CHAPTER 4

SPECTRAL CHARACTERISTICS OF ORGANIC DYES

4.1 INTRODUCTION

The nonlinear optical (NLO) materials with large and fast optical response are gaining interest both in research as well as in industrial point of view. The last decade has seen an increasing trend towards the use of organic polymers as photonic components because of their ease of processing and fabrication, compatibility with metals, ceramics, semiconductors, and glasses, good mechanical strength, and flexibility to tailor nonlinear optical properties. The potential use in optical information processing devices has been the driving force behind most of the research into characterization of nonlinear optical properties of materials. For this purpose, considerable attention has been paid in particular to the third order nonlinearities of organic dyes.

With the rapid development of the optical communication, people have the higher demand for the photoelectron device and light storage medium. Not only the rapid response but also the large third-order nonlinear susceptibility for materials are needed. A thorough investigation of the dyes in solid and liquid media is necessary to understand the lasing characteristics of dyes in polymers which is modified with additive solvent. The spectral characteristics of these dyes give an insight about their lasing characteristics. The spectral characteristics of these dyes are studied by recording the absorption and fluorescence spectra.

In this chapter a study of the absorption and fluorescence spectra and lifetime of the dyes in liquid and solid environment are studied. The absorption curve does not mention the nonlinear effects as the light source in the spectrophotometer is insufficient to cause these effects, yet the absorption measurements are used to determine the suitable wavelength of the light source for which the optical material can act as an optical limiter. The molecular structures of dyes chosen are shown in Figure 2.1(a to f).

4.2 SPECTRAL CHARATERISTICS OF AZO DYES

4.2.1 Spectral Characteristics of Acid Red 27

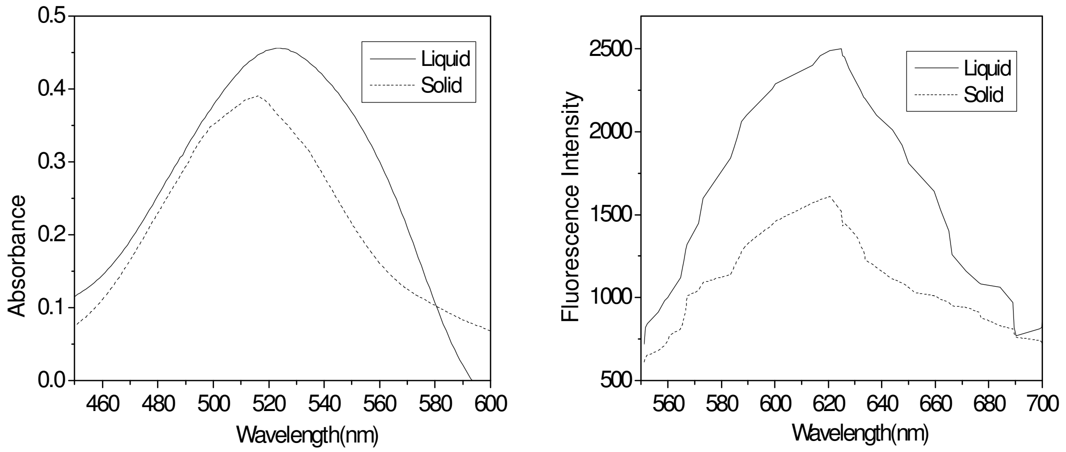
The dye, Acid Red 27 is obtained from Sigma Aldrich India. The chemical structure of the dye is given in Table 2.1. Thin layer chromatography (TLC) test confirms the absence of any impurities. Methanol is chosen as solvent.

4.2.1.1 Synthesis of Acid Red 27 DDP Rods

The Acid Red 27 dye doped polymer rod is synthesized by thermal bulk free radical polymerization method as explained in section 2.7.1. MMA is used as monomer and benzoyl peroxide is chosen as the initiator for polymerization. The spectral characteristics of Acid Red 27 in liquid media (in methanol) and solid media (MPMMA matrix) are studied. The synthesized dye doped polymer rod is of concentration 0.05 mM. The rod is in the form of rectangular shape with 2-3 cm length and 0.9 cm thickness. The optical quality of dye doped polymer rod is checked by passing a 5mW He-Ne laser beam (λ = 632.8 nm) through it. The rod shows no dispersion or distortion. The photograph of synthesized Acid Red 27 dye doped polymer rod is shown in Figure 2.1.

