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# Photoacoustic study on the photostability of polymethyl methacrylate films doped with Rhodamine 6G–Rhodamine B dye mixture system

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## Abstract

The photosensitivity of dye mixture-doped polymethyl methacrylate (PMMA) films are investigated as a function of laser power, concentration of the dyes, modulation frequency and the irradiation wavelength. Energy transfer from a donor molecule to an acceptor molecule affects the emission output of the dye mixture system. Photosensitivity is found to change with changes in donor–acceptor concentrations. PMMA samples doped with the dye mixture are found to be more photosensitive when the dyes are mixed in the same proportion.

## 1. Introduction

Dye-doped polymers have applications as active laser media and as active device components in modern photonic technology [1–3]. A large number of inorganic and organic high-density optical information storage media have also been reported [3, 4]. Organic emitters doped in a polymer layer offer an inexpensive, malleable and easy-to-produce alternative to conventional crystalline materials. Organic dyes are also of interest for sensors [5], optical amplifiers [6] and fibre optics [7]. 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 denatures the dye, thereby limiting the applications of such organic material under exposure to high optical intensities. A non-linear absorber of light has the unique property of its optical absorption being capable of alteration by introducing changes in the intensity of radiation incident upon it. Organic dye molecules undergo optical bleaching when subjected to high intensity radiation and are

useful as passive Q switches for lasers and as recording media [8]. Photoinduced changes in laser dyes [9] can be monitored either by optical methods or by photothermal methods. In optical methods the radiative relaxation from excited states are investigated, whereas in the photothermal technique, the energy liberated as a result of non-radiative relaxation is measured. The latter technique is found to be more sensitive when compared with the former.

Spectroscopic studies based on photothermal effects, such as photoacoustic spectroscopy (PAS) [10] and photothermal deflection spectroscopy (PDS) [11] offer powerful techniques for studying the absorption of highly fluorescent dyes and give complementary information on fluorescence spectroscopy through the detection of non-radiative relaxation processes. A dominant feature of laser heating is that a large amount of energy may be absorbed within a short interval of time. Photothermal methods measure a signal, directly related to the amount of electromagnetic energy absorbed by the sample, which is subsequently converted into heat. These methods have the additional advantage of being much less sensitive to the light scattered by surface roughness and volume inhomogeneities. The photoacoustic (PA) technique has already been used by many researchers to study the energy transfer mechanisms in a number of dye systems [12, 13].

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Embedding a dye in solid matrices can modify its non-linear optical properties. Although both inorganic glasses [14], and polymeric materials [3, 9] have been successfully used as host matrices for lasing dyes, polymers offer a number of advantages such as high optical homogeneity, better chemical compatibility with organic dyes, control over medium polarity and viscoelasticity in a manner similar to conventional solvents [15] and adaptability to inexpensive fabrication techniques. Synthetic polymer hosts have additional advantages when compared to other matrices, because these polymers exhibit good compatibility with organic dyes, permitting miniaturization and low-cost integrated optical system designs [16]. One of the important advantages of transparent polymers when compared to traditional optical materials (inorganic glasses and crystals) is that it is possible to introduce organic dyes which play the role of active components in polymers and which change appreciably, 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 [17]. The chief 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, the absorption characteristics and the photostability of the mixture can be changed.

Different organic polymers can be used as solid host material [8] and the basic requirements imposed on a polymeric host for lasing dye molecules are: (i) good optical transparency at both pump and lasing wavelengths; (ii) good solubility of the dye in the material; and (iii) resistance to pump laser radiations. Commonly used polymeric materials are based on methylmethacrylate (MMA) such as polymethyl methacrylate (PMMA), or compositions of the methacrylate co-polymers such as 2-hydroxyethyl methacrylate (HEMA): MMA among others. PMMA is the most frequently used host for lasing dyes owing to its excellent optical transparency in the visible region and its relatively high laser damage resistance. The low solubility of the majority of the conventional laser dyes in PMMA causes some limitations. Good solubility of dyes is achieved by introducing proper additives, which also enhances laser damage resistance [18]. Ethyl alcohol is chosen as an additive because it combines good solubility for xanthene dyes with the enhancement of the laser damage threshold.

