CHAPTER : 2

EXPERIMENTAL

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The solid materials are used to prepare fluorescent thin films by spin coating technique in rigid polymer matrix. The thin film preparation involves following stages.

1) Purification of polynuclear aromatic hydrocarbons : (Purification of fluorescent materials).
2) Preparation of solutions.
3) Cleaning of the Substrate.
4) Preparation of thin films by spin coating technique.
5) Determination of thickness of the film.
6) Measurement of absorption spectra of thin films.
7) Recording of fluorescence and fluorescence excitation spectra.
8) Storage of the films.

2.1 Purification of Polynuclear Aromatic Hydrocarbons

Even a trace of impurity in the compound markedly changes the fluorescence properties and therefore purification of organic compounds was done before optical measurements.

Anthracene, 9-methylanthracene, 9-anthracene carboxylic acid naphthalene, pyrene, perylene and Biphenyls were used in present study. Scintillation grade Anthracene produced from Fluka grade (AG Buchur SG Switzerland) while 9-methyl, anthracene, 9-anthracene carboxylic acid, Biphenyl, pyrene and perylene were obtained from Merck. (Schuchardt Hohenbreme Germany).

Anthracene and pyrene were recrystallized from saturated solution in hexane. Biphenyl was recrystallized from its saturated solution in benzene (AR) while perylene, 9-methyl anthracene and 9-anthracene carboxylic acid (9ACA) were used without further purification.

The purity of these materials was further confirmed by testing their melting points, paper chromatogram and the photoluminescence spectra.

2.2 Preparation of Solutions

The solvents used for the preparation of solution were benzene, cyclohexane, methanol, ethanol and water. AR grade benzene, cyclohexane, methanol and ethanol were distilled twice before use.

2.3 Cleaning of the Substrates

The non fluorescent glass microslides were cut into the dimensions 75 x 15 x 2 mm and were utilized as the substrate support. The thickness of the film layer has a direct bearing on the cleanliness of the substrates, therefore, the key precaution taken is the careful cleaning of the substrates. The substrates were cleaned by the following procedure.

a) Substrates were first washed with the tap water and then boiled in a concentrated chromic acid (0.5 M) for 30 minutes and then kept in it for 48 hours.

b) Glass slides were taken out and washed with double distilled water.

c) The substrates were again degreased with medium concentrated detergent solution and washed several times with a double distilled water.

d) Acetone was used to remove water traces if any and then dried under IR lamp in a chamber. All substrates were preserved in dust free and dry atmosphere maintained in a dessicator.

2.4 Thin Film Preparation

The fluorescent thin films were prepared by spin coating technique. The spin coating unit used in this work was fabricated in our laboratory. Highly volatile solvents like benzene, hexane, methanol, ethanol etc. were used for the preparation of solutions.

In order to make the film adhesive to the substrate a definite quantity of polymer soluble in solvent is added. Polymers like polystyrene, polyvinyl alcohol (PVA) etc. have been used. The amount of polymer used depends on the concentration of the solution and volume of the solution to be prepared. A solution containing 4 wt. % of polymer was used during preparation of the film.. The solution of definite concentration of the fluorescent material and polymer was spread on to the substrate. The substrate was kept rotating by mechanical device as shown in figure 2.1. The rotation speed (spin rates) was 1400 rpm regulated by the facility provided on the motor. The substrate was spun for 30 seconds. For deposition of thin films, substrates of different size and shapes were used. The commonly used substrates for film preparation (deposition) are glass, ceramics, fused silica and quartz. In present work microscope glass slides and cover slips have been used as substrates. The spin coater was enclosed in a air tight cabinet in order to avoid contamination.

2.5 Determination of Thickness of the Film.

In the present study thin films of polymer doped by fluorescent material were determined by weight difference method. The weight of the film was

