Chapter 6

Photoacoustic investigations on photostability of Rhodamine 6G doped PMMA

Synthesis of rhodamine 6G doped poly (methyl methacrylate) samples and their photostability studies using a laser induced photoacoustic technique are discussed in this chapter. The linear dependence of photoacoustic signal amplitude on the optical absorption coefficient of the sample is made use of in these measurements. Rhodamine 6G doped PMMA samples are prepared using conventional free-radical polymerization method. Investigations are carried out at different incident light intensities, wavelengths, dye concentrations and modulation frequencies. The photobleaching rate is found to increase monotonically with increase in pump power and decrease with increase in dye concentration. Various aspects of the mechanisms of the photodegradation of the dye molecules and the role of different externally influencing parameters such as wavelength, modulation frequency etc. are discussed in detail.
6.1 Importance of dye doped polymers

Conventional laser systems employing solutions of organic dyes have been in existence for many years and are widely used as tunable lasers, from the ultraviolet to the near infrared range [1-10]. However, the need of complex and bulky laser designs, requirement of large volumes of the organic solvents and handling problems have limited their use in many applications. Consequently, from the early days of the development of liquid state dye lasers, people are looking for an alternative, a solid state strategy, to employ these organic chromophores. In fact a direct employment of the dye materials as solid-state cast films is not feasible because of increased luminescence quenching resulting from a strong interaction of excited-state molecules [7-10]. This molecular quenching mechanism leads to a complete suppression of stimulated emission in pure dye films. A strategy to circumvent this concentration quenching due to molecular interaction is, therefore, to spatially separate the dye molecules by incorporating them as guests in host materials [11-14].

As a result of the search for new laser materials in the last decade there has been a renewed interest in the use of solid matrices containing laser dyes to produce tunable solid-state dye lasers [13-27]. A solid host for lasing dyes is an attractive alternative to the liquid-phase dye lasers with obvious advantages such as compactness, manageability, lack of toxicity and flammability, suppression of flow fluctuations, solvent evaporation etc. In the dye doped solid matrix systems, the dye molecules are dispersed in a solid host medium which is either chosen to be polymers or sol-gel materials. Soffer and McFarland in 1967 [11] and Peterson and Snavely in 1968 [12] independently reported stimulated emission from polymer matrices doped with organic dyes. Since then a number of solid organic and inorganic polymer matrices have been described, where the laser dyes have been in most cases merely dispersed. Although this approach is very attractive, the first results are not very encouraging, with low lasing efficiencies, fast dye photodegradation and low laser damage threshold of the solid host. Consequently, the research on solid-state dye lasers remained almost dormant for more than a decade. During the past two decades new and optimized approaches have led to significant advances in these systems with respect to laser efficiency and damage threshold. Late 1980's have witnessed the development of improved host materials with higher laser damage resistance, which gave a new interest in this field [15,16,28,29]. Also, in the past decade the synthesis of new high-performance dyes and the implementation of new ways of incorporating the organic molecules into the solid matrix have resulted in significant advances towards the development of practical tunable solid-state dye lasers [30-36].
Even though the recently reported works with silica gels [37-41] have indicated that the sol-gel materials might show higher photostability and better lasing properties than those based on organic polymers, the polymeric matrix approach offers various advantages. Most frequently used polymeric materials are based on methyl methacrylate (MMA), such as poly methyl methacrylate (PMMA) or compositions of methacrylate copolymers like HEMA: MMA etc. [16-21,27,30]. The advantages of these synthetic polymer hosts are better optical transparency, homogeneity of refractive index, good compatibility with the organic dye, inexpensive fabrication techniques, lightweight etc. In addition to these, chemical control of the polarity in the visible range and the modification of viscoelasticity are possible in polymers. Furthermore, new modified polymeric organic materials have been developed with a laser radiation threshold that is comparable to or higher than those of most laser-damage-resistant inorganic glasses and crystals [18,42].