At present, work in the dye-doped polymer has been carried out with dyes of the xanthene family. Xanthene derivatives, Rhodamine 6G (Rh 6G) and Rhodamine B (Rh 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

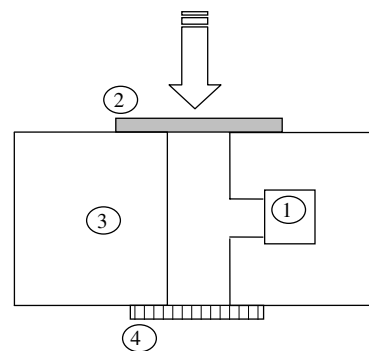
matrices. For the present investigations, Rh 6G chloride ( $C_{28}H_{31}ClN_2O_3$ , LOBA Chemie, GR, molecular weight 479.02) and Rh B ( $C_{28}H_{31}ClN_2O_3$ , Merck, GR, molecular weight 479.02) are used. Eventhough Rh 6G and Rh B have the same molecular formula, they have different molecular structures.

## 2. Preparation of dye-doped polymer samples

MMA (CDH Chemicals, AR Grade) is washed three times with 2% sodium hydroxide solution to remove foreign inclusions and then with distilled water till the solution is clear. A few pellets of anhydrous calcium chloride are added to the MMA and kept for 24 h. The dry MMA is then filtered. Since Rhodamine dye has limited solubility in the monomer MMA, ethyl alcohol (Merck, AR Grade) is used as a solvent. The addition of ethanol as a plasticizer has also been reported to increase the laser damage threshold of PMMA [18]. Accurately weighed dyes are dissolved in ethanol to prepare stock solutions of the two dyes from which solutions of different concentrations are prepared. Different dye-doped samples are prepared by mixing the monomer, MMA, with the respective dye dissolved in ethyl alcohol in the ratio of 4 : 1. Solutions of the monomer–alcohol mixture with different volume ratios of the two dyes at different dye concentrations are prepared. One gram of benzoyl peroxide per 100 ml of the solution is used as an initiator for polymerization. The monomer–alcohol mixture containing the dye and the initiator is put in a glass test tube and 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. After 24 h, the completely polymerized sample is removed from the water bath [13]. A spot casting method is used to prepare the samples in which the dye-doped polymer mixture drops are placed on clean microscopic glass slides to form thin coatings of the sample. The slides coated with the samples are kept at room temperature for one week to dry. Perfect drying is necessary to avoid shrinkage of the sample.

## 3. Experimental details

A continuous wave (CW) laser-induced PA technique is used to investigate the photoinduced degradation of the dye-doped polymer samples. For the PA signal measurements, the reflection mode geometry of the PA cell is employed (figure 1).



**Figure 1.** Reflection mode geometry of the PA cell. (1) Microphone, (2) glass window, (3) acrylic body of the cell, (4) sample.

The excitation source used is a highly stabilized argon ion laser (Liconix 5000) and its different emission lines (488 and 496 nm) are used for the study. The CW laser emission is intensity-modulated using a mechanical chopper (Ithaco HMS 230).

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 is amplified using a digital lock-in amplifier (Stanford Research Systems SR 830). Laser radiation at wavelengths of 488 and 496 nm of the Ar<sup>+</sup> laser and of 532 nm of a diode-pumped solid state laser (DPSS BWT 50) are used for the investigation. The influence of the excitation radiation on the rate of dye photodegradation is studied at power levels of 20, 30 and 40 mW. Investigations are also carried out by varying parameters such as dye concentration and the laser modulation frequency.

