CHAPTER 2

MATERIALS AND EXPERIMENTAL SETUP

2.1 INTRODUCTION

This chapter describes briefly about the laser dyes used for the energy transfer dye lasers, various polymerization techniques, synthesis of dye doped polymer films, and the equipments used such as the spectrophotometer for recording absorption spectra and spectrofluorometer for recording fluorescence spectra respectively. This chapter presents an account of the experimental procedure for the production of energy transfer distributed feedback dye laser using Q-switched Nd:YAG laser.

2.2 MATERIALS

Laser dyes of Neutral Red, Pyronin-Y, Coumarin-503, Crystal Violet, Thionine and Coumarin-540 were purchased from Central Drug House, Mumbai, India. Spectroscopic-grade Ethanol was used as a solvent. Absorption spectra of the dyes were recorded using a UV/VIS Spectrophotometer (Perkin Elmer-LS25) and their fluorescence spectra measured using a Spectrofluorimeter (Perkin Elmer-LS45). Fluorescence lifetime of the dyes was obtained using a single photon counting spectrometer. For pumping, the second harmonic of a 6-ns, Nd:YAG Laser (model LAB-170-10; Quanta Ray) of 10 Hz repetition rate was used.
2.2.1 Xanthene Dyes

Xanthene dyes cover the wavelength region from 500 to 700 nm and are generally very efficient. Most of the commercial dye lasers are from this class – Fluorescein and RhodamineB are the two widely used laser dyes. The electron distribution in the chromophore in the xanthenes dyes can be described by the following two identical mesomeric structures which is shown in Figure 2.1.

![Figure 2.1 Structure of Xanthene dyes]

2.2.2 Coumarin Dyes

Coumarins, as a family of molecules, exhibit a wide range of fluorescence emission properties. In many cases, this fluorescence is extremely sensitive to the local environment of the molecule, especially the local polarity and microviscosity. In addition, coumarins show a wide range of size, shape, and hydrophobicity. These properties make them especially useful as fluorescent probes of heterogeneous environments, such as supramolecular host cavities, micelles, polymers and solids.
Coumarins, or benzo-α-pyrone, are a very large and important family of compounds. Their defining structure consists of fused pyrone and benzene rings, with the pyrone carbonyl group at position 2 (Song & Gordon 1970) this structure is illustrated in Figure 2.2 for the coumarin parent molecule (IUPAC name: 2H-chromen-2-one, and also known as 1-benzopyran-2-one). Coumarins are widely occurring in nature, with coumarin itself first isolated in 1820 from a specific variety of bean, and many other coumarin derivatives found in a wide range of plants (Song & Gordon 1970). As a group, coumarins exhibit interesting fluorescence properties, which include a high degree of sensitivity to their local environment, including polarity and viscosity. This sensitivity has led to their widespread application as sensitive fluorescent probes of a wide range of systems, including homogeneous solvents and mixtures.

![Chemical structure of coumarin](image)

**Figure 2.2 The chemical structure and numbering scheme of coumarin**

Numerous fluorescent coumarin derivatives have been reported, with a wide range of polarity, pH, viscosity, and other sensitivities, and varying underlying photophysical mechanisms for the observed fluorescence properties. A group of widely used laser dyes emitting in the blue-green region of the spectrum are derived from coumarins by substituting 7-position with auxochromes such as –OH, –OCH₃ , –NH₂ , –NHCH₃ , –N(CH₃)₂ and other electron-donating substituents. The first coumarin laser dye was 7-diethylamino-4- methylcoumarin which exhibits laser action at about 460 nm
under flash lamp excitation. The amino analogue, 7-amino-4-methylcoumarin (coumarin 120) shows laser action at 440 nm.

Coumarin dyes have the tendency for low photo-stability. Coumarins degrade due to laser light. The side products formed after degradation also absorb in the laser region which may give undesired effects. Coumarin molecule as such is non-fluorescent, but it exhibits intense fluorescence on substitution of various functional groups at different positions. In general, electron-donating substituents tend to enhance emission intensity while electron-withdrawing substituents tend to diminish it. The intensity of the dye laser beam cannot be increased over a certain range of the pump power and is limited by saturation. This is due to photo quenching effect. Studies on the photo-quenching properties in various dyes have shown that the effect plays a crucial role in the performance of pulsed laser pumped dye laser systems.

