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Effect of different donors and a polymer environment on photophysical and energy transfer studies using C540 as the acceptor

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Abstract. The dyes (C450, C480 and C540) and their dye mixtures (C450:C540 and C480:C540) were doped in polymer matrices (solid). Their photophysical studies were recorded. These results were analysed by comparing them with the data of the dyes and the dye mixtures in monomer compositions (liquid). The absorption and fluorescence spectral profiles of the dyes in the polymer matrix were found to be identical to those in the monomer compositions. The effect of different donors on the energy transfer technique using C540 as acceptor, in polymer matrix and monomer compositions, was studied in detail. The results obtained for the energy transfer technique in two binary dye mixtures containing different donors but same acceptor, in solid and liquid media, were intercompared. The gain of the acceptor without donor and with different donors was determined experimentally. The gain coefficient in the polymer matrix (solid) was less than that in the monomer medium (liquid). Also, the gain of the acceptor C540 was found to be more when C450 was used as the donor compared to that when C480 was used as the donor. Using nitrogen laser, the photobleaching effect in the two binary dye-doped polymer rods (with different donors but same acceptor) was studied. It was observed that photobleaching of the acceptor C540 in the presence of C450 as donor is slower than that in the presence of C480 as donor.

Keywords. Energy transfer; gain coefficient; amplified spontaneous emission; photobleaching; polymer matrix; photophysical studies.

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1. Introduction

Energy transfer techniques using organic dyes are widely used due to various valuable advantages [1–9]. But as these organic dyes in liquid solutions have various drawbacks, the solid-state medium containing the organic dyes was developed. Out of the various solid-state media, the transparent polymers were found to have high damage threshold

and have played a significant role in the advancement of solid-state dye laser systems [10–13]. Good optical transparency and laser damage resistance properties of polymethyl methacrylate (PMMA) compared to other polymeric materials made it the most frequently used transparent polymer matrix [14–16]. Hence, PMMA was chosen as the host, for the binary dye mixtures, in this work.

Various literatures are available on studies conducted on the energy transfer technique in binary dye mixtures in PMMA matrices [17–21]. To improve the photostability and conversion efficiency of PMMA matrix, modified polymethyl methacrylate (MPMMA) was used as the host material. PMMA was modified with the solvent ethanol (EtOH) as it provided good solubility for the coumarin dyes and also increased the optical resistance of PMMA [22,23]. The energy transfer studies were done in detail using C540 as the acceptor and C450 and C480 dyes as donors, in polymer matrix. The results obtained were compared with those in the liquid monomeric media. The effectiveness, reason and the technique behind using energy transfer in dyes are already discussed in many literatures including those from our group [22–27]. Nitrogen laser was used as the pumping source for our work. The C540 dye was chosen as the acceptor because review of literature showed laser action from C540 only at high concentrations. Since we wanted to study the effect of donor on the acceptor, we chose C450 and C480 as donors as both had good absorption cross-sections at the nitrogen laser pumping source of 337.1 nm.

To study the energy transfer mechanism from donor to acceptor, many spectroscopic parameters were calculated by recording the absorption and fluorescence spectra of the dyes and dye mixtures, in polymer matrix and monomer compositions [3,22–25,28–30]. The time-resolved fluorescence lifetime (τ) of the donor dye in the presence and absence of the acceptor was recorded. Only very little detailed information was available on gain characteristics of coumarin dyes and dye mixtures in MPMMA matrix except for a few from our group [17,22,23,31–33]. To establish the bandwidth and wavelength of operation under varying donor–acceptor concentrations, the peak of the amplified spontaneous emission (ASE) and gain of the acceptor dye (with donor) in the binary dye mixture were recorded by transverse excitation using nitrogen laser, in polymer matrix and monomer compositions. The photobleaching effect of the acceptor dye C540 in the presence of C450 as donor and C480 as donor, in MPMMA, was studied separately in MPMMA using nitrogen laser excitation. These data, thus recorded, were used to determine the most favourable donor to be used with the acceptor C540 so that higher gain and lesser photobleaching take place.

2. Experimental details

2.1 *Materials used*

Laser grade dye Coumarin 540 (C540) was used as the acceptor and laser grade dyes Coumarin 450 (C450) and Coumarin 480 (C480) were used as the donors. All these dyes were obtained from Exciton Inc., USA and were used without purification. The molecular structures of the dyes used are shown in figure 1. The absence of impurities was confirmed by the thin layer chromatography (TLC) test. For the synthesis of dye-doped polymer (DDP) and binary dye-doped polymer (BDDP) rods, methyl methacrylate (MMA) obtained from Lancaster Ltd., UK was used. The purification process of MMA is

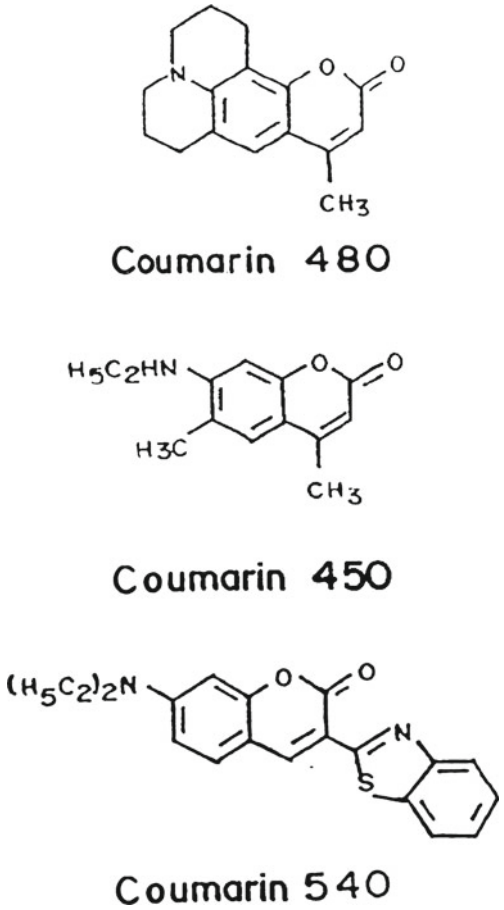

Figure 1. Molecular structure of the dyes used.

already mentioned in our previous papers [17,18,22,23,31]. The modifying additive used was the solvent ethanol (EtOH) which was of HPLC grade in purity. It was obtained from E-Merck (India) Ltd. The initiator used for polymerization of MMA was 2,2′-azo-bis (isobutyronitrile) or AIBN.

2.2 *Synthesis of DDP and BDDP rods*

The synthesis of DDP and BDDP rods is already well explained in all our previous papers [17,18,22,23,31]. Accordingly, BDDP rods of two donor–acceptor combinations (C450:C540 and C480:C540) and also at different acceptor concentrations were synthesized.