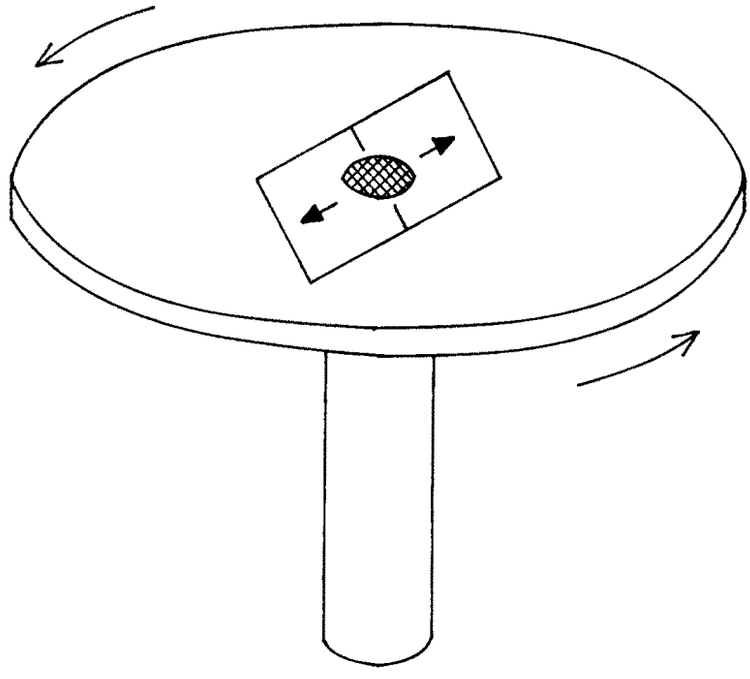

Fig.2·1 - Schematic diagram for a spinner.

measured accurately by using the balance micro processor based balance of Mettler Toledo (Model AB 204-S) Switzerland of accuracy ± 0.1 mg. In thickness measurement sets of films were prepared on microscope glass slides as well as on thin cover slips under similar experimental conditions.

It is confirmed that nature of absorption and fluorescence from both the films were similar. The films on coverslip were used for film thickness determination. This is necessary because the films are so thin that the films on microscope glass slide could not give the appreciable difference. In contrast the coverslips are light in weight and the weight measurements before and after film preparation have given the correct weight of the material deposited.

The thickness of the film was calculated from the weight of film deposited and area of coverslip on which film is deposited.

Following equation have been used to determine the thickness of the film.

$$t = \frac{m}{A \times d}$$

where t = thickness of film

A = Area of the substrate on which film is deposited

m = mass of film

d = density of sample

2.6 Recording of Absorption Spectra

The absorption spectra of the spin coated thin films recorded in UV-visible spectrophotometer-159 Elico, India at room temperature. For absorption study the films were coated on a quartz plate substrates of dimensions 50 mm x 10 mm. The thin transparent films of bare polymer on similar dimension of quartz plate was used as a reference. The dimension of quartz plate was such that it can fit into the space provided in the sample holder of spectrophotometer. Absorption spectra were measured with deuterium lamp in the UV from 250

to 380 nm and a quartz tungsten halogen lamp in the visible region from 380-750 nm.

2.7 Recording of Fluorescence and Fluorescence Excitation Spectra.

The fluorescence and fluorescence excitation spectrum of the spin coated thin films in solid polymer matrix were recorded on PC based spectro-fluorometer (JASCO model FP-750 JAPAN). The block diagram of the PC Based spectrofluorometer is shown in fig. 2.2. The light from the source (150 w xenon arc) is focused on to the entrance slit of the excitation monochromator by the ellipsoidal and spherical mirror. The incident light from the slit is dispersed by the diffraction grating and monochromatic light is taken at by the exit slit. A part of monochromatic light is led on the silicon photodiode detector by beam splitter while the light that has transmitted the beam splitter is led to the sample chamber by plane mirror and ellipsoidal mirror and focused on the center of sample cell. The emission from the sample film is focused on to the entrance slit of the emission monochromator by the ellipsoidal and plane mirror. The light dispersed by the diffraction grating of the emission monochromator going through the exit slit finally led to the photometric photomultiplier tube (PMT) by the special mirror.

The light incident on the monitoring detector (silica photodiode) and the emission detector PMT is converted into an electrical signal and then converted into a digital signal by A/D converter. The signal is then subjected to arithmetic operation by the micro computer and outputted to the display unit as a digital data or spectra.

