

Photoacoustic study on photobleaching of Rhodamine 6G doped in poly(methyl methacrylate)

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Abstract. The photobleaching of the lasing dye Rhodamine 6G embedded in the solid matrix poly(methyl methacrylate) was investigated using a photoacoustic technique. Chopped laser radiation from an argon ion laser at four different wavelengths was used for the study. Experimental results indicate that the photobleaching rate is directly proportional to the incident laser power while it decreases with increase in concentration of the dye molecules. In the present case we have not observed any dependence of photobleaching on the chopping frequency. One-photon absorption is found to be responsible for the photobleaching of the dye within the selected range of laser power.

1. Introduction

Several studies on photo-induced bleaching of organic dyes impregnated in solid matrices have been reported during the past few decades [1–10]. Such studies have great importance due to the various applications of these materials, such as for active laser elements, passive Q-switches, optical data storage, photonic displays, optical waveguides etc. Suitable materials for different applications can be prepared by properly selecting the type of solid matrix and the dye incorporated into it. For example, lasing dyes doped in polymers can be used as laser active elements, phthalocyanines doped in polymers can be used as Q-switches and dye-sensitized gelatin or poly(vinyl alcohol) can be used as a holographic recording medium [4, 5, 11, 12]. Lasing dyes doped in a solid matrix are reported to be a good alternative to the conventional liquid-phase dye lasers. The advantages of the former over the latter are their compactness, simplicity of handling, ease of preparation and low cost. However, the low laser damage resistance of the host material (usually a polymer) and low photostability of dyes in the solid matrix have somewhat limited the widespread use of these elements as a lasing medium.

In all the above applications, a thorough knowledge of the photostability of the dyes incorporated in a solid matrix is necessary. Several theoretical models have been developed to explain photobleaching of the dye under pulsed and continuous-wave (cw) irradiation. Dyumaev *et al* [4] have studied the dye photodegradation in a polymer matrix under high-power pulsed irradiation. They have also developed a theoretical model for the photodestruction

of lasing dyes by correlating the dye concentration, pump power, pulse duration and number of pump pulses. Newell *et al* [8] have developed a model to explain their observations on dye photobleaching using transmission studies under cw irradiation. Torres *et al* [13] have studied the laser-induced iodine desorption from polystyrene and compared the results with the theoretical model that they have developed. However, these models for cw irradiation are reported to be valid only at low pump powers. In the present paper, we report photostability studies on Rhodamine 6G (Rh 6G) doped in poly(methyl methacrylate) (PMMA) using a photoacoustic (PA) technique at relatively high pump powers.

The PA technique is reported to be a versatile tool for optical and thermal characterization of a variety of samples [14–19]. The PA technique makes use of the detection of acoustic waves generated by a modulated optical irradiation when it interacts with a sample kept inside a closed cavity. According to Rosencwaig–Gersho theory [20], for a thermally thick sample, the complex amplitude of the pressure variation inside the cavity is given by

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

where β and μ are the optical absorption coefficient and the thermal diffusion length of the sample, respectively; γ is the ratio of heat capacities of air; P_0 and T_0 are the ambient pressure and temperature, respectively; I_0 is the incident light intensity and l' is the length of the gas column inside the cavity; a' and k are the thermal diffusion coefficient of the gas inside the cavity and the thermal conductivity of

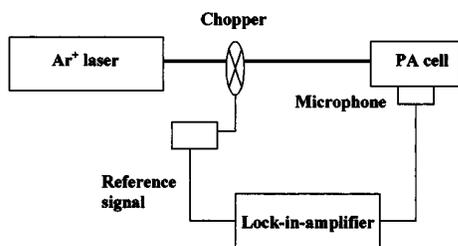


Figure 1. Schematic diagram of the experimental set-up.