4.2.1.2 Absorption and Fluorescence Spectra of Acid Red 27

The absorption spectra of the dye Acid Red 27, in methanol (liquid media) and in PMMA modified with methanol are recorded and are shown in Figure 4.1 (a). The fluorescence spectra of the dye in methanol and in dye doped polymer rod are recorded and are shown in Figure 4.1 (b).The peak wavelengths of the absorption and fluorescence spectra are measured, and the spectral parameters such as molecular absorption coefficient ($\in$), oscillator strength (f), absorption bandwidth ($\Delta\upsilon_{1/2}$), fluorescence bandwidth (FWHM) and Stoke's shift are calculated and these values are given in Table 4.1.



(a) **(b)**

Figure 4.1 (a) Absorption and (b) Fluorescence spectra of Acid Red 27 dye in liquid (methanol) and solid (MPMMA)

Table 4.1 Spectral characteristics of Acid Red 27 in liquid and solid media

Solvent/ Medium	Absorption spectra				Fluorescence spectra		
	Peak wavelength in nm	ε x10^4 L mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$ cm^{-1}	f x10^{-24} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}
methanol	523	4.5544	3246.4	0.64	624.8	100	3094.8
MPMMA	516	3.8994	2969.4	0.501	620.6	125	3250.8

The peak wavelength of the absorption spectra of Acid Red 27 in MPMMA showed a blue shift from that in methanol. The oscillator strength of Acid Red 27 in solid matrix was less than that of Acid Red 27 in liquid medium. The peak emission wavelength of Acid Red 27 in solid matrix showed a blue shift from that in liquid medium. The FWHM of the flourescence spectrum of Acid Red 27 in solid medium was found to be broader than that in liquid medium. The Stoke's shift of Acid Red 27 in solid matrix was more when compared to that in liquid media

4.2.2 Spectral Characteristics of Sudan IV

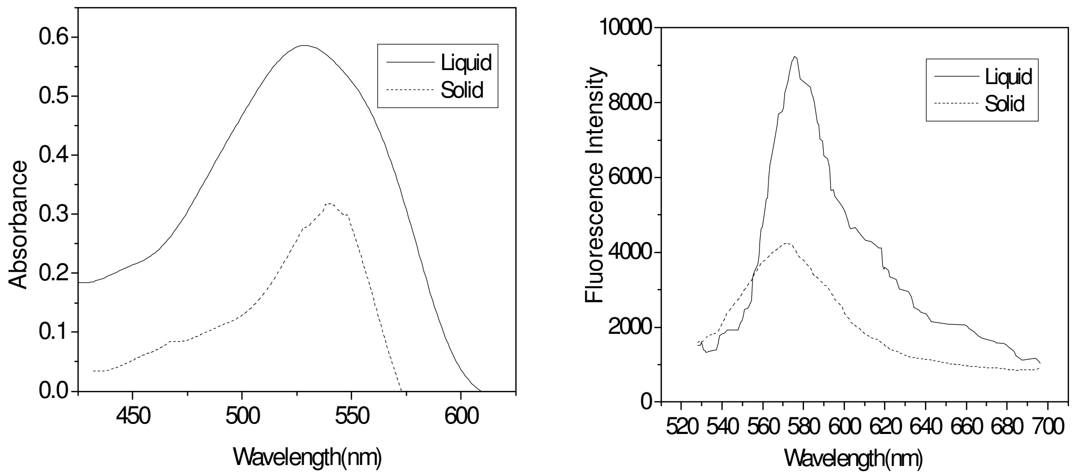
The dye, Sudan IV is obtained from Sigma Aldrich, India. The chemical structure of the dye is given in Table 2.1. Thin layer chromatography (TLC) test confirms the absence of any impurities. Benzene is chosen as solvent.

4.2.2.1 Synthesis of Sudan IV DDP Rods

The Sudan IV dye doped polymer rod is synthesized by thermal bulk free radical polymerization method as explained in section 2.7.1. MMA is used as monomer and benzoyl peroxide is chosen as the initiator for polymerization. The spectral characteristics of Sudan IV in liquid media (in benzene) and solid media (MPMMA matrix) are studied. The synthesized dye doped polymer rod is of concentration 0.05 mM. The rod is in the form of rectangular shape with 2-3 cm length and 0.9 cm thickness. The optical quality of dye doped polymer rod is checked by passing a 5mW He-Ne laser beam (λ = 632.8 nm) through it. The rod shows no dispersion or distortion. The photograph of synthesized Sudan IV dye doped polymer rod is shown in Figure 2.1.

