CHAPTER : 3

RESULT AND DISCUSSION

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3.1 Fluorescence of Pyrene Doped Polystyrene Films

Pyrene doped polystyrene (PS) films have been prepared from the benzene solution. Fig3.1shows fluorescence spectrum of PS films containing 1.1517 wt % and 0.1152 wt % pyrene. The spectrum of film containing low wt % of pyrene is structured and shows emission bands at 378, 385 and 397 nm. The spectrum is similar to those reported for the dilute solution of pyrene[16,70,101-107] and in L-B films.[16,70,108-110] The structured emission band is assigned to the monomer emission of pyrene. The fluorescence spectrum of film containing high wt % of pyrene is a broad band peaking at 479 nm. This band corresponds to a well known excimer emission band of pyrene; observed from its concentrated solution in inert solvent[101,102] and from crystalline pyrene.[106,107,111] The excitation spectrum of low weight % pyrene film monitored at 397 nm emission wavelength is structured with maximum at 340 nm. This spectrum matches well with the absorption spectrum of pyrene in dilute solution.[103-106] The similarity observed between absorption and excitation spectrum of pyrene film, suggests the monomeric existence of pyrene molecules in the film. The excitation spectrum of polystyrene films containing higher weight % of pyrene and monitored at excimer emission wavelength is a broad band in the region 300-400 nm. The lack of vibronic transition and broadening is an indication of aggregation of molecules in the excited state. We believe that as in concentrated solution, the excited pyrene monomer undergoes a π-orbital vibronic coupling with ground state pyrene molecule to form a dimeric species.[16,44,70,112,113] The excited dimer known as

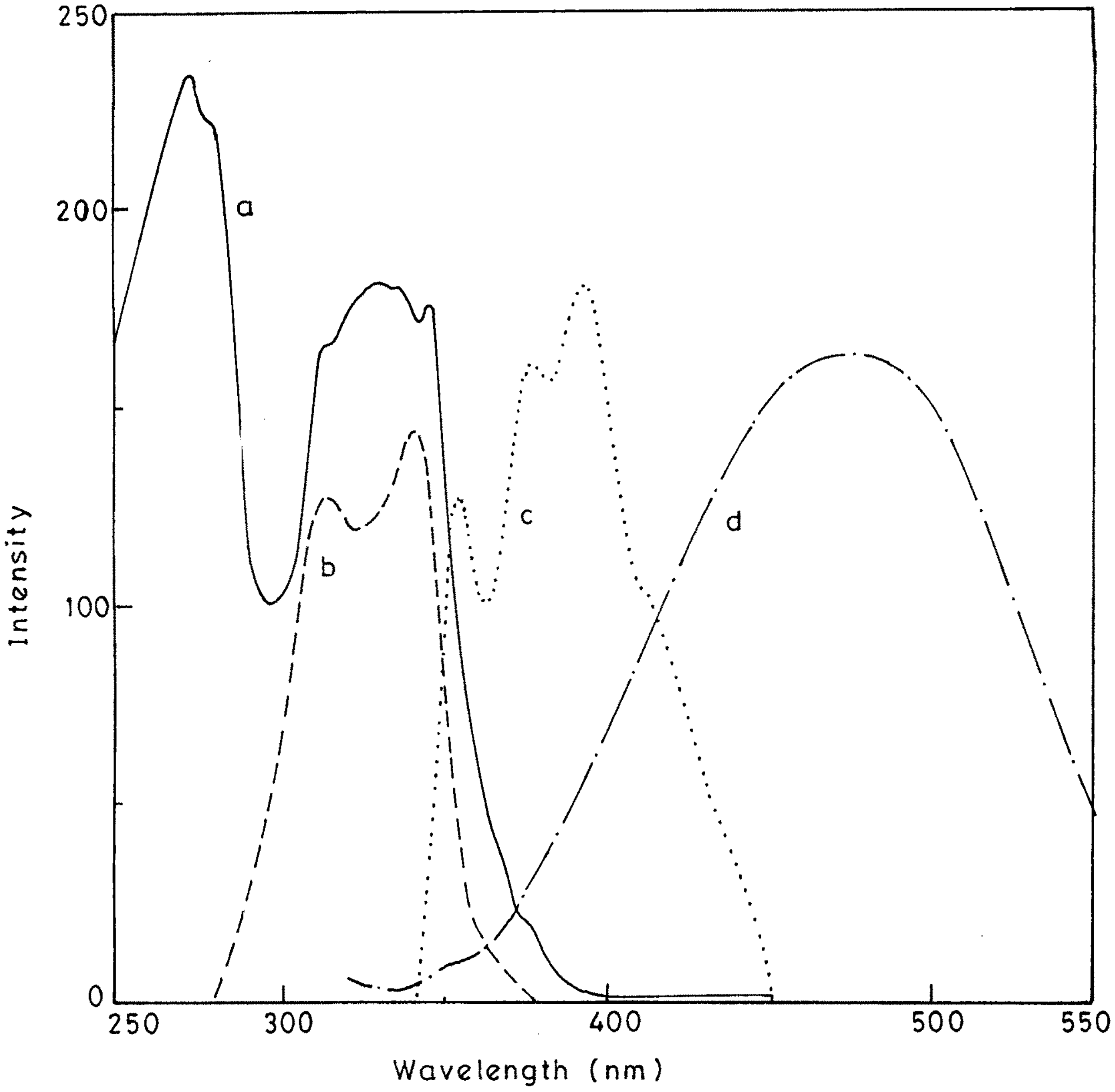


Fig. 3·1 – Fluorescence and Excitation spectra of 0·1152 wt % (a&c) and 1·152 wt % (b&d) Pyrene doped Polystyrene films. c

a) Exitation spectrum monitored at monomer emission (397 nm)

b) Excitation spectrum monitored at excimer emission (477 nm)

c) Emission spectrum monitored at λex = 340 nm

d) Emission spectrum monitored at λex = 340 nm excimer dissociates to give its characteristic broad excimer like emission seen at 479 nm in the fluorescence spectrum of the film. The absorption spectrum of the films containing low and high weight % of pyrene are shown in fig. 3.2. The similarity observed between both the spectra suggests that in ground state the pyrene exists as monomer and rules out the possibility of aggregation in the ground state. Hence aggregation is probable only in the excited state.

The systematic variation of pyrene in the PS film has given the monomer and excimer emission from the same film and the critical wt % of pyrene giving transition from monomer to excimer emission was determined. Fig.3.3 shows fluorescence spectra of PS films containing varying wt % of pyrene. The spectrum of film containing 0.1728 wt % is structured with the maximum emission at 397 nm. This emission is arising from the isolated pyrene molecule. The broad eximer like emission band corresponding to pyrene excimer is not observed from this film. Careful examination of the spectra shown in figure 3.3 reveals the quenching of monomer emission as wt % of pyrene in polystyrene film increases. At pyrene concentration 0.2303 wt %, a broad tail seems to appear in the range 410-550 nm. Further increase in wt % of pyrene has increased the intensity of this broad band with simultaneous quenching of its monomer emission. The spectra of films containing pyrene above 0.9214 wt % show complete quenching of monomer emission and prominent broad structureless band peaking at 479 nm are seen. The position of band found to be independent of pyrene wt. % in polystyrene matrix. However, intensity of band increases with pyrene wt % linearly and seems to saturate at higher wt %. It is interesting to note that some of the films containing 0.5758, 0.461, 0.3455, 0.2303 wt % of pyrene show both monomer and excimer like emission from the same film. Transition from monomer to excimer starts at concentration 0.2303 wt %. Fig. 3.4 shows