2.3 *Experimental methods*

The experimental work carried out on the donor dye (C450) with and without the acceptor dye (C540) in the C450:C540 binary dye system are explained in our previous papers

[22,23]. The absorption and fluorescence spectra of the donor C450 (alone) and the acceptor C540 (alone), in MPMMA (solid) and MMA+EtOH (liquid), were recorded with 0.05 mM concentration of the dyes in the solid and liquid media, using Elico SL 159 spectrophotometer and Hitachi F2000 spectrofluorometer, respectively. The emission spectra of the C450:C540 binary dye mixture, in solid and liquid media, as a function of the acceptor concentration were recorded. Fluorescence lifetime measurements were carried out using picosecond time-correlated single photon counting technique with a Ti:sapphire laser (Tsunami Spectra Physics, USA) operating with an intensity maximum at 375 nm. A single pass gain measurement using the ASE method proposed by Shank *et al* [34] was used for calculating the gain of the acceptor (with donor) in the binary dye mixture. The ASE and gain of the acceptor dye (with donor) in the binary dye mixture were studied by transverse excitation using a home-built nitrogen laser, radiating at 337.1 nm and operating at a repetition rate of 1 Hz with a peak power of 100 kW and a pulse width of 10 ns. The same procedure was repeated for C480:C540 binary dye mixture. The recording

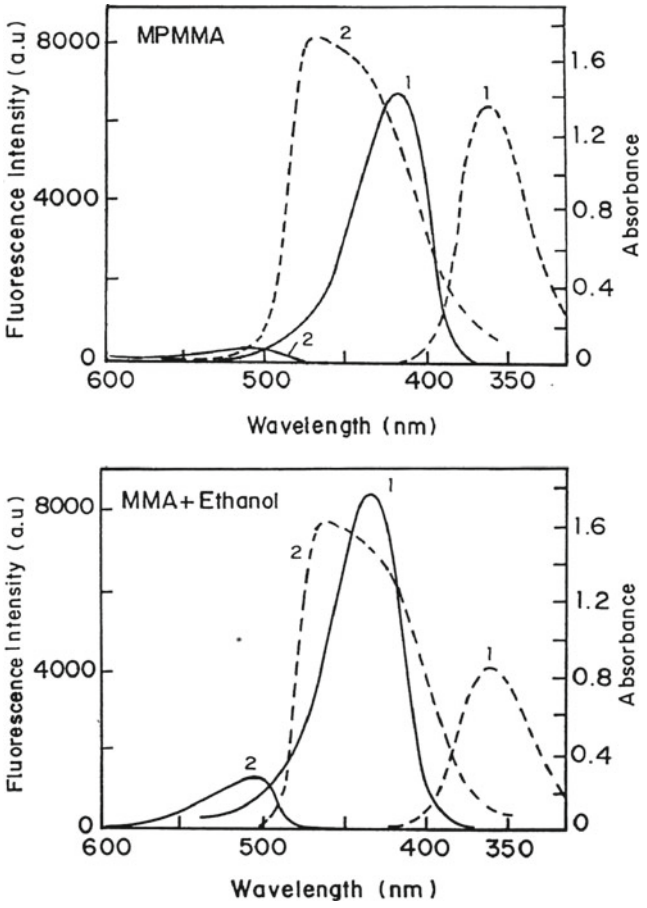

Figure 2. Absorption (- - -) and fluorescence (—) spectra of C450 (Curve 1) and C540 (Curve 2) at 0.05 mM concentration.

of absorption and fluorescence spectra, fluorescence lifetime, gain, ASE, photobleaching and the calculation of the various spectroscopic parameters such as critical transfer radius, transfer efficiencies, rate constants etc., were done as explained in [3,22–26,34].

3. Results and discussion

3.1 *Photophysical studies*

For the C450:C540 binary dye mixture system, the absorption and fluorescence spectra of the donor C450 (alone) and the acceptor C540 (alone) each at a concentration of 0.05 mM, in MPMMA and MMA+EtOH were recorded as shown in figure 2. The same

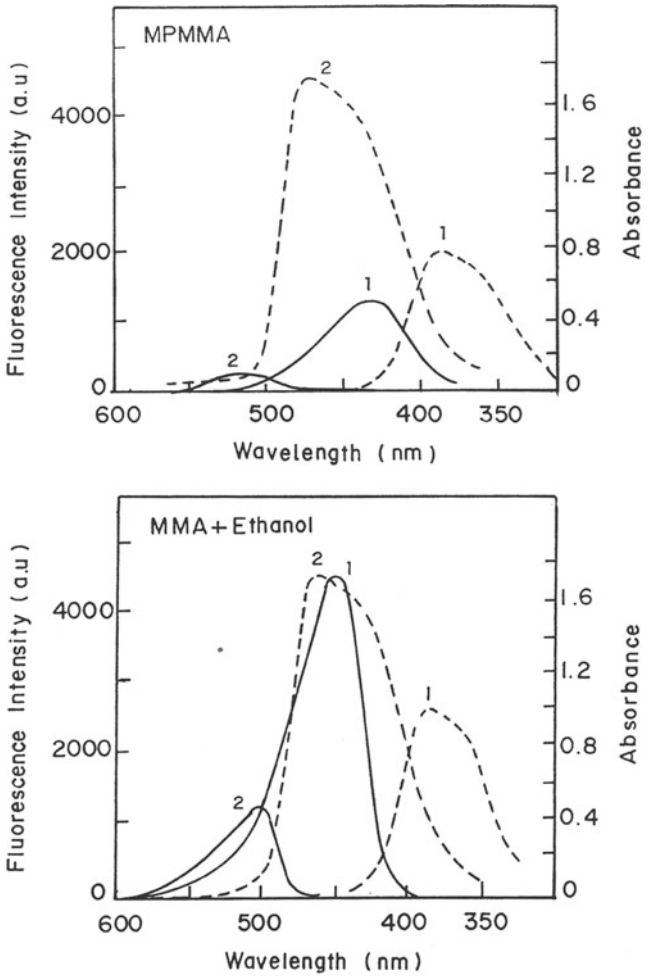

Figure 3. Absorption (- - -) and fluorescence (—) spectra of C480 (Curve 1) and C540 (Curve 2) at 0.05 mM concentration.

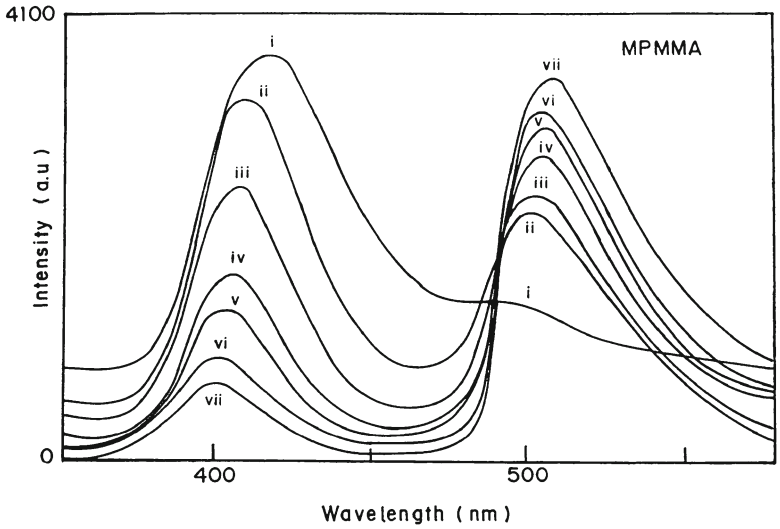

Figure 4. Variation of fluorescence intensity of C450:C540 binary dye mixture for different acceptor concentrations and fixed donor concentration of 0.05 mM. (i) 0.01 mM, (ii) 0.03 mM, (iii) 0.05 mM, (iv) 0.07 mM, (v) 0.09 mM, (vi) 0.11 mM, (vii) 0.13 mM.

procedure was repeated for the C480:C540 binary dye mixture system and the profiles are shown in figure 3. In both the binary systems, the spectral overlap of the absorption spectra of the acceptor with the fluorescence spectra of the donor indicated the presence of radiative and non-radiative types of energy transfer processes. The emission spectra