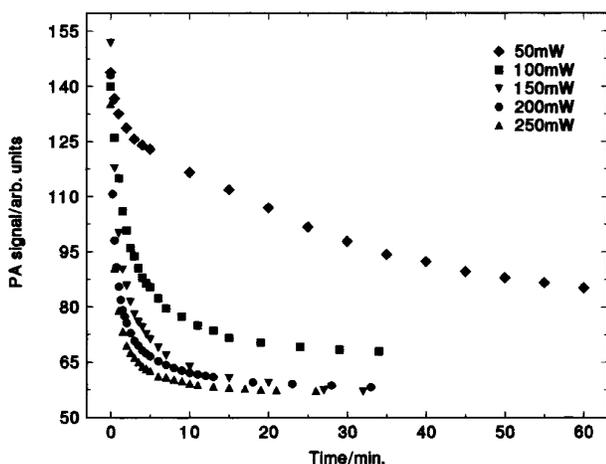


Figure 2. A plot of PA signal versus time for Rh 6G doped PMMA samples at different pump powers ($\lambda = 488$ nm, sample thickness 2.7 mm, dye concentration 1×10^{-3} mol l $^{-1}$).

the sample, respectively. We have selected the chopping frequency and the sample thickness in such a way that the sample under investigation is thermally thick in all the experiments. From the above equation, it is clear that under identical experimental conditions, the PA signal amplitude is directly proportional to the optical absorption coefficient of the sample. We have employed this relation to analyse the photobleaching of the samples under chopped laser pulses of millisecond duration. One major advantage of the PA technique over conventional transmission studies is that even bulk samples with greater dye concentrations can be studied using this technique. Also the sample surface need not be highly polished.

2. Experimental details

Rhodamine 6G (chloride salt, Loba Chemie Wien) was used as received. It was dissolved in a mixture of methyl methacrylate and ethyl alcohol taken in the ratio 4:1. Ethyl alcohol was added to the monomer to enhance the solubility as well as the photostability of the dye. Solutions of three different concentrations (1×10^{-3} mol l $^{-1}$, 5×10^{-4} mol l $^{-1}$ and 1×10^{-4} mol l $^{-1}$) were prepared and benzoyl peroxide was used as the polymerization initiator. The mixture held in thin glass bottles was kept in a constant temperature bath maintained at 50 °C for thermal polymerization. After about 48 hours the completely polymerized samples were cut into pieces of desired thickness and were polished to minimize the scattering losses.

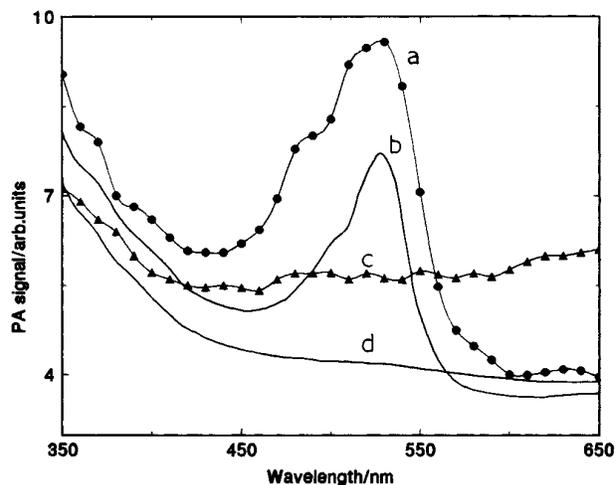


Figure 3. PA spectra and optical absorption spectra of the Rh 6G doped PMMA sample before and after bleaching (dye concentration 1×10^{-3} mol l $^{-1}$). (a) PA spectrum before bleaching, (b) optical absorption spectrum before bleaching, (c) PA spectrum after bleaching and (d) optical absorption spectrum after bleaching.

A schematic diagram of the experimental set-up used for the present study is shown in figure 1. Highly stabilized laser radiation from an argon ion laser (Liconix 5000 series) was intensity modulated using a mechanical chopper (Ithaco, HMS 230) before it was made to fall on the sample kept inside a non-resonant PA cell. The unfocused laser beam has a diameter of 1.2 mm at the irradiation site on the sample. The acoustic signal generated in the closed cavity was detected using an electret microphone (Knowles BT-1834) coupled to the PA cell and was processed using a lock-in-amplifier (Stanford Research Systems SR 510). Laser emissions at 476 nm, 488 nm, 506 nm and 514 nm were used for the present study. The photodegradation of the samples was studied at different pump powers namely 50 mW, 100 mW, 150 mW, 200 mW and 250 mW. The observed PA signal variations at these pump powers are shown in figure 2. The experiments were also carried out at different dye concentrations and chopping frequencies.