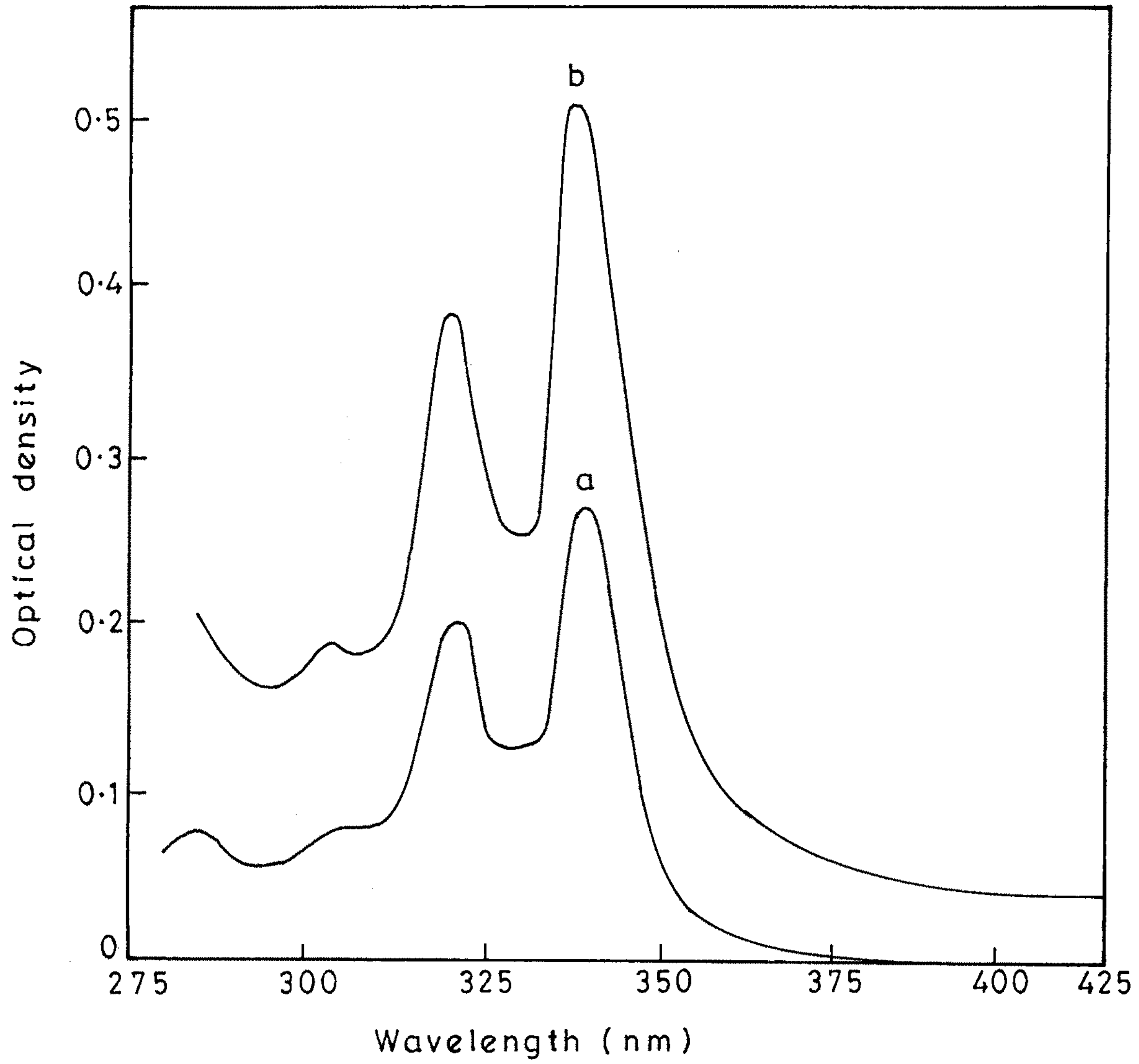


Fig. 3·2 — Absorption spectra of Pyrene doped PS films.
a) 0·1152 wt % Pyrene
b) 1·152 wt % Pyrene

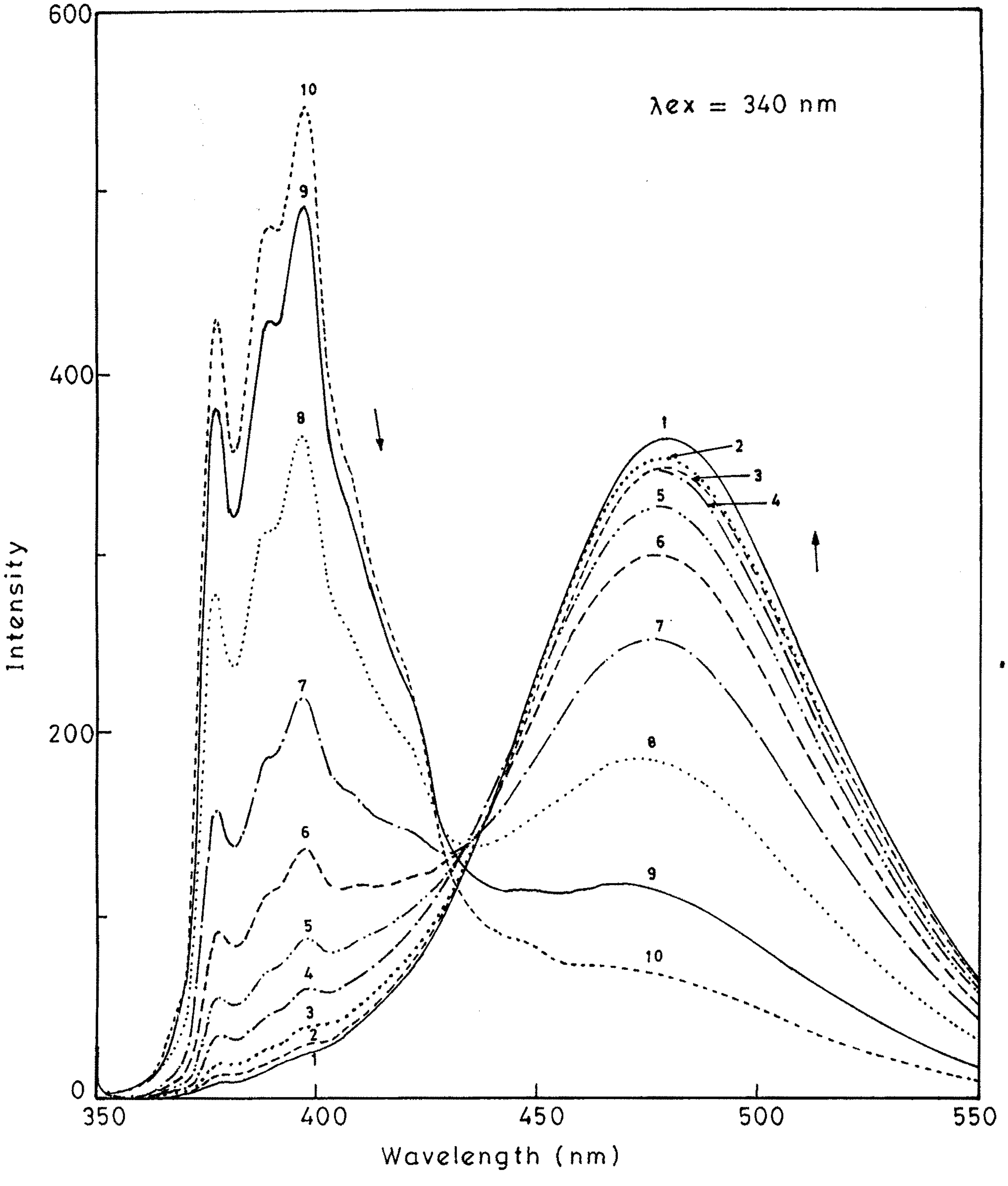


Fig. 3·3 - Fluorescence spectrum of Pyrene doped Polystyrene films - monomer to eximer transition.
1) 1·152 2) 1·0365 3) 0·9214 4) 0·8062 5) 0·6910
6) 0·5758 7) 0·461 8) 0·3455 9) 0·2303 10) 0·1728 wt % of Pyrene.

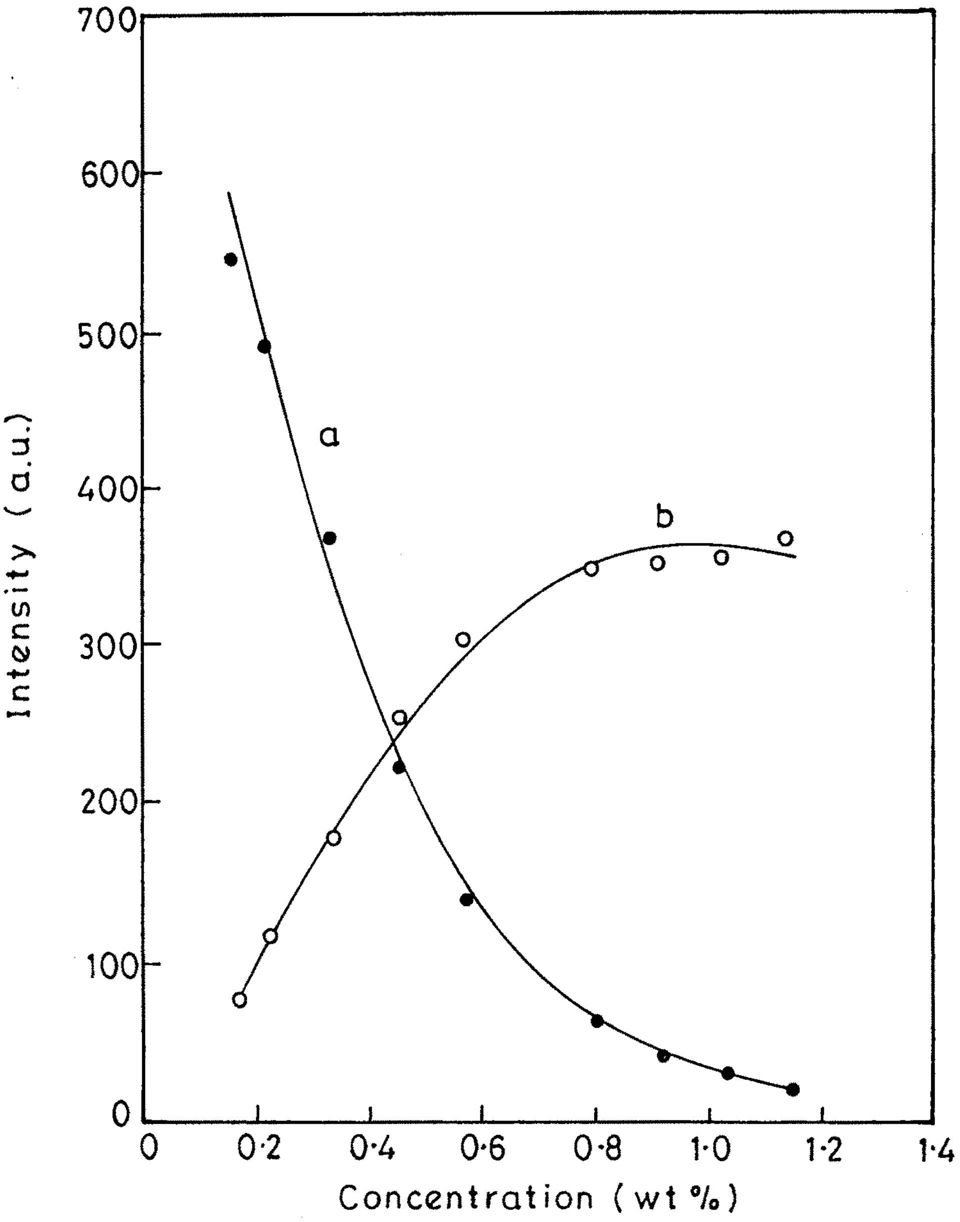


Fig. 3·4 – Fluoescence intensity dependence with weight % of Pyrene in film.
a) Monomer emission λem = (397 nm)
b) Excimer emission λem = (477 nm)