4.2.2.2 Absorption and Fluorescence Spectra of Sudan IV

The absorption spectra of the dye Sudan IV, in benzene(liquid media) and in PMMA modified with benzene are recorded and are shown in Figure 4.2 (a). The fluorescence spectra of the dye in benzene and in dye doped polymer rod are recorded and are shown in Figure 4.2 (b).The peak wavelengths of the absorption and fluorescence spectra are measured, and the spectral parameters such as molecular absorption coefficient ($\in$), oscillator strength (f), absorption bandwidth ($\Delta\upsilon_{1/2}$), fluorescence bandwidth (FWHM) and Stoke's shift are calculated and these values are given in Table 4.2.



(a) (b)

Figure 4.2 (a) Absorption and (b) fluorescence spectra of Sudan IV dye in Liquid (benzene) and Solid (MPMMA)

Table 4.2 Spectral characteristics of Sudan IV in liquid and solid media

Solvent/ Medium	Absorption spectra				Fluorescence spectra		
	Peak wavelength in nm	ε x10^4 L mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$ cm^{-1}	f x10^{-24} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}
benzene	529	5.8611	3780	0.9594	575.5	44	1521.3
MPMMA	540	3.1835	1828	0.2519	572.5	63	1036

The peak wavelength of the absorption spectra of Sudan IV in MPMMA showed a red shift from that in benzene. The oscillator strength of Sudan IV in solid matrix was less than that of Sudan IV in liquid medium. The peak emission wavelength of Sudan IV in solid matrix showed a blue shift from that in liquid medium. The FWHM of the flourescence spectrum of Sudan IV in solid medium was found to be broader than that in liquid medium. The Stoke's shift of Sudan IV in solid matrix was less when compared to that in liquid media

4.3 SPECTRAL CHARATERISTICS OF NATURAL DYE

4.3.1 Spectral Characteristics of Natural Red 25

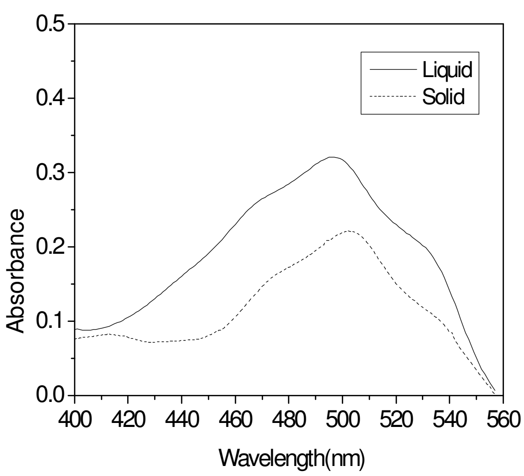
The dye, Natural Red 25 is obtained from Sigma Aldrich, India. The chemical structure of the dye is given in Table 2.1. Thin layer chromatography (TLC) test confirms the absence of any impurities. Ethanol is chosen as solvent.

4.3.1.1 Synthesis of Natural Red 25 DDP Rods

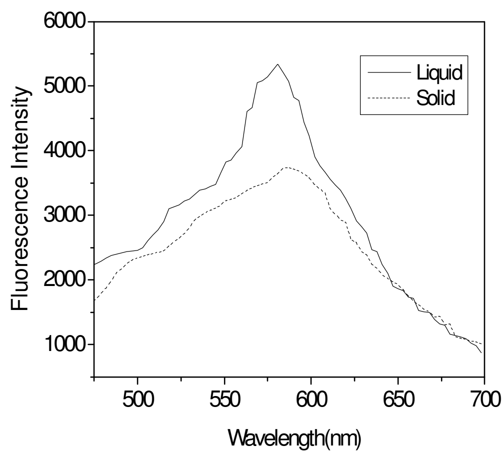
The Natural Red 25 dye doped polymer rod is synthesized by thermal bulk free radical polymerization method as explained in section 2.7.1. MMA is used as monomer and benzoyl peroxide is chosen as the initiator for polymerization. The spectral characteristics of Natural Red 25 in liquid media (in ethanol) and solid media (MPMMA matrix) are studied. The synthesized dye doped polymer rod is of concentration 0.05 mM. The rod is in the form of rectangular shape with 2-3 cm length and 0.9 cm thickness. The optical quality of dye doped polymer rod is checked by passing a 5mW He-Ne laser beam (λ = 632.8 nm) through it. The rod shows no dispersion or distortion. The photograph of synthesized Natural Red 25 dye doped polymer rod is shown in Figure 2.1.