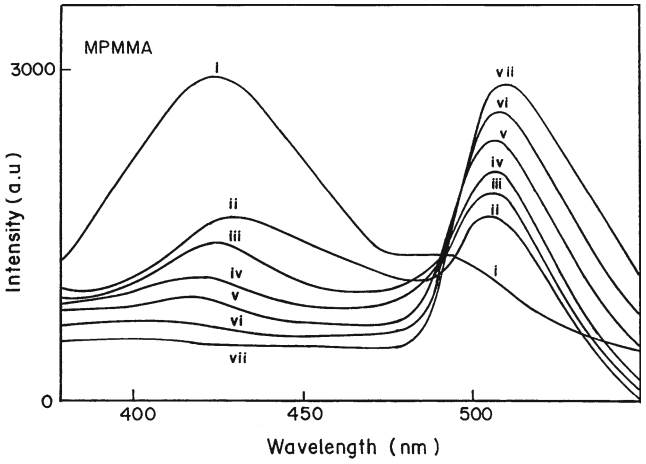

Figure 5. Variation of fluorescence intensity of C480:C540 binary dye mixture for different acceptor concentrations and fixed donor concentration of 0.05 mM. (i) 0.01 mM, (ii) 0.03 mM, (iii) 0.05 mM, (iv) 0.07 mM, (v) 0.09 mM, (vi) 0.11 mM, (vii) 0.13 mM.

of C450:C540 binary dye mixture, in MPMMA and MMA+EtOH, were recorded with a donor–acceptor concentration of (0.05 : 0.05) mM. Also, the variation in the fluorescence intensity of C450:C540 binary dye mixture for different acceptor concentrations but fixed donor concentration of 0.05 mM was recorded. Figure 4 shows the variation of fluorescence intensity of C450:C540 binary dye mixture in MPMMA only. A similar plot was obtained for C450:C540 in MMA + EtOH. Figure 4 shows only two peaks, one around C450 peak emission wavelength and the other around C540 peak emission wavelength indicating the absence of any new fluorescence peak formation for this binary dye mixture. Hence, this showed the absence of complex formation in C450:C540 binary dye mixture, in both polymer matrix and monomer composition. Also, the low concentration of the dyes in the liquid monomer medium and the restricted mobility of the molecules in

Table 1. Spectroscopic parameters of C450 and C540.

In MPMMA (Solid)	
Fluorescence lifetime of C450 without C540	$\tau_{od} = 3.34$ ns
Fluorescence lifetime of C450 with C540	$\tau_{d} = 3.27$ ns
Calculated critical transfer radius	$R_0 = 51.6$ Å
Critical concentration	$C_0 = 3.243$ mM
Radiative type transfer rate	$K_r = 2.647 \times 10^{13}$ l/mol/s
Non-radiative type transfer rate	$K_{nr} = 1.933 \times 10^{11}$ l/mol/s
Absorption cross-section of the donor C450 at 337 nm	$\sigma_D^L(337) = 6.072 \times 10^{-17}$ cm^2
Absorption cross-section of the acceptor C540 at 337 nm	$\sigma_A^L(337) = 1.003 \times 10^{-17}$ cm^2
Emission cross-section of the donor C450 at 521 nm	$\sigma_{SED}(521) = 4.112 \times 10^{-18}$ cm^2
Emission cross-section of the acceptor C540 at 521 nm	$\sigma_{SEA}(521) = 2.437 \times 10^{-16}$ cm^2
In MMA+EtOH (Liquid)	
Fluorescence lifetime of C450 without C540	$\tau_{od} = 3.02$ ns
Fluorescence lifetime of C450 with C540	$\tau_{d} = 2.97$ ns
Calculated critical transfer radius	$R_0 = 51.8$ Å
Critical concentration	$C_0 = 3.23$ mM
Radiative type transfer rate	$K_r = 7.959 \times 10^{13}$ l/mol/s
Non-radiative type transfer rate	$K_{nr} = 2.149 \times 10^{11}$ l/mol/s
Absorption cross-section of the donor C450 at 337 nm	$\sigma_D^L(337) = 3.762 \times 10^{-17}$ cm^2
Absorption cross-section of the acceptor C540 at 337 nm	$\sigma_A^L(337) = 6.308 \times 10^{-18}$ cm^2
Emission cross-section of the donor C450 at 513 nm	$\sigma_{SED}(513) = 1.333 \times 10^{-17}$ cm^2
Emission cross-section of the acceptor C540 at 513 nm	$\sigma_{SEA}(513) = 3.157 \times 10^{-16}$ cm^2

Donor = D = C450
Acceptor = A = C540

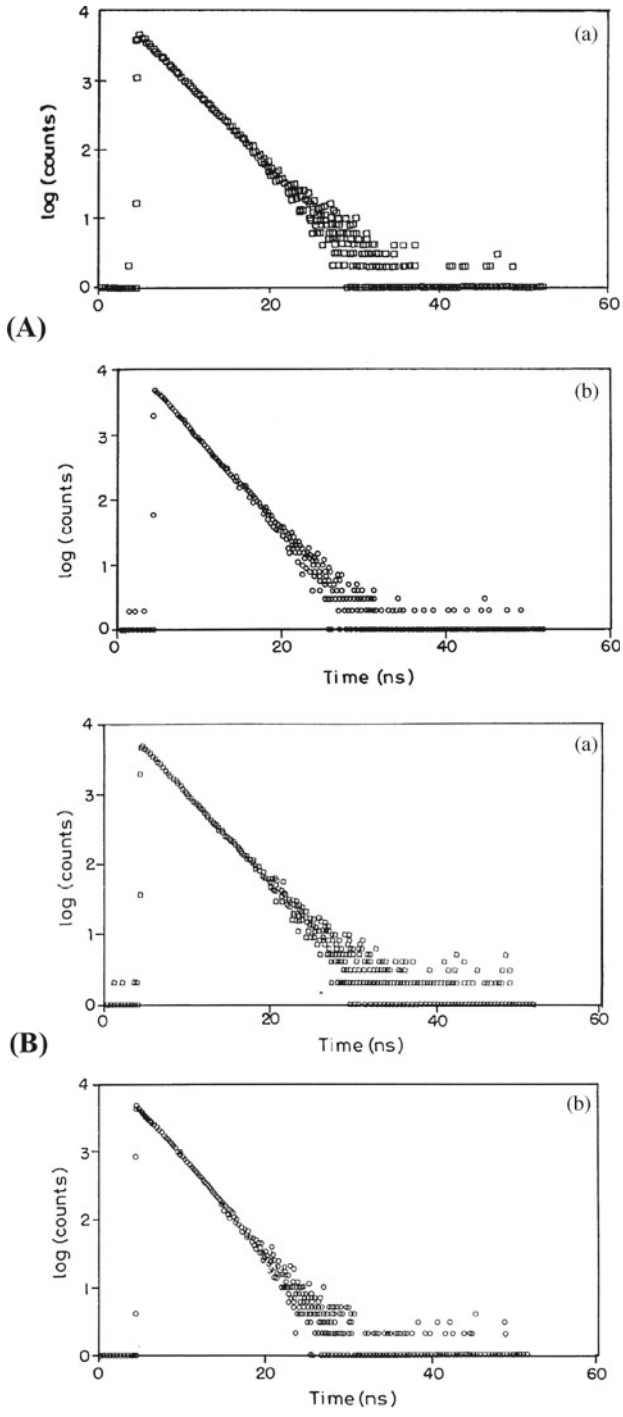

Figure 6. Fluorescence decay profiles of (A) C450 and (B) C450 with C540 in (**a**) MPMMA and (**b**) MMA+ethanol.

the solid polymer medium were the reasons for neglecting the collisional type of energy transfer in both liquid and solid media respectively [22–24,27,29]. In the same way, it was observed that there was no complex formation, in both solid and liquid media, in the C480:C540 binary dye mixture as shown in figure 5. Due to the same reasons already mentioned, the collisional type of energy transfer was neglected in C480:C540 binary mixture.

As already mentioned in our previous papers [22,23], the fluorescence lifetime measurements of the donor C450 without the acceptor C540 (τ_{od}) and with the acceptor C540 (τ_d), in MPMMA and MMA+EtOH, was determined experimentally using time-correlated single-photon counting technique. The data for the C450:C540 binary dye mixture are given in table 1 while the fluorescence decay profiles are given in figure 6.