#### 4. 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 [10]. The complex amplitude of the PA signal produced is given by the relation

$$Q = \frac{-i\beta\mu^2\gamma P_0 I_0}{4\sqrt{2}T_0 l_g a_g k}, \quad (1)$$

where  $\beta$  is the optical absorption coefficient of the sample and  $\mu$  the thermal diffusion length in the medium,  $\gamma$  the ratio of specific heat capacities for air,  $P_0$  and  $T_0$  the ambient pressure and temperature, respectively,  $I_0$  the intensity of incident light,  $l_g$  and  $a_g$  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, if by some means, the absorption coefficient value changes, then the PA signal amplitude will also accordingly, vary. 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 [19]. Any change in the PA signal amplitude from the sample is essentially a measure of the rate of photodegradation of the dye.

The absorption spectra for mixtures of Rh 6G and Rh B are shown in figure 2. The absorption peak of Rh 6G-doped PMMA is around 520 nm, and that of Rh B-doped PMMA is around 550 nm. Absorption of Rh B-doped PMMA is very low when 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 520 nm.

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

From the plot, it is clear that PA signal degradation rate changes from sample to sample. Plots are shown separated from each other for the sake of clarity. All the

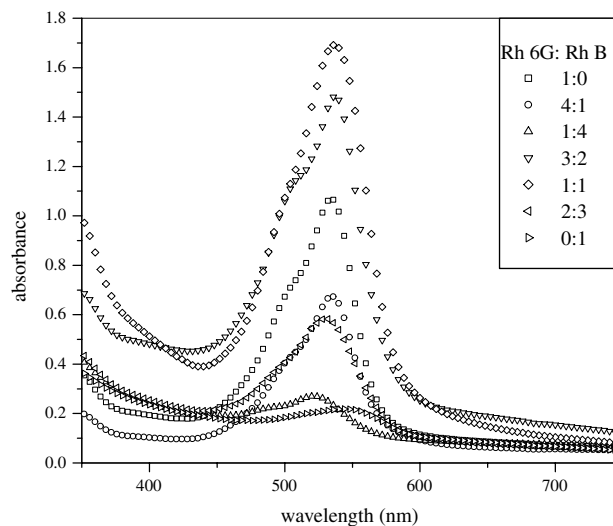


Figure 2. Absorption spectra of dye mixture system.

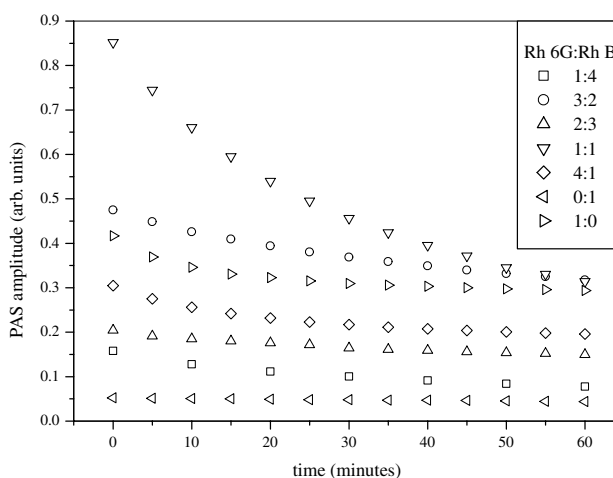
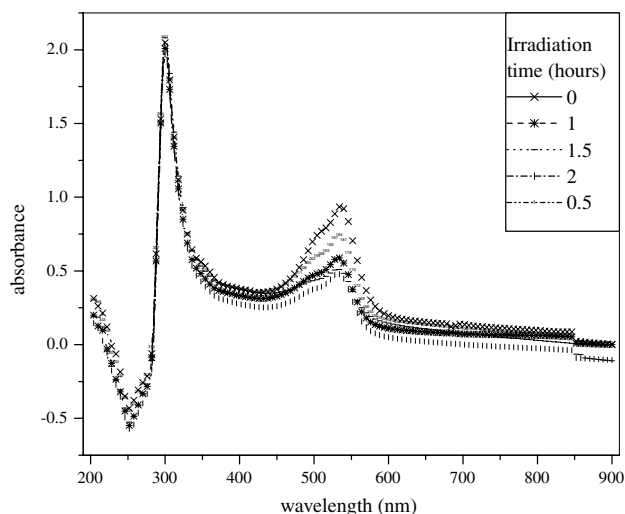