4.3.1.2 Absorption and Fluorescence Spectra of Natural Red 25

The absorption spectra of the dye Natural Red 25, in ethanol (liquid media) and in PMMA modified with ethanol are recorded and are shown in Figure 4.3 (a). The fluorescence spectra of the dye in ethanol and in dye doped polymer rod are recorded and are shown in Figure 4.3 (b).The peak wavelengths of the absorption and fluorescence spectra are measured, and the spectral parameters such as molecular absorption coefficient ($\in$), oscillator strength (f), absorption bandwidth ($\Delta\upsilon_{1/2}$), fluorescence bandwidth (FWHM) and Stoke's shift are calculated and these values are given in Table 4.3.



(a)



(b)

Figure 4.3 (a) Absorption and (b) Fluorescence spectra of Natural Red 25 dye in liquid (ethanol) and Solid (MPMMA)

Table 4.3 Spectral characteristics of Natural Red 25 in liquid and solid media

Solvent/ Medium	Absorption spectra				Fluorescence spectra		
	Peak wavelength in nm	ε x10^4 L mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$ cm^{-1}	f x10^{-24} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}
ethanol	496	3.2133	4139	0.576	581	123	2949.6
MPMMA	502	2.213	2930.2	0.2808	587	171	2884.5

The peak wavelength of the absorption spectra of Natural Red 25in MPMMA showed a red shift from that in ethanol. The oscillator strength of Natural Red 25in solid matrix was less than that of Natural Red 25 in liquid medium. The peak emission wavelength of Natural Red 25 in solid matrix showed a red shift from that in liquid medium. The FWHM of the flourescence spectrum of Natural Red 25 in solid medium was found to be broader than that in liquid medium. The Stoke's shift of Natural Red 25 in solid matrix was less when compared to that in liquid media

4.4 SPECTRAL CHARATERISTICS OF TRIARYLMETHANE DYE

4.4.1 Spectral Characteristics of Ethyl Violet

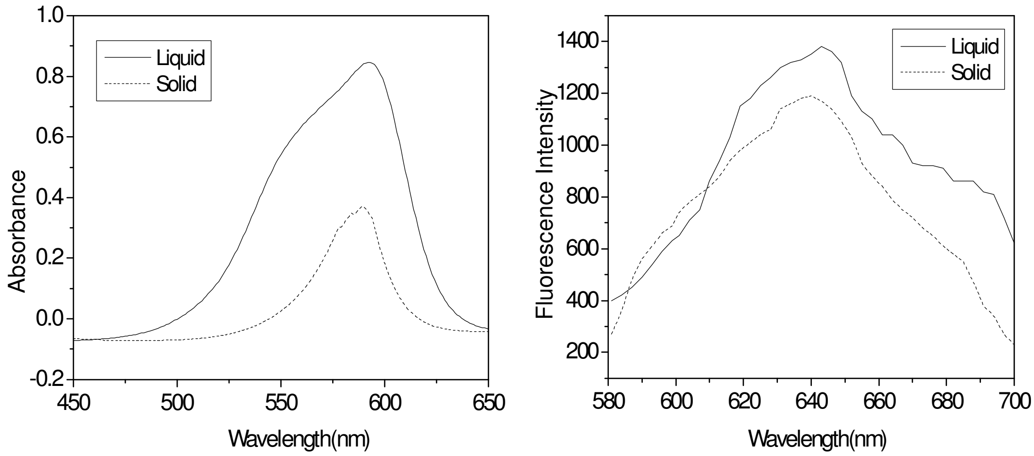
The dye, Ethyl Violet is obtained from Sigma Aldrich, India. The chemical structure of the dye is given in Table 2.1. Thin layer chromatography (TLC) test confirms the absence of any impurities. Ethanol is chosen as solvent.

4.4.1.1 Synthesis of Ethyl Violet DDP Rods

The Ethyl Violet dye doped polymer rod is synthesized by thermal bulk free radical polymerization method as explained in section 2.7.1. MMA is used as monomer and benzoyl peroxide is chosen as the initiator for polymerization. The spectral characteristics of Ethyl Violet in liquid media (in ethanol) and solid media (MPMMA matrix) are studied. The synthesized dye doped polymer rod is of concentration 0.05 mM. The rod is in the form of rectangular shape with 2-3 cm length and 0.9 cm thickness. The optical quality of dye doped polymer rod is checked by passing a 5mW He-Ne laser beam (λ = 632.8 nm) through it. The rod shows no dispersion or distortion. The photograph of synthesized Ethyl Violet dye doped polymer rod is shown in Figure 2.1.

