

Emission characteristics of laser dyes C1 and Rh6G in cross-linked polyvinyl alcohol solutions

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Abstract. The lifetimes and the relative quantum yields for fluorescence of two laser dyes Coumarin 1 and Rhodamine 6G have been determined in cross-linked polyvinyl alcohol matrix. The cross-linking has been achieved using gamma radiation. The relative fluorescence quantum yields of the dyes increased with increasing cross-linking of the polymer, but the fluorescence lifetimes remained unchanged within experimental error. The results have been attributed to a reduction in the loss of the excitation energy via the internal conversion of the excited singlet state due to increase in the viscosity of the medium brought about by the increased cross-linking of the polymer.

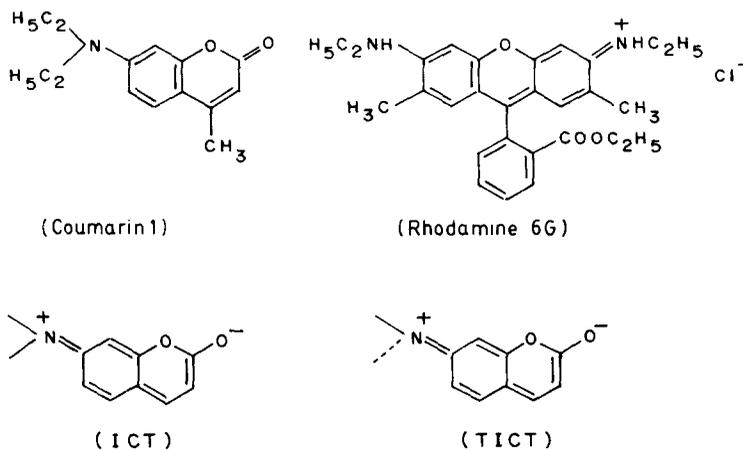
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1. Introduction

Dye lasers are now in widespread use due to their tunability. But their only drawback is the low conversion efficiency (Schafer 1983). Improving the efficiency of such dye lasers is thus of paramount importance. One way of approaching this goal is to increase the fluorescence quantum yields (Drexhage 1973). Quantum yield can be increased only when the rates of the processes leading to non-radiative decay of the excited state decrease. The processes are highly dependent on the medium, and hence it is necessary to find a suitable medium where they are minimised. Among many other factors, viscosity of the medium influences the emission characteristics to a great extent. Polymeric solutions are often used to increase the viscosity of the medium. In literature, there are many reports available on the fluorescence and absorption studies of dye molecules in polymeric matrices (Tazuke *et al* 1980; Ghiggino *et al* 1981; Kalyana Sundaram 1987). The photophysical and chemical properties of the probes mostly depend on the type of polymer (open chain, coiled or cyclic), tacticity of the polymer, nature of the solvent in which the polymer is dissolved and the binding sites available on the polymer backbone.

In the present work, we have studied solutions of the laser dyes, 7-diethylamino-4-methyl coumarin (also known as Coumarin 1, C1) and Rhodamine 6G (Rh6G) (the structures of these dyes are given in scheme 1) in aqueous solutions containing polyvinyl alcohol (PVA), the polymer being used to increase the viscosity of the solutions. In addition, further increases in viscosity have been obtained by

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Scheme 1.

cross-linking the polymer in solution with gamma radiation. The actual structure of cross-linked polyvinyl alcohol is not known very well yet. But it contains both hydrophilic and hydrophobic groups in a three-dimensional network and hence can influence the fluorescence characteristics to a great extent, depending on the nature of the probe. In this work, measurements on fluorescence quantum yields using steady state fluorescence techniques and fluorescence lifetimes, using single-photon counting techniques, of the two dyes at various stages of cross-linking have been carried out and the results presented.