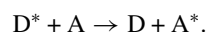
Figure 3. PA signal amplitude versus irradiation time plot for different volume ratios of Rh 6G and Rh B-doped polymer samples  $P = 30$  mW,  $\lambda = 488$  nm,  $f = 80$  Hz; concentration of Rh 6G = 1 mM, concentration of Rh B = 1 mM.

samples containing Rh 6G exhibit signal degradation and then saturation on continued irradiation. This indicates that on irradiating the dye-doped PMMA sample with a strong laser beam, photodegradation of the dye molecules takes place and the resultant product does not absorb radiation in the spectral region where the original dye molecules absorb it. The reduction in absorbance is evident in the absorption spectrum (figure 4). Therefore, the observed decrease in PA signal amplitude is because of the gradual decomposition of the dye molecules. The time taken to attain saturation is found to vary from sample to sample. As Rh B has very low absorption at the irradiation wavelength, the photo-reaction 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 photochemically stable at this particular concentration and irradiation wavelength. The addition of Rh B changes the photosensitivity of Rh 6G. The reduction in photochemical



**Figure 4.** Absorption spectra of the sample (Rh 6G–Rh B volume ratio 1 : 1 with the same concentration) before and after irradiation.

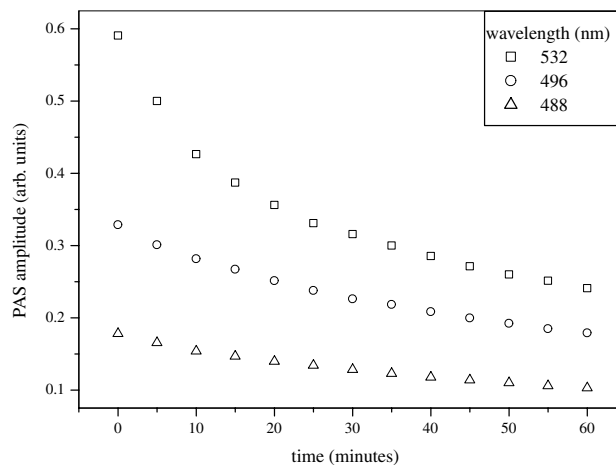
reaction of Rh 6G can be attributed to the enhancement in energy exchange to Rh B. Non-radiative energy transfer from an excited state donor ( $D^*$ ) molecule can occur owing to the coulombic or electron exchange interaction between  $D^*$  and the acceptor (A) molecule. Non-radiative transfer of electronic 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:



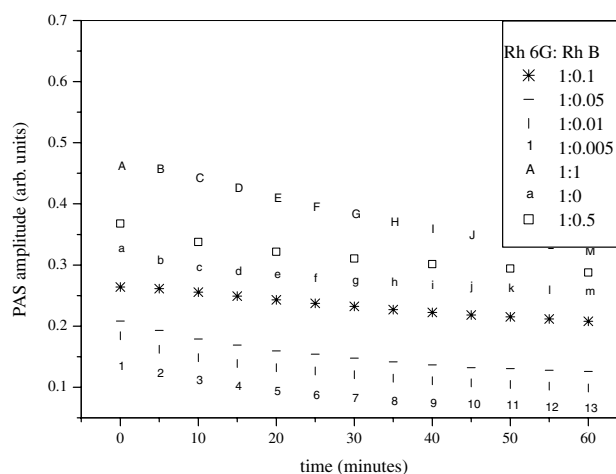
This type of energy transfer occurs when the energies involved in  $D^* \rightarrow D$  and  $A \rightarrow A^*$  transitions are the same, the excitation transfer being the simultaneous occurrence of the two coupled or resonant transitions.