Though the polymers possess a large number of advantages over the conventional dye lasers, the finite lifetime for stable operation of the dye incorporated into the solid host still persists as a limitation to the commercial exploitation of this kind of active laser materials. One of the important parameters to reduce the photodegradation of the dye is to optimize the rigidity of the host. Dissipation of the excess energy of photoexcitation can be favoured by a more efficient phononic coupling of the dye molecule to the host media. This can be achieved by using optimized copolymer mixtures as matrix materials or by covalent linkage of the dye molecules to the polymeric chain [15,20,43].

Apart from the use as active laser media, dye doped polymers find many other applications in the modern photonic technology. Though the photodegradation of the dyes is a disadvantage when these materials are used as a laser medium, the dye degradation can be made use of in many other applications such as holographic recording [44,45]. Several studies on photo-induced bleaching of organic dyes impregnated in solid matrices have been reported during the past few decades [46-49]. Such studies have great importance due to various applications of these materials such as active laser elements, passive Q-switches, optical data storage, photonic displays, optical wave-guides 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, dye doped polymer can be used as an active laser medium, phthalocyanines doped polymers can be used as Q-switches and dye-sensitized gelatin or poly(vinyl alcohol) can be used as holographic recording media [18,35,49].

In all the applications discussed above, 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. have studied the dye photodegradation in a polymer matrix under high power pulsed irradiation [18]. 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. have developed a model to explain their observations on dye photobleaching using transmission studies under cw laser irradiation [50]. Filho et al. have studied the laser-induced iodine desorption from polystyrene and compared the results with the theoretical model developed by them [51]. However, these models for cw laser irradiation are generally found to be valid only at low pump powers.

6.2 Methods to measure dye photodegradation

The photodegradation of organic dyes in a solid matrix is essentially due to a photoinduced reaction. Since the primary photo-process is absorption of a photon to create a photoexcited molecule, photochemistry and spectroscopy are intimately related. In a quantitative study, therefore, a radiation source of known intensity and wavelength and an appropriate detector are necessary to detect a photochemical reaction or any other photoinduced changes.

A molecule excited to a higher energy state must return to the ground state, unless it gets involved in a photochemical reaction and loses its identity. In condensed systems there exist a number of ways for the excited molecule to dissipate the excitation energy. Out of these different paths, commonly occurring and most important channels are radiative relaxation (fluorescence or phosphorescence), nonradiative relaxation (usually thermal relaxation) and excited state chemical reaction [52-57].

In the case of a photoexcited dye molecule, any of the above mentioned relaxation mechanisms are possible. Irrespective of whether the dye molecules are in a solution form or embedded in a solid matrix, the amount of energy liberated via radiative or nonradiative relaxation mechanisms is determined by the number of original dye molecules in the ground state as well as those in the excited state. Any kind of a photochemical reaction will result in a change in the number density of the original dye molecules. Consequently, the optical absorption as well as the amount of energy liberated through the radiative or nonradiative channels may change. Hence, by measuring either of these two quantities or both, one can easily make a quantitative evaluation of the photochemical processes that the sample (dye) undergoes. Another way to monitor a photochemical change is the analysis of the resultant products.
In order to induce a photochemical process as well as for its detection one can use either a steady state light source or a pulsed optical radiation. In its broadest sense, we can divide the detection methods into two categories. The first one is purely optical methods in which the radiative relaxation or the optical absorption (or transmission) is investigated. The second method is the photothermal techniques in which the sample is excited using an optical radiation and the quantity detected is the energy released through nonradiative relaxation processes.