### 2.3 HOST MATERIAL

Solid-state dye lasers based on polymeric and sol-gel glass have been reported extensively in literature. Polymers, porous glasses, organically modified silicate and polycon glass have also been identified as suitable. Compared with other host materials, polymeric materials are easy to prepare. For our laser configuration, PMMA was preferred because it has high optical transparency and thermal stability.

### 2.4 POLYMERIZATION

The formation of a polymer from the monomer or monomers is called polymerization. In other words, polymerization is the union of two or more smaller and simpler molecules of similar or different types, with or without the elimination of water etc, leading to the formation of new
C-C bonds or linkages. There should at least be two reactive or bonding sites in a substance which has to act as a monomer in the formation of the polymer. This number of bonding sites in a monomer is generally called as functionality. The reactions used to synthesize polymers in the laboratory are of two types. These are addition reactions in which monomers add to one another to give a polymer whose molecular weight is the sum of those of the monomer units from which it is formed, and condensation reactions in which successive monomer units combine by splitting out a small molecule such as water. On this basis, polymerization may be classified into two parts: (a) Condensation polymerization and (b) Addition polymerization

2.4.1  Condensation Polymerization

Condensation polymerization may be regarded as analogous to condensation reaction of low molecular weight compounds, condensation taking place between two or more poly functional groups to form large poly functional molecules, which in turn could condense with each other or in the early stages of the reaction with some of the original reactants. A condensation polymer must be made from monomers that contain more than one functional group so as to enable intermolecular reactions to take place, e.g. bakelite.

2.4.2  Addition Polymerization

Addition polymerizations are those involving chain reactions. These polymerizations pass through successive stages of initiation, propagation and termination common to chain reactions. The chain carriers are usually free radicals, cations and anions. In such type of polymerization, the primary molecule reacts with another usually in the presence of a catalyst to form a large molecule, called dimer. The latter in turn reacts with another monomer to give a trimer and this process continues until some termination
occurs or the stock of monomer is finished. One such common addition polymer is Polymethylmethacrylate. It is obtained from the monomer methyl methacrylate whose chemical structure is given below.

### 2.4.3 Matrix Preparation

The polymer matrix was prepared by bulk polymerization method. Firstly, dyes in concentration as small as \(10^{-6}\) M and \(10^{-3}\) M were taken, because a high concentration of dyes could reduce the photostability of the host material or lead to aggregation of dye molecules to form dimers. To eliminate impurities from the dyes, they were mixed with aqueous sodium hydroxide, filtered and distilled. Dye dissolution was carried out in a sonicator. Benzyl peroxide (3 g/l) was used to initiate polymerization. Dissolution of the initiator was done in a sonicator. Polymerization was carried out under controlled temperature conditions (70°C) using a constant temperature bath.

### 2.5 EXPERIMENTAL SET-UP TO STUDY THE ETDFDL

The energy transfer distributed feedback dye laser (ETDFDL) is obtained using an isosceles right angled quartz prism. The dye-doped polymer film (solid type) was coated on one of the sides of an isosceles right-angled quartz prism by spin-coating method is shown in Figure 2.3 and its experimental setup for DFDL in liquid type is shown in Figure 2.4 (a). The distributed feedback prism dye cell set-up is used for the creation of the interference pattern on the surface of dye cell. The DFDL is pumped by Q-switched Nd:YAG laser (QUANTA RAY Model: LAB-170-10) that emit pulses of 6ns duration at a repetition rate of 10 Hz. The pump beam (532 nm or 355 nm) is focused by a cylindrical quartz lens of focal length 5 cm into a line image, which is incident on the hypotenuse AB of the prism. The light transmitted by hypotenuse of the prism is totally reflected from the side AC of
the prism and interferes to form fringes on a dye cell attached to the prism producing periodic modulation of refractive index and also the gain. The DFDL output beam is obtained from the side of BCDE of the prism which is shown in Figure 2.4 (b) and its photograph is shown in Figures 2.5 and 2.6 which is used to measure the wavelength and output power of the DFDL. The feedback is obtained from the Bragg reflection from the periodic structure incorporated throughout the active medium. The pumping beam of wavelength $\lambda_p$ incident at an angle $\theta$ on the medium the DFDL wavelength is given by