monomer and excimer intensity dependence with wt % of pyrene in the film. The emission also found to depend upon the thickness of the film. Table no.1 shows thickness of the film and emission nature. It is found that the thinner film gives monomer emission while thicker film exhibits excimer emission. Thickness variation of the films reveals a transition from monomer to excimer emission. The concentration dependence of emission peak intensity for the films of varying thickness is presented in fig. 3.5. Figure reveals the linearity for the films containing lower wt % and deviation from linearity at higher wt % of pyrene. The linearity indicating validity of Beer's law supports the monomeric emission and existence of pyrene as an isolated molecule in the films. The observed deviation indicates the aggregation of neighbouring molecules due to parallel alignment in polymer environment.

3.2 Structural characterization of the Films

The X-ray diffractogram of spin coated pyrene doped polymer film is shown in figure 3.6. X-ray diffractogram of undoped polystyrene film was substracted. The figure shows well defined peaks, which were indexed on the basis of monoclinic unit cell. The values of lattice constants of pyrene being a = 13.649 A°, b = 9.256 A°, c = 8.47 A° and β = 100.28°.[114] Calculated 'd' values are in good agreement with those reported for the bulk material in the ASTM card No. 4.0410 and given in Table – 2. This observation indicates that the film possesses same crystalline structure as that of the bulk.

The prominent band (201) was used to calculate particle size by using Scherrer formula[115]

In order to determine the grain/particle size of the pyrene a prominent peak [201] in the XRD profile was used by making use of Scherrer formula the particle size was calculated as

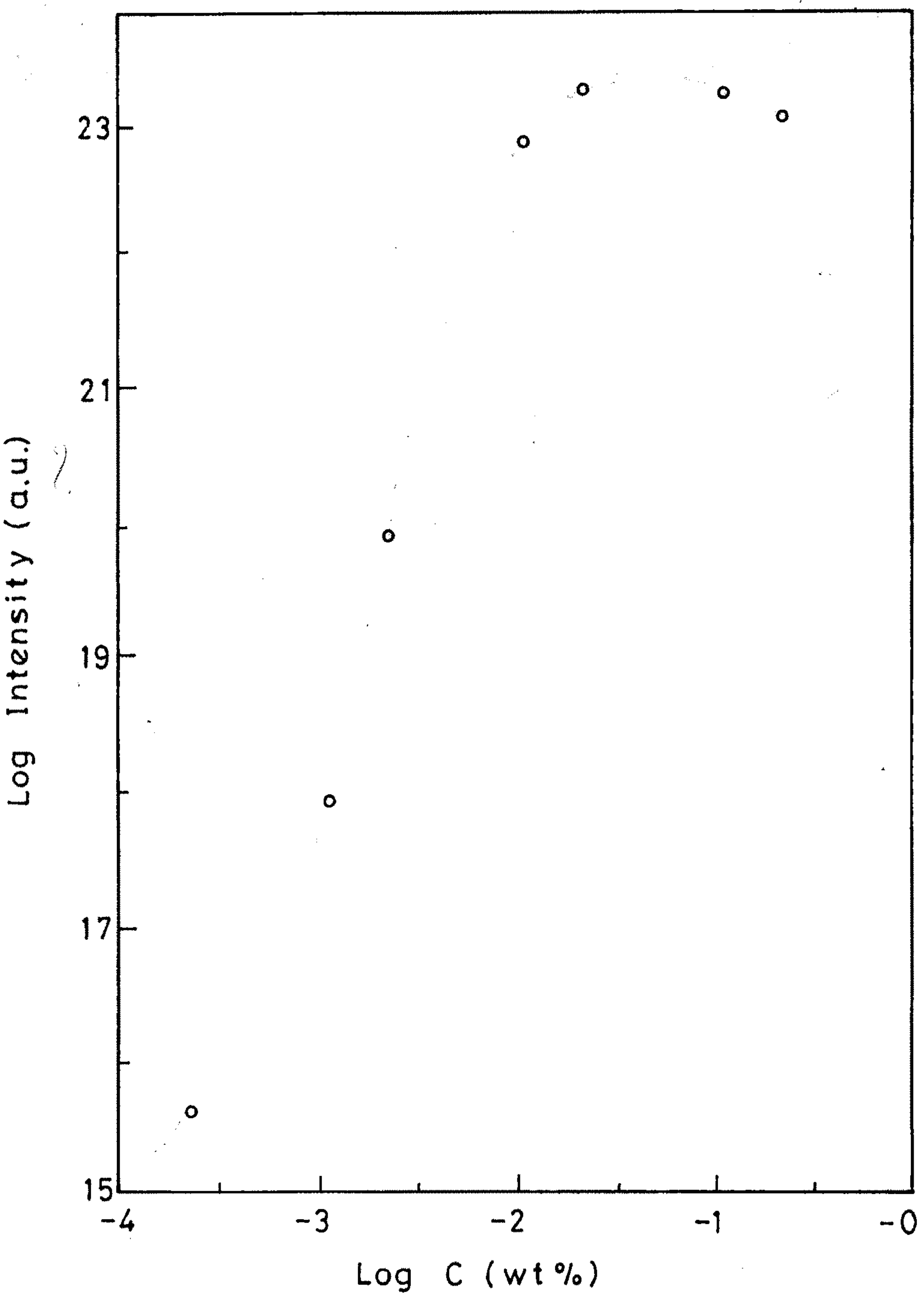


Fig. 3·5 — Concentration dependence of emission intensity with thickness of the films.

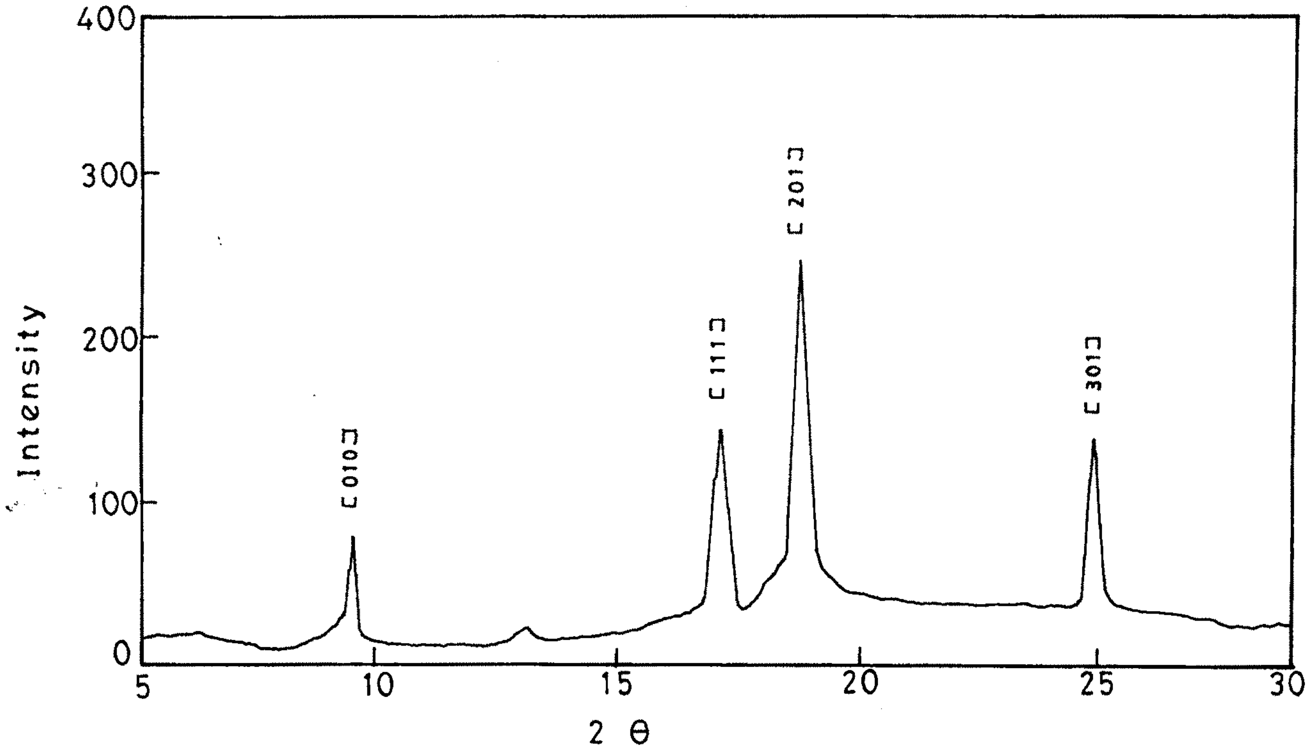


Fig. 3·6 — X-ray diffractogram of Pyrene doped PS film.

$$t = \frac{0.9\,\lambda}{B\cos\theta} \qquad \ldots \qquad (1)$$

where λ is the X-ray wavelength, 'B' is angular line width at the half maximum intensity and θ is the Bragg angle. The angular line width was obtained from the instrument directly.