6.2 Optical methods

Pure optical methods are the oldest and the simplest techniques to study the photodegradation of organic dyes in a solution form or when they are impregnated in a solid matrix [45-50]. Optical transmission studies, fluorescence or phosphorescence methods are some of the major optical methods that can be used for the dye photostability studies. The basic theory applied in the optical transmission studies is the Beer-Lambert law, expressed as

\[ I = I_o \exp(-\alpha \nu \cdot C \cdot l) \]  

where \( I_o \) and \( I \) are the incident and transmitted intensities of the light beam with a frequency \( \nu \). \( \alpha \nu \) is the optical absorption coefficient which is a function of the frequency (wavelength) of radiation. \( C \) and \( l \) are the concentration of the absorbing species and the optical path length, respectively. Hence, a change in the number density of the absorbing species (say, the organic dye in the solution or solid matrix) can be detected very easily by simply measuring the transmitted light intensity. This can be done either as a function of time or as a function of wavelength of the incident light, depending on the experimental situation. If the photochemical reaction takes place in a faster time scale, then the time dependent measurements are more suitable; whereas, if it is a very slow process then the wavelength scanning (optical absorption spectrum) is ideal [45]. The advantage of wavelength scanning is that it not only carries the signals of the degradation of the original molecules but also the signatures of the creation of new products and their absorption properties will be visible in the spectrum. Usually a single source of light is used for inducing a photochemical change and for detecting it. Since most of the dyes absorb in the ultraviolet or visible region, lasers and arc lamps are the most suitable sources for this kind of studies. A large number of reports are available in the literature where this simple photon transmission method is used for the photobleaching studies of different dyes in solid matrices [46, 48-50]. The experimental set up usually used for the optical transmission studies is very simple and is shown below.
However, the necessary requirements for employing this method are the need of a good surface optical quality for the sample and it should not be optically opaque. Apart from these, the methods discussed above suffer from many other constraints and hence its application in a detailed study of the different mechanisms responsible for the photodegradation is strictly limited.

![Diagram of a typical optical transmission set-up for the photostability studies.](image)

**Figure 1.** Block diagram of a typical optical transmission set-up for the photostability studies.

In the case of a luminescent dye such as a laser dye, a still better approach is to study the radiative relaxation (fluorescence or phosphorescence). In this approach, the sample is excited using a suitable optical radiation and the variation in the radiative emission during a photochemical change is detected. This method has been employed in many of the photostability studies on dye doped polymers [15,19]. Apart from mere fluorescent studies to investigate the photostability of the dyes, people have also used the decay of laser output when these materials are used as an active laser media [16,20,24,27,30]. If the excitation radiation has sufficiently high energy, then multi-photon absorption may take place and hence the photochemical process will become more complicated [58,59]. In such situations pure optical methods are not sufficient to understand the intricate intermediate steps as well as a complete quantitative evaluation of the photochemical process. The major reason for this is that many of the intermediate steps are associated with nonradiative relaxation processes and this cannot be effectively detected using an all-optical method. In such situations the photothermal methods play a vital role.

### 6.2.2 Photothermal methods

Photothermal methods are a group of highly sensitive techniques used to measure optical absorption and thermal characteristics of a sample. The fundamental principle of a photothermal method is the *photo-induced* change in the *thermal* state of a sample. Measurements of the temperature, pressure or density changes that occur due to optical absorption form the basis of the photothermal spectroscopic method [60-63]. Sample heating is a direct consequence of optical absorption and hence the photothermal signal is directly dependent on the quantity of the light absorbed. Scattering and reflection losses do not produce photothermal signals. Subsequently, photothermal spectroscopy more accurately measures optical absorption in scattering solutions, solids and at interfaces.
In a photochemical process, generally, intermediate species (radicals) are created and eventually the free radicals convert into some other products. Usually these intermediate steps are associated with nonradiative energy transfer which in turn produces the thermal effects. Hence, photothermal methods are more suitable for detecting these ultrafast processes [64-71]. They can also be used to detect the photochemical changes that occur during a steady state excitation of the molecules. As in the case of thermal and optical characterisation of materials, almost all the photothermal methods can be employed to investigate the photochemical processes. Though many of the photothermal methods are used in the photochemical study of gases or liquids, they are not yet widely employed in solid samples such as dye doped polymers. Photothermal interferometry, photoacoustics, thermal lens, photothermal beam deflection, transient grating etc. are some of the most useful photothermal methods that can be used to investigate photodegradation of organic materials.