2. Experimental

The laser dye C1 was synthesised and purified to laser grade in our laboratory (Rao *et al* 1988). Rh6G from E Merck, AG grade, was used as received. The polyvinyl alcohol received from the Robert Johnson Company, Bombay, was of the cold-water soluble crystalline variety. Molecular weight of the PVA, as measured by the viscosity method, was 27 000. Gamma irradiation was carried out in a Co-60 gamma cell with a dose rate of 960 Gy per hour as measured by the Fricke dosimeter. All irradiations of PVA solutions were carried out prior to the addition of the laser dye in order to prevent radiolytic decomposition of the dye. The concentration of the dyes used for all these studies was $\approx 5 \times 10^{-5} \text{ mol dm}^{-3}$. The irradiated PVA solutions were kept for a few hours to allow the trapped radicals to decay partially. The viscosity measurements were carried out using an Ubbelohde viscometer at 30°C. Nanopure water was used for all these measurements. The fluorescence lifetimes were measured using a fluorescence time domain spectrometer with a nanosecond discharge lamp (EI-199 system from Edinburgh instruments, UK) interfaced with a LSI-11/23 (Plessey, UK) microcomputer and reconvolution programs. The quantum yield determinations were carried out using Hitachi F-4010 spectrofluorometer. The concentration of PVA was 5% w/v. These solutions were irradiated in 25 ml flasks with bulb diameters of 2.5 cm. The nature of the cross-linking obtained with the absorbed dose is highly dependent on the geometry of the flask (Gopinathan and Balan 1991).

3. Results and discussion

The absorption and emission spectra of the two dyes, C1 and Rh6G, in cross-linked PVA were found to be identical to those in noncross-linked systems. However there is a shift in the λ_{max} of these dyes in PVA-containing solutions as compared to that in water. The absorption maximum of Rh6G in water is 525 nm whereas that in cross-linked gel-like PVA is 531 nm. This shift, though not very high, indicates greater stabilisation of the dye in the cross-linked polymer. It is likely that PVA has a microcage where clusters of water molecules exist and therefore the polarity would be different. There may be a change in the hydrogen-bonding nature of the dye in the cluster as compared to that in the aqueous solution. All these factors may be responsible for the stabilisation of the dye in the polymer. Initially we discuss our results with the more water-soluble and positively charged dye Rh6G and then with those of C1.

When an aqueous solution of PVA is irradiated, there are primary radicals produced by the radiolysis of water (such as H, OH, e_{aq}^- etc.) (Charlesby 1958). These radicals create some reactive radical sites on the polymer, which cause cross-linking of the polymer leading to a three-dimensional network. This results in increase in the viscosity of the medium. The change in viscosity with increasing absorbed dose (after every hour of irradiation) was measured and the values are listed in table 1. While most of the radicals are used up in cross-linking of the polymer, some of them are trapped inside the network and remain stable for periods ranging from a few hours to many days (Gopinathan *et al* 1983). In the initial stages of cross-linking it is not significant, because after a few hours the radicals decay almost completely. But this becomes more prominent as the cross-linking increases (when it forms a gel). However, some of them may be scavenged by the presence of oxygen. But it is also possible that oxygen may lead to the formation of peroxy radicals which are also known to cause damage to the dye. When a solute is added to these solutions, some of these radicals, depending on their reactivities with the solute, can cause degradation of the dye. However, reduction in the dye absorption cannot be attributed to the formation of aggregates at the concentrations employed in the study ($\sim 10^{-5}$ mol dm $^{-3}$). As a result of this degradation, the actual dye concentration available for excitation is reduced. Thus in case of Rh6G there is a reduction of $\approx 35\%$ in the absorbance at its λ_{max} near the gelling point, whereas in case of C1 no such effect is seen. Hence, in case of Rh6G, the fluorescence intensities have been corrected for these reductions.

The plots of fluorescence quantum yields and lifetime data are given in figures 1c and d (the solutions were excited at 348 nm). It can be seen from figure 1d that the

Table 1. Viscosity change on 5% PVA solution on irradiation.

Dose (Gray)	Viscosity (CPS)
Unirradiated	28-30
961	35-71
1442	43-40
1992	51-28
2403	70-34
2884	116-40

