Nonlinear optical properties of polymer [PMMA] thin films doped with dye lasing compounds, Rhodamine 6G and Acriflavine in chloroform solvent by using dip coating method

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Abstract

The fluorescence emission of Rhodamine 6G (R6G) and Acriflavine dyes in PMMA polymer have been studied by changing the irradiation and exposure time of laser light to know the effect of this parameter. It was found that the fluorescence intensity decreases in the polymer samples doped dyes as the exposure time increases and then reaches stabilization at long times, this behavior called photobleaching, which have been shown in liquid phase less than solid phase. Using 2nd harmonic with wavelength 530 nm laser, the photobleaching effect in the two dye-doped polymers different solvent but same was studied. It was observed that photobleaching of by different solution and by using dip spin coating the photobleaching seem in liquid phase more than the thin films from the mixing solutions with a thickness of (0.1 to 1 micrometer). The maximum peak of fluorescence seems as red shift with different solvent concentration.

Key words

Polymer, lasing compounds, photobleaching, dip coating.

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السلوك البصري اللاخطي لاغشيه بوليمر البولى مثيل ميثا اكريليت مشوب بصبغات ليزريه الرودامين والكرفلافين باعتماد الكلوروفرم كمذيب مرسب بطريقة الترسيب بالتغطيس

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الخلاصة

عملية انبعاث الفلوره من صبغتي الرودامين 6G والكرفلافين في بوليمر(البولي مثيل ميثا اكرليت) قد تم دراستها بتغير بعض الاعلومات مثل شدة التعرض وزمنه باعتماد اشعة ليزر معينة وذلك لمعرفة تاثير ذلك على السلوك البصري للوسط المدروس. لقد وجد ان شدة الفلوره تقل بوسط البوليمر المشوب بالصبغه عند زيادة زمن التعرض ليصل الى حد نستطيع ان نعتبره حد الاستقرار هذه الظاهره يطلق عليها بالتبيض البصري حيث بدت هذه الظاهرة واضحة في الاوساط الصلبة ولم تبدو واضحة في الاوساط السائلة. استخدم ليزر النديميوم الياك بطول موجي 1.064 مايكروميتر منصفه ببلوره لاخطيه للحصول على طول موجي 530 نانومتر اخضر اللون للحصول على ظاهرة التبيض في كلا الصبغتين المدروسة وايضا دراسة سلوك الصبغتين بتغير المذيب قبل التشويب. ان ظاهرة التبيض درست باغشيه محضره بـطريقة الترسيب بالتغطيس و بمنظومة صنعت لهذا الغرض وقد كان سمك الاغشية المحضرة بحدود من 0.1 الى 1 مايكروميتر. بينت الدراسة الطيفية حدوث زحزحه نحو الاحمر بتغير التركيز.

Introduction

Organic lasing compounds have various applications, especially in the polymer. There are many scientific branches application due to their high fluorescence quantum efficacy and yield and they have a broad gain that it makes them suitable for tunable short time pulse generation in the range of nanometer and below.

Polymer doped with different concentrations of dye lasers are the good pipe dream that was as old as the laser itself to have a laser study that is easily tunable over a wide range of frequency or wavelength. From the UV to the near-IR [1]. The polymethyl methacrylate (PMMA) has a good optical transparency and resistance [2] of laser damage properties compared with other polymeric materials that may be used as the transparent polymer matrix. There are many important reasons to use the polymer as a solid media(matrix) i.e. as a host for lasing compounds is due it have many advantages as rigidity, no toxicity, solvent evaporation, and compactness. There is also the polymer have many other advantages in the commercial usage and easy technical properties as the safety of operation and low cost.

The polymers have high homogeneity which is important to get narrow line width spectra of fluorescence, and the researchers can easily control the physical and chemical composition when the sample formation stage, and there is better compatibility with lasing compounds lasing dyes materials [3]. There is the main problem facing the study when using additive lasing dye to polymer for solid lasing materials. This behavior called the photobleching or fast decay. The simple definition of the photobleaching is the process describing the organic materials as laser dyes molecules inability to be a transition from excited state to ground states then again returns to excited states. This process is simple but complexity in something.

One of the important organic materials that used in this study is fluorescent materials. The study of fluorescent dyes has an important branch in laser study as organic molecules which has aromatic ring structures that have delocalized pi electrons which are easily excited in studies by using photons. The important for any molecular design for any optical study is to know the characteristic of the absorption and emission spectra and then to know the characteristic of the molecule. The average fluorescence molecule size is about 1 nm. The lasing compounds molecules can be dissolved in different solvents with different concentrations. The optical properties like absorption and florescence spectra are very sensitive to the type of solvent and its concentration can be used. In this study, two lasing compounds were investigated, Rhodamine 6G and Acriflavine, one polymer which is polymethyl methacrylate (PMMA) as host for the lasing compounds that be used.