6.3 Experimental details

6.3.1 Preparation of rhodamine 6G doped PMMA samples

Rhodamine dyes, belonging to the Xanthene family, with fluorescence emission in the yellow-red region of the spectrum are well known for their excellent laser performance in liquid solutions as well as in solid matrices [7-9]. For the present investigation rhodamine 6G chloride (Loba Chemie Wien) is used as received. Initially, the monomer methyl methacrylate (CDH Chemicals) is mixed with ethyl alcohol (Merck) in the ratio 4:1. Reasons for using ethyl alcohol as an additive to MMA are discussed in the next section. Solutions of monomer - alcohol mixture at three different dye concentrations namely, 1×10⁻³ mol/l, 5×10⁻⁴ mol/l and 1×10⁻⁴ mol/l are used for polymerisation. Benzoylperoxide (CDH chemicals) is used as the polymerisation initiator (1% by weight). The monomer-alcohol mixture containing the dye and the initiator held in thin glass test tubes is kept in a constant temperature bath maintained at 50 (±0.5) °C for polymerisation. Completely polymerised samples obtained after 48 hours is then kept at room temperature for one week for drying. Perfect drying is necessary to avoid shrinkage of the sample. Careful examination (including the absorption spectra) of the polymerised samples confirmed that the dye is homogeneously dispersed in the polymer matrix. Plane undoped PMMA samples are also prepared under the same experimental conditions for using it as a reference sample in optical absorption recording. The dried samples are then cut into small disc like pieces of thickness 1.2 mm and their faces are polished using fine emery paper and finally with woolen cloth. Polishing is done only to reduce the scattering losses.
6.3.2 Recording of photoacoustic spectra

The linear dependence of the PA signal amplitude on the absorption coefficient of the sample is used to record the PA spectrum, which is essentially the optical absorption spectrum, of the dye doped PMMA matrix. For this purpose a 1000W Xe arc lamp (Oriel 6269) is used as the excitation source and a 0.1m monochromator (Oriel 7250) to select the desired wavelength. The block diagram of the experimental setup is shown in figure 2. To protect the monochromator from thermal damage due to the large infrared emission from the arc lamp, a water cell (5cm long) is used in front of the monochromator. The water will effectively filter out the infrared portion of the spectrum. In order to achieve a large signal to noise ratio, the entrance and exit slits of the monochromator are adjusted to get maximum signal (bandwidth 10nm). Light coming out of the monochromator is intensity modulated using a mechanical chopper (Ithaco HMS 230) and the PA signal is processed using a lock-in-amplifier (Stanford Research Systems SR 510).

![Figure 2. Schematic diagram of the experimental setup used to record the photoacoustic spectra. WC, the water column; L₁, L₂ and L₃, the focusing lenses.](image)

Though the xenon arc emission spectrum is a continuum, its intensity varies from wavelength to wavelength and hence, an intensity normalisation procedure is required. For this purpose carbon black thin film coated on a glass plate is used as the sample. Being a perfectly black body, the absorption and emission of carbon black throughout the spectral region of interest is uniform and hence the PA spectrum recorded using this sample will be essentially the emission spectrum of the arc. The emission spectrum of Xe arc recorded using PA method is shown in figure 3. This spectrum is used to normalise the PA spectrum of the dye doped PMMA samples and the photodegraded samples. In addition to the PA spectrum, optical absorption spectra of the samples are also recorded using a spectrophotometer (Milton Roy, Genesys 5).
Figure 3. The emission spectrum of Xe arc recorded using PA method.

Figure 4. PA spectra and optical absorption spectra of rhodamine 6G samples before and after bleaching (dye concentration: $1 \times 10^{-3}$ mol/l). (a,c)PA spectrum before and after bleaching, (b,d) optical absorption spectrum before and after bleaching.
6.3.3 Experimental setup used to study the dye photodegradation

A continuous wave (cw) laser induced photoacoustic technique is employed to investigate the photo-induced degradation of the laser dye rhodamine 6G doped in PMMA. The experimental setup used for the present investigation is schematically shown in figure 5. The excitation source used is a highly stabilised 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). The modulated light beam at specific power levels is then allowed to fall on the sample kept in a home-built non-resonant PA cell. The details of the cell are given in the next paragraph. A highly sensitive electret microphone (Knowles BT 1834) is used to detect the PA signal. Finally, the PA signal is processed using a single phase, analog lock-in-amplifier (Stanford Research Systems SR 510). Laser lines at 476nm, 488nm, 506nm and 514.5nm wavelengths are used for the investigations. Influence of the excitation light intensity on the rate of dye photodegradation is studied at 50mW, 100mw, 150mW, 200mW and 250mW. Other parameters that are varied are the dye concentration and the laser modulation frequency.

