

# Photosensitivity of Laser Dye Mixtures in Polymer Matrix – A Photoacoustic Study

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## ABSTRACT

Laser induced photoacoustic (PA) technique is used in the study of photostability of polymethyl methacrylate (PMMA) films doped with Rhodamine 6G-Rhodamine B dye system. Energy transfer from a donor molecule to an acceptor molecule in a dye mixture affects the output of the dye system. Details of investigations on the role of laser power, modulation frequency and the irradiation wavelength on the photosensitivity of the dye mixture doped PMMA films are presented.

**Keywords:** optical bleaching, laser dyes, recording medium, photo-degradation

## 1. INTRODUCTION

High-density information storage is an important technological objective and large number of optical storage media which fulfill this aim has been reported. Dye doped polymers find applications in similar fields of modern photonic technology apart from its use as an alternative to solid state laser media [1, 2]. Current interests in photonic materials are in the write-once optical media and compact disk recordable media. The modification of the dye is necessary for writing and reading with laser radiations at short wavelengths. The promising candidates for information storage are organic dyes doped in polymer matrices. One area that may be revolutionized by the use of organic luminophores in plastics is the flat screen monitor industry. Current flat screens typically use expensive, delicate technique like plasma technology. Organic emitters doped in a polymer layer offer an inexpensive, malleable and easy-to-produce alternative. Organic dyes are also of interest for sensors, optical amplifiers and fiber optics. If organic fluorescent molecules are to be effectively used in such applications, they must be able to withstand repeated excitations and the large amounts of energy that will be cycled through them. Unfortunately upon repeated absorption, the dye molecules begin to photo-oxidize. This permanently destroys the dye, thereby limiting applications of such organic materials under exposure to high optical intensities. A nonlinear absorber of light has the unique property that its optical absorption can be altered by introducing changes in the intensity of radiation incident upon it. Different types of organic molecules undergo optical bleaching [3] when subjected to high intensity radiation and are useful as passive Q switches for lasers and as recording media [4]. A number of techniques have been used to study photo-induced changes in laser dyes [5]. Photochemical changes induced in a medium can be monitored either by optical methods or photo-thermal methods. In optical methods the radiative relaxation or optical absorption (or transmission) is investigated whereas in photo-thermal technique, the energy liberated as a result of non-radiative relaxation is measured.

Spectroscopic studies based on photo-thermal effects, like photoacoustic spectroscopy (PAS) [6] and photo-thermal deflection spectroscopy (PDS) [7] offer powerful techniques to study the absorption of highly fluorescent dyes and gives complementary information to fluorescence spectroscopy through the detection of non-radiative relaxation processes. The dominant feature of laser heating is that a considerable amount of energy may be absorbed in a short interval of time. Photo-thermal methods measure a signal, which is directly related to the amount of electromagnetic energy absorbed by the sample, which is converted into heat. These methods present the additional advantage of being immune to the light scattered by surface roughness and volume inhomogeneities. The PA technique has already been used by many researchers to study the energy transfer mechanisms in a number of dye systems [8].

Embedding it in solid matrices can modify the non-linear optical properties of a dye. Although both inorganic glasses and polymeric materials have been successfully used as host matrices for lasing dyes, polymers offer a number of advantages both from the technical and economical point of view, which include high optical homogeneity, better chemical compatibility with organic dyes, control over medium polarity and viscosity in a way similar to conventional solvents [9], and adaptability to inexpensive fabrication techniques. Synthetic polymer hosts have additional advantages compared to other matrices because these polymers exhibit good compatibility with organic dyes permitting miniaturization and low cost integrated optical system designs. One of the important advantages of transparent polymers compared to traditional optical materials (inorganic glasses and crystals) is that it

is possible to introduce organic dyes that play the role of active components into polymers, which appreciably changes the characteristics of the polymer matrix. Suitable materials for different applications can be prepared by properly selecting the type of solid matrix and the dye incorporated into it. Intermolecular energy transfer between two molecular species separated by a distance in the condensed phase has been observed in numerous molecular systems [10, 11]. Main mechanisms involved in the electronic energy transfer in molecular systems are radiative transfer, non-radiative transfer and excitation migration. Non-radiative transfer of electronic energy involves the simultaneous de-excitation of the donor and the excitation of the acceptor, a one step process that does not involve the intermediacy of a photon. A necessary condition for non-radiative energy transfer between two molecules is that the distance between the donor and the acceptor must be very small. The energy transfer mechanism results in the quenching of absorption of the donor molecule. Through suitable selection of dye combinations, absorption characteristics and the photo-stability of the mixture can be changed.