As the quantity of Rh B in the mixture is increased, the Rh B–light interaction increases while that of Rh 6G decreases. Samples with small amounts of Rh B show gradual photodegradation in the early stages followed by saturation. In these cases, the influence of Rh 6G is maximum. As the volume ratio of Rh B is increased above that of Rh 6G, certain modifications are introduced in the energy exchange process so that signal degradation is very slow. This indicates that the presence of Rh B stabilizes the sample against damage. The sample with the two dyes mixed in a 1 : 1 ratio takes a longer time for photodegradation and more than an hour to attain saturation. The PA signal amplitude is also found to be maximum for this particular combination. This may occur owing to the fact that the energy exchange between the two dyes is maximum for this particular combination, thereby reducing the rate of photochemical reaction. In all other cases, the photochemical reaction is very fast in the initial stage and hence the samples attain saturation within a short time. Even though a large number of studies have been reported in the field of dye-doped polymers, the exact mechanism responsible for the photodegradation of laser dyes in polymers has not yet been fully explained [20, 21].

In order to investigate the influence of irradiation wavelength on the photodegradation of the dye system-doped PMMA, PA studies are carried out using 532 nm radiation from



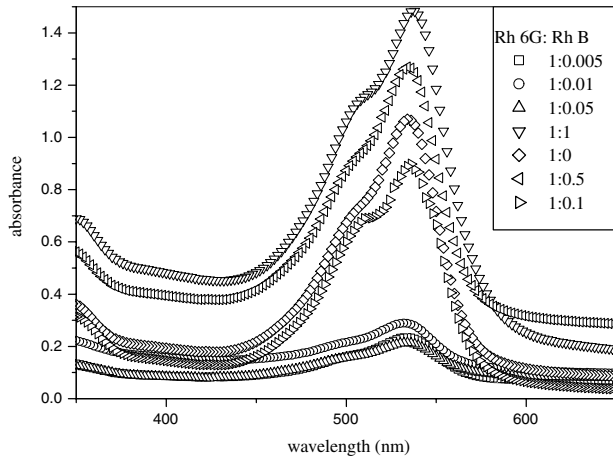
**Figure 5.** PA signal versus time plot for different wavelengths (dyes of same concentration (1 mM) are mixed in the ratio 1 : 1). Laser power = 30 mW, modulation frequency  $f = 80$  Hz.



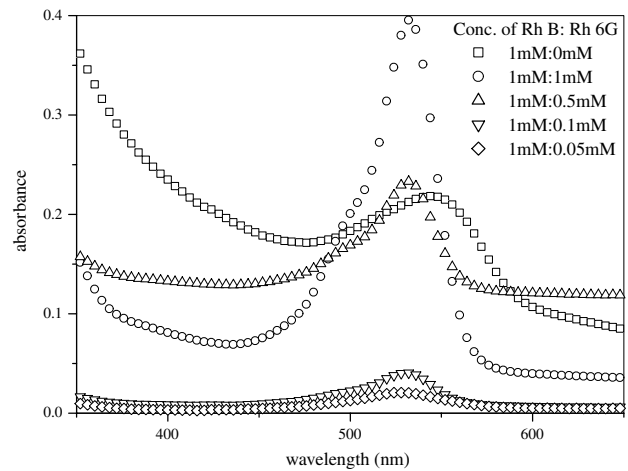
**Figure 6.** PA signal amplitude versus irradiation time plot for PMMA doped with Rh 6G–Rh B system. Rh 6G concentration is fixed at 1 mM and Rh B concentration (mM) is changed. Laser power = 30 mW,  $\lambda = 488$  nm, modulation frequency  $f = 80$  Hz.

the DPSS laser, and 496 and 488 nm radiations from the argon ion laser. The PA signal amplitude is plotted as a function of irradiation time (figure 5). The photodegradation rate is found to increase as the irradiation wavelength increases from 488 to 532 nm. This is understandable as the absorption of Rh 6G is maximum at around 520 nm. The PA signal amplitude also increases as the irradiation wavelength approaches the peak absorption wavelength. Even though higher wavelengths give higher values for the PA signal, investigations are carried out using 488 nm, because of the steady operational conditions for longer time durations at this wavelength.