There are two types, are the most favored of coating techniques where used dip coating depending on the effect to be obtained and the polymer to be used for organic dye dissolved in a polymer like PMMA. The organic lasing dyes have large and broad absorption and emission spectra and are extended from the 400 to 900 nm.

Dip coating system

Dip coating technique is one of the process that can be coated the substrate by immersing it in a polymer doped lasing dye where a thin layer is formed by well defined speed under temperature must be controlled, by using controled oven under atmospheric conditions. Fig. 1 shows the dip coating process. The controls of evaporation in atmosphere condition caused the solvent evaporated and it leads to a gelation process and the results in polymer doped dye laser formation of film. The resulting films are densified thermally by using controled oven the densification and treatment are composition depends on the temperature. The thikness of the films dpendes on: viscosity, liquid-vapour surface tension, and density by the relation:

$$h = 0.94 \cdot \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}}$$

h = coating thickness η = viscosity

γ_{LV} = liquid-vapor surface tension

ρ = density, g = gravity

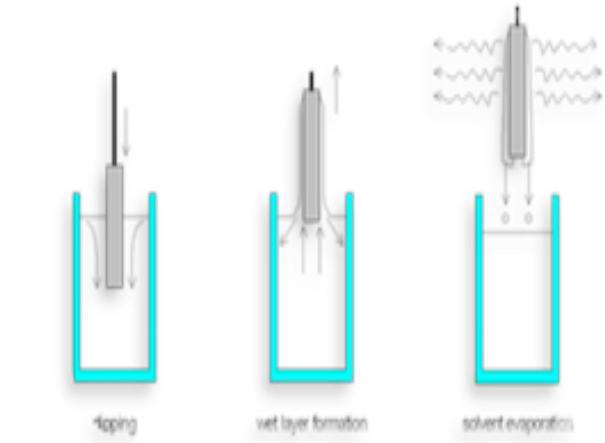
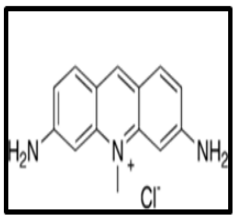


Fig. 1: Dip coating principle process.

The speed withdrawal of the dip coatting is the process of hard coating started by cleaning the glass substrate slides and then dipping into a lasing dyes doped in polymer solutions. There is an adhesion between glass substrate and polymer doped dyes laser. After the dip hard coating process samples are thermally annealed for 1-3 houre in thermal oven. There are many advantages and disadvantages of the dip coatting the advantages are; Same coating on both sides, b (est scratch resistance, index matching of lacquer and substrate and inexpensive chemistry if slides volume is high,the disadvantages are clean room is required, requires high level of discipline good dip coating equipment is expensive and training to avoid yield issues. The main advantages is the reduction significantly of the newton rings effect, that is generated in the passesing light through samples media with many refractive indices.

Meterial and method

The following materials were used, Lasing compounds in this study used two dye molecules Rhodamine 6G and Acriflavine dyes of the xanthene family as active media.

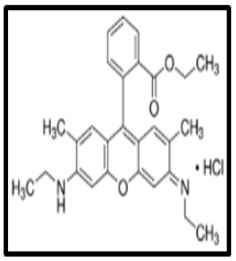


Acriflavine dyes:

Linear Formula $C_{14}H_{14}ClN_3$

Molecular Weight 259.74 g•mol^{-1}

(laser grade) supplied by lambda physics



Rhodamine 6G

Linear Formula $C_{28}H_{31}N_2O_3Cl$

Molecular Weight 479.0 g•mol^{-1}

(laser grade) supplied by lambda physics

The host material was used the poly(methyl methacrylate) (PMMA) is one of in general Poly(methacrylates) which is polymer companied with esters of methacrylic acids, this PMMA is commonly used with chemical formula $(C_5H_8O_2)_n$. It is a clear polymer and colorless when it available on the market. It is produced by polymerization the free-radical of methyl methacrylate according to the below relation Fig. 2:

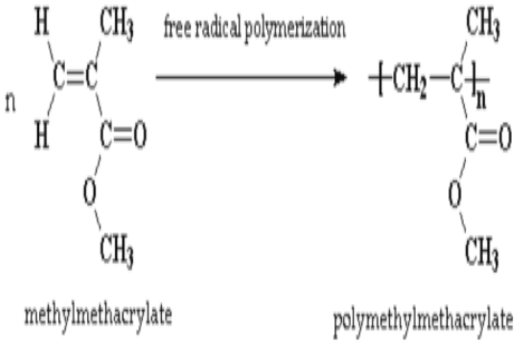


Fig.2: Preparation of the polymer PMMA.