Different organic polymers can be used as solid host material and the basic requirements imposed on a polymeric host for lasing dye molecules are good optical transparency at both the pump and lasing wavelengths, good solubility of the dye in the material, and resistance to pump laser radiations. Most frequently used polymeric materials are based on methacrylate (MMA), such as polymethyl methacrylate (PMMA) or compositions of the methacrylate co-polymers like hydroxyethyl methacrylate (HEMA): MMA etc. PMMA is the most frequently used host for laser dyes due to its excellent optical transparency in the visible region and its relatively high laser damage resistance. The low solubility of majority of the conventional laser dyes in PMMA causes some limitations. Good solubility of dyes is achieved by introducing modifying additives, which also enhances laser damage resistance [12]. In the present study ethyl alcohol is chosen as an additive because it combines good solubility for xanthenes dyes and enhancement of host laser damage resistance.

## 2. EXPERIMENTAL DETAILS

### 2.1 Rhodamine 6G- Rhodamine B Systems

Present work in the dye-doped polymer has been carried out with dyes of the xanthenes family. Xanthenes derivatives, Rhodamine 6G and Rhodamine B, with fluorescence emission in the yellow-red region of the electromagnetic spectrum are well known for their excellent laser performance in liquid solutions as well as in solid matrices. For the present investigations Rhodamine 6G chloride ( $C_{28}H_{31}ClN_2O_3$ , LOBA Chemie, GR, molecular weight 479.02) and Rhodamine B ( $C_{28}H_{31}N_2O_3$ , Merck, GR, molecular weight 479.02) are used as received.

### 2.2 Preparation of dye doped polymer samples

Methyl methacrylate (MMA) (CDH Chemicals) is washed three times with 2% sodium hydroxide solution to remove foreign inclusions and then with distilled water till the solution is clear. Few pellets of anhydrous calcium chloride are added to the MMA and kept for 24 hours. The dry MMA is then filtered. Since Rhodamine dye has limited solubility in the monomer MMA, ethyl alcohol (Merck) is used as a solvent. The addition of ethanol as a plasticizer has also been reported to increase the laser damage threshold of PMMA. Accurately weighed dyes are dissolved in ethanol to prepare stock solutions of the two dyes. For the preparation of different dye doped samples, the monomer MMA is mixed with the respective dye dissolved ethyl alcohol in the ratio 4:1. Solutions of monomer – alcohol mixture with different volume ratios but of same concentration of the two dyes are prepared for polymerization. 1gm of benzoyl peroxide per 100ml of the solution is used as an initiator for polymerization. The monomer-alcohol mixture containing the dye and the initiator, taken in a glass test tube is kept in a constant temperature bath maintained at 50°C for polymerization. Care is taken to see that the dye is homogeneously distributed in the polymer matrix. Completely polymerized sample obtained after 24 hours is taken out of the water bath. Placing the dye doped polymer mixture drops on clean microscopic glass slides results in thin coatings (spot casting) of the sample. The sample coated slides are kept at room temperature for one week for drying. Perfect drying is necessary to avoid shrinkage of the sample.

### 2.3 Photoacoustic study

Photo-thermal methods measure the photon energy that has been converted into heat. A continuous wave (CW) laser induced PA technique is used to investigate the photo-induced degradation of the dye doped polymer samples. For the PA signal measurements the reflection mode geometry of the PA cell is employed. The excitation source used is a highly stabilized argon ion laser (Liconix 5000) and its different emission lines are used for the study. The CW laser emission is intensity modulated using a mechanical chopper (Ithaco HMS 230) (figure 1).

The modulated light beam at specific power levels is allowed to fall on the sample kept within the non-resonant PA cell. The PA signal detected by the microphone (BT 1834) is amplified using a digital lock-in amplifier (Stanford Research Systems SR 830). Laser lines of wavelengths 488nm, 496nm from the argon ion laser and 532nm radiation from a diode pumped solid state laser (DPSS) (BWT 50) are used for the present studies. Influence of the

excitation light on the rate of dye photo-degradation is studied at power levels of 20mW, 30mW and 40mW. The influence of the laser modulation frequency is also studied.

The absorption spectra of the samples are taken by using a spectrophotometer (Jasco V570, UV/ VIS/ NIR Spectrophotometer).