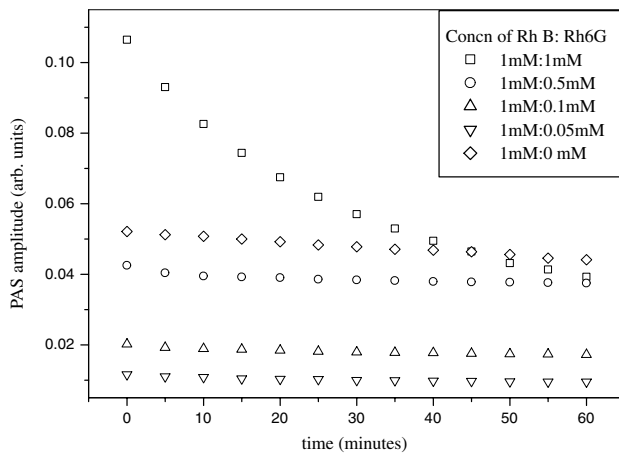
The variation in PA signal amplitude for PMMA samples doped with Rh 6G and Rh B in the same volume ratio for a constant concentration of Rh 6G, and different concentrations of Rh B, is shown in figure 6. From the plot, it is clear that the decay time is more for the PMMA film in which dyes are doped in the ratio of 1 : 1. As equal amounts of both the dyes are present in the mixture, photons are equally shared between the two. In the case of films with low concentrations of Rh B (0.005 and 0.1 mM) the PA signal is found to be lower than that



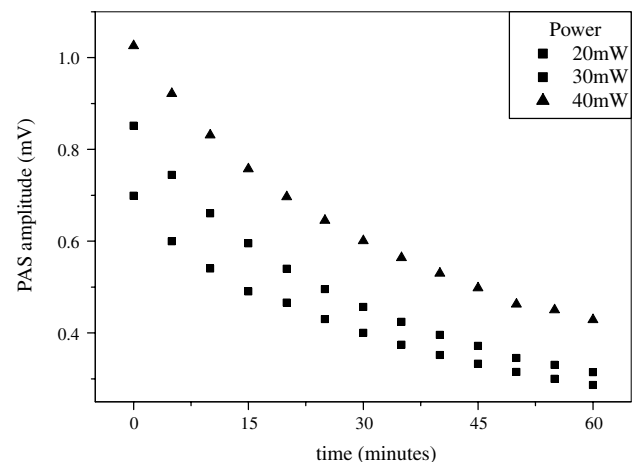
**Figure 7.** Absorption spectra of dye mixture-doped PMMA samples for constant Rh 6G and different Rh B concentrations.



**Figure 9.** Absorption spectra of dye mixture-doped PMMA samples for constant Rh B and different Rh 6G concentrations.



**Figure 8.** PA signal amplitude versus irradiation time plot for PMMA doped with Rh 6G–Rh B system. Rh B concentration is fixed at 1 mM and Rh 6G concentration is changed. Laser power = 30 mW,  $\lambda = 488$  nm, modulation frequency  $f = 80$  Hz.



**Figure 10.** PA signal amplitude versus time plot for dye system-doped PMMA at different irradiation intensities (dyes of same concentration (1 mM) are mixed in the ratio 1 : 1).  $f = 80$  Hz,  $\lambda = 488$  nm.

corresponding to Rh 6G alone. Here, the presence of Rh B has a damping effect on the non-radiative relaxation processes, which in turn, reduces the PA signal amplitude. Energy exchange takes place between Rh 6G and Rh B molecules. When the concentration of Rh B is increased above 0.1 mM, the PA signal is found to be more than that corresponding to PMMA doped with Rh 6G alone, and is maximum for the 1 : 1 ratio with the same concentrations.

