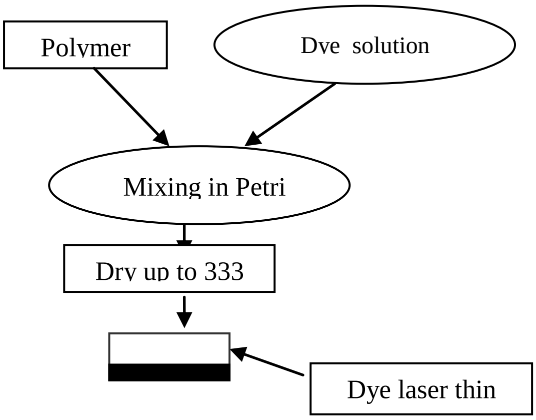


Fig (2) Steps of preparation of the thin film dye laser.

C – Spectrophotometer

Absorption spectrum was measured by a (CARY 100 cone .UV – visible spectrophotometer) by the processor (Varian) Japanese.

D – Spectrofluorophotometer

Fluorescence emission and excitation were measured from the samples prepared at section using a Shimadz Rf – 510 – spectrofluorophotometer . The instrument computerized and operates in the wavelength range (200 – 800) nm and a scanning speed of 480 (nm ⁄ min) .

E – Refractometer

Refractometer index was measured by using refractometer model ABBE – 60 manufactured by (Bellingham and Stanley LTD, Tunbridg wells, England) with in the rang (1.3 – 1.77)

F – Optical microscope.

Are a standard microscope (light) with a digital camera and a microscope that has a permeability and reflectivity, with five different amplifications x (50 – 100 – 200 – 500 – 2000)

The quality of the microscope and the camera is (Nikon Eclipse EME 600 with digital camera DXM 1200 F). Attached camera and microscope to computer and can be calculator through a special program called (Act.1).

G – Thickness measurement

Michelsoń s interferometer was used to measure the thickness of dye – doped thin film. Using He – Ne laser (632.8nm) the film thickness can be determined by the following formula.

$$t = \frac{\Delta x}{x} \cdot \frac{\lambda}{x} \quad \ldots\ldots\ldots\ldots \quad (6)$$

where, x :- the fringe width.
Δx:- the fringe spacing
λ :- the wavelength of laser

Results and Discussion:

To study the absorption spectrum for the chloroform, it can be shown from figure (3) that it has no absorption at the spectral range of C_{47} dye within wavelength range (300 – 500nm). Absorption spectra of C_{47} dissolved in chloroform with different concentration ($1x10^{-4}$, $5x10^{-5}$ and $1x10^{-5}$ M) are shown in figures 4, 5 and 6 respectively. From these figures one can deduced that C_{47} solution absorption spectrum has a wide spectral range at wavelength range (300 – 500nm). It has also be shown that maximum absorption appears at higher concentration at a wavelength (393nm) and red shifted by ≈ 13nm, while at lower concentration ($1 x 10^{-5}$M) in other word at wavelength 380nm this is due to the fact that an increase in concentration produce an increase in number of molecules in volumetric unit which effect the energy state. This increase in concentration produce an increase in perturbation field of the molecules and while at the concentration decreases the relative intensity decrease which is in agreement with Beer – Lambrat law. Table (1) presents the concentration variation with the maximum absorption wavelength (λ_{abs}) and relative intensity.

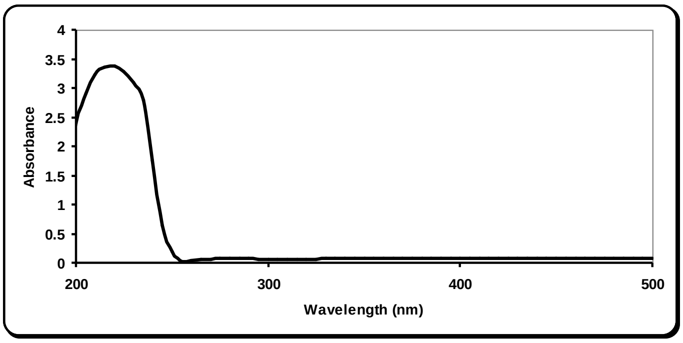


Fig (3) Absorption spectra of chloroform

Table (1) The effect of dye concentration variation on the absorption spectra and the relative intensity