The grain size is of the order of $160\ A^{o}$ and reveals the crystallanity of the film.

3.3 Absorption studies and Band gap energy estimation

Pyrene is a wide band organic semiconductor. The valence band and conduction band are separated and this band gap energy was calculated from the absorption curves. The molar absorption coefficient (α) were obtained from the absorption curve shown in fig. 3.2. and given in Table-3. The absorption spectrum of pyrene film is very much identical with its spectrum in solution state. For allowed transitions the absorption coefficient is related to the incident photon energy by the relation.[17]

$$\alpha = A\,(h\nu - Eg)^{1/2}$$

where A is constant, and Eg is the energy gap. The curve has been plotted between α^2 and $h\nu$ for the film of thickness 172 nm and is shown in fig.3.7. The value of energy gap estimated from the curve is 2.42 eV. This value is in close agreement with the value reported for pyrene film prepared by ion plating technique.[17]

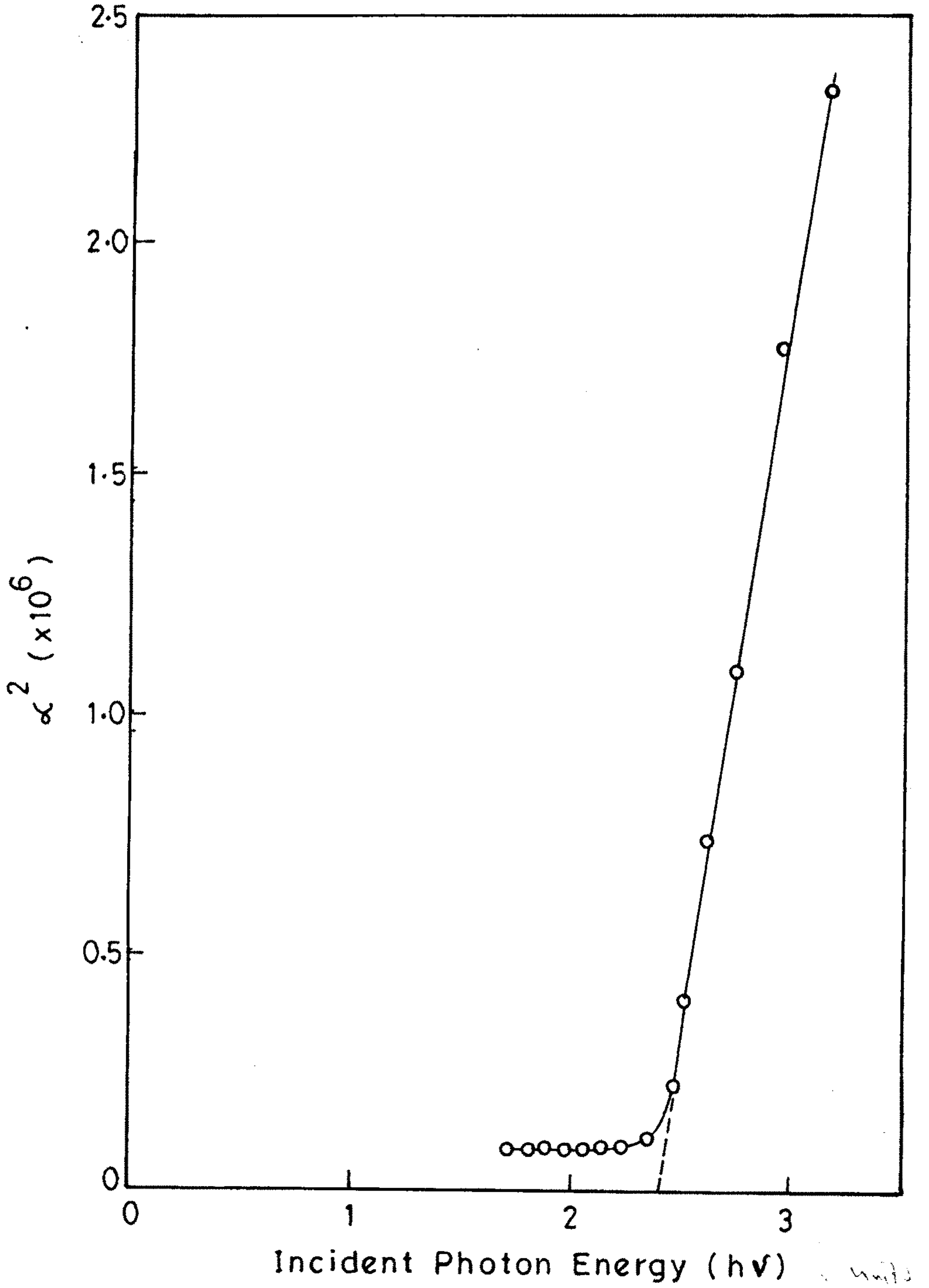


Fig. 3·7 - Curve plotted be in α^2 and hν.

Table No. 1 : Fluorescence Behaviour and Thickness of the Film.

Sr. No.	wt % of Pyrene	Thickness Å	λ_{max} (nm)	Intensity of emission at λ_{max}	
				397 nm	479 nm
1	0.1728	160.96	397	546.03	
2	0.2303	172.63	397	492.06	
3	0.3455	207.82	397, 479	368.25	177.78
4	0.4610	279.58	397, 479	222.22	253.97
5	0.5758	310.70	397,479	139.68	303.18
6	0.6910	391.14	397, 479	95.24	330.16
7	0.8062	423.27	497		349.21
8	0.9214	447.58	479		352.38
9	1.0365	478.92	479		355.56
10	1.152	520.64	479		368.56

Table No. 2 : ASTM data on bulk and experimental data on spin coating pyrene doped polymer films.

ASTM data on Bulk		Experimental data on Pyrene thin film	
d (A°)	2 θ (cal)	2 θ (obs)	d (A°) (cal)
9.2	9.7	9.6	9.06
4.84	17.61	17.0	4.67
4.23	19.13	18.7	4.13
3.58	24.7	24.6	3.56

Table No.3 : Molar Absorption Coefficient (α) and energy of wavelength ($h\nu$)

Sr.No.	$\alpha \times 10^3$	$h\nu$	$\alpha^2 \times 10^6$
1	0.3020	1.77	0.0912
2	0.3020	1.83	0.0912
3	0.3020	1.90	0.0912
4	0.3020	1.98	0.0912
5	0.3020	2.06	0.0912
6	0.3020	2.15	0.0912
7	0.3020	2.25	0.0912
8	0.3550	2.36	0.126
9	0.4785	2.48	0.229
10	0.8631	2.61	0.745
11	1.054	2.75	1.11
12	1.3454	2.91	1.81
13	1.5395	3.10	2.37

3.4 Fluorescence of Polystyrene Films doped by Perylene

Fig. 3.8 shows fluorescence spectra of polystyrene films doped by perylene. The weight of perylene were monitored from lower to higher wt % so as to obtain fluorescence properties of perylene those would be similar to solution. As per expectation fluorescence spectrum 'a' of the polymer film containing 0.00061 wt % perylene is structured and emission bands appeared at 450, 480 and at 510 nm. The maximum emission has occurred at wavelength 450 nm. This spectrum matches well with spectrum of perylene reported in literature for its dilute solution in benzene solvent.[35] It is observed that as wt % of perylene in polymer film increases, intensity of emission bands at 450 and 480 nm decreased and the band at 510 nm not only gets broadened but also slightly red shitted at wt % of perylene 0.09188 in polymer. The fluorescence spectrum of polymer film containing 0.2756 wt % is absolutely a broad band. The broad band is an indication of emission arising from excited dimer or an excimer. It is known that perylene is exhibiting its α and β excimer emission at wavelength 560 and 630 nm.[24,33-35,116] Hence the broad structureless emission observed at 510 nm is not due to an excimer but may be due to excitation of ground state dimer.