2.8 Storage of the Films

The thin films were protected from environmental poisoning. In order to avoid contamination the chamber was enclosed with air tight cabinet. The thin

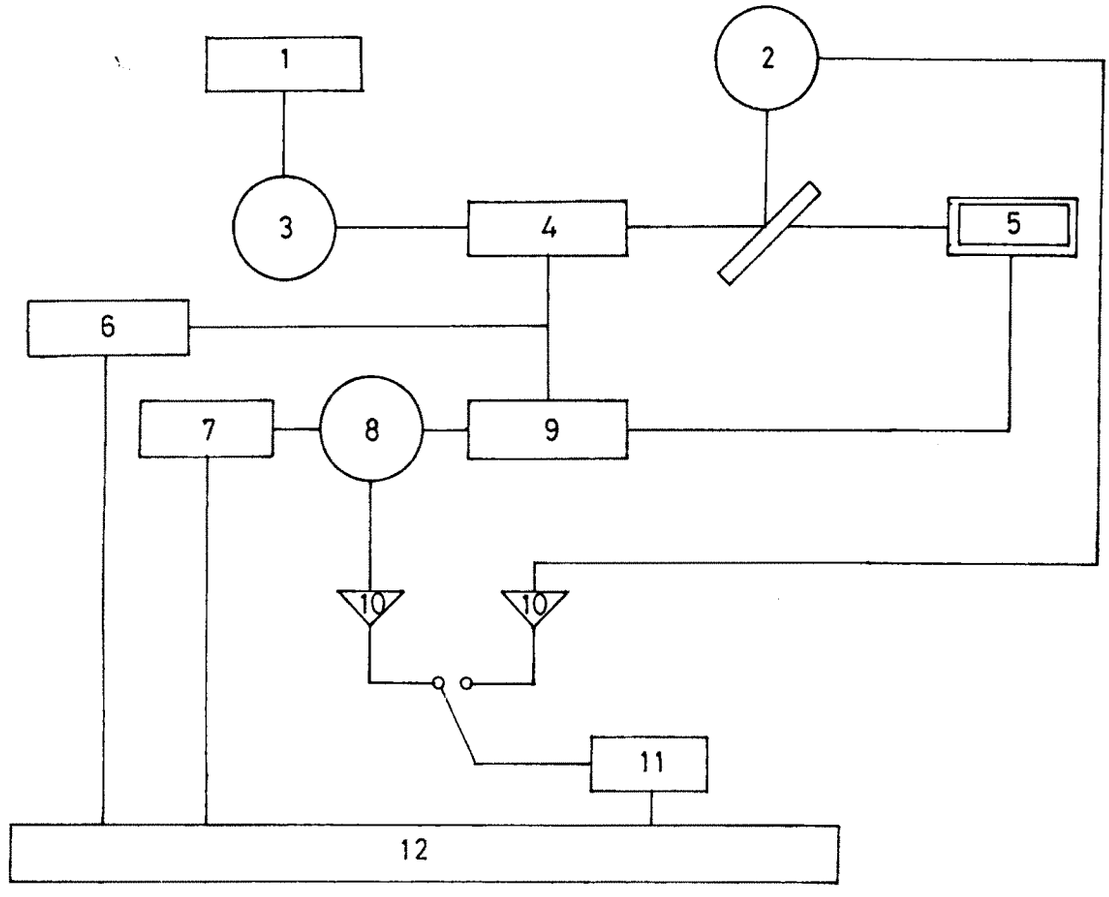

Fig. 2·2 - Schematic diagram of JASCO FP-750 Spectrofluorometer.

1 - Power 2 - Monitoring detector 3 - Light source
4 - Excitation monochromator 5 - Cell 6 - Driver
7 - H.T. 8 - Emission detector 9 - Emission monochromator
10 - Amplifier 11 - A/D Convertor 12 - CPU & I/F.

films were also protected from dust and moisture. To avoid this the films were kept in a dry and air tight chamber.

2.9 Comparison between Langmuir Blodgett and Spin Coating Films

L.B. and S.P. films show similar characteristics. Both LB and SC films are homogeneous with small particles uniformly distributed throughout the surface. The LB and SC techniques have the advantage of introducing some degree of anisotropic ordering of molecules within film monomer and dimer.

The results of fluorescence spectrum measurement show that the films prepared by LB method and spin coating method possess similar molecular arrangements or morphology which are mainly controlled by molecular aggression. So less expensive more convenient spin coating method is a alternative for Langmuir Blodgett method.

The spin coating technique has the merit of convenience. Fast operating and use of low cost instrument. It is possible to deposit moderately well ordered films on to substrate of all kinds using materials with molecules which possess good solubility. spin coating method allows the deposition of organic thin films with structural properties similar to those of LB films.[42,43,49,50]

The drawback in using LB technique is that it relies on a specific character of the organic molecules which should possess an amphiphilic nature as well as precise treatment of the solid substrate.