Concentration (mol/liter)	I_{abs} (a.u)	λ_{max} (abs) (nm)	$\Delta\lambda_{abs}$ (nm)	$\Delta\lambda_{abs}$(FWHM)(nm)
$1x10^{-5}$	20.5	380	50	20
$5x10^{-5}$	61.5	385	70	25
$1x10^{-4}$	66.1	393	90	30

The spectral properties of chloroform with C_{47} were studied by recording the fluorescence emission spectra for different concentrations ($1x10^{-4}$, $5x10^{-5}$ and $1x10^{-5}$ M) as shown in figures (4),(5) and (6). The peak wavelength of fluorescence for the chloroform with C_{47} dye shows red shift from that for pure dye. This change may be attribute to the structure of dye, the fluorescence from the excited state dye molecule is reabsorbed by the ground state molecule which shifts the fluorescence peak to lower energies. The fluorescence bandwidth of the dye in chloroform solvent is boarder than that for pure dye, this is due to the fact that the spectral characteristics of the dye insolvent depends on the intermolecular between the dye and chloroform molecules.

The relative intensity was determined as a function of the dye concentrations and the results are tabulated in table (2).It can be shown that the highest relative intensity for the peak wavelength at the highest dye concentration.

Table (2) The effect of dye concentration variation on the fluorescence spectra and the relative intensity

Concentration (mol/liter)	I_{flo} (a.u)	λ_{max} (flo) (nm)	$\Delta\lambda_{flo}$ (nm)	$\Delta\lambda_{flo}$ (FWHM) (nm)
$1x10^{-5}$	18	402	30	25
$5x10^{-5}$	44.5	405	60	40
$1x10^{-4}$	64.6	410	70	45

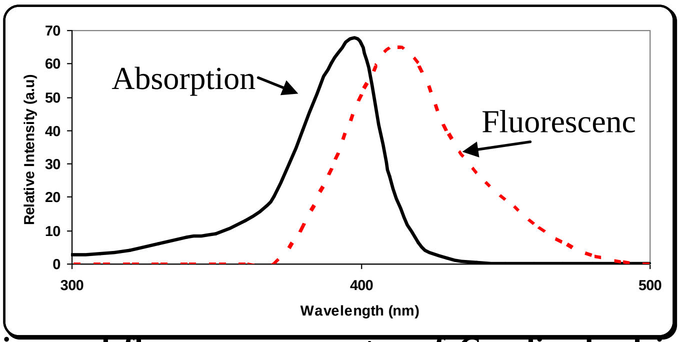


Fig (4) Absorption and fluorescence spectra of C_{47} dissolved in chloroform at concentration ($1x10^{-4}$ M)

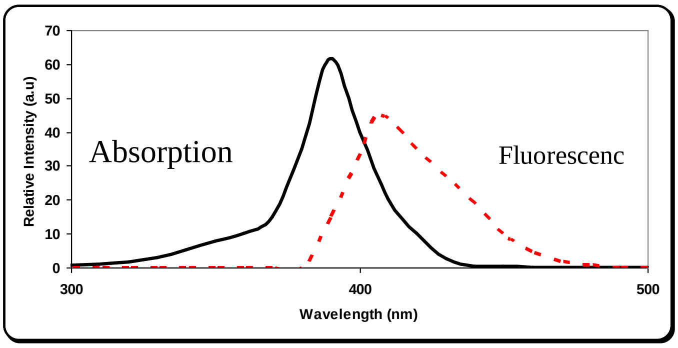


Fig (5) Absorption and fluorescence spectra of C_{47} dissolved in chloroform at concentration ($5x10^{-5}$ M)