In order to record the PA spectrum of the sample, the laser source in figure 1 was replaced by a 1000 W Xenon arc lamp (Oriel 6269) and a monochromator. The output of the monochromator (10 nm bandwidth) was focused to the sample kept inside the PA cell. The PA spectrum of the sample before laser irradiation was recorded using this set-up. The PA spectrum of the completely bleached sample after the laser irradiation was also recorded. The lamp emission profile was recorded using carbon black as the sample. Both the spectra of the sample before and after bleaching were normalized using the lamp emission profile and are shown in figure 3.

The optical absorption spectra of the sample before and after laser irradiation were also recorded using a spectrophotometer. Both the spectra are shown along with the PA spectra in figure 3.

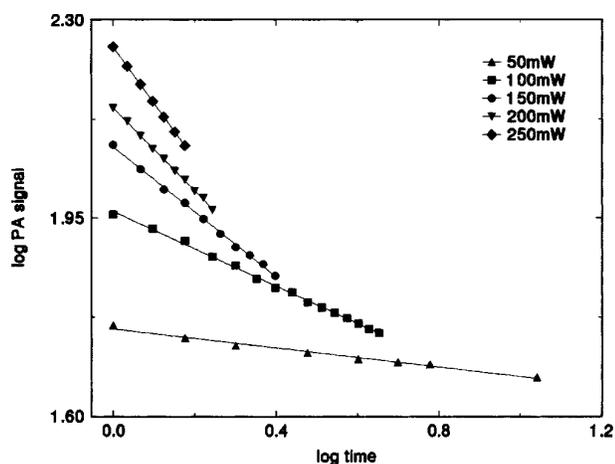


Figure 4. The log–log plot connecting the PA signal and time at different pump powers ($\lambda = 488$ nm).

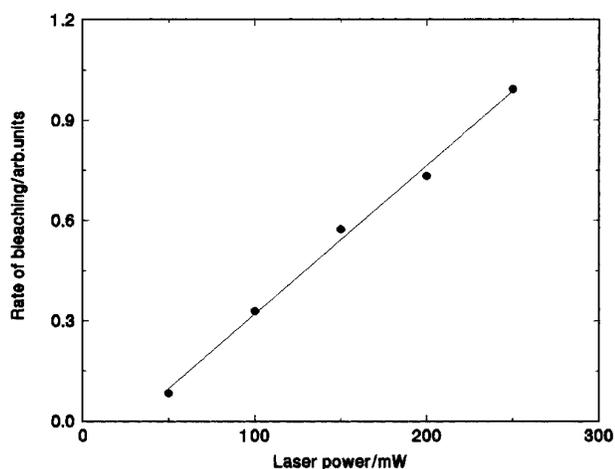


Figure 5. Variation of the rate of bleaching of Rh 6G doped in PMMA with incident laser power ($\lambda = 488$ nm, dye concentration 1×10^{-3} mol l $^{-1}$).

3. Results and discussion

The effect of laser power on photobleaching rate of the dye molecules was studied at different pump powers in the range 50–250 mW. The variation of PA signal amplitude with time for different pump powers is shown in figure 2. From this plot it is clear that the PA signal decreases quickly during the initial stage followed by a saturation. This obviously corresponds to a decrease in the absorption coefficient of the sample (from equation (1)). The saturation in the PA signal corresponds to the complete photodegradation of the dye molecules from their original state. This was confirmed from the recorded PA spectrum as well as from the optical absorption spectrum of the sample shown in figure 3. From the spectra it is clear that the sample before bleaching has strong absorption centred around 530 nm, whereas after bleaching it does not have any absorption at this wavelength. This leads to the conclusion that on irradiating with a strong laser beam, photodegradation of the dye molecules takes place so that there is no absorption of optical energy in the 530 nm region. Therefore, the observed decrease in PA signal amplitude is purely due to the gradual photodecomposition