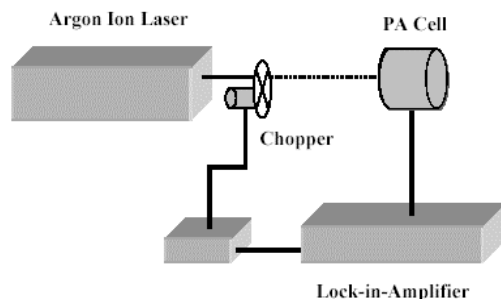


Figure 1 schematic diagram of the experimental set-up

### 3. RESULTS AND DISCUSSIONS

The process of PA signal generation in condensed media has already been experimentally established and a satisfactory theoretical explanation has been given by Rosencwaig and Gersho [6]. The complex amplitude of the PA signal produced is given by the relation,

$$Q = \frac{-i\beta m^2 g p_0 I_0}{4\sqrt{2}T_0 l_g a_g k}$$

where  $\beta$  is the optical absorption coefficient of the sample and  $\mu$  is the thermal diffusion length in the medium;  $\gamma$  is the ratio of specific heat capacities for air,  $B$  and  $T_0$  are the ambient pressure and temperature respectively.  $I_0$  is the intensity of incident light,  $l_g$  and  $a_g$  are the length of the gas column inside the cavity and the thermal diffusion length in the gas respectively and  $k$  is the thermal conductivity of the sample. Hence, by any means, if the absorption coefficient value changes, then the PA signal amplitude will also vary accordingly. Any kind of photochemical reaction will result in a change in the number density or concentration of the original species and this, in turn, will result in a change in the optical absorption properties of the sample. Doping of an organic dye in a solid matrix will not alter the thermal properties of the host [9]. So when a dye doped polymer is investigated using PA technique, any change in the PA signal amplitude is essentially a measure of the rate of photodecomposition of the dye. Results of the studies carried out to investigate the rapidity with which an optical dye in a solid host irreversibly degrades when it is illuminated by visible light are presented here.

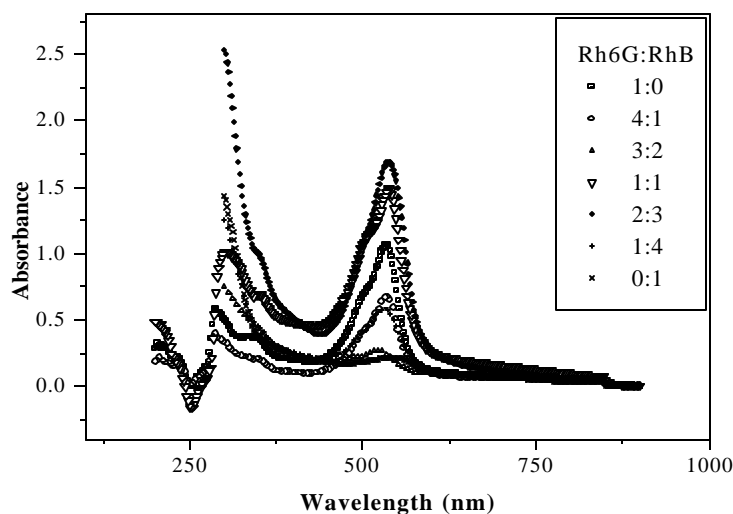


Figure 2. Absorption spectra of Rh 6G: Rh B mixture in PMMA film

The absorption spectra for mixtures of Rh 6G and Rh B are shown in figure (2). Absorption peak of Rh6G doped PMMA is around 520nm and that of Rh B doped PMMA is at 550nm. Absorption of Rh B doped PMMA is very low compared to that of Rh 6G doped PMMA in the wavelength range selected for investigations. It is observed that the addition of Rh B dye decreases the effective absorption of the mixture at 520nm.

Initial investigations are carried out on dye doped PMMA samples with varying volume ratios of the constituent dyes, Rhodamine 6G and Rhodamine B. The variation of PA signal amplitude as a function of time for the different samples is shown in figure 3

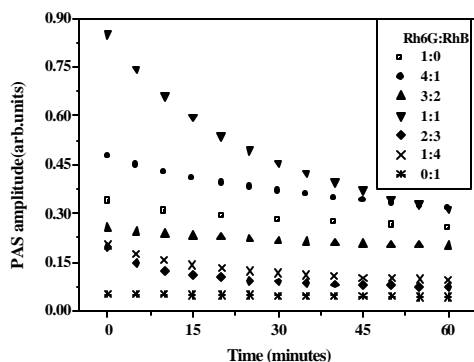


Figure 3. PA signal amplitude versus irradiation time plot for different volume ratios of Rh 6G and Rh B doped polymer samples  
 Conc Rh 6G = 1mM Conc Rh B = 1mM  
 P = 30mW  $\lambda = 488\text{nm}$   $f = 80\text{Hz}$