4.4.1.2 Absorption and Fluorescence Spectra of Ethyl Violet

The absorption spectra of the dye Ethyl Violet, in ethanol (liquid media) and in PMMA modified with ethanol are recorded and are shown in Figure 4.4 (a). The fluorescence spectra of the dye in ethanol and in dye doped polymer rod are recorded and are shown in Figure 4.4 (b).The peak wavelengths of the absorption and fluorescence spectra are measured, and the spectral parameters such as molecular absorption coefficient ($\in$), oscillator strength (f), absorption bandwidth ($\Delta\upsilon_{1/2}$), fluorescence bandwidth (FWHM) and Stoke's shift are calculated and these values are given in Table 4.4.



(a) **(b)**

Figure 4.4 (a) Absorption and (b) Fluorescence spectra of Ethyl Violet dye in liquid (ethanol) and solid (MPMMA)

Table 4.4 Spectral characteristics of Ethyl Violet in liquid and solid media

Solvent/ Medium	Absorption spectra				Fluorescence spectra		
	Peak wavelength in nm	ε x10^4 L mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$ cm^{-1}	f x10^{-24} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}
ethanol	592	8.4574	2110	0.772	643	93	1339.8
MPMMA	589	3.712	877.1	0.140	640	86	1352.9

The peak wavelength of the absorption spectra of Ethyl Violet in MPMMA showed a blue shift from that in ethanol. The oscillator strength of Ethyl Violet in solid matrix was less than that of Ethyl Violet in liquid medium. The peak emission wavelength of Ethyl Violet in solid matrix showed a blue shift from that in liquid medium. The FWHM of the flourescence spectrum of Natural Red 25 in solid medium was found to be shorter than that in liquid medium. The Stoke's shift of Ethyl Violet in solid matrix was more when compared to that in liquid media

4.5 SPECTRAL CHARATERISTICS OF SAFRANIN DYE

4.5.1 Spectral Characteristics of Safranin O

The dye, Safranin O is obtained from Sigma Aldrich India. The chemical structure of the dye is given in Table 2.1. Thin layer chromatography (TLC) test confirms the absence of any impurities. Methanol is chosen as solvent.

4.5.1.1 Synthesis of Safranin O DDP Rods

The Safranin O dye doped polymer rod is synthesized by thermal bulk free radical polymerization method as explained in section 2.7.1. MMA is used as monomer and benzoyl peroxide is chosen as the initiator for polymerization. The spectral characteristics of Safranin O in liquid media (in methanol) and solid media (MPMMA matrix) are studied. The dye doped polymer rod is of concentration 0.05 mM. The synthesized rod is in the form of rectangular shape with 2-3 cm length and 0.9 cm thickness. The optical quality of dye doped polymer rod is checked by passing a 5mW He-Ne laser beam (λ = 632.8 nm) through it. The rod shows no dispersion or distortion. The photograph of synthesized Safranin O dye doped polymer rod is shown in Figure 2.1.

4.5.1.2 Absorption and Fluorescence Spectra of Safranin O

The absorption spectra of the dye Safranin O, in methanol (liquid media) and in PMMA modified with methanol are recorded and are shown in Figure 4.5. The fluorescence spectra of the dye in methanol and in dye doped polymer rod are recorded and are shown in Figures 4.6 (a) and 4.6 (b) respectively. The peak wavelengths of the absorption and fluorescence spectra are measured and the spectral parameters such as molecular absorption coefficient ($\in$), oscillator strength (f), absorption bandwidth ($\Delta\upsilon_{1/2}$), fluorescence bandwidth (FWHM) and Stoke's shift are calculated and these values are given in Table 4.5.