Table 2. Spectroscopic parameters of C480 and C540.

In MPMMA (Solid)	
Fluorescence lifetime of C480 without C540	$\tau_{od} = 4.16$ ns
Fluorescence lifetime of C480 with C540	$\tau_d = 2.92$ ns
Calculated critical transfer radius	$R_0 = 45.5$ Å
Critical concentration	$C_0 = 4.742$ mM
Radiative type transfer rate	$K_r = 1.688 \times 10^{13}$ l/mol/s
Non-radiative type transfer rate	$K_{nr} = 0.642 \times 10^{11}$ l/mol/s
Absorption cross-section of the donor C480 at 337 nm	$\sigma_D^L(337) = 2.47 \times 10^{-17}$ cm^2
Absorption cross-section of the acceptor C540 at 337 nm	$\sigma_A^L(337) = 1.003 \times 10^{-17}$ cm^2
Emission cross-section of the donor C480 at 513 nm	$\sigma_{SED}(513) = 1.327 \times 10^{-17}$ cm^2
Emission cross-section of the acceptor C540 at 513 nm	$\sigma_{SEA}(513) = 2.649 \times 10^{-16}$ cm^2
In MMA+EtOH (Liquid)	
Fluorescence lifetime of C480 without C540	$\tau_{od} = 3.65$ ns
Fluorescence lifetime of C480 with C540	$\tau_d = 3.46$ ns
Calculated critical transfer radius	$R_0 = 59$ Å
Critical concentration	$C_0 = 2.179$ mM
Radiative type transfer rate	$K_r = 53.65 \times 10^{13}$ l/mol/s
Non-radiative type transfer rate	$K_{nr} = 2.699 \times 10^{11}$ l/mol/s
Absorption cross-section of the donor C480 at 337 nm	$\sigma_D^L(337) = 2.265 \times 10^{-17}$ cm^2
Absorption cross-section of the acceptor C540 at 337 nm	$\sigma_A^L(337) = 6.308 \times 10^{-18}$ cm^2
Emission cross-section of the donor C480 at 510 nm	$\sigma_{SED}(510) = 3.926 \times 10^{-17}$ cm^2
Emission cross-section of the acceptor C540 at 510 nm	$\sigma_{SEA}(510) = 3.226 \times 10^{-16}$ cm^2

Donor = D = C480
Acceptor = A = C540

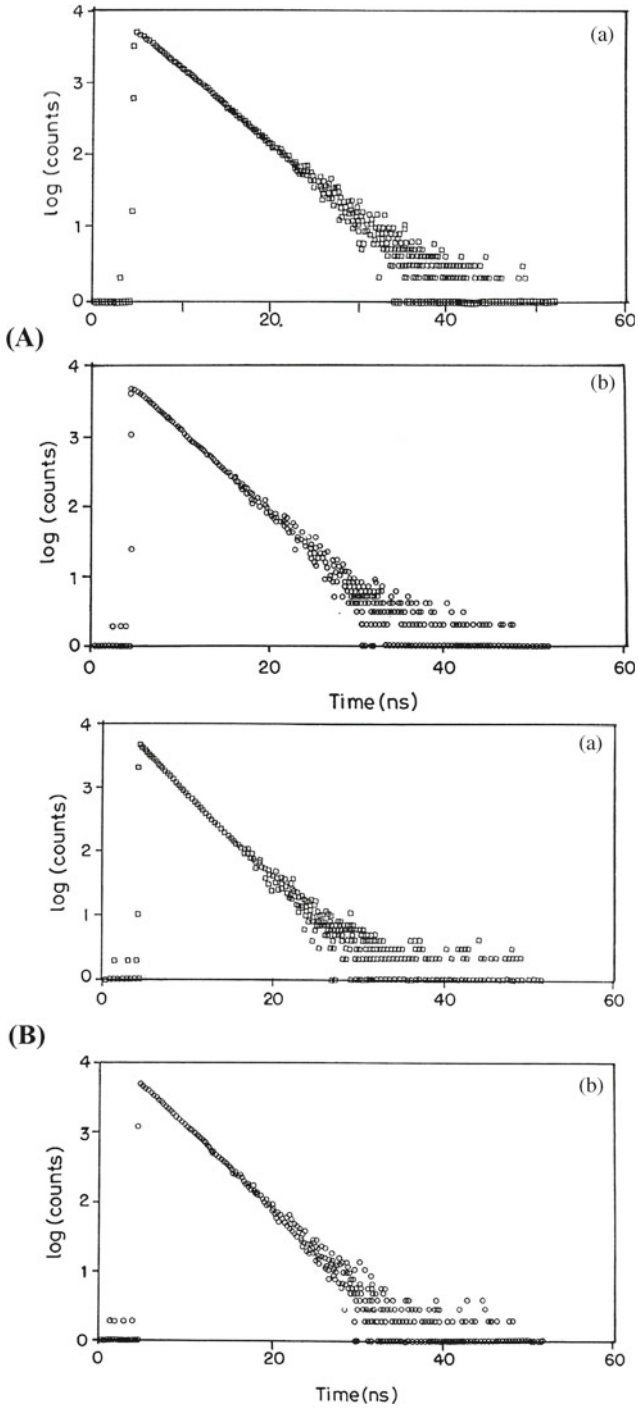

Figure 7. Fluorescence decay profiles of (A) C480 and (B) C480 with C540 in (**a**) MPMMA and (**b**) MMA+ethanol.

The same experimental procedure as above was repeated for the C480:C540 binary dye mixture. The values and fluorescence decay profiles of this dye mixture are shown in table 2 and figure 7. From tables 1 and 2 and figures 6 and 7, it was observed that, for

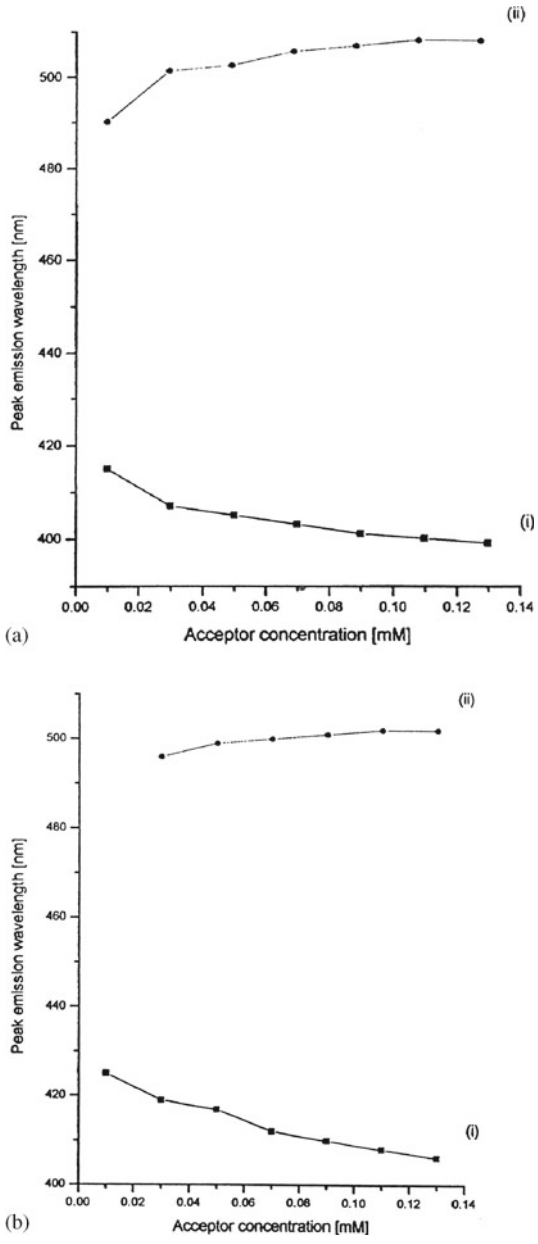

Figure 8. Spectral shift in fluorescence peak wavelength of the donor C450 (Curve i) and the acceptor C540 (Curve ii) in (**a**) MPMMA and (**b**) MMA+ethanol for different acceptor concentrations keeping donor concentration fixed at 0.05 mM.