The UV absorption studies and excitation spectroscopy helps to confirm the emission at 510 nm. Fig.3.9 shows excitation spectra of perylene films containing 0.00061 wt % and 0.2756 wt % perylene and monitored at emission wavelength 450 nm (monomer emission maximum) and at 510 nm. The excitation spectra are identical in all respects except their intensities and shows sturcutred bands. The bands were observed at wavelength 410 and 420 nm. The excimer formation is indicated in excitation spectrum as broad bands. Hence absence of

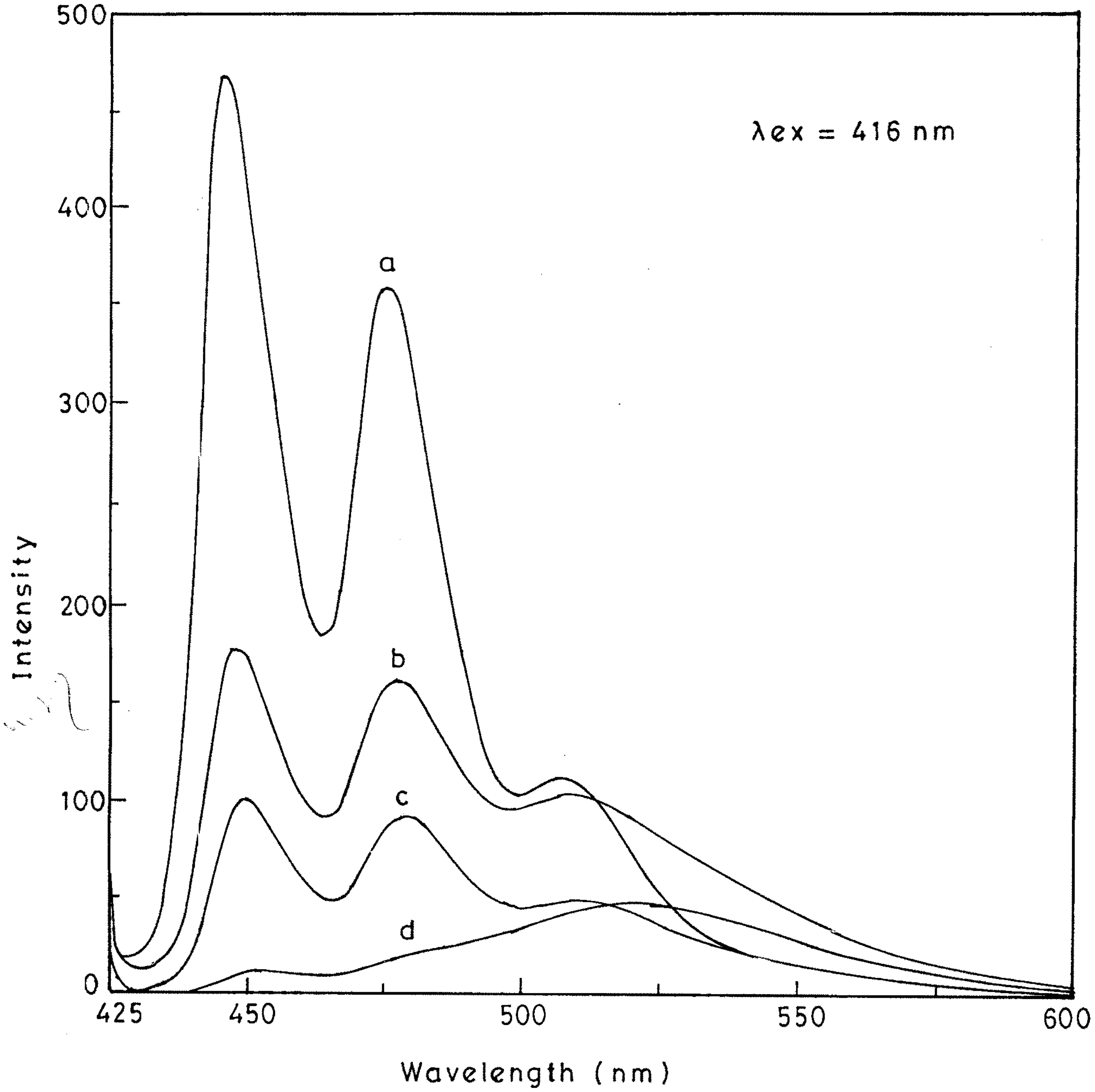


Fig. 3·8 – Fluorescence spectra of PS films doped by Perylene.
a) 0·00061 wt % b) 0·0183 wt %
c) 0·09188 wt % d) 0·2756 wt %

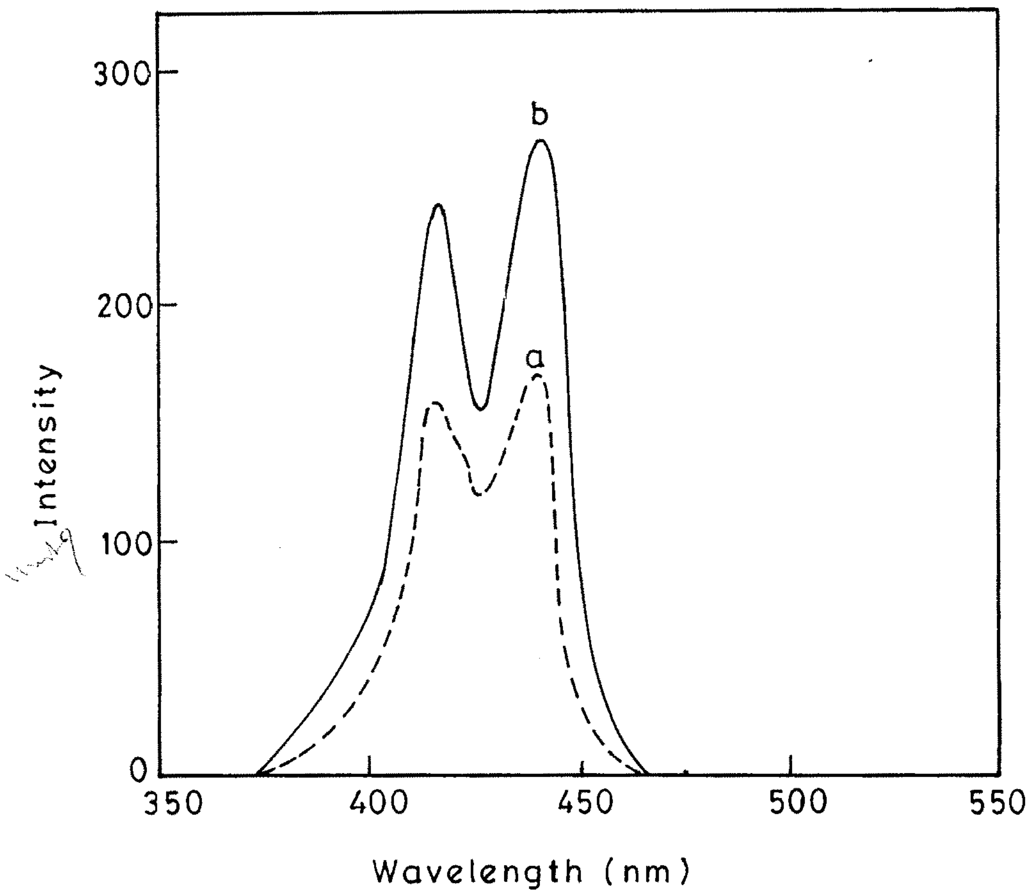


Fig. 3·9 – Excitation spectra of Perylene doped PS films.
a) (0·00061 wt %) monitered at monomer emission wavelength 450 nm.
b) (0·2756 wt %) monitored at 510 nm.

broad band suggests that the emission arising from the film containing higher wt % of perylene is not excimer emission. This conclusion is further confirmed by absorption spectrum of the films of perylene recorded onUV-visible absorption spectrophotometer. Fig.3.10 shows absorption spectra of polystyrene films containing lower and higher wt % of perylene. The spectrum containing 0.00061 wt % of perylene is structured and corresponds well with those reported for perylene in dilute solution.[35] The structured absorption spectrum indicates the monomeric nature of perylene in dilute solution and emission must be arising from single isolated molecule. However, the absorption spectrum of films, giving structureless emission is broad as compared to absorption spectrum of the film containing lower wt %. The broadening of the absorption spectrum led to assume the formation of ground state perylene dimer due to association of two neighbouring molecules in the film containing 0.2756 wt % of perylene. When such film is exposed to radiation the ground state dimer gets excited and after its life time deactivates to give structureless emission as seen at wavelength 510 nm in fig. 3.8.

3.5 Solute-Solute Interaction in Polymer Matrix : Pyrene-Perylene doped polystyrene films

Pyrene is an efficient photo absorbing material. It absorbs long wave UV radiation in the range 250-360 nm; and either emits its monomeric fluorescence or undergo energetic interactions with its ground state neighbour to form excimer. The monomer and excimer fluorescence depends upon the environment and its concentration in which it is placed. It is hoped that if the environment contain another solute with which excited pyrene can undergo energetic interaction or by energy transfer may activate the solute to emit its characteristic fluorescence. With this view, polystyrene films were doubly doped by pyrene and perylene. The concentration of one in relation to other is systematically varied so as to