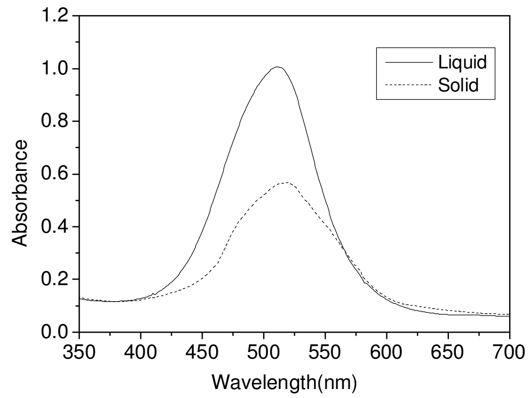
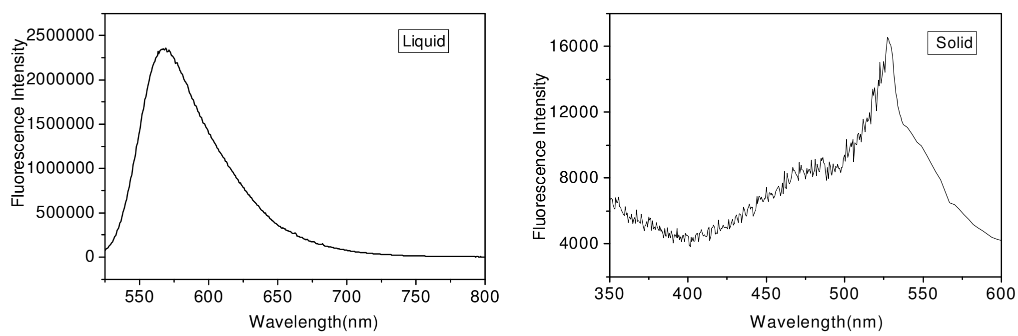


Figure 4.5 Absorption spectra of Safranin O dye in liquid (methanol) and solid (MPMMA)



(a) **(b)**

Figure 4.6 Fluorescence spectra of Safranin O dye (a) in Liquid (methanol) (b) solid (MPMMA)

Table 4.5 Spectral characteristics of Safranin O in liquid and solid media

Solvent/ Medium	Absorption spectra				Fluorescence spectra			Average Life time (ns)
	Peak wavelength in nm	ε x10^4 L mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$ cm^{-1}	f x10^{-24} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}	
methanol	512	10.066	3557.3	1.5504	562.8	64	1762.9	2.41
MPMMA	518	5.675	3961.5	0.9734	527.4	64	344	-

The peak wavelength of the absorption spectra of Safranin O in MPMMA showed a red shift from that in methanol. The oscillator strength of Safranin O in solid matrix was less than that of Safranin O in liquid medium. The peak emission wavelength of Safranin O in solid matrix showed a blue shift from that in liquid medium. The FWHM of the flourescence spectrum of Safranin O in solid medium and in liquid medium are found to be equal. The Stoke's shift of Safranin O in solid matrix was less when compared to that in liquid media

4.5.1.3 Fluorescence Lifetime Measurements

The fluorescence decay profile and the residuals of the dye Safranin O in solvent methanol are shown in Figure 4.7. The residuals shown in the Figure are well within the error limits. The average life time values of the dye are shown in Table 4.5. The dye exhibits bi-exponential decay.

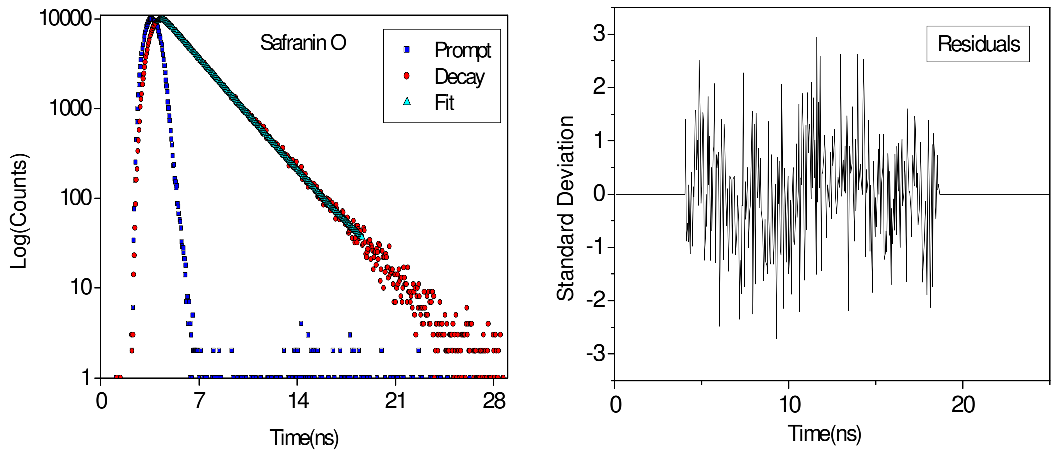


Figure 4.7 Fluorescence decay profile and residuals of Safranin O dye

4.6 SPECTRAL CHARATERISTICS OF COUMARIN DYE

4.6.1 Spectral Characteristics of LD 490

The dye, LD 490 is obtained from Sigma Aldrich India. The chemical structure of the dye is given in Table 2.1. Thin layer chromatography (TLC) test confirms the absence of any impurities. Methanol is chosen as solvent.