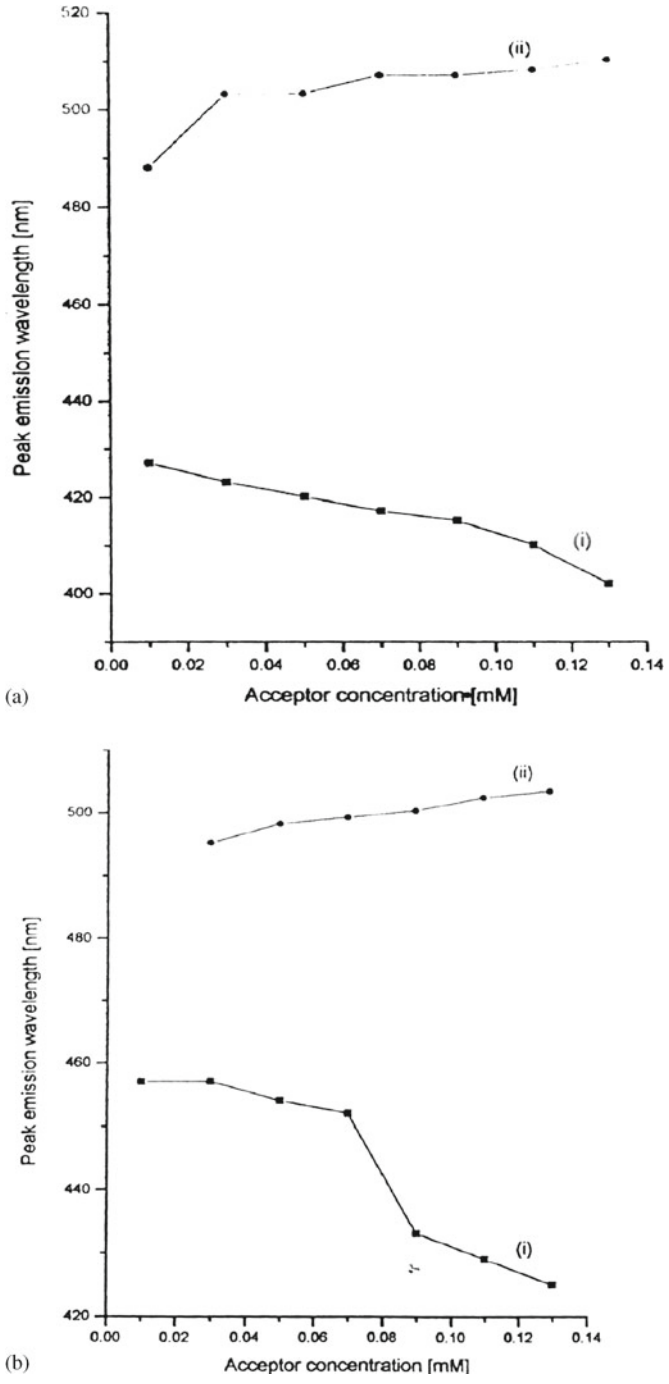

Figure 9. Spectral shift in fluorescence peak wavelength of the donor C480 (Curve i) and the acceptor C540 (Curve ii) in (**a**) MPMMA and (**b**) MMA+ethanol for different acceptor concentrations keeping donor concentration fixed at 0.05 mM.

both the binary systems, the fluorescence lifetime of the donor decreased in the presence of the acceptor C540. This decrease in the lifetime of the donor on addition of acceptor was observed in both the polymer matrix as well as the monomer composition. Such a decrease in the fluorescence lifetime of a donor on addition of an acceptor indicated that there was transfer of energy from the donor to the acceptor [14,22,23,35,36].

3.2 *Spectroscopic parameters*

The various spectral parameters, for both the binary dye mixtures, were calculated using the absorption and emission spectra shown in figures 2 and 3. The calculated values are given in tables 1 and 2. From the tables, it was evident that the critical transfer radius, in both C450:C540 and C480:C540 binary systems, in solid and liquid media, was in good agreement with Forster kinetics.

3.3 *Stern–Volmer analysis*

The effect of acceptor concentration $[A]$ on the fluorescence spectra of the donor dye in the absence (I_{od}) and presence of acceptor (I_d) was analysed in figures 2–5, respectively. Figures 4 and 5 give the fluorescence spectral profiles of each of the binary dye mixture as a function of acceptor concentration $[A]$. From the figures, it was evident that when the acceptor was added, the fluorescence intensity of the donor decreased from I_{od} to I_d as a function of the acceptor concentration $[A]$, in both the binary systems in polymer matrix and monomer composition. This decrease in the fluorescence intensity of the donor in the presence of the acceptor was due to the transfer of energy from the donor to acceptor [3,14,19,22,23,28,37]. Results were similar for both the binary systems in polymer matrix as well as in the monomer composition. The emission peak wavelength of the donor and the acceptor as a function of $[A]$ is shown in figure 8 for C450:C540 binary system and in figure 9 for C480:C540 binary system. For both the binary systems, the donor fluorescence peak wavelength exhibited a blue-shift while the acceptor C540 fluorescence peak wavelength exhibited a red-shift with increasing acceptor concentration.

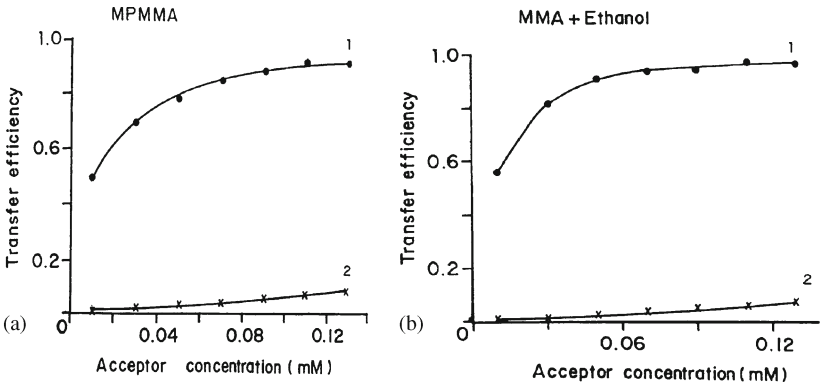

Figure 10. Acceptor concentration dependence of f (Curve 1) and f_{nr} (Curve 2) for the C450:C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

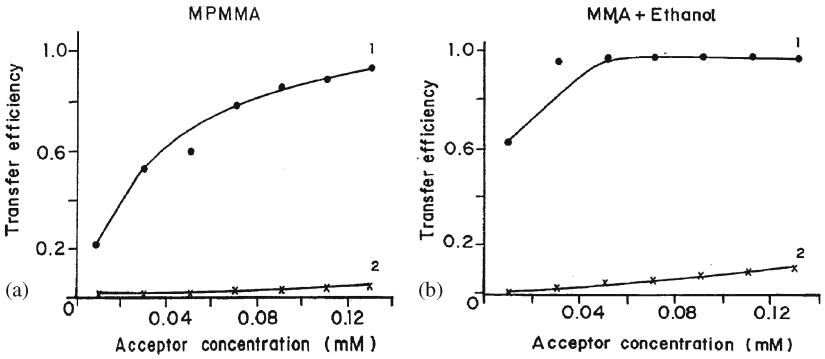

Figure 11. Acceptor concentration dependence of f (Curve 1) and f_{nr} (Curve 2) for C480:C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

This observed blue-shift in the donor fluorescence with $[A]$ may be due to radiative transfer to the acceptor, which will increase as $[A]$ increases. Likewise, the successive red-shift in the fluorescence maximum of the acceptor may be attributed to radiative migration due to self-absorption [19,22,23,38]. The trend was similar in the polymer matrix as well as in the monomer composition, for both the binary systems.