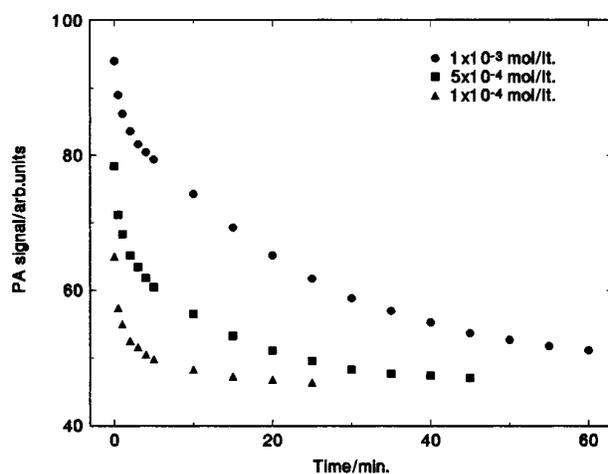


Figure 6. A plot of PA signal versus time for three different dye concentrations ($\lambda = 514$ nm, laser power 100 mW).

of the dye molecules. The finite value of the PA signal even after complete degradation of the dye molecules is the contribution of the solid matrix PMMA. The bleaching of the dye molecules causes a colour change of the sample from yellowish-orange to colourless. It is also clear from figure 2 that as the pump power increases the plot becomes steeper or the dye degradation takes place at a faster rate. The sharp increase in the rate of bleaching is more clearly displayed in the log–log plot connecting the PA signal and time as given in figure 4. The slope of the plot, which gives the rate of bleaching, was found to increase with the increase in laser power. Figure 5 shows the plot connecting the rate of bleaching and pump power. This plot indicates that the photobleaching rate varies linearly with the pump power within the range studied. The plot also indicates that there exists a threshold power level below which there is no appreciable degradation of the dye molecules in a reasonable time duration.

The variation of photobleaching with the concentration of the dye molecules was studied at three different concentration values, namely 1×10^{-3} mol l $^{-1}$, 5×10^{-4} mol l $^{-1}$ and 1×10^{-4} mol l $^{-1}$. The laser power was fixed at 100 mW in all these experiments. The observed PA signal variation with time for these dye concentration values is shown in figure 6. From this figure it can be seen that there is a considerable increase in the photobleaching rate with decrease in dye concentration. The rate of bleaching at a concentration of 1×10^{-4} mol l $^{-1}$ is found to be 2.61 times greater than that at a concentration of 1×10^{-3} mol l $^{-1}$ and for a concentration of 5×10^{-4} mol l $^{-1}$, it is 1.77 times greater than that at a concentration of 1×10^{-3} mol l $^{-1}$. For the bleached sample no perceptible change in absorption at 530 nm or at any other wavelength has been observed even after several weeks. This means that the photobleaching in the present case is an irreversible process. The PMMA matrix is found to be very stable and it can neatly withstand a chopped laser radiation at a power level of 250 mW. Also the unbleached sample does not show any noticeable degradation after its storage for two months at room temperature.

We have investigated the effect of chopping frequency on the photobleaching rate of the dye molecules at different

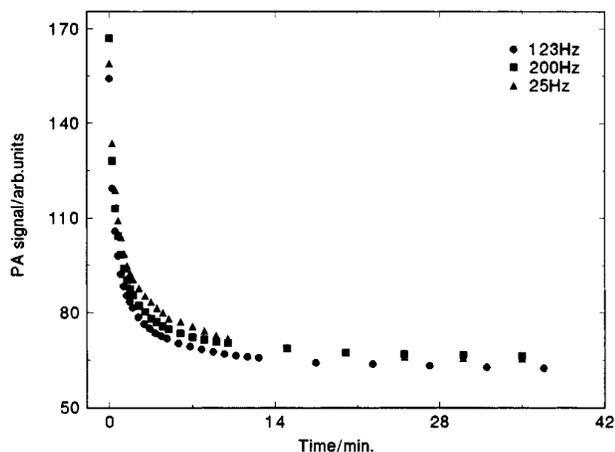


Figure 7. A plot of PA signal versus time for three different chopping frequencies ($\lambda = 488$ nm, laser power 200 mW).