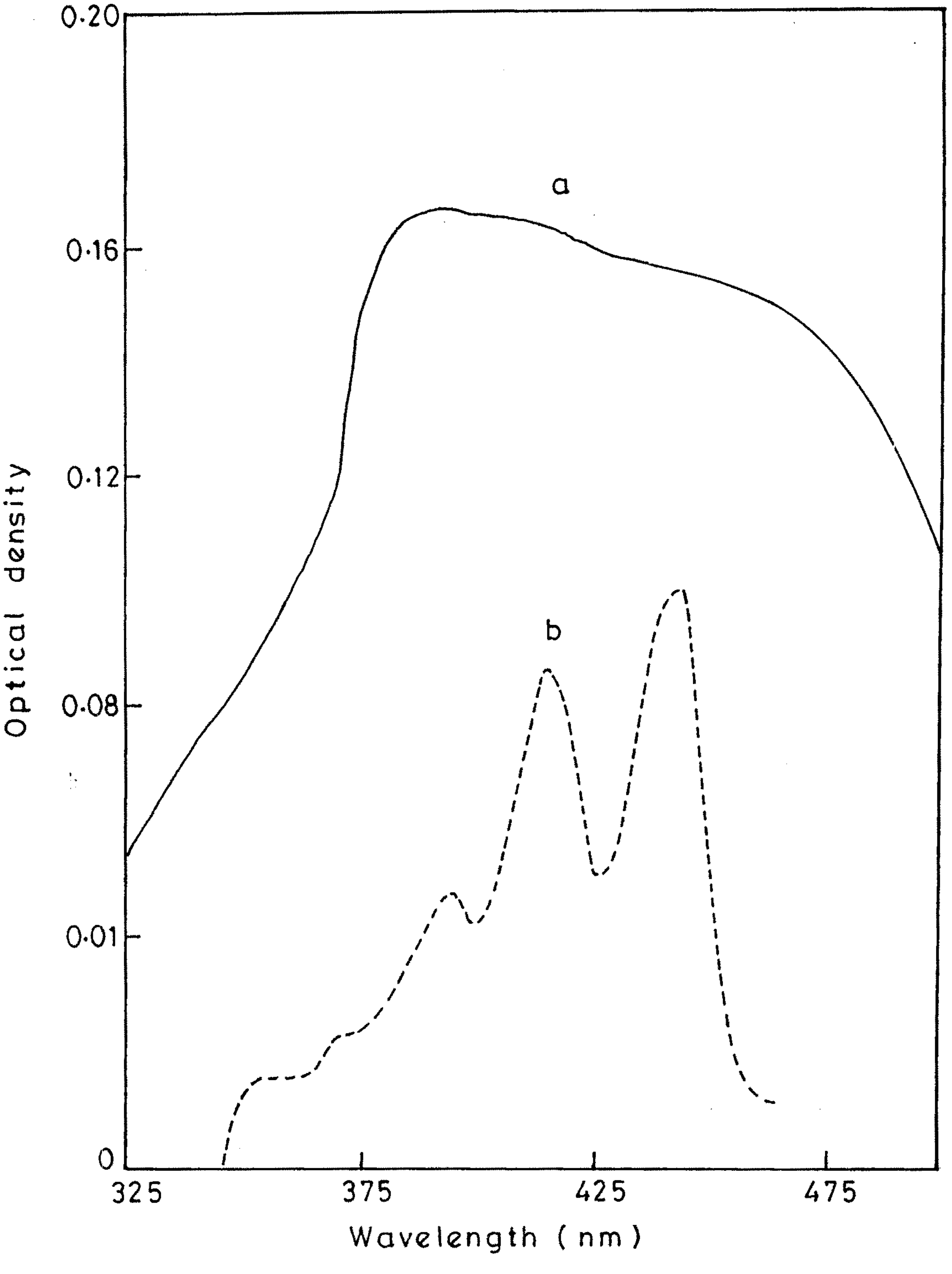


Fig. 3·10 - Absorption spectra of perylene doped polystyrene thin films a) 0·2756 wt % b) 0·00061 wt % .

obtain interesting emission properties in polymer matrix. The perylene is chosen because it is known to have energetic interactions with pyrene in their condensed systems.[117] Such energetic interactions are not yet observed in their solutions and films.

Fig. 3.11 represents fluorescence spectra of pyrene and perylene doped monolayer films of polystyrene. All the spectra were recorded by monitoring excitation wavelength to 340 nm which corresponds to pyrene excitation energy. The concentration of pyrene is kept constant to 0.1728 wt % which exhibits monomer fluorescence while that of perylene is varied from 0.00027 to 0.9188 wt %. Spectrum No.1 is monomer emission of pure pyrene without perylene. A careful observation of the spectra shown in figure reveals that the pyrene monomer fluorescence is quenched gradually as concentration of perylene in the film increases. It is also observed that another structured emission band appears in the region 420-500 nm. This region corresponds to perylene monomer emission as is described in section 3.4. The perylene monomer emission found to increase with concentration of perylene in polystyrene film. The film containing 0.08262 perylene exhibited the complete quenching of pyrene as well as perylene monomer. However, on further increase in perylene concentrations a new structureless emission band with maximum emission at about 520 nm has appeared in the fluorescence spectra of polystyrene film with increase in concentration of perylene above 0.08262 wt %, the intensity of this emission band seems to increase. The spectrum no.11 is of the film prepared from 0.1728 wt % of pyrene solution saturated by perylene (0.9188 wt % perylene).

Polystyrene films containing pyrene and perylene were excited by wavelength 340 nm which corresponds to excitation energy of pyrene. Therefore in the film pyrene molecules get excited to their first excitated singlet level. The

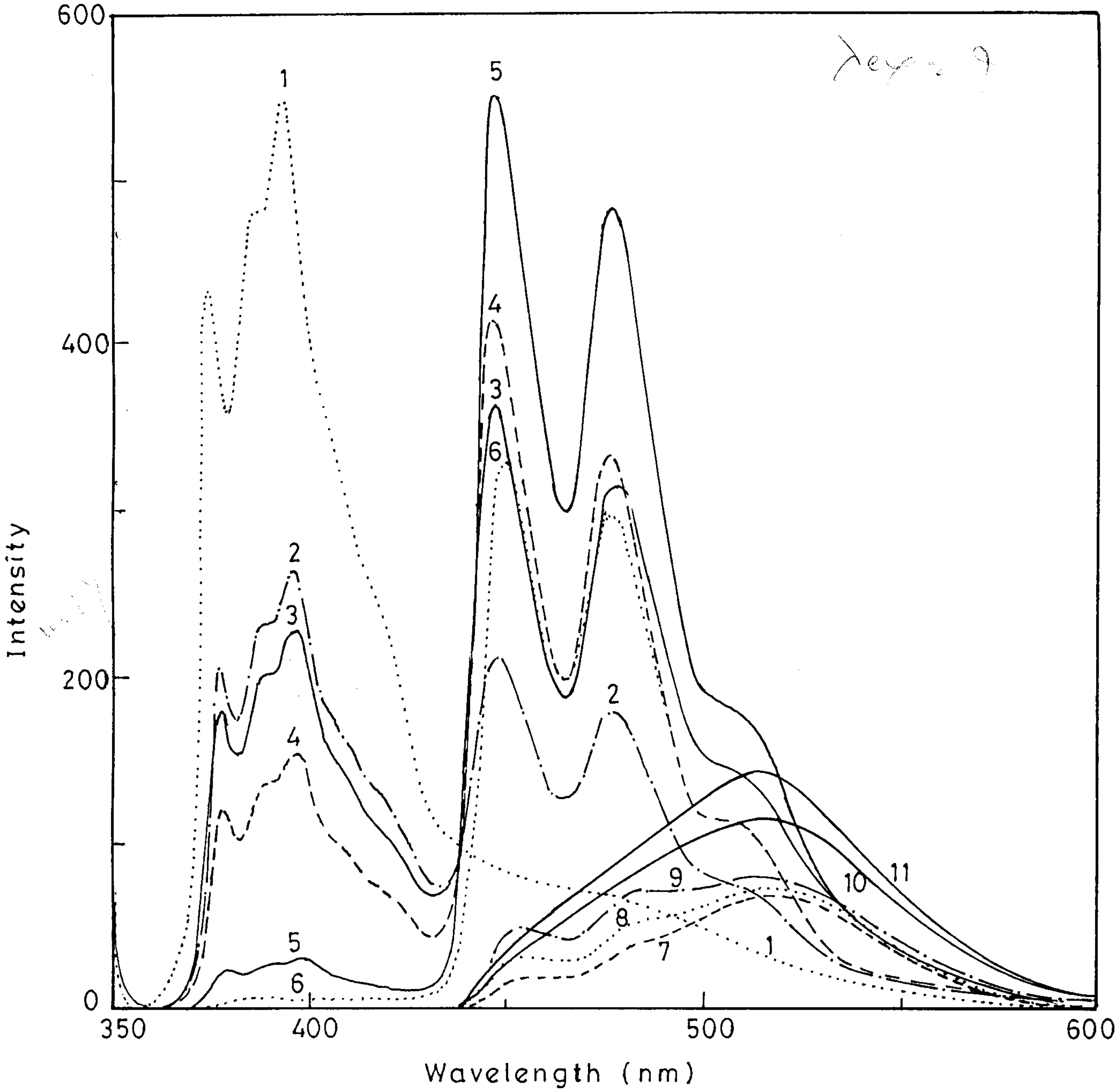


Fig. 3·11 - Fluorescence spectra of Polystyrene film doped by Pyrene and Perylene

1) 0·1728 wt % Pyrene (without Perylene) and

2-11) Spectra containing 0·1728 wt % Pyrene and varying amounts of Perylene.

2) 0·00027 wt %   3) 0·00137 wt %   4) 0·00275 wt %
5) 0·01378 wt %   6) 0·02756 wt %   7) 0·08262 wt %
8) 0·1105 wt %   9) 0·1385 wt %   10) 0·25394 wt %
11) 0·9188 wt %

structured emission observed in the film without perylene is its monomeric emission. The presence of perylene in the film quenches pyrene monomer emission may be because of EET from excited pyrene to ground state perylene. The efficient EET probability is indicated by the strong overlap observed between monomer emission spectrum of pyrene and excitation spectrum of perylene shown in fig. 3.12. Thus excited pyrene transfer its energy to ground state perylene to form singlet excited perylene. The observed structured emission in the range 430-510 nm must be due to deactivation of singlet excited perylene radiatively. The emission in this range are therefore assigned to perylene monomer emission. The higher perylene concentrations in the film completely quenches pyrene monomer emission as well as perylene monomer emission, which may be due to the fact that at higher concentrations lateral π orbital overlap between adjacent pyrene and perylene molecule increases which favours energetic interaction to form dimeric species between excited perylene and neighbouring ground state pyrene. The heterodimeric species is responsible for structureless, broad emission observed in the region 450-600 nm with maximum emission at about 520 nm. This band is assigned to well known exciplex emission of pyrene and perylene occurring in the polystyrene film. Following mechanism is proposed to explain observed emission from doubly doped polystyrene films.

