ABSTRACT

Dye lasers have proved to be very useful laser systems because of their intrinsic high gain and wide range of frequency tunability. Due to high gain of the dyes in liquid medium, they can work either as a superradiant or conventional laser. The laser pumped dye laser provides a simple and inexpensive optical frequency converter. The emission band of dye laser can be shifted markedly by simple means such as changing of solvents and solutes. The dye laser medium is cheap and can be pumped by flash lamps or lasers (Nitrogen laser, 2nd and 3rd harmonic Nd: YAG laser, argon-ion laser etc.). The dye laser medium is, in general, a liquid solution or a solid matrix, which can be pumped in CW mode as well as pulsed mode. Eventhough, dye lasers in liquid medium have some advantages such as self curing and so on, they have more disadvantageous due to evaporation of solvent, fluctuation in the flow of the dye, solvent or dye poisoning, etc. Hence, dye lasers in solid medium was experimented successfully in this work as it averts many of the common problems associated with static or flowing liquid dye systems.

In the last few years, significant advances have been made towards the development of practical tunable solid state dye lasers. Most of the work has been done using either polymer or silica as the host material for the dye lasers. The polymer materials show better optical homogeneity than the
available silicate materials, which is extremely important for narrow line width oscillators. Hence, only polymer materials were utilised throughout the course of this work. Polymer based elements can improve systems performance considerably. Also, organic dyes were used as they show better solubility and therefore better compatibility with the polymeric materials. Such dye doped polymer rods are compact, rugged, easy to use and provides low cost tunable laser.

This thesis reports a study of laser spectral and laser gain studies of coumarin dyes doped polymeric material under nitrogen laser, 2\textsuperscript{nd} and 3\textsuperscript{rd} harmonic Nd: YAG laser excitation. Further steady state fluorescence and absorption measurements have been made to provide additional information for understanding the laser behaviour. A Study of photodegradation of dye incorporated in polymeric materials and energy conversion efficiency have also been made to understand the behaviour of coumarin dyes in solid matrix. The gain of mixture of two dyes has also been studied in order to investigate the energy transfer process involved in the mixture. The photophysical behaviour of coumarin dyes in the excited state has also been investigated by studying the superradiant emission.

In chapter 1, the photophysical properties of organic laser dyes and the important features of polymeric materials have been discussed. Accordingly, polymethyl methacrylate (PMMA) was chosen as host material
for this work. This chapter also discusses the different methods of polymerisation. The utility of the small signal optical gain parameter of a dye environment has also been discussed.

Chapter 2 described the synthesis of dye doped polymer rod, design and construction of nitrogen laser, details of 2nd and 3rd harmonic Nd: YAG laser, details of spectrophotometer, spectrofluorometer and details of experimental setup for amplified spontaneous emission recording and for gain studies of dyes in solid and liquid environment.

Chapter 3 presents the results of the spectral and laser gain studies of Rh6G and coumarin dyes (C1, C490, C503 and LD490) were investigated by us and the results discussed. In this chapter the details of synthesis of these dye doped polymers are given. The steady state absorption and fluorescence spectra of these dyes in solid and liquid environment were studied and their wavelengths compared. Most of these dyes in solid environment showed a shift in the fluorescence and the absorption peak of the wavelength. This is due to variation in the dielectric constant of the environment. The dielectric constant of the liquid environment is higher than that of the solid environment. The ASE spectra of these dyes in solid and liquid environment were studied.

The peak ASE maximum of C490 and C503 showed a red shift with that of the fluorescence maximum. This is due to $\lambda^4$ dependence of the gain.
The gain of these dyes in solid and liquid medium under nitrogen laser excitation was compared. It is found that the gain in solid medium is less than that in the liquid medium. The gain of dye depends on the dielectric constant of the medium. This causes the changes.