![Diagram of the photoacoustic set-up](image)

**Figure 5.** Schematic diagram of the photoacoustic set-up for the photostability studies

The photoacoustic cell used for the present investigation is made of a heavy stainless steel block which effectively protects the PA signal from the ambient noises. The cross-sectional view of the cell is shown in figure 6. The cell is designed in such a way that it can be used either in the front illumination configuration or in the rear side illumination configuration. W₁ and W₂ are two glass windows and M is the microphone. The sample chamber is 5mm long and 4mm in
diameter. The microphone is kept 3mm away from the sample chamber and is coupled to the sample compartment through a bore of 3mm diameter. For the photostability studies, thin disk like sample is kept in the space between the window (W₂) and the PA cavity. Laser irradiation is made through the other window W₁ (front illumination).

![Figure 6. Cross-sectional view of the photoacoustic cell. W₁ and W₂ are the glass windows, M is the microphone, C is the PA cavity and S is the position to keep the sample.](image)

6.4 Results and discussion

In chapter 2 we have discussed the Rosencwaig-Gersho theory (R-G theory) which gives a satisfactory explanation to the generation of photoacoustic effect in condensed media. The dye doped PMMA samples are optically transparent and thermally thick, as the thermal diffusion length in PMMA is only a few tens of microns in the frequency range of investigations. Then, the complex amplitude of the PA signal produced is given by

\[ Q = \frac{-i\beta\mu^2 \gamma P_o I_o}{4\sqrt{2}T_o l_g a_g k} \]  

(2)

where \( \beta \) is the optical absorption coefficient of the sample and \( \mu \) is the thermal diffusion length in the solid material; \( \gamma \) is the ratio of specific heat capacities of air; \( P_o \) and \( T_o \) are the ambient pressure and temperature, respectively; \( I_o \) is the incident light intensity; \( l_g \) 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 \( \beta \) 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. Equation (2) is not only valid for optically transparent samples but also for opaque samples, provided the sample is thermally thick. Moreover, doping of an organic dye in a solid matrix will not alter the thermal properties of the host. Therefore, in the present case photodecomposition of the dye (and hence a change in its concentration) will not alter the thermal parameters of the host material. The above discussed facts clearly indicate that when a dye doped PMMA sample is investigated using PA method, any change in the PA signal amplitude is essentially a measure of the rate of photodecomposition of the dye.

Before going to the details of the experimental results, let us discuss the reasons for choosing ethyl alcohol as an additive to the monomer (and hence the polymer). One of the major reasons is that it combines good solubility for xanthene dyes and enhancement of the host laser-damage resistance [17,18]. Another reason, from the point of view of the use of dye doped PMMA as an active laser medium, is that polymerisation causes a decrease in the dielectric constant ($\varepsilon_{\text{MMA}} \approx 4$ and $\varepsilon_{\text{PMMA}} \approx 2.9$). This results in a shift of equilibrium between the dye monomer molecules and their aggregates towards the latter and consequently, the conversion efficiency decreases. Introduction of ethyl alcohol into MMA and PMMA causes $\varepsilon$ to increase and results in a reduction of the interaction between the cation and the anion in a dye ionic pair. This leads to expansion of the tight ionic pairs and shifts the equilibrium between the monomer and the dimer configurations toward the former; thereby increasing the quantum yield and the conversion efficiency of rhodamine 6G chloride [17]. This increase in quantum yield and the conversion efficiency on going from tight ionic pair to the expanded one is due to a decrease in the luminescence quenching of the dye-cation excited state that is associated with electron transfer from the anion to the cation.