The fundamental schematic diagram of the experimental setup Fig. 3 are combination of Nd-YAG laser with wavelength (1.064μm) and 2nd harmonic crystal to get 532 nm green lasers, sample holder, 0.5 m Monochrometer connected with PMT (photomultiplier tube) with H.V. power supply and output recorder. The samples are placed in the quartz cavity and confined the laser beam in the cavity and the laser-induced fluorescence is detected at right angles. In this setup the integrated fluorescence with accurate wavelength is recorded. The elastically radiation which is scattered with the same wavelength of the laser radiation but the fluorescence emission spectral band in the wavelength and detected by using PMT(R666) Side-On Type Photomultiplier Tubes supplied from Hamamatsu company through the use (0.5 m) monochrometer. The UV-Vis absorption and fluorescence spectroscopy is one of the quantitative studying and the most suitable methods for the study of the properties of dyes with different of concentration, the range of the concentration used in this study is (10^{-3} – 10^{-6}M) which is monomer-dimer equilibrium exists by using chloroform as solvent.

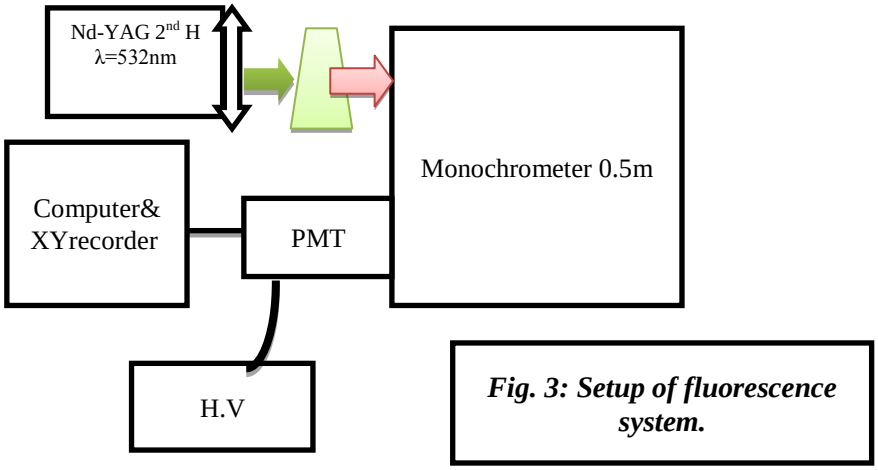


Fig. 3: Setup of fluorescence system.

Results and discussion

The double-beam spectrophotometer was used to recored the absorption spectra, but fluorescence spectra were recorded by using the system illustrated in Fig. 3. The photophysics processes like absorption and fluorescence of Acriflavine and R(6G) doped in PMMA with different concentrations (1×10^{-5} to 1×10^{-4}) mol/ℓ. Films were made by dip coating and gravity settling techniques,the polymer PMMA doped dye solutions concentration ratio 1ml of (10^{-3}) mol/ℓ rhodamine 6G and acriflavine dyes in 9 ml of PMMA polymer. The adsorption of R6G and Acriflavine molecules in PMMA shown in Fig. 4 (a, c). The absorption of these dyes lead some modifications in spectrum. From this figure the red shift clearly occurs in all samples for R6G and Acriflavine when the increasing concentration in the range (10^{-4} to 10^{-5}), and also the intensity of fluorescence from Fig. 4 (b, d). It can be seen from Fig. 4 (b, d) that the intensity increased as increasing the concentration of polymer doped dye in its intensity with increasing the concentration of polymer doped dye. Table 1 represent the red shift in both spectrum absorption and fluorescence. The same result with different dyes illustrated in [7].