3.3.1 *Efficiencies of energy transfer.* The energy transfer efficiencies and rate constants were calculated as already discussed in our previous papers [22,23]. The total transfer efficiency (f), non-radiative transfer efficiency (f_{nr}) and radiative transfer efficiency (f_r) of the binary systems, in MPMMA and MMA+EtOH were calculated. The transfer efficiencies thus calculated are shown in figures 10–13 as functions of acceptor concentration. It was observed that the radiative transfer efficiency is more predominant than the non-radiative transfer efficiency in both the binary systems and in both the media.

3.3.2 *Rate constants of energy transfer.* The fluorescence quantum yield of the donor in the absence (Φ_{od}) and presence of acceptor (Φ_d) was calculated as in our previous

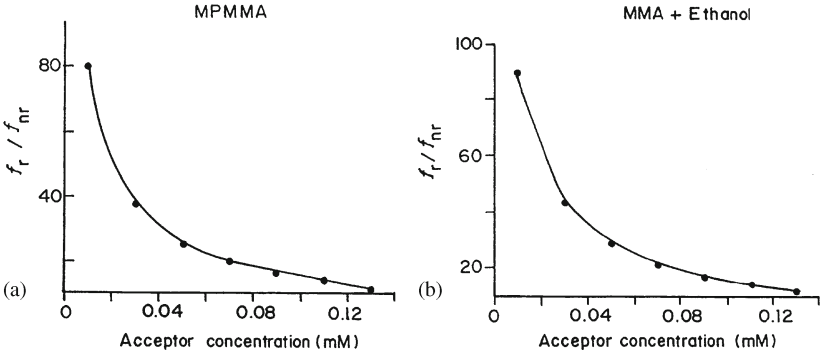

Figure 12. Acceptor concentration dependence of f_r/f_{nr} for C450:C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

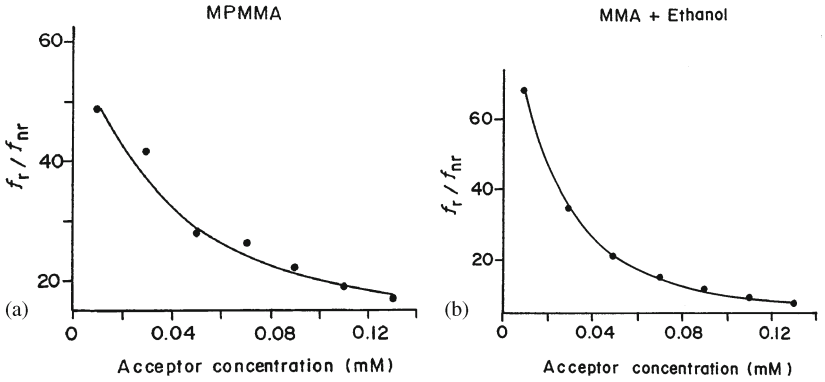

Figure 13. Acceptor concentration dependence of f_r/f_{nr} for the C480:C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

papers [22,23]. As shown in figures 14–17, the variation of I_{od}/I_d vs. $[A]$ and the relative quantum yields of the donor (Φ_{od}/Φ_d) as a function of $[A]$ was plotted and found to be linear. Here, the radiative and non-radiative rate constants were calculated as already discussed in the previous papers [3,22,23]. The values calculated are given in tables 1 and 2 for the two binary systems. It was observed that under the acceptor concentration ranges considered, the radiative energy transfer mechanism is more predominant than the non-radiative energy transfer mechanism for both C450:C540 and C480:C540 binary systems in polymer and monomer environments.

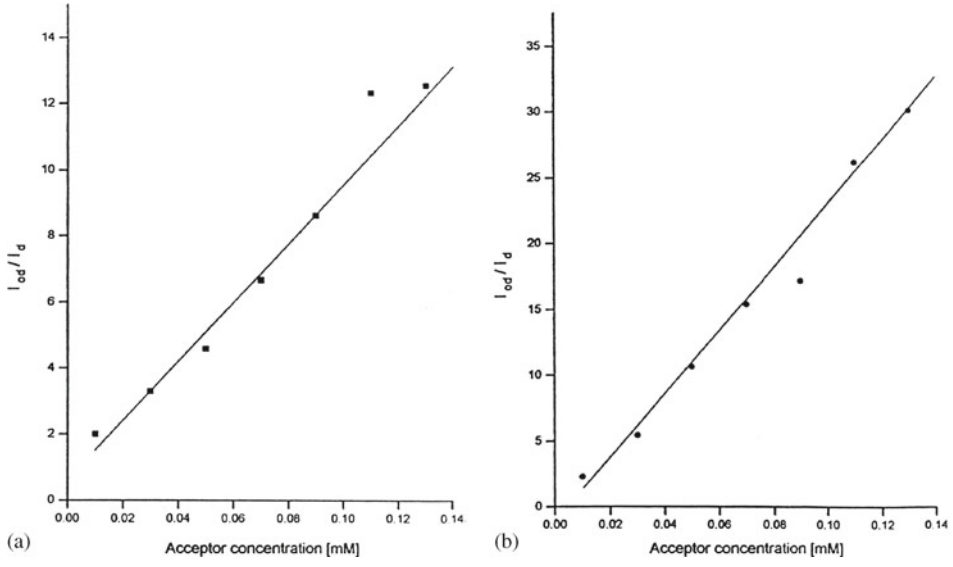

Figure 14. Fluorescence intensity I_{od}/I_d vs. acceptor concentration for the C450:C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

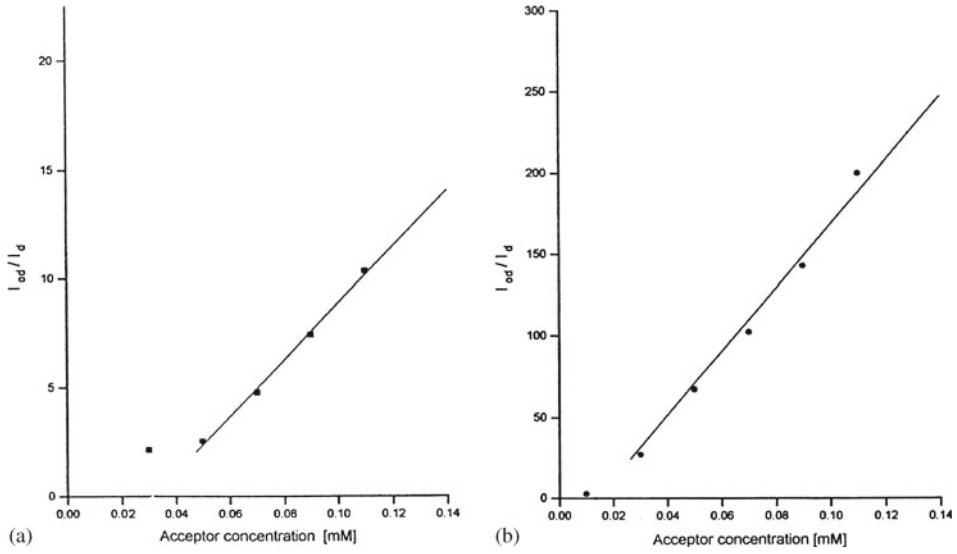

Figure 15. Fluorescence intensity I_{od}/I_d vs. acceptor concentration for the C480: C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