The effect of laser power on photobleaching rate of the dye molecules is investigated at different pump powers ranging from 50mW to 250mW. The variation of PA signal amplitude as a function of time for different pump powers is shown in figure 7. From this plot it is clear that the PA signal amplitude decreases quickly during the initial stage followed by a saturation. This obviously corresponds to a decrease in the absorption coefficient of the sample at 488nm. The saturation in the PA signal corresponds to the complete photodegradation of the dye molecules from their original state. The PA spectrum as well as the optical absorption spectrum of the sample shown in figure 4 also confirms this observation.
From the spectra it is clear that the long-wavelength absorption band of rhodamine 6G in PMMA matrix falls in the blue-green region with the peak at 530nm. However, the photodecomposition of the dye completely wipes out this long-wavelength band. This indicates that on irradiating the dye doped PMMA sample with strong laser beam, photodegradation of the dye molecules takes place and the resultant product does not absorb in the spectral region where the original dye molecules absorb. Therefore the observed decrease in PA signal amplitude is purely due to the gradual photodecomposition 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 PMMA matrix. The bleaching of the dye molecules causes a colour change of the sample from yellowish-orange to a colourless one. It is also clear from figure 6 that as the pump power increases the plot becomes steeper or the dye degradation takes place at a faster rate. This is more clearly displayed in a logarithmic plot connecting PA signal and time as given in figure 8.
The slope of the plot, which gives the rate of bleaching, is found to monotonically increase with the increase in laser power. Figure 9 shows the plot connecting the rate of bleaching (in arbitrary units) and pump power. This observation is in accordance with many of the earlier reported studies on photodegradation of dyes in solutions and in polymer matrices [18]. 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 for a reasonable time duration.

The variation of photobleaching with concentration of the dye molecules is studied at three different concentration values namely $1 \times 10^{-3}$ mol/lt, $5 \times 10^{-4}$ mol/lt and $1 \times 10^{-4}$ mol/lt. In all these measurements the laser power is kept fixed at 100mW and the wavelength used is 488nm. The observed PA signal variation with time for these dye concentration values is shown in figure 10. From this figure it can be seen that there is a considerable increase in the photobleaching rate with decrease in dye concentration. This observation is in good agreement with the earlier reported results based on the lasing studies on rhodamine 6G doped PMMA [17]. The rate of bleaching at a concentration of $1 \times 10^{-4}$ mol/lt is found to be 2.61 times greater than that at a concentration of $1 \times 10^{-3}$ mol/lt and for a concentration of $5 \times 10^{-4}$ mol/lt, it is 1.77 times greater than that at a concentration of $1 \times 10^{-3}$ mol/lt. Also, the photobleaching of
Figure 9. Variation of the rate of bleaching of rhodamine 6G doped PMMA with incident laser power (\(\lambda = 488\text{nm}\), dye concentration \(1 \times 10^{-3}\text{ mol/l}\)).

Figure 10. PA signal versus time plot for three different dye concentrations (\(\lambda = 514.5\text{nm}\), laser power 100mW).
rhodamine 6G in PMMA is observed to be an irreversible process. The PMMA matrix is found to be very stable and it can neatly withstand an intensity modulated laser radiation at a power level of 250mW. Also, the unbleached sample does not show any noticeable degradation even after its storage for two months at room temperature.

Another possible parameter that may influence the rate of photodegradation is the excitation pulse duration or the modulation frequency. The effect of modulation frequency on photobleaching rate of the dye is investigated at three distinct frequencies namely, 25Hz, 123 Hz and 200Hz. The PA signal variations at these chopping frequencies are given in figure 11. 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 implies that the photodestruction of rhodamine 6G in PMMA matrix depends only on the total incident energy per unit time on the sample, which is same for all the chopping frequencies. However, for certain other dyes doped in certain other polymers, a dependence of chopping frequency on photobleaching has been noticed earlier [72].