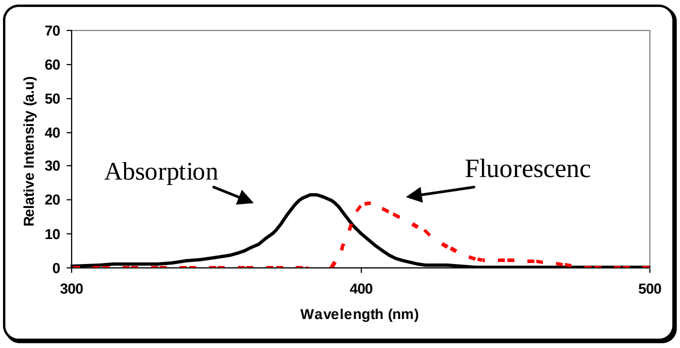


Fig (6) Absorption and fluorescence spectra of C_{47} dissolved in chloroform at concentration ($1x10^{-5}$ M)

The spectral study of polymeric thin film for dye solution:

Through the study of the absorption spectra of the polyermer PMMA in chloroform as shown in fig(7) it observes that no absorption in the rang of the C_{47} dye.

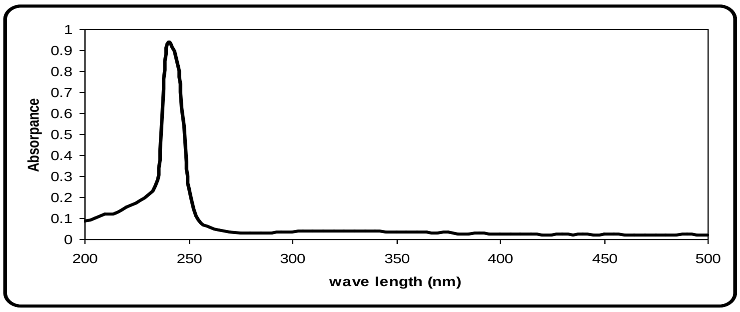


Fig (7) The absorbance of the polymer in a chloroform

The absorption specter of polymeric thin film for the dye solution C_{47}+PMMA in chloroform at a different concentration ($1x10^{-4}$, $5x 10^{-4}$ and $1x 10^{-3}$) M as shown in figure (8,9 and 10)

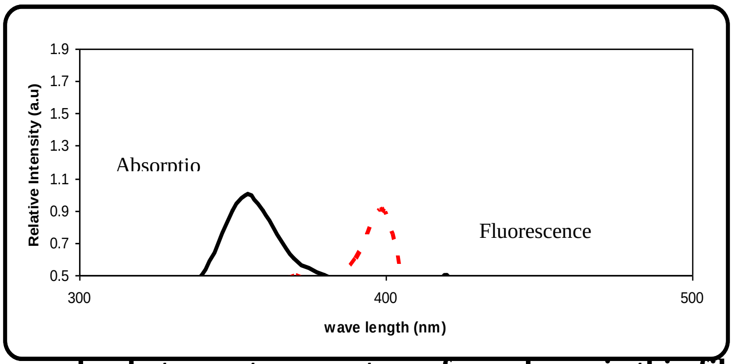


Fig (8) The overlap between two spectrum for polymeric thin film at [$1x10^{-4}$)] M of dye doped polymer (C_{47}+PMMA)

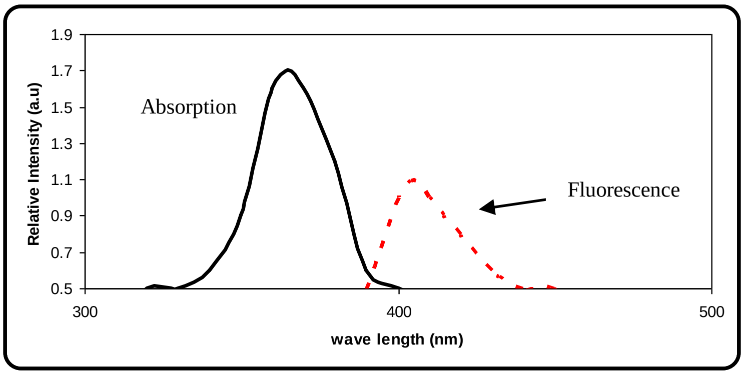


Fig (9)The overlap between two spectrum for polymeric thin film at [$5x10^{-4}$)] M of dye doped polymer (C_{47}+PMMA)