4.6.1.1 Synthesis of LD 490 DDP Rods

The LD 490 dye doped polymer rod is synthesized by thermal bulk free radical polymerization method as explained in section 2.7.1. MMA is used as monomer and benzoyl peroxide is chosen as the initiator for polymerization. The spectral characteristics of LD 490 in liquid media (in methanol) and solid media (MPMMA matrix) are studied. The synthesized dye doped polymer rod is of concentration 0.05 mM. The rod is in the form of rectangular shape with 2-3 cm length and 0.9 cm thickness. The optical quality of dye doped polymer rod is checked by passing a 5mW He-Ne laser beam (λ = 632.8 nm) through it. The rod shows no dispersion or distortion.

The photograph of synthesized LD 490 dye doped polymer rod is shown in Figure 2.1.

4.6.1.2 Absorption and Fluorescence Spectra of LD 490

The absorption spectra of the dye LD 490 in methanol (liquid media) and in PMMA modified with methanol are recorded and are shown in Figure 4.8. The fluorescence spectra of the dye in methanol and in dye doped polymer rod are recorded and are shown in Figures 4.9 (a) and 4.9 (b) respectively. The peak wavelengths of the absorption and fluorescence spectra are measured, and the spectral parameters such as molecular absorption coefficient ($\in$), oscillator strength (f), absorption bandwidth ($\Delta\upsilon_{1/2}$), fluorescence bandwidth (FWHM) and Stoke's shift are calculated and these values are given in Table 4.6.

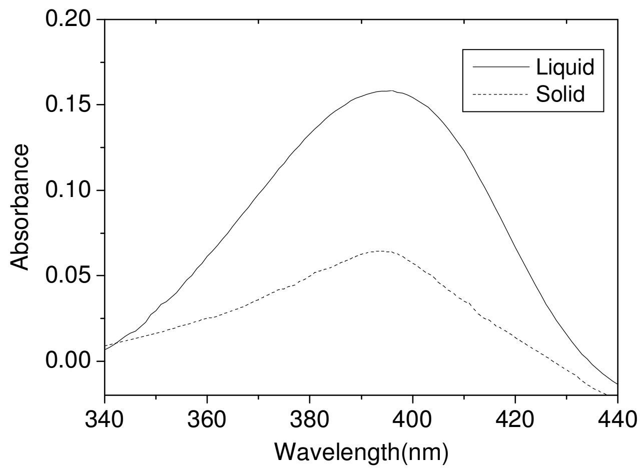
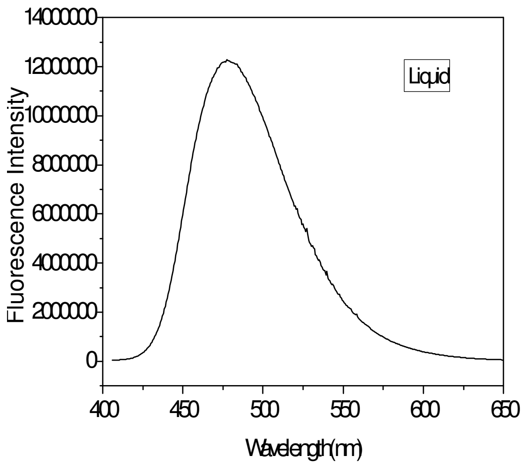
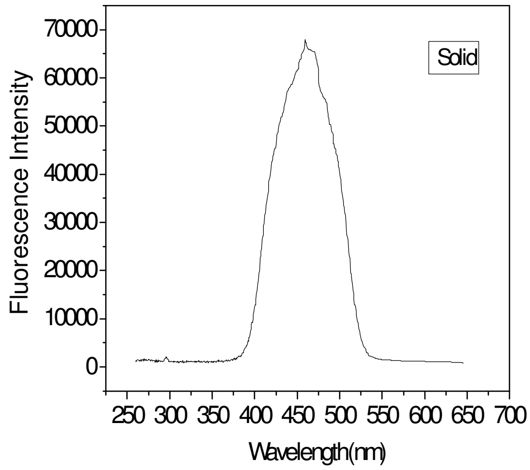


Figure 4.8 Absorption spectra of LD 490 dye in liquid (methanol) and solid (MPMMA)



(a)



(b)

Figure 4.9 Fluorescence spectra of LD 490 dye (a) in liquid(methanol) (b) solid (MPMMA)