Figure 11. PA signal versus time plot for three different modulation frequencies ($\lambda = 488\text{nm}$, laser power 200mW).
Figure 12. PA signal versus time plot for different wavelengths (laser power used is 50mW, concentration of the dye is $1 \times 10^{-3}$ mol/l). Plots corresponding to different wavelengths are shifted from each other for the sake of clarity.

Generally, laser dyes have two broad absorption bands, one in the short-wavelength region (usually in UV) and the other in the long-wavelength region [8,9]. Even in a particular band, one can use different wavelengths for pumping a dye laser. In the case of rhodamine 6G, different emission lines of an argon ion laser come under the long-wavelength absorption band of the dye. In order to investigate whether these distinct lines have any influence on the photodegradation rate of the dye, four different wavelengths namely 476nm, 488nm, 506nm and 514nm are employed. The laser power is kept constant at 50mW for all the wavelengths. The time evolution of the PA signal amplitude for different excitation wavelengths are shown in figure 12. From this plot it is clear that the selected wavelengths have no significant influence on the photobleaching rate of the dye.

Even though a large number of studies have been reported in the field of dye doped polymers, the exact mechanism responsible for photodegradation of laser dyes in polymers is not yet fully brought out. There exist a large number of channels for the photochemical reaction processes. The reaction will takes place only when the molecules are in the excited state. Most of the analyses available in the literature are based on the pulsed laser excitation. Under such high energy ($>10^7$ W/cm$^2$) excitation, multi-photon absorption process is possible and the dye
photodecomposition mechanism becomes very complex as the reaction may happen from any of the excited states. In a recent paper published by Ferrer et al., it is pointed out that the dyes undergo a thermal degradation due to the poor thermal conductivity of the polymer matrix [32]. However, this explanation does not seem to be reasonable as temperatures as high as 80 °C are used for the polymerisation of the dye doped samples. Also, considering the very high fluorescence quantum yield of laser dyes such as rhodamine 6G, the thermal energy liberated will be very small. However, a more reasonable and genuine explanation is given by Dyumaev et al. They have recently reported that the excitation of the dye molecules can give rise to electron energy transfer from the dye molecules to the polymer macromolecules. Subsequently vibrational relaxation of the first excited state of the polymer macromolecules results in the formation of radicals by a mechanism similar to that for UV or γ irradiation of polymers [18]. These radicals interact efficiently with the dye molecules in any of the excited states, resulting in their destruction. If this is the major mechanism responsible for the photobleaching of the dye, then the addition of a low molecular weight additive such as ethyl alcohol may improve the photostability of the dye to some extent. The addition of a low molecular weight additive may significantly improve the dye photoresistance through resonance vibrational cross relaxation, which hampers the formation of macroradicals.

It is a clearly established fact that at relatively low radiation intensities ( < 10^6 W/cm²) the dye destruction occurs from the first excited (singlet or triplet) electronic states and the photobleaching rate is linearly dependent on the radiation intensity [18]. The laser intensities used for the present investigations falls in this range and hence the dye destruction takes place while the system is either in the first excited singlet-state or lowest triplet state. Also, a linear dependence of dye degradation rate on the incident intensity is observed as reported earlier. It is expected that in the present case the dye degradation is due to the excited state reactions with the polymer macromolecules or with the free radicals formed in the matrix during polymerisation.

### 6.5 Conclusions

The photoacoustic technique has been implemented successfully to investigate the bleaching of organic dye molecules embedded in PMMA matrix. Based on the experimental observations using the PA technique, the following conclusions have been made. 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 concentration of the dye molecules. Moreover, it is found that the photobleaching rate of the dye is insensitive to modulation
frequency when the dye is irradiated with an intensity modulated cw laser. This means that the
time scale of photo-induced reaction is shorter than milliseconds, as the investigated time scales
are in the millisecond regime. 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
is observed for the four different irradiation wavelengths used.

It is obvious that an increase in dye concentration increases the optical density of the
sample. The present observation indicates 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 ensure that the selected
concentration values do not bring them to 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.
References