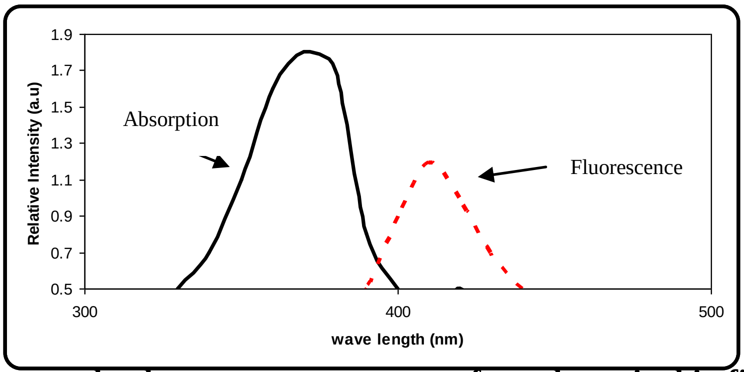


Fig (10)The overlap between two spectrums for polymeric thin film at ($1x10^{-3}$)M of dye doped polymer (C_{47}+PMMA)

The result of the absorption spectra of the polymeric thin film as described in the table 3

Table (3) The effect of concentration change on absorption spectra of thin film (C_{47}+PMMA) on a mount relative intensity and wavelength.

Concentration (mol/liter)	I_{abs} (a.u)	λ_{max} (abs) (nm)	$\Delta\lambda_{abs}$ (nm)	$\Delta\lambda_{abs}$(FWHM)(nm)
1×10^{-4}	1	355	30	16
5×10^{-4}	1.7	357	40	27
1×10^{-3}	1.8	360	50	37

The study of the fluorescence spectra.

Through the study of the fluorescence spectra , as shown in figures (8 , 9 and 10) of thin film for dye solution Coumarine -47 doped in the polymer PMMA at [(1x10^{-4}), (5x10^{-4}), (1x10^{-3})] M respectively.

It can be shown one that the fluorescence spectra shifted toward the long wavelengths (Red Shift) (410 nm) at the concentration (5 x 10 $^{-5}$)M when increase the concentration to (1x10^{-3}) M, the relative intensity of fluorescence is increase and also the Bandwidth will increase.

Table (4) shows the effect of the concentration changing on the relative intensity value and Bandwidth for fluorescence spectra yield of polymeric thin film (C_{47} + PMMA). So the figures. (8, 9 and 10) shows the overlap absorption and fluorescence spectra of polymeric thin film at [(1x10^{-4}), (5x10^{-4}), (1x10^{-3})] M will be increase

Table (4) The effect of the concentration change for fluorescence spectra of thin film (C_{47}+PMMA) on a mount relative intensity and wavelength .

Concentration (mol/liter)	I_{abs} (a.u)	λ_{max} (abs) (nm)	$\Delta\lambda_{abs}$ (nm)	$\Delta\lambda_{abs}$ (FWHM) (nm)
1×10^{-4}	0.9	405	10	7
5×10^{-4}	1.1	410	30	22
1×10^{-3}	1.2	415	40	25

Discussion of the results of polymeric thin film (C_{47}+PMMA) in chloroform solvent:

The use of polymeric thin film as active medium lasers is more important than the liquid solution, when doped the dye in polymer as foil, we observed that it stops the molecules from spread to the surface, and leads to increase optical stability, In this respect we can use the polymeric elements of high concentrations and used them as well as to reduce the self-absorption. Also can be keeping the foil for a long time without damage. The overlap between the absorption and fluorescence spectral of the thin film is lower than in the dye solution and this leads to shift toward the longer wavelength (Red shift). Increase the amount of absorption and fluorescence intensity of polymeric thin film by increase of concentration due to increase the number of molecular which is agreement with Beer-Lambert law, when increase the concentration cause to shifted the peak of absorption toward the long wavelengths because of the dipole moment of the excited state, is higher than the ground state.