The photobleaching rate of these dyes under the nitrogen laser, second and third harmonic Nd: YAG Q-switched and mode locked lasers was measured. This showed that the dyes in the solid environment exhibited photobleaching. These dyes offered high laser damage resistance for low powers of nitrogen laser excitation. The photobleaching rate was faster for 3rd harmonic Q-switched Nd:YAG laser. The photobleaching was rapid for mode locked laser. The photobleaching rate can be reduced by rotating the polymer rod. The decrease of ASE intensity is faster when the polymer rod is fixed rigidly. When the rod was kept rotating, the decrease of ASE intensity is less. The dye was undergoing photobleaching, when exposed continuously to laser radiation. When the rod was rotated the exposed region was continuously changing and a new region was exposed to laser radiation and rotation of the rod prevents the laser damage to the dye.

Chapter 4 discusses the energy transfer technique in solid state dye laser. Dyes which have low absorption cross section at the pumping wavelength are not efficient dye laser medium, for that pumping source. Increasing the dye concentration can overcome this difficulty to some extent.
But this leads to energy reabsorption and narrowing of gain spectra. To overcome this, energy transfer technique can be used by including another dye, which can absorb the pump radiation efficiently and transfer it to the dye to be pumped. This avoids the re-structuring of the dye molecule itself and also helps to increase the tunability range. In energy transfer technique, the energy absorbed by one dye (donor) is transferred to another dye (acceptor) in order to increase the lasing efficiency of the acceptor dye. In this work, energy transfer has been observed and studied in various binary dye mixtures in solid environment. It is suggested that energy transfer in such binary dye doped polymer mixtures may be due to Forster type or radiative type or complexing type of energy transfer. The ASE of the acceptor has been observed for the C1:Rh6G binary dye doped polymer rod. The gain of the acceptor in the absence and presence of the donor has been calculated and compared. These gain studies have been used to prove the presence of energy transfer technique in this binary dye doped polymer rod. Dyes Coumarin521, Coumarin535 and Coumarin540 experienced poor solubility in MMA modified with EtOH. Also, these dye doped polymer rods did not show ASE output under laser excitation at this low concentration. To avoid this problem, energy transfer technique is used to obtain ASE output in dye doped polymers, at such low concentrations, by choosing a suitable donor dye which absorbs the excitation energy and transfers it effectively to an acceptor dye. Using such a technique, the gain per acceptor molecule in the absence and presence of the donor dye has been measured and analysed. From this, it is seen that the gain per acceptor
molecule is considerably increased. Such observations prove that energy transfer has taken place. It is inferred that this energy transfer may be due to radiative or non-radiative (Forster) or complexing type of energy transfer processes.

The stability of the acceptor dye doped polymer rods in the absence and presence of the donor under nitrogen laser excitation has been studied. The analysis of these observations shows that the photobleaching resistance of the acceptor dye doped polymer rod in the absence of the donor is more than that of the acceptor dye doped polymer rod in the presence of the donor.

The photobleaching effect of Cl:Rh6G binary dye doped polymer rod has been studied for stable and rotating system using nitrogen laser excitation. Similar studies were carried out for various other binary dye doped polymer mixtures such as Cl: C503, Cl: LD490, Cl: C521, Cl: C535, Cl: C540, C490: C521 and C490: C540.

Chapter 5 discusses the dual amplified spontaneous emission of Cl dye doped polymer rod modified with n-butyl acetate and Cl dye doped polymer rod modified with dioxane. Certain coumarin dyes having mobile alkyl amino substitutents in the seventh position exhibited dual amplified spontaneous emission in certain solvents under nitrogen laser excitation. Eventhough there is only one detectable fluorescence peak, the two ASE bands
appear to be from the top different excited species. One of which is the precursor of the other. Coumarin 1 has a mobile amino group in the seventh position, which can reorient itself in the polymer matrix during the life of the excited state of the dye molecules. The orientation is stabilised by forming a complex between the excited solute and polar solvent and these complexes are stabilised by long range interaction. This may be the cause for anomalous emission. Thus, a study of photophysics of coumarin 1 in solid environment under condition of unsaturated gain would be useful in understanding its behaviour. The dual ASE of coumarin1 in polymer matrix modified with dioxane and coumarin 1 in polymer matrix modified with n-butyl acetate has been recorded. This may be due to complex formation.

The last chapter of the thesis presents the general conclusion of this study, also, giving suggestion for further work.