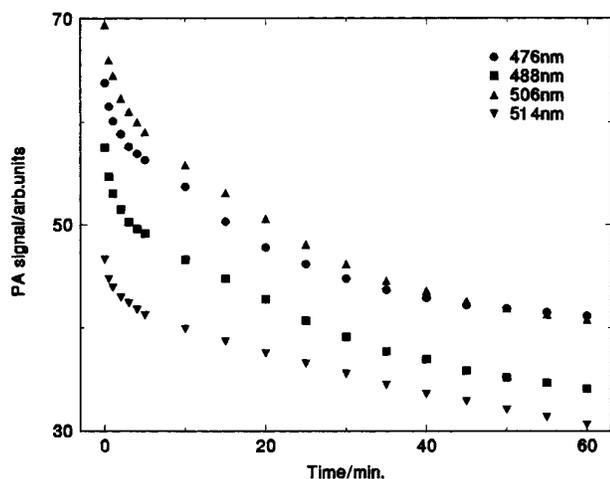


Figure 8. A plot of PA signal versus time for four different wavelengths (laser power 50 mW, dye concentration 1×10^{-3} mol l^{-1}).

chopping frequencies in the range 25–200 Hz. The PA signal variations at these chopping frequencies are given in figure 7. It can be seen from this figure that, within the range selected, the chopping frequency does not have any noticeable dependence on the photobleaching rate of the dye molecules. This leads to the conclusion that the photodestruction of Rh 6G in PMMA depends only on the total energy incident on the sample, which is the same for all the chopping frequencies. However, for certain other dyes doped in some other polymers, the dependence of chopping frequency on photobleaching has been noticed earlier [12].

We have also studied the bleaching behaviour of the sample at four different irradiation wavelengths, namely 476 nm, 488 nm, 506 nm and 514 nm at a constant pump power of 50 mW. The PA signal variations in this case are shown in figure 8. From this plot it is clear that the selected wavelengths have no influence on the photobleaching rate of the dye. This could be due to the fact that the wavelengths used are not well separated and are lying close to the optical absorption maximum of the sample.

It is obvious that an increase in dye concentration increases the optical density of the sample. Hence from

our observations it is clear that by increasing the optical density of the sample one can decrease the photobleaching rate. Therefore, if we use a dye-doped polymeric material as a laser active element, the lifetime for stable operation can be increased by increasing the dye concentration. However, in this case care should be taken to see that the concentration values selected do not take them into the range of fluorescence quenching. Alternatively, if one uses such a material as a medium for optical data storage, then by decreasing the dye concentration one can decrease the time for recording.

Even though the exact mechanism responsible for photodegradation is not yet known, there are several possibilities for the photochemical reaction process. However, the reaction takes place only when the molecules are in the excited state. We have measured the PA signal amplitude at different pump powers in the range 50–250 mW and the log–log plot connecting laser power and PA signal (not shown) was found to be linear with a slope of 0.84, which corresponds to single-photon absorption. This strongly indicates that multi-photon processes do not contribute significantly to the photobleaching process of rhodamine 6G doped in PMMA under cw laser irradiation. Therefore, in the present case the dye destruction takes place while the system is either in the first excited singlet state or lowest triplet state. The major possibilities for dye degradation are the excited state reactions with the polymer macromolecules or with the free radicals formed in the matrix during polymerization. The impurities present in the matrix may also affect such decomposition processes

4. Conclusions

To conclude, the photoacoustic technique has been implemented successfully to the investigation of the bleaching of organic dye molecules embedded in the solid matrix PMMA. Using this technique we have confirmed that the bleaching of Rh 6G molecules within the laser power range 50–250 mW is due to a one-photon process. Based on our experimental observations using the PA technique, we have arrived at the following results. In the case of Rh 6G doped in the solid matrix PMMA, the rate of photobleaching is directly proportional to the incident laser power and it decreases with increase in the concentration of the dye molecules. Moreover, we have found that the photobleaching rate of the dye is insensitive to the chopping frequency. This means that the time scale of the photo-induced reaction is less than a few milliseconds. Hence in the present case the rate of photodegradation depends only on the total energy incident on the sample. Also no noticeable change in the bleaching rate was observed for the four different irradiation wavelengths used.

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