Quantum efficiency

The fluorescence quantum yield of the dye solution and thin film were determined on the basis of the absorption and fluorescence spectra. This was calculated by using the following equation:

$$q_{fm} = \frac{Area \quad underthe \quad fluorescence \quad spectrum \quad curve}{Area \quad underthe \quad absorption \quad spectrum \quad curve}$$

From the results of calculation by using computer model (Matlab 6.5) and the results tabulated in table (5) and(6) .

Table (5) Represents quantum efficiencies of the C_{47} in chloroform solvent

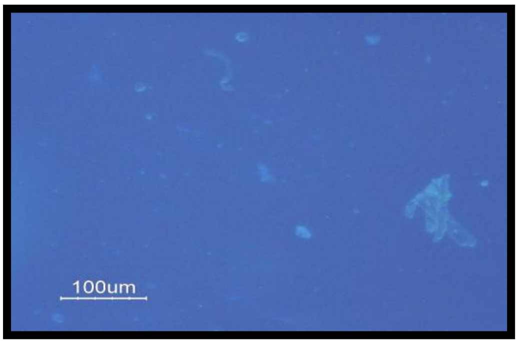
Concentration (mol/liter)	Quantum efficiency% q_{fm}
1x10^{-5}	69%
5x10^{-5}	63%
1x10^{-4}	45%

Table (6) Represents quantum efficiencies of the(C_{47+} PMMA) in chloroform solvent

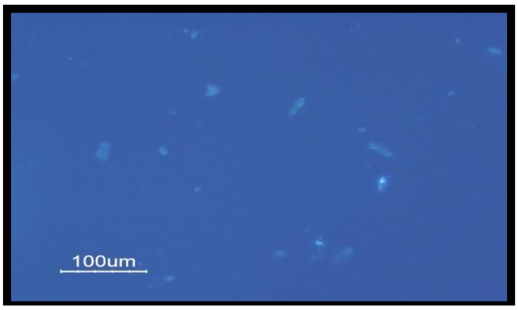
Concentration (mol/liter)	Quantum efficiency% q_{fm}
1×10^{-4}	80%
5×10^{-4}	74%
1×10^{-3}	59%

Morphological study of polymer thin film doped with dye laser:

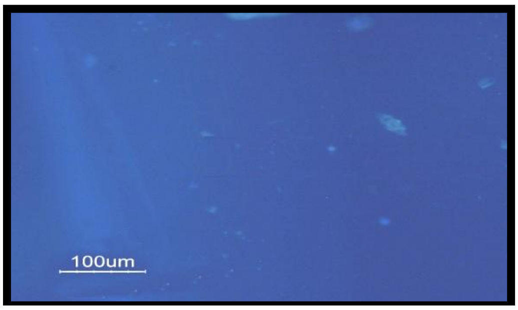
From the microscopic study as shown in fig.(11 a,b,c), the regions of non-homogeneous of polymer thin film doped with dye laser C_{47} in a chloroform solvent in three different concentrations [a($1x10^{-3}$), b($5x10^{-4}$) and ($1x10^{-4}$)]M respectively. It's noticed that when increasing the concentration the defects and less the homogeneity was apparent due to increase the (dissolved molecules) as a dimmer molecule.



a



b



c

Fig (11) Regions of non-homogeneous of polymeric thin film doped dye laser at three concentrations [a($1x10^{-3}$), b($5x10^{-4}$),c ($1x10^{-4}$)] M with a magnification (X 200)

Conclusion:

The study of the Coumarine -.47 dye solutions in the solvent a chloroform and the same dye doped in polymer PMMA with increase concentration one could conclude the following: Shifted the fluorescence spectrum of Coumarine -47 dye solution in the solvent a chloroform and polymeric thin film, in the same solvent toward the longer wavelength (Red shift). Increase in the relative intensity of the absorption and fluorescence spectrum for Coumarine -47 dye solution and the polymeric thin film. Decrease the fluorescence life time as compared with radiative life time of dye solution and polymeric thin film. Decrease quantum efficiency of dye solutions and polymeric thin film. Decrease the overlap between the absorption spectrum and the fluorescence of polymeric thin film due to increase of stokes shift, compare with dye solution, so it's better to use polymeric thin film because of reduce self absorption process. Decreasing the refraction index. The inhomogeneous of dye laser thin film will be increase.