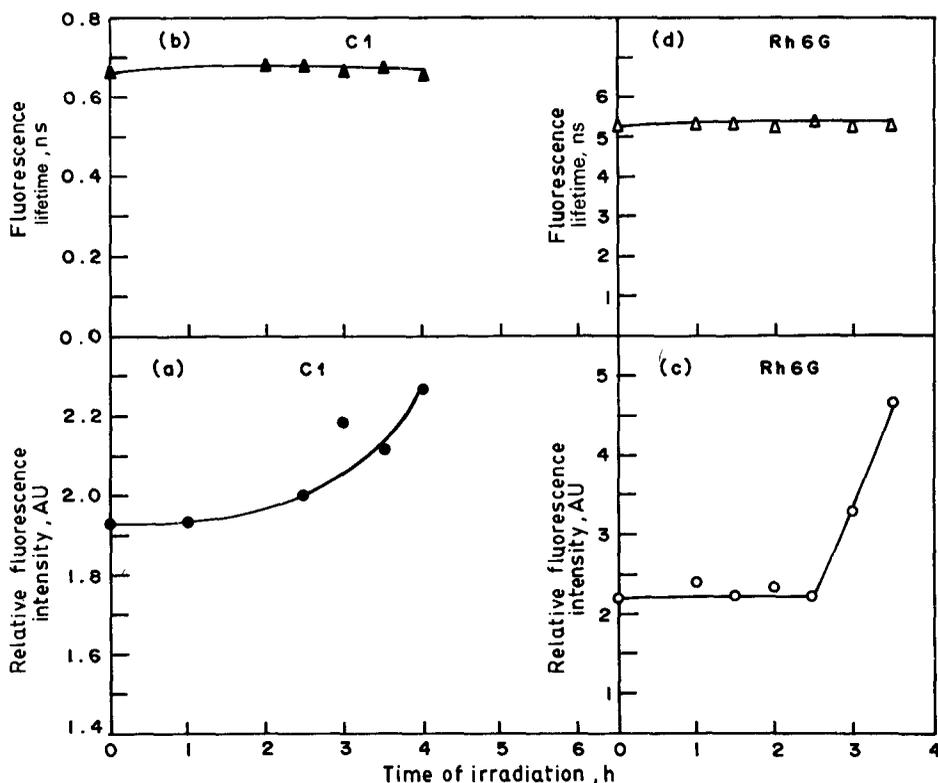
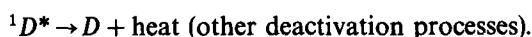
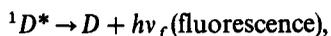
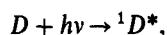


Figure 1. Variation of the fluorescence yields and the lifetimes of the dyes Coumarin 1 and Rhodamine 6G with the time of irradiation. 1 hour of irradiation = 961 Gy absorbed dose.

fluorescence lifetimes of Rh6G remain unchanged with cross-linking. All the fluorescence decay plots gave good fits for single exponential decay with a lifetime of 5.2 ns. However, the fluorescence intensity was found to increase with increasing cross-linking. Irradiation upto an absorbed dose of 2000 Gy caused hardly any change in the fluorescence intensity, but a sharp increase in the fluorescence was observed when the dose absorbed was more than 2700 Gy. Just before the gelling point, when the absorbed dose was 3200 Gy, the intensity was more than doubled. The various processes leading to the increase in fluorescence are represented and explained as follows:



Here D is a dye molecule, which is excited to its first excited singlet state. The fluorescence lifetime τ_f is defined as

$$\tau_f = 1/(k_f + k_{IC} + \Sigma k_i).$$

Here k_f , k_{IC} and k_i are the rate constants for fluorescence, internal conversion and all other deactivation processes of the singlet excited states of Rh6G. The fluorescence quantum yield ϕ_f is defined as

$$\phi_f = k_f / (k_f + k_{IC} + \Sigma k_i).$$

By examining these two expressions it can be concluded that if τ_f ($1/k_f$) remains the same and ϕ_f increases in cross-linked polymers, when the dye is trapped inside the three-dimensional network, the rate of nonradiative decay decreases and the radiative process increases, there is an increase in the fluorescence efficiency but the sum of all these rate constants remains unaffected. As a result of this, the lifetime remains unchanged. Up to the absorbed dose of 2000 Gy, not much change in the viscosity and cross-linking is expected (table 1), hence the fluorescence intensity remains unaffected.