3.4 *Gain*

The optical gain and ASE of the acceptor dye with and without the donor dye were experimentally evaluated as explained in our previous papers. In each of the two binary systems and also in the polymer and monomer environments, the optimum acceptor concentration

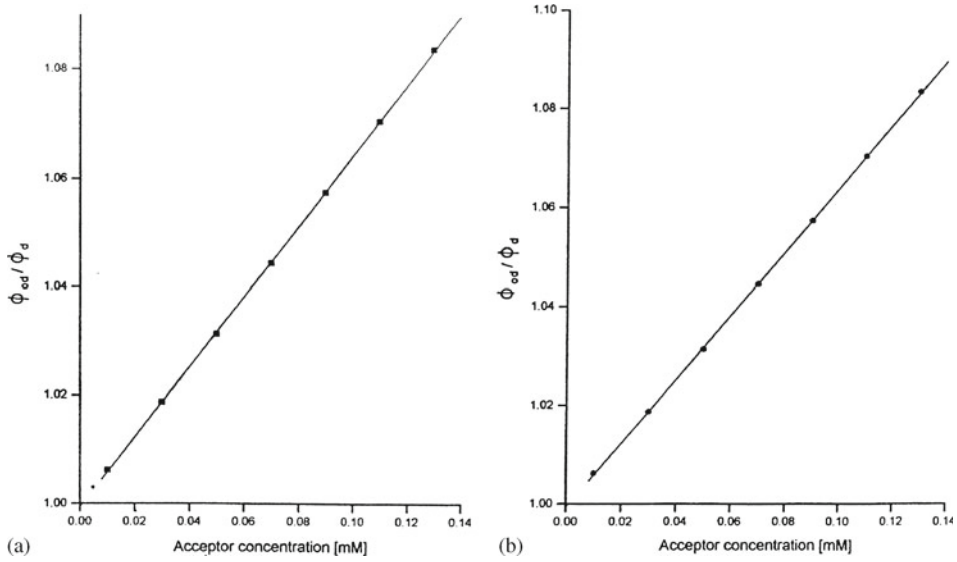

Figure 16. Relative quantum yields Φ_{od}/Φ_d vs. acceptor concentration for the C450:C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

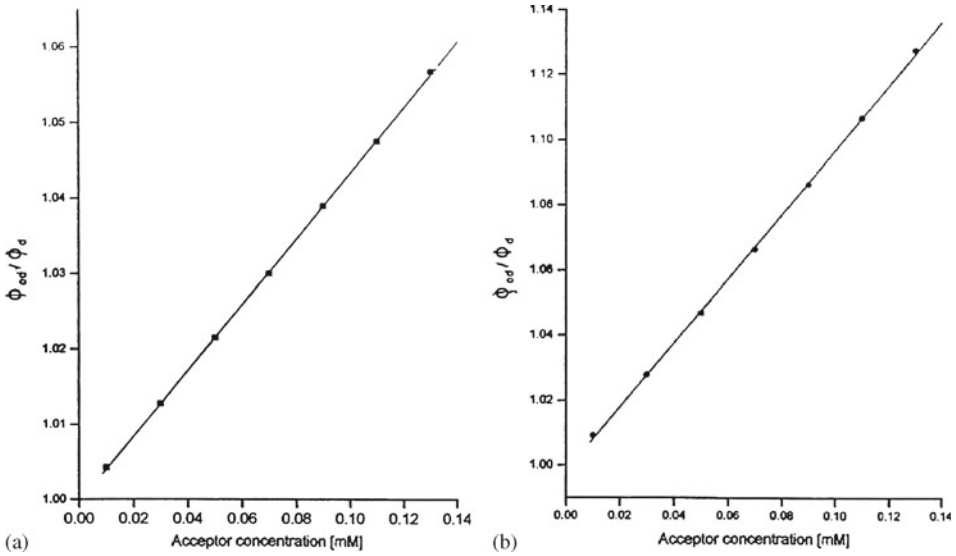

Figure 17. Relative quantum yields Φ_{od}/Φ_d vs. acceptor concentration for the C480:C540 binary dye mixture in (**a**) MPMMA and (**b**) MMA+ethanol.

needed for laser action so that the gain measured was unsaturated gain was determined as already explained [22,23]. This optimum acceptor concentration [A] was used to calculate the gain of the acceptor in the presence of the donor, in the respective medium.

For the C450:C540 binary system, the optimum donor–acceptor concentration needed to obtain unsaturated gain was found to be (20 : 1) mM in MPMMA and (4 : 0.75) mM in MMA+EtOH. Similarly, for the C480:C540 binary system, the optimum donor–acceptor concentration needed to obtain unsaturated gain was found to be (25 : 2) mM in MPMMA and (5 : 1) mM in MMA+EtOH. The gain studies of C540 in C450:C540 and C480:C540 binary dye mixtures were repeated in MMA and EtOH using donor–acceptor concentrations optimized as above in each case. These values of gain of the acceptor C540 in the presence of each of the two donors in polymer and monomer environments is shown in tables 3 and 4 while the corresponding gain curves are shown in figures 18 and 19 respectively. From tables 3 and 4, it was noted that the gain of C540 in the presence of the

Table 3. ASE and gain of C540 in C450:C540 binary dye mixture in solid and liquid media.

Concentration of C450:C540 (mM)	Medium	ASE (nm)	Gain $\times 10^{-19}$ (cm^2/mol/kW)
4:0.75	MMA	501	5.699
4:0.75	EtOH	519	8.759
4:0.75	MMA+EtOH	513	6.442
20:1	MPMMA	521	3.273

Table 4. ASE and gain of C540 in C480:C540 binary dye mixture in solid and liquid media.

Concentration of C480:C540 (mM)	Medium	ASE (nm)	Gain $\times 10^{-19}$ (cm^2/mol/kW)
5:1	MMA	515	2.228
5:1	EtOH	503	2.643
5:1	MMA+EtOH	510	2.638
25:2	MPMMA	513	0.603

donor (either C450 or C480) in the solid polymer matrix of MPMMA was less than that in the liquid media (MMA+EtOH, MMA, EtOH). This decrease in the gain coefficient in each of the binary dye mixtures in the solid polymer matrix from that in the liquid media may be due to the increase in the refractive index of MPMMA [22,23,34]. Also, dye re-absorption and inhomogeneity produced at higher concentrations in the solid medium may have caused a decrease in gain in the polymer medium [22,23,36].

Also, from tables 3 and 4, it was observed that the gain of the acceptor C540 in the presence of C450 as the donor was much higher than the gain of the acceptor C540 in the presence of C480 as the donor. The same result was observed in all the media. This indicated that under similar conditions, the gain of the acceptor dye, in both solid and liquid media, predominantly depends on the structure of the donor dyes used. This fall in gain of the acceptor C540 in the presence of C480 as the donor compared to that in the presence of C450 as the donor may be because the dye C450 has a mobile amino group in the seventh position and a CH_3 substitution in the sixth position while dye C480 has a rigidized amino group in the seventh position.

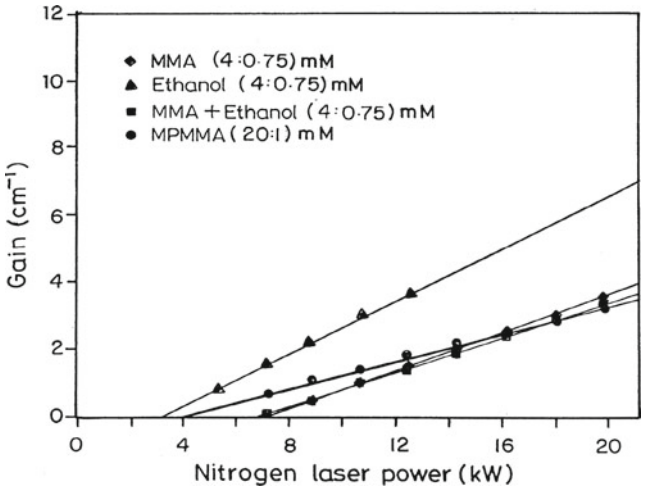

Figure 18. Variation of gain with nitrogen laser power for C540 in the C450:C540 binary dye mixture.