$$\lambda_{DFDL} = \frac{n\lambda_p}{n_p \sin \theta}$$

(2.1)

Here $n$ and $n_p$ are the refractive indices of the dye solution and the material of the prism respectively (Chandra & Takeuchi 1972).

Figure 2.3 Experimental set-up of DFDL (Solid)
Figure 2.4 (a) Experimental set-up of DFDL (Liquid)

Figure 2.4 (b) Schematic diagram of prism a dye cell

Figure 2.5 Photograph of Experimental set-up of DFDL
2.6 SPECTROPHOTOMETER

The basic block diagram of spectrophotometer (LS 45 UV-VIS spectrophotometer) is shown in Figure 2.7. It measures the intensity of light passing through a sample $I$, and compares it to the intensity of light before it passes through the sample $I_0$. The ratio $I / I_0$ is called the transmittance, and is usually expressed as a percentage (% T). The absorbance $A$ is based on the transmittance:

$$A = -\log\left(\frac{T}{100}\right)$$

The UV-visible spectrophotometer can also be configured to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample $I$, and compares it to the intensity of light reflected from a reference material ($I_0$). The ratio $I / I_0$ is called the reflectance, and is usually expressed as a percentage (% R). The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often
a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), Xenon arc lamp, which is continuous from 160-2,000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths.

![Block diagram of UV – VIS spectrophotometer (LS-25)](image)

**Figure 2.7** Block diagram of UV – VIS spectrophotometer (LS-25)

The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.
2.6.1 Working Principle

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case, the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken. Samples for UV/Vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, L, in the Beer-Lambert law.) Test tubes can also be used as cuvettes in some instruments. The type of sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. Glass and plastic cuvettes are also common, although glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths. Specialized instruments have also been made. These include attaching spectrophotometers to telescopes to measure the spectra of astronomical features. UV-visible microspectrophotometers consist of a UV-visible microscope integrated with a UV-visible spectrophotometer. A complete spectrum of the absorption at all wavelengths...
of interest can often be produced directly by a more sophisticated spectrophotometer. In simpler instruments the absorption is determined one wavelength at a time and then compiled into a spectrum by the operator. By removing the concentration dependence, the extinction coefficient ($\varepsilon$) can be determined as a function of wavelength.

### 2.7 SPECTROFLUOROMETER

To obtain the fluorescence or excitation spectrum of the liquid sample, this is a vital instrument. This instrument is interfaced with a computer, so that a small program can be written and the required excitation wavelength, emission scan range, scan speed etc., can be fed to the instrument through the computer. The fluorescence spectrum and the excitation spectrum can be obtained either on the CRT or on a dot matrix printer. The basic block diagram of spectrofluorometer is shown in Figure 2.8.

**Figure 2.8 Block Diagram of Spectrofluorometer (LS-45)**

Spectrofluorometer consists of a Xenon lamp which excites the sample. The fluorescence is collected at right angles to the direction of excitation. The Xenon lamp emits light in the entire spectrum including UV,
visible and IR. Therefore, using monochromator, we have to select a particular wavelength out of this band to excite the sample, which is controlled by stepper motor. Similarly, the fluorescence of the sample is also broad band and this is also passed through the monochromator to get a single spectrum. The output fluorescence is directed by a photo detector and this signal is amplified (variable gain amplifier) so that the output relative intensity can be calibrated to a fixed value. LS 45 spectrofluorometer was used to record the fluorescence spectra of the dye solutions. Fluorescence spectra of the solid samples were obtained by using rectangular shaped polymer rods directly.