In figures 1a and 1b, the fluorescence lifetimes and the relative quantum yields of Coumarin 1 as a function of cross-linking are depicted (the solutions were excited at 375 nm). Here also the fluorescence intensity did not show much variation up to a dose of 2000 Gy, after that it started increasing. However, unlike as in Rh6G, C1 did not show drastic change in the fluorescence intensity, it only increased by ≈ 10 to 15% even after irradiation corresponding to an absorbed dose of > 3000 Gy (near the gelling point). The fluorescence lifetime of C1 in pure water is 0.33 ns and shows good single exponential fit, whereas in the unirradiated PVA solution the lifetime is 0.66 ns and did not vary much with cross-linking as in the case of Rh6G. However, it changed from single to double exponential decay in cross-linked PVA and its contribution increased with cross-linking. The second component has a lifetime of ≈ 2.5 ns and does not arise from PVA, which was confirmed by running a blank experiment with cross-linked PVA. This may be explained as due to the presence of different clusters present in the cross-linked network. The longer lifetime is due to the presence of the more viscous and non-polar environment available for the dye. The fluorescence lifetimes and quantum yields of C1 are very sensitive to the polarity of the solvent environment (Jones *et al* 1989). For example, in cyclohexane the fluorescence quantum yield and lifetime, respectively, of C1 are 0.49 and 2.8 ns, whereas in 20% ethanol and water they are 0.11 and 0.70 ns, and in water the quantum yield reduces to 0.055. The excited state of 7-amino coumarins is represented as an intramolecular charge transfer state (ICT) (Jones and Jackson 1980). In polar solvents, there exists another state which is non-fluorescent, i.e. the twisted intramolecular charge transfer state (TICT) (the structures are represented in scheme 1). The increased contribution of the TICT state in polar hydrogen-bonded solvents is considered to be responsible for reduced fluorescence yield and lifetime. Thus when C1 is incorporated in the cross-linked polymer, it may be distributed in two different clusters, leading to a biexponential decay. For example, Coumarin 1 in 5% aqueous solution of PVA showed a fluorescence lifetime of 0.7 ns and after exposure to a dose of ≈ 3000 Gy, the lifetimes changed to 0.66 (75%) and 2.5 ns (25%). If C1 experiences a more viscous and non-polar environment, there is increase in fluorescence yield due to reduction in free rotation of the amino group, but when it is in a polar environment, the formation of non-fluorescent TICT structure reduces the fluorescence intensity. As a result, the overall fluorescence quantum yield does not show much increase. Such biexponential decays and inhomogeneous distribution of

aromatic hydrocarbon probes in coiled polymers have already been reported in the literature (Snare *et al* 1982). On the other hand, Rhodamine 6G, which is cationic in nature, experiences strong hydrophilic interactions that act as the driving force to push the molecule into the polymer network. As a result, there is a drastic reduction in the internal conversion and sharp increase in fluorescence.

The photodegradation of Rh6G was carried out in water as well as in PVA and the results were compared. The light source was a Rayonet photochemical chamber reactor model RPR 100 (Priyadarsini *et al* 1987). It consisted of 16 low-pressure mercury lamps, coated with phosphors emitting at 300 nm. Preliminary results suggested that the dye when incorporated in 5% PVA solution exhibits almost 10 times more stability than in water, whereas in cross-linked PVA it did not undergo any degradation. For example, after 2 hours of irradiation, Rh6G in water showed 19% degradation, whereas in PVA solution it showed only 2% and in cross-linked PVA no degradation was observed. Further work on this is being carried out.

4. Conclusions

The results obtained in this work indicate that laser dyes when incorporated in polymer networks show increased fluorescence efficiency. This results in increase in the efficiency of dye lasers using these dyes. The effect is stronger in case of cationic and anionic dyes as compared to neutral dyes. The photostability of the dye also increases considerably in the cross-linked PVA.

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References

- Charlesby A 1958 *Effects of radiation on materials* (New York: Rheinhold)
- Drexhage K H 1973 *Topics in applied physics* (ed.) F P Schafer (Berlin: Springer-Verlag) vol. 1, p. 145
- Ghiggino K P, Roberts A J and Phillips D 1981 *Adv. Polym. Sci.* **40** 69
- Gopinathan C and Balan T P 1991 *Proceedings of Rad. Tech. Asia '91*, Radiation Curing Conference, Osaka, Japan, p. 600
- Gopinathan C, Balan T P and Antani D U 1983 *Indian J. Med. Res.* **78** 567
- Jones G II and Jackson W R 1980 *Chem. Phys. Lett.* **72** 3913
- Jones G II, Jackson W R, Choi C and Bergmark W R 1989 *J. Phys. Chem.* **89** 294
- Kalyana Sundaram K 1987 in *Photochemistry in microheterogeneous systems* (New York: Academic Press) chap. 8
- Priyadarsini K I, Kunjappu J T and Moorthy P N 1987 *Indian J. Chem.* **A26** 899
- Rao K N, Moorthy P N, Prasad C V C, Kunjappu J T and Priyadarsini K I 1988 Synthesis, purification and characterisation of some 7-amino coumarin laser dyes, BARC Report 1400
- Schafer F P 1983 *Laser Chem.* **3** 265
- Snare M J, Tan K L and Treloar F E 1982 *J. Macromol. Sci.* **A17** 189
- Tazuke, Ooki H and Sato K 1980 *Macromolecules* **15** 400