References:

1. Masilamani, V., and Aldwayyan, A.S., 2004,"Structural and Solvent Dependence of Superexciplex", Spectrochimica Acta Part A 60, 2099-2160.
2. Hoagland R.P., 1999, "Handbook of Fluorescent Probes and Research Chemicals", 7th (Molecular probes, Eugene, OR).
3. Duarte, F.J. and Hillman, L.W.(eds), 1990,"Dye Laser Principles", (Academic Press, New York).
4. Dudley, C., 2004 " Absorption, Fluorescence and Amplified Spontaneous Emission of Blue-Emitting Dyes", M.Sc. Thesis, Washington State University.
5. Abd El Mongy, S., 2009, "Preparation of Spectroscopic

Studies of Rodamine 6G Doped Polystyrene", Australian Journal of Basic and Applied Science, 3(3), 1954 – 1963.

6. Bindhu, C. V., Harilal, S.S., Nampoori, V. P. N. and Vallabhan, C. P. G., 1999, "Solvent Effect on Absolute Fluorescence Quantum Yield of Rhodamine 6G Determined using Transient Thermal Lens Technique", Modern Physics Letters B, 13,(16), 563-576.
7. Darzi, A. K. R., 1977,"Fluorescence Life Time Measurement of Rhodamine "B"&"6G" indifferent Solvent using Mode-Locked Nd-YAG Class Laser, M. Sc. Thesis Baghdad University.
8. Jacobs, S., Sargent, M., Scott, J. F., and Scully, M.O.,1975, "Laser Application to Optics and Spectroscopy", Addison, Wesly Publishing Company, London, Amsterdam 2nd ed.
9. Hirschfeld,T., 1976,"Quatum Efficiency Independent of the Time Integrated Emission from a Fluorescence Molecule", Applied Optics,15(12), 3135-3139.

دراسة الخواص الطيفية لصبغة الكومرين – 47 المطعمة بالبوليمرPMMA

محمد تقي حسين* ***رفاه عبد الهادي عمر***** ***لمياء قند خليف*****

*جامعة بغداد / كلية العلوم / قسم الفيزياء
**جامعة بغداد / كلية العلوم للبنات / قسم الفيزياء

الخلاصة:

تحضير غشاء رقيق من صبغة الكومارين (47) ومزجها مع البولمر (PMMA) وبنفس النسب وبمذيب الكلورفورم وبتراكيز ($1x\ 10^{-4}$, $5x\ 10^{-4}$, $1x\ 10^{-3}$) مولاري . لقد تم تحضير الأغشية بأستخدام فرن حراري وبدرجة 333 كلفن وبضغط 10^{-2}تور ولمدة ساعة. وقد تم قياس سمك الغشاء بأستخدام تداخل مايكلسن حيث كان بحدود 0.2 ملم . تم حساب الكفاءة الكمية حيث كانت (80% , 47% , 59%) على التوالي . كذلك تم حساب العمر الأشعاعي وزمن الفلوره للأغشية المحضره وبالتراكيز أعلاه حيث كانت (, 3.35 , 2.5 8.57) نانوثانية وكذلك (6.58 , 1.97 , 1.85) نانوثانية على التوالي . لقد وجد بأن التداخل الحاصل بين الأمتصاص والفلوره بالنسبة للأغشية هو أقل من ما عليه بالنسبة للسوائل وأن أزاحة ستوك تكون أعلى . ومن خلال دراسة الشكل المضهري للأغشية لوحضة بأن العيوب تزداد مع زيادة التركيز.