From the plot it is clear that PA signal degradation rate change from sample to sample. It is observed that the decay time is more for the PMMA film in which dyes are doped in the ratio 1:1. Plots are shifted from each other for the sake of clarity. All the samples containing Rh6G exhibit signal degradation and then saturation on continuous irradiation. This indicates that on irradiating the dye doped PMMA sample with strong laser beam, photo-degradation of the dye molecules take place and the resultant product does not absorb in the spectral region where the original dye molecules absorb. The reduction in absorbance is evident in the absorption spectrum (Figure 4). Therefore the observed decrease in PA signal amplitude is due to the gradual decomposition of the dye molecules. The time taken to attain saturation is found to vary from sample to sample. This clearly shows the photo-

sensitivity of the dye doped PMMA samples. As Rh B has very low absorption at the irradiation wavelength, the photoreaction is more for Rh 6G. The PMMA sample doped with Rh B alone does not show considerable change in PA signal on continuous irradiation whereas samples with Rh 6G exhibit signal degradation. From this it can be deduced that Rh B doped PMMA is photo-chemically stable at this particular concentration. Addition of Rh B changes the photosensitivity of Rh 6G. The reduction in photochemical reaction of Rh 6G can be attributed to the enhancement in energy exchange to Rh B. Non-radiative energy transfer from an excited state donor ( $D^*$ ) molecule can occur due to coulombic or electron exchange interaction between  $D^*$  and the acceptor (A) molecule. Non-radiative transfer of electronic energy involves the simultaneous de-excitation of the donor and the excitation of the acceptor, a one step process that does not involve the intermediacy of a photon.

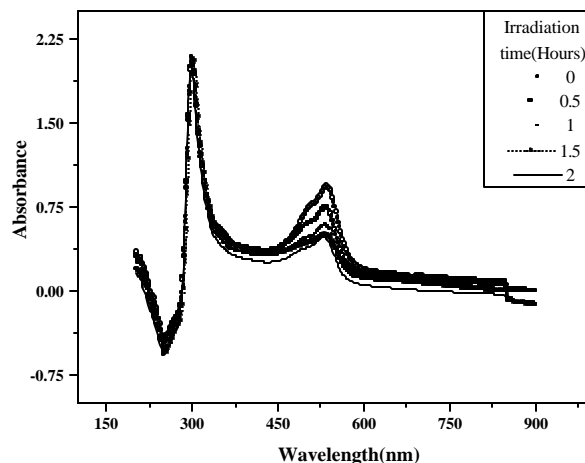
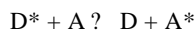


Figure 4. Absorption spectra of the sample before and after irradiation



This type of energy transfer occurs when the energies involved in  $D^* \rightarrow D$  and  $A \rightarrow A^*$  transitions are same, the excitation transfer being the simultaneous occurrence of the two coupled or resonant transitions.

As the amount of Rh B in the mixture is increased, the light interaction with Rh B increases which reduces the light interaction with Rh 6G. Samples with small amounts of Rh B show gradual photo-degradation in the early stage followed by saturation. In these cases the influence of Rhodamine 6G is maximum. As the volume ratio of Rh B is increased above that of Rh 6G, somehow changes are introduced in the energy exchange process so that signal degradation is very slow and saturation is attained within a short time. This indicates that the presence of RhB stabilizes the sample against damage. The sample with the two dyes mixed in 1:1 ratio takes a long time for photo-degradation and takes more than one hour to attain saturation. The PA signal magnitude is also found to be maximum for this particular combination. This may be because of the fact that the energy exchange between the two dyes is maximum for this particular combination and it reduces the rate of photochemical reaction. Further investigations are carried out on samples with dyes mixed in the same ratio. Even though a large number of studies have been reported in the field of dye doped polymers, the exact mechanism responsible for the photo-degradation of laser dyes in polymers is not yet fully brought out [11].

In order to investigate the influence of irradiation wavelength on the photo-degradation of the dye system doped PMMA, PA studies are carried out at different wavelengths. 532nm line from the DPSS laser, and, 496nm and 488nm lines of the argon ion laser are used for investigations and the PA signal amplitude is plotted as a function of irradiation time (figure 5).