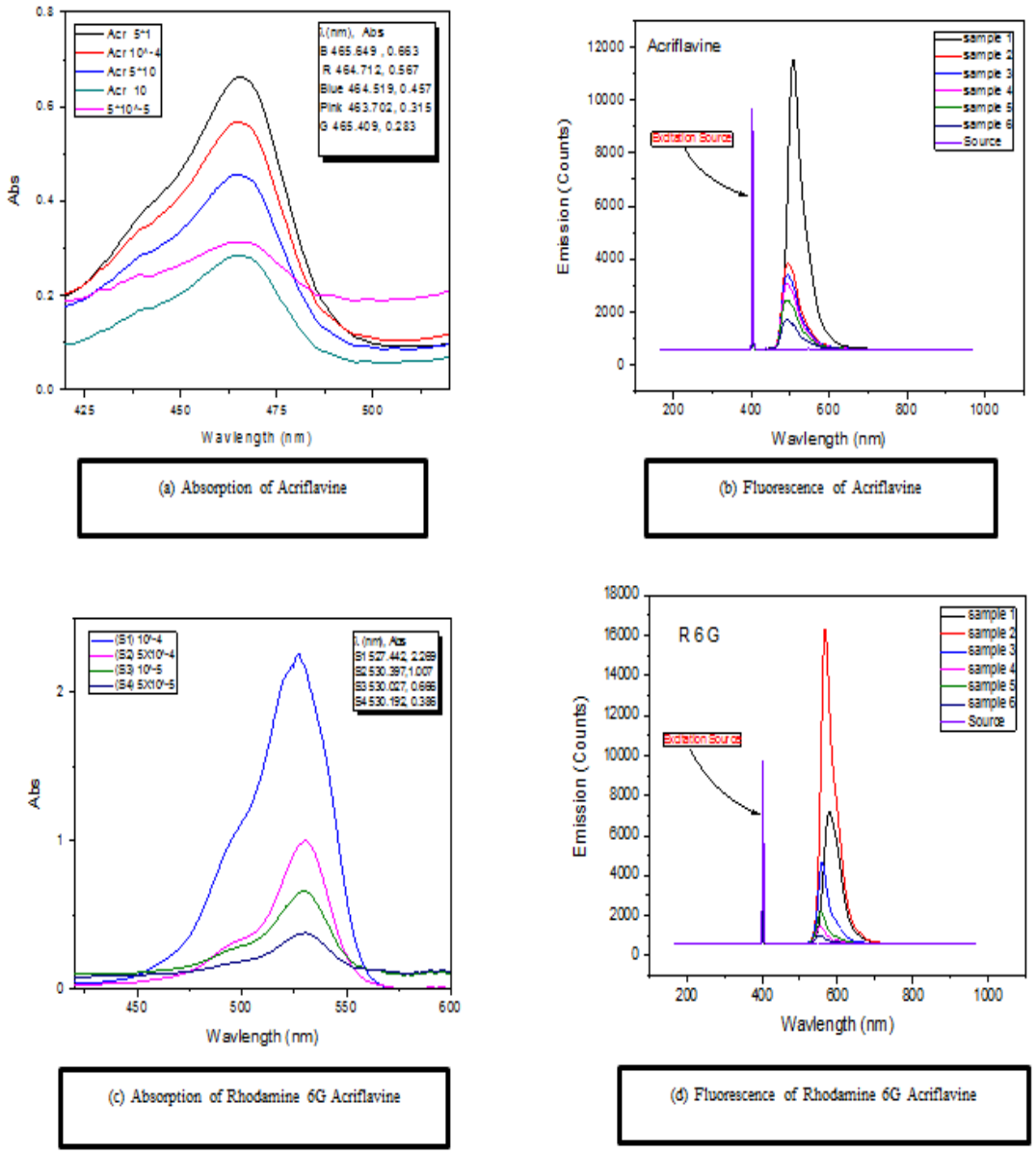


Fig. 4: Absorption of a: Acriflavine, b: Acriflavine, c: Rhodamine 6G and florescence, d: Rhodamine 6G.

Table 1: Illustrated the red shift of 1: Acriflavine 2: Rhodamine 6G in absorption and fluorescence spectra.

C mole/litter	λ_{abs} (nm)		λ **fluo** (nm)	
	Acriflavine	Rhodamine 6G	Acriflavine	Rhodamine 6G
$1x10^{-5}$	465.5	527.4	594.5	553.8
$5x10^{-5}$	465.4	530.02	493.2	554.3
$1x10^{-4}$	464.8	530.2	492.6	555.6
$5x10^{-4}$	464.5	530.4	490.8	559.4
$1x10^{-3}$	463.7		490.3	578.1

The fast response of of the polymer films doped dye laser at the UV irradiation due to the surface relief formation and the dye molecules a spontaneous reorientation Fig. 5. The dips spontaneous and non-exponential

emission of the molecules spectra decay kinetics containing two components, accelerated and inhibited that compared to the fluorescence dye homogeneous matrix as a reference.