Presentation	Process
$Py_{(So)} + h\nu \longrightarrow Py^{*}_{(S1)}$	Pyrene excited
$Py^{*}_{(S1)} \longrightarrow Py_{(So)} + h\nu_f$	Pyrene manomer emission.
$Py^{*}_{(S1)} + Pe_{(So)} \longrightarrow Py_{(So)} + Pe^{*}_{(S1)}$	Excited energy transfer.
$Pe^{*}_{(S1)} \longrightarrow Pe_{(So)} + h\nu_f$	Perylene monomer emission.
$Pe^{*}_{(S1)} + Py_{(So)} \longrightarrow [PePy]^{*}$	Exciplex formation.
$[PePy]^{*} \longrightarrow Pe_{(So)} + Py_{(So)} + h\nu_f$	Exciplex emission.

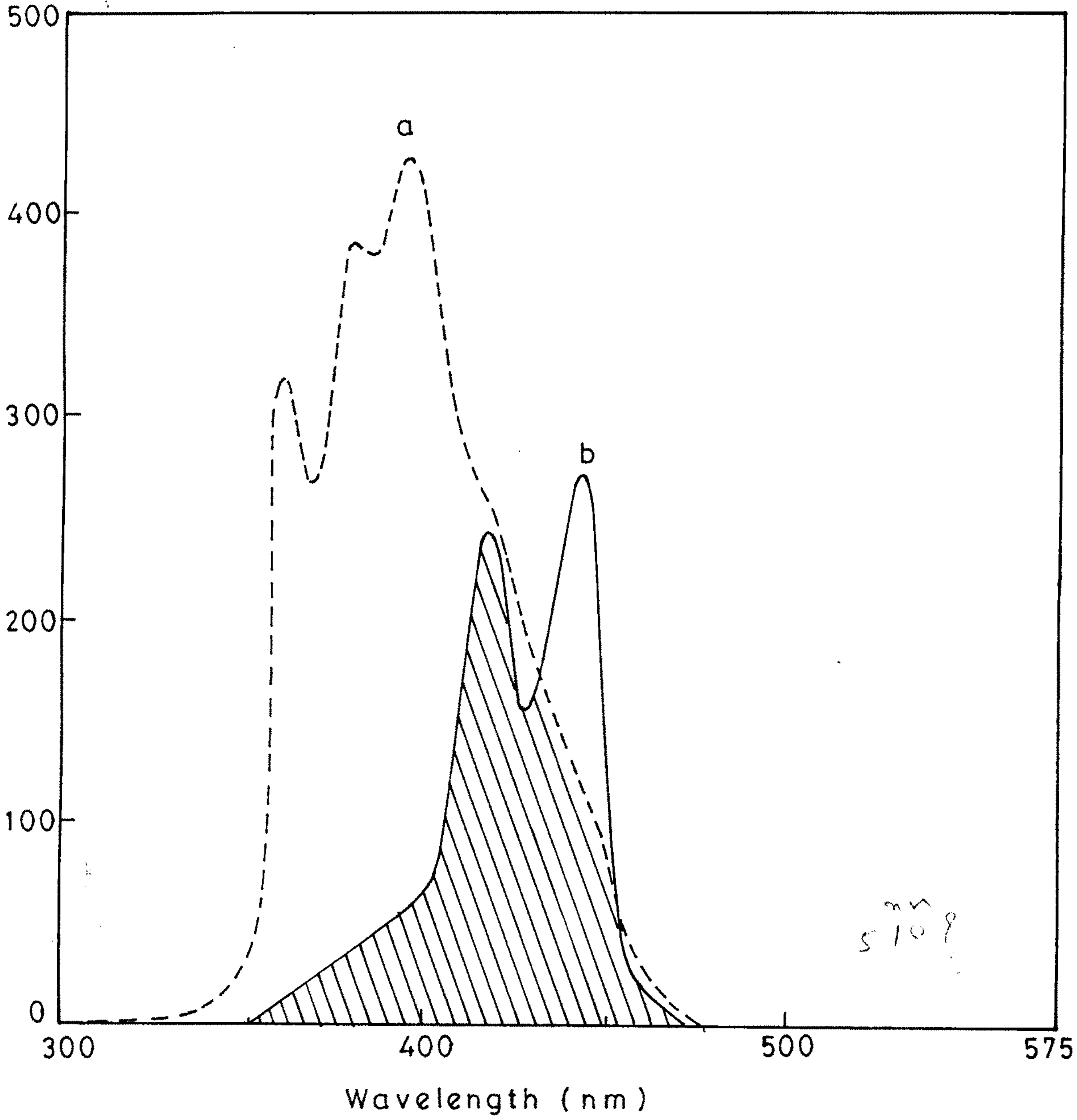


Fig. 3·12 - Excitation spectrum of Perylene and emission spectrum of Pyrene in Polystyrene film.
Region of overlap shown by shaded lines
a) Emission spectrum of Pyrene monitored at 340 nm.
b) Excitation spectrum of Perylene monitored at 450 nm.

Films of pyrene and perylene in polystyrene matrix have also been prepared by changing concentrations. Fig.3.13 shows spectrum 'a' of the film~~s~~ cointaining 0.27564 wt % perylene and 0.001152 wt % pyrene in polymer. The spectrum reveals perylene monomer emission while pyrene monomer is quenched by larger amount of perylene. The expected perylene dimeric emission is also not observed. In contrast when wt % of perylene is low and that of pyrene is high i.e. 0.00061 perylene and 1.152 wt % pyrene, then spectrum 'b' appears as shown in the same figure. The spectrum shows broad excimer emission of pyrene and emission of perylene are absent. This is due to the fact that at higher pyrene concentration, the tendency of pyrene molecule to form excimer dominates rather than to transfer excitation energy (EE) to perylene molecule. Hence for exciplex emission between pyrene and perylene to occur it is necessary to maintain low wt. % of pyrene corresponding to its monomer emission. The advantage of the studies is that when perylene alone containing 0.27564 wt % in the film is excited by 340 nm radiation, it could not fluoresce and only a base line is recorded as shown in Fig. 3.14 (spectrum d). However, when pyrene absorbing 340 nm radiation strongly is present with perylene, both perylene monomer and its dimeric emissions are highly sensitized by excited pyrene due to excitation energy transfer. By controlling amount of perylene in polymer, (pyrene) the emission of the polymer film can be tuned from violet to green.

3.6 Fluorescence and Absorption Studies of Naphthalene doped Polymer films

Polystyrene solubalise naphthalene in benzene solution. Thin polystyrene films doped by Naphthalene molecules were prepared and their fluorescence and absorption spectra were recorded. Fig. 3.15 shows absorption, excitation and fluorescence spectra of the naphthalene in polystyrene films. The excitation spectrum monitored at 350 nm is structured and shows bands at 263, 314 and 360