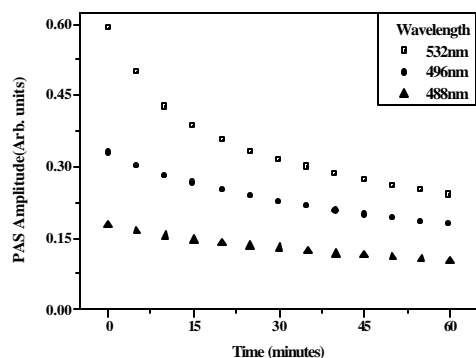


Figure 5. PA signal versus time plot for different wavelengths (dyes of same concentration (1mM) are mixed in the ratio 1:1) Laser power = 30mW Modulation frequency = 80Hz

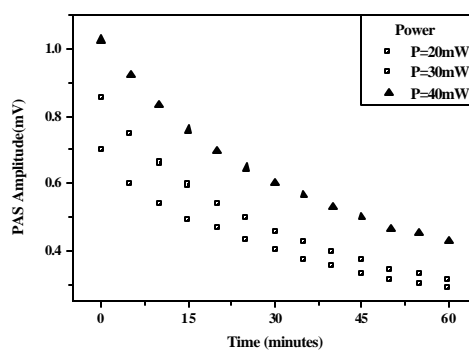


Figure 6. PA signal amplitude versus time plot for dye system doped PMMA at different irradiation intensities (dyes of same concentration (1mM) are mixed in the ratio 1:1)  $f = 80\text{Hz}$   $\lambda = 488\text{nm}$

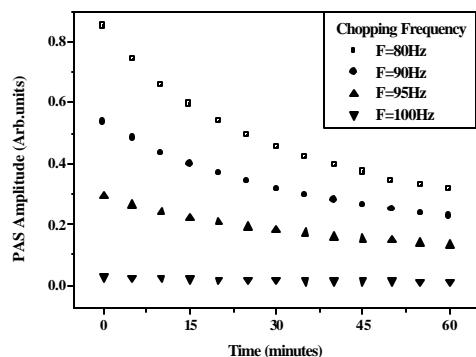


Figure 7. PA signal amplitude versus time plot for dye system doped PMMA for different modulation frequencies (dyes of same concentration (1mM) are mixed in the ratio 1:1) Laser power = 30mW  $\lambda = 488\text{nm}$

The photo-degradation rate is found to increase as the irradiation wavelength increases from 488nm to 532nm. This is understandable as the absorption of Rh 6G is maximum at around 520nm. The PA signal amplitude also increases as the irradiation wavelength approaches the peak absorption wavelength. Even though higher wavelengths give higher magnitudes of PA signal, investigations are carried out using 488nm because of the steady operational conditions for longer time durations at this wavelength.

From figure 6 it is clear that PA signal degradation increases with increase in pump power. The plots show that degradation rate is not uniform throughout. Initial degradation occurs at a faster rate followed by slower decay, which is clearly visible at lower pump levels.

The PA signal decreases with increase in modulation frequency as seen in figure 7. If ' $f$ ' is the modulation frequency, the number of light pulses falling on the sample in ' $t$ ' seconds will be ' $ft$ '. With increase in the value of either frequency or irradiation time, number of photons falling on the sample and hence absorbed by it will increase. This increased absorption results in faster photo-degradation. At higher modulation frequencies the degradation will be complete within a short time so that no change in PA signal can be observed. At lower frequencies photochemical changes take place at a slow rate and decrease in PA signal amplitude is gradual. The plot also reveals that signal degradation is slow at low chopping frequencies.

#### 4. CONCLUSIONS

The PA technique has been implemented successfully to investigate the bleaching of organic dye molecules embedded in PMMA matrix. From the observations it can be concluded that the bleaching rate of dye mixture doped PMMA matrix is directly proportional to the incident laser power and can be controlled by changing the modulation frequency. Addition of another dye into the system to form donor-acceptor combination can change the photostability of a dye doped polymer matrix. Adding Rhodamine B can enhance photostability of Rhodamine6G and photosensitivity of Rhodamine B can be enhanced by adding Rhodamine6G. If the dye doped polymeric material is to be used as an active medium for laser operations, the life-time of stable operation can be increased through proper selection of dye combinations. The dye doped PMMA can also be used as an optical recording medium. Through suitable selection of dye combinations and proper choice of concentrations of individual dyes, the time for optical recording can also be adjusted

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