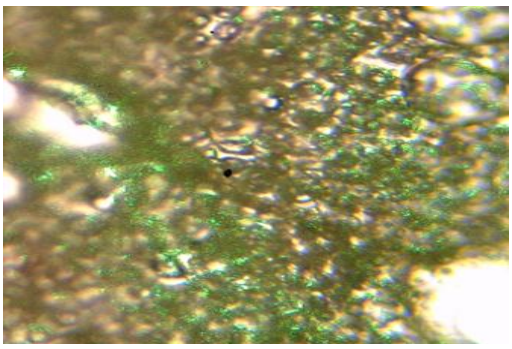


Fig. 5: The dye molecules a spontaneous reorientation by green laser.

The photobleaching rate baseline of R6G and Acriflavine is shown in Fig. 6 using solution after adding the polymer, from Fig. 6 shows the photobleaching behavior as a decay curves in Acriflavine one can see that at low concentrations more bleaching rate than high concentrations. This behavior seem because the molecules dye quantity in the low concentration is less than at high concentration then, the laser beam radiation interact with number of dye molecules at low concentration less than these at high concentration. B.T. chiad et al. in 2013 get the simillar behaviour by using another dye laser.

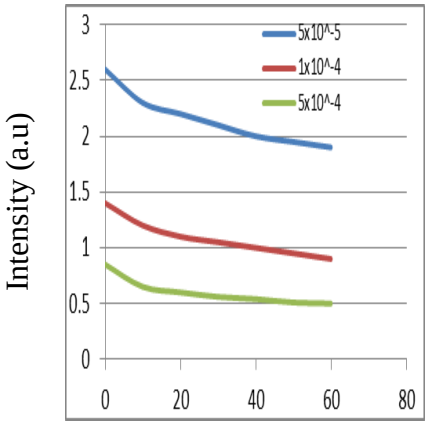


Fig. 6: Time of exposure vs. fiuorescence intensity at the maximum peak for Acriflavine polymer PMMA doped with different concentrations of Acriflavine dye.

The morphology of thin films sample on the glass surface prepared by dip coating and gravity settling after 48h was studied, during the thin films preparation on top of glass substrates, the common solvent was evaporated. By using a special optical system can study the surface structure and distribution.

The distribution of polymer appeared in Fig. 7 and as dark areas. from this figuer one can see the distrbiution of dye seems in between of polymwer molecules as colored area. Quantitative analysis of PMMA is indicates that still continuous throughout the sample and wets the rims of the polymer as evidenced by the halo around PMMA. The trans-cis isomerisation effect is the mean reasons for surface volume structuration. Using SEM [4] and AFM [5] the result compataple with this study resulte. There are many studies using other methods like SEM [5], this resalt can compatible with the present stydy using improving optical system as shown in Fig. 7.

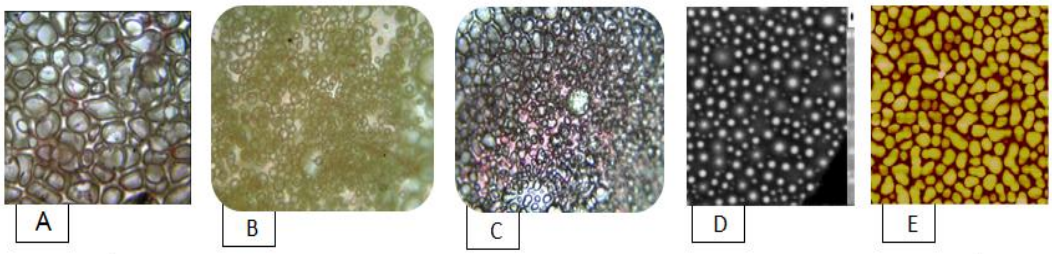


Fig. 7: The morphology of thin films sample on the glass surface, a, b, c, present work using optical system with ccd camera, d, ref(4), e, ref (5) by using AFM system.

Conclosions

The polymer effect when doped by lasing compounds on the photophysical behavior of lasing dyes was studied in spectral profiles of absorption and fluorescence. the red shifted in the absorption and fluorescence of the samples were studies in different concentrations for both dye in the liquid phase and sold state as thin films, another behavior seems in spectral profiles the relative intensity was increasing. Also this study concluded a photobleaching behavior of Acriflavine and Rhodamine6G with time of excitation in solid state.

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