The absorption spectra of the samples also show maximum absorption for the sample in which dyes are mixed in the same proportion (figures 7 and 9). For lower concentrations of Rh B, signal degradation is not appreciable, whereas for higher concentrations, signal degradation is gradual and signal saturation takes a longer time. The presence of small amounts of Rh B stabilizes the dye mixture against photodegradation.

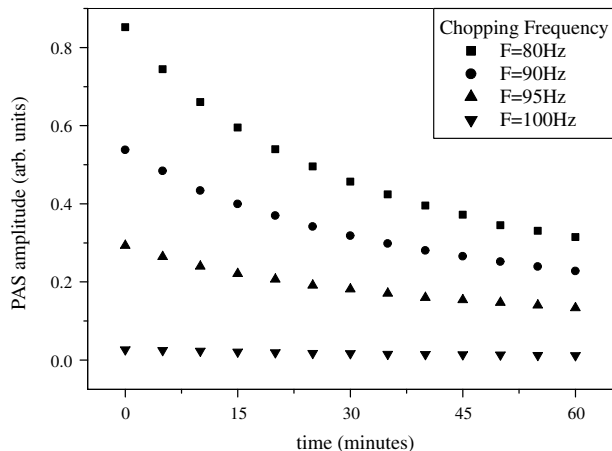
The variation in PA signal amplitude for PMMA samples doped with Rh 6G and Rh B in the same volume ratio for constant concentration of Rh B and different concentrations of Rh 6G is shown in figure 8.

Rh B dye has lower absorbance than Rh 6G at 488 nm. When the concentration of Rh 6G in the system is very low, the

influence of Rh B will be predominant and the signal is almost stable under continuous irradiation. As the concentration of Rh 6G is increased to 0.5 mM, PA signal increases and degradation becomes visible. Signal saturation occurs within a short time. The presence of Rh 6G is found to enhance the photosensitivity of the Rh B–Rh 6G system and hence, results in faster bleaching.

Studies were also carried out on the dye mixture system to study the photostability at various power levels and chopping frequencies. From figure 10, it is clear that PA signal degradation increases with an increase in pump power. These plots show that the degradation rate is not uniform throughout. Initial degradation occurs at a faster rate followed by slower decay, which is more visible at lower pump levels.

The PA signal decreases with the increase in modulation frequency. This is due to the shortening of the thermal diffusion length  $\mu$  on increasing the modulation frequency, as is clear from equation (1). At lower frequencies, PA signals from deeper sample layers will be generated resulting in slow signal degradation. Therefore, at lower frequencies it takes longer to complete the photochemical changes and



**Figure 11.** PA signal amplitude versus time plot for dye system-doped PMMA for different modulation frequencies (dyes of the same concentration (1 mM) are mixed in the ratio 1 : 1). Laser power = 30 mW,  $\lambda = 488$  nm.

the decrease in PA signal amplitude is gradual (figure 11). Since, the penetration depth is low for higher modulation frequencies, photobleaching is completed within a short time and no appreciable change in the signal amplitude is observed. Enhancement in the signal decay with exposure time as observed in figure 11 can be attributed to the effect of thermal degradation of the sample along with the photon-induced bleaching. Thus, by changing the frequency of modulation, the bleaching rate can be varied.

## 5. Conclusions

The PA technique has been used 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 a donor-acceptor combination can change the photostability of the dye-doped polymer matrix. For example, adding Rh B can enhance photostability of Rh 6G and photosensitivity of Rh B can be enhanced by adding Rh 6G. If the dye-doped polymeric material is to be used as an active medium for laser operations, the life-time of a stable operation can be increased through proper selection of dye combinations and their concentrations. The dye-doped PMMA can also be

considered a good medium for optical recording applications. Through suitable selection of dye combinations and the proper choice of concentrations of individual dyes, the time for optical recording can be adjusted.

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