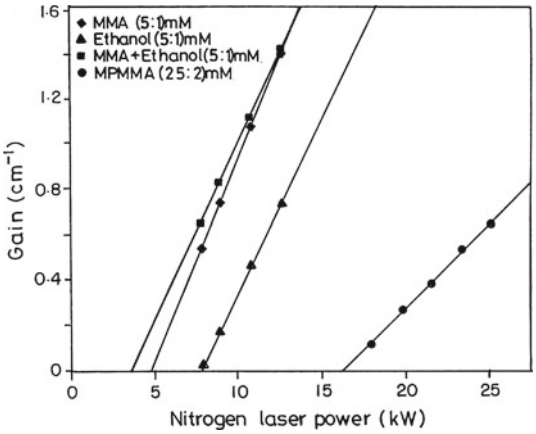

Figure 19. Variation of gain with nitrogen laser power for C540 in the C480:C540 binary dye mixture.

3.5 *Photobleaching*

Nitrogen laser excitation was used to study the photobleaching characteristics of the acceptor C540 in the presence of each of the two donors, namely C450 and C480 in MPMMA, as already explained in our previous publications [22,23]. The photobleaching characteristics of the acceptor C540 in the presence of the donor C450 in MPMMA at a

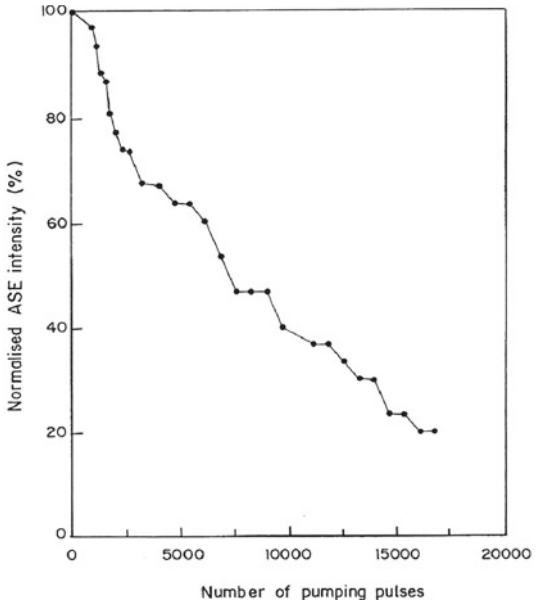

Figure 20. Variation of ASE intensity with the number of nitrogen laser pumping pulses of the acceptor C540 with the donor C450 in MPMMA.

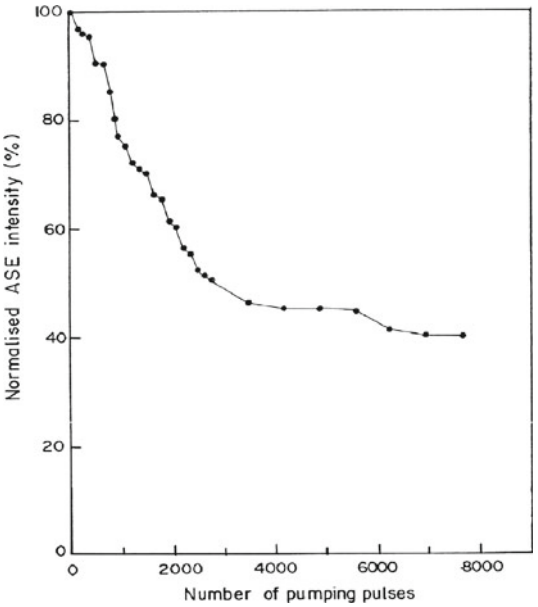

Figure 21. Variation of ASE intensity with the number of the nitrogen laser pumping pulses of the acceptor C540 with the donor C480 in MPMMA.

concentration of (20 : 1) mM were studied. Similarly, the photobleaching characteristics of the acceptor C540 in the presence of the donor C480 in MPMMA at a concentration of (25 : 2) mM were studied. These characteristics are shown in figures 20 and 21. From figures 20 and 21, it was observed that the acceptor C540 in the presence of the donor C450 took more number of pumping pulses to bleach than in the presence of the donor C480. Acceptor dye C540 in the presence of donor C450 withstood 7210 pulses before its ASE intensity was reduced to 50% of its initial value while acceptor dye C540 in the presence of the donor C480 withstood only 2750 pulses before its ASE intensity was reduced to 50% of its initial value. This longer photobleaching rate of the acceptor dye C540 in the presence of donor C450 when compared to the shorter photobleaching rate of the acceptor dye C540 in the presence of donor C480 may be due to the presence of the mobile amino group in the seventh position and a CH_3 substitution in the sixth position of the dye C450 while dye C480 has a rigidized amino group in the seventh position.

4. Conclusion

The effect of polymer environment on the photophysical characteristics of dyes and dye mixtures was studied by comparing the results in the corresponding monomer environment. Accordingly, the absorption and fluorescence spectral profiles of the dyes and dye mixtures were identical in the polymer and monomer environments. In both binary dye mixture systems of C450:C540 and C480:C540, there was a spectral overlap of the donor and the acceptor dyes, in polymer and monomer environments. This proved

that energy transfer from the donor to the acceptor was possible. This overlap also indicated the presence of radiative and non-radiative energy transfer processes. In both the binary dye mixture systems, in both polymer and monomer environments, the radiative energy transfer mechanism predominated the non-radiative energy transfer mechanism under the concentration ranges considered. The fluorescence lifetime of the donor dye, with and without the acceptor C540 dye, recorded using single photon counting technique was found to decrease in the presence of the acceptor due to transfer of energy from the donor to the acceptor. The optical gain and ASE of the acceptor C540 in both the binary dye mixture systems, in the polymer and monomer media, were recorded using transverse excitation by nitrogen laser. The acceptor dye C540 did not exhibit any gain when taken at a low concentration. But when each of the donor dyes at a high concentration was added, the acceptor C540 gave an ASE output at the acceptor wavelength. So, it was observed that without the presence of each of the donors to act as an energy transfer dye, the excited state population of the acceptor C540 was apparently too low for lasing at that concentration. The binary dye mixtures exhibited similar trends in the polymer and monomer environments. The gain measured was the unsaturated gain of the acceptor C540 in each of the binary systems. In each of the two binary systems of C450:C540 and C480:C540, the gain of the acceptor in the presence of the donor in the polymer environment (MPMMA) was less than that in the corresponding monomer composition. Also, the acceptor C540 exhibited higher gain in the presence of donor C450 compared to that in the presence of donor C480, in both polymer and monomer environments. Under nitrogen laser pumping, the photobleaching studies of the acceptor C540 in the BDDP rod exhibited slower bleaching in the presence of donor C450 and faster bleaching in the presence of donor C480. This higher gain and slower photobleaching of the acceptor the C540 in the presence of donor C450 when compared to that in the presence of donor C480 may be due to the dependence of the above on the structure of the donor dyes when used under similar environmental conditions. Hence, this higher gain of the acceptor C540 in the presence of donor C450 may be because the dye C450 has a mobile amino group in the seventh position and a CH_3 substitution in the sixth position while dye C480 has a rigidized amino group in the seventh position.

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