Table 4.6 Spectral characteristics of LD 490 in liquid and solid media

Solvent/ Medium	Absorption spectra				Fluorescence spectra			Average Life time (ns)
	Peak wavelength in nm	ε x10^4 L mol^{-1} cm^{-1}	$(\Delta\nu)_{1/2}$ cm^{-1}	f x10^{-25} L mol^{-1} cm^{-2}	Peak wavelength in nm	FWHM nm	Stoke's shift cm^{-1}	
methanol	396	1.5831	3267	2.239	477.4	70.2	4305	4.64
MPMMA	395	0.641	2917	0.809	458.6	93.6	3511	-

The peak wavelength of the absorption spectra of LD 490 in MPMMA showed a blue shift from that in methanol. The oscillator strength of LD 490 in solid matrix was less than that of LD 490 in liquid medium. The peak emission wavelength of LD 490 in solid matrix showed a blue shift from that in liquid medium. The FWHM of the flourescence spectrum of Natural Red 25 in solid medium was found to be broader than that in liquid medium. The Stoke's shift of LD 490 in solid matrix was less when compared to that in liquid media.

4.6.1.3 Fluorescence Lifetime Measurements

The fluorescence decay profile and the residuals of the dye LD 490 in solvent methanol is shown in Figure 4.10. The residuals shown in the Figure are well within the error limits. The average life time values of the dye is shown in Table 4.6. The dye exhibits bi-exponential decay.

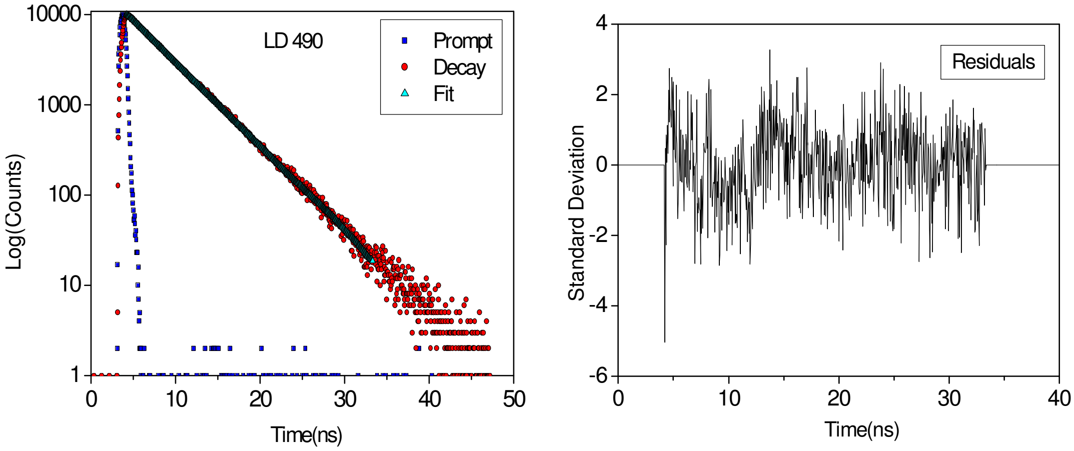


Figure 4.10 Fluorescence decay profile and residuals of LD 490 dye

4.7 CONCLUSION

The spectral parameters such as absorption peak wavelength, molar extinction coefficient (€), bandwidth $(\Delta\nu)_{1/2}$, oscillator strength (f), fluorescence peak wavelength, full width at half maximum (FWHM), Stoke's shift of the dyes, in liquid and solid media are calculated. The peak wavelength of absorption of Sudan IV, Natural Red 25 and Safranin O in the solid matrix (MPMMA) showed a red shift from that of the liquid media. This may be due to the increase in the rigidity of the polymeric matrix. The peak wavelength of absorption of Acid Red 27, Ethyl Violet and LD 490 in the solid matrix showed a blue shift from the peak wavelength of absorption of the dye in the liquid medium. This may be due to the decrease in the dielectric constant of the solid medium when compared to that of the liquid medium.

The fluorescence emission peak wavelength of Acid Red 27, Sudan IV, Ethyl Violet 25, Safranin O and LD 490 in the solid matrix showed a blue shift from the peak wavelength of fluorescence of the above dyes in the liquid medium. This may be attributed to the decrease in the dielectric constant of the polymeric medium when compared to that of the liquid medium. The shifts produced in the absorption and fluorescence spectra of the dye molecule are due to the interaction between the solute dipole and the solvent dipole. The fluorescence lifetime of Safranin O and LD 490 are 195ps and 305ps in methanol, respectively. The residuals shown along with the decay are well within the error limits.