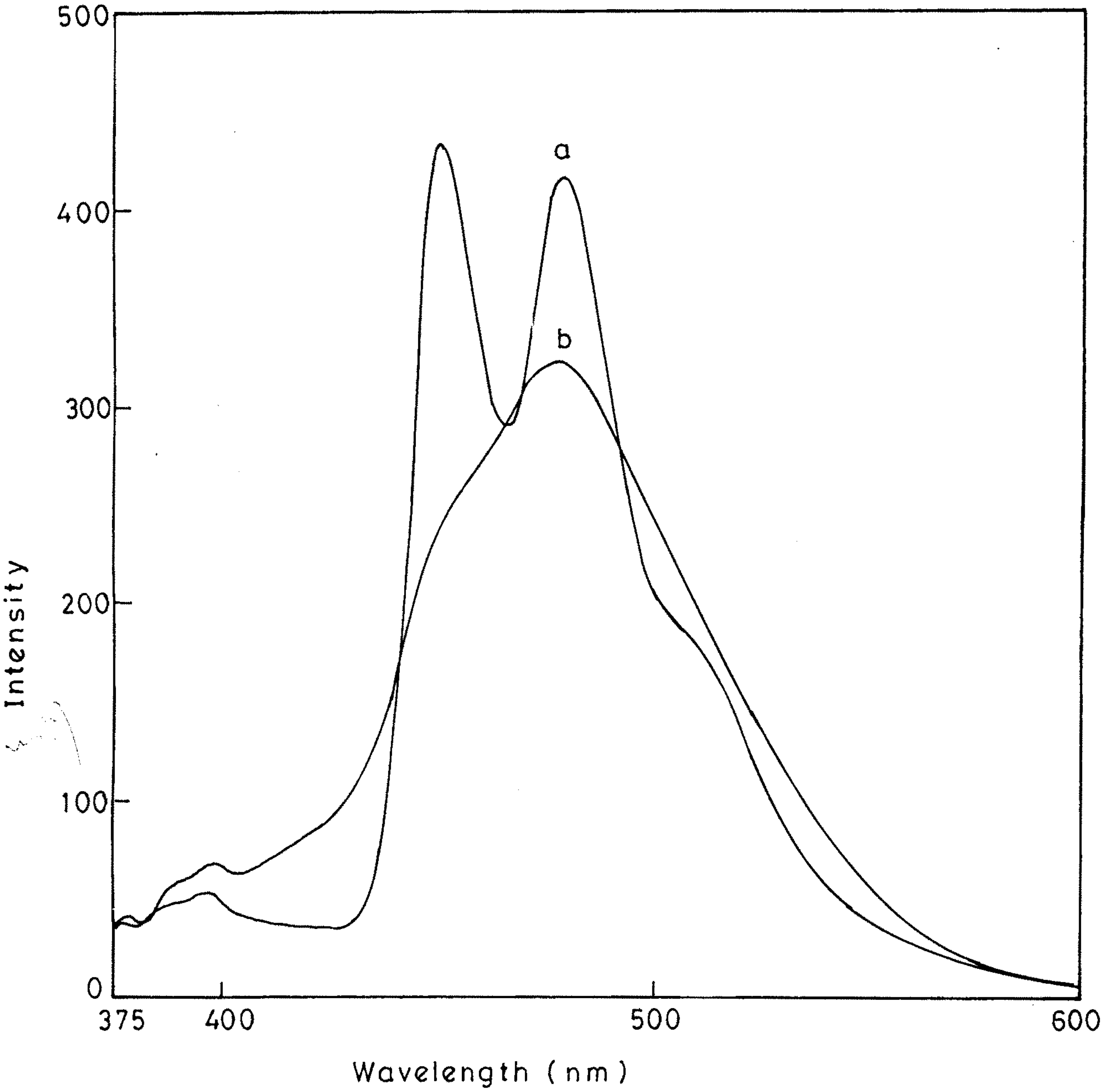
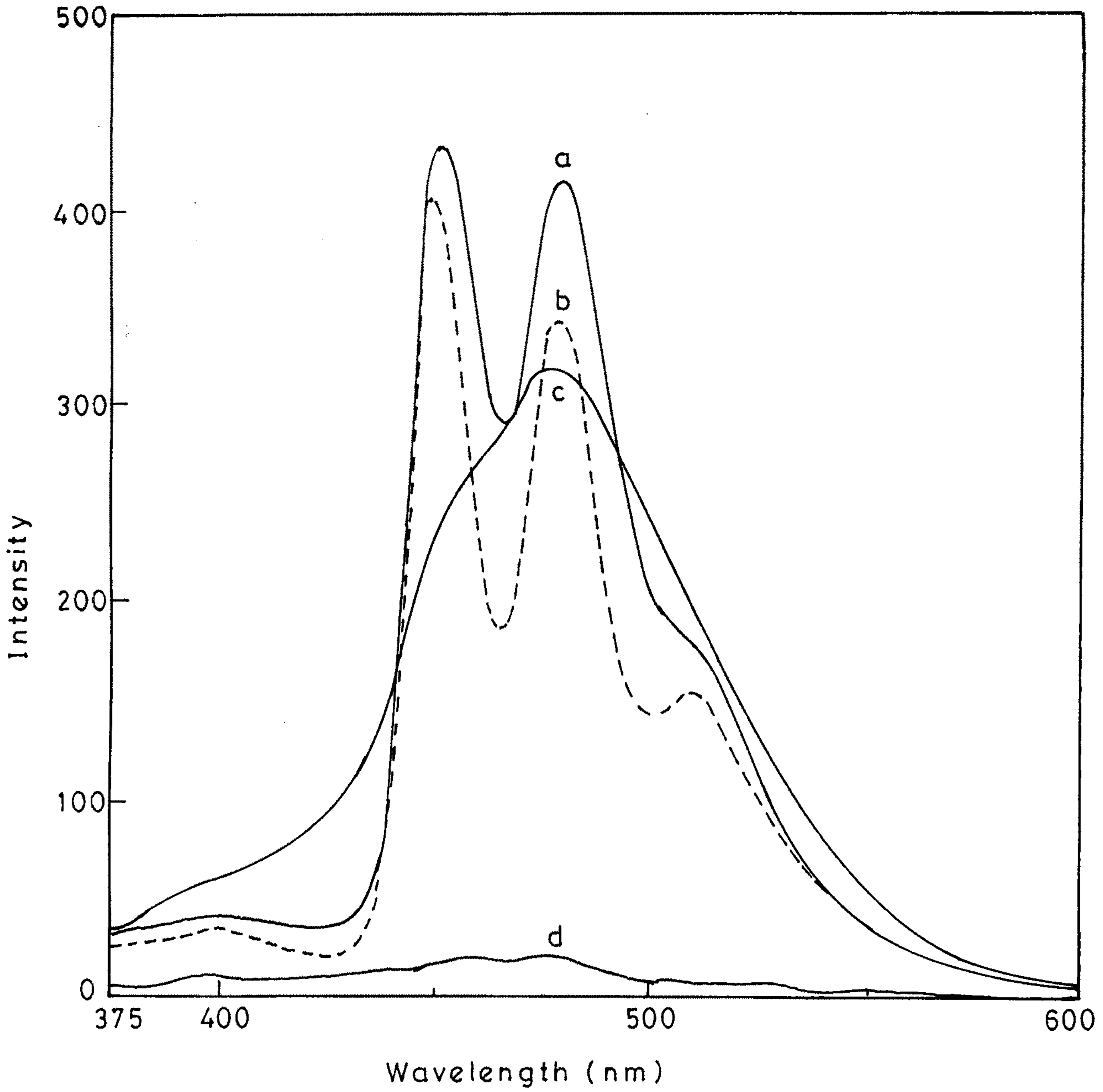


Fig. 3·13 – Fluorescence spectrum of PS films containing varying amounts of Pyrene and Perylene.

a) Pyrene (0·001152 wt %) + Perylene (0·27564 wt %)

b) Pyrene (1·152 wt %) + Perylene (0·00061 wt %)



[illegible]

Fig. 3·14 - Fluorescence spectrum of PS films containing varying amounts of Pyrene and Perylene.

a) Pyrene (0.001152 wt %) + Perylene (0·27564 wt %)
b) Pyrene (1·152 wt %) + Perylene (0·27564 wt %)
c) Pyrene (1·152 wt %) + Perylene (0·000609 wt %)
d) Perylene (0·27564 wt %)

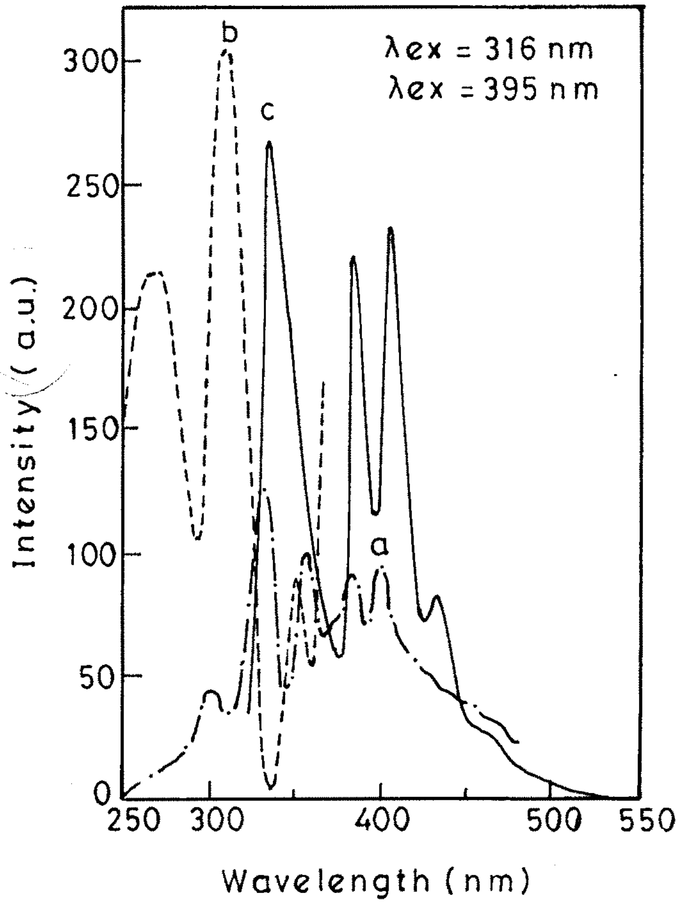


Fig. 3·15 - Absorption (a) Excitation (b) and Fluorescence (c) spectra of Naphthalene doped PS film.

nm. The intensity of the excitation band is maximum at the wavelength 314 nm. Hence the fluorescence spectra of naphthalene doped polystyrene films were monitored at excitation wavelength 314 nm.

The absorption spectrum is structured and has vibrational envelope at the wavelengths 263, 314 and 360 nm the maximum absorption being at the wavelength 314 nm. The absorption spectrum is slightly red shifted in comparison with its excitation spectrum. However excitation and emission spectra are mirror images of each other. The fluorescence spectrum is structured and has emission bands at 328, 340, 377, 397, 425 nm. The structured emission band indicates that the emission is arising from single molecule. Thus naphthalene exists as isolated molecule in polystyrene matrix. The possibility of aggregation of naphthalene molecules in polystyrene matrix has been checked from the fluorescence of polystyrene films containing varying amounts of naphthalene. The spectra of the films are shown in fig.3.16.

From the Fig. 3.16, it is seen that all the spectra are structured and identical in shape. The emission bands are observed at the wavelength 328, 340, 377, 397, 425 and 444 nm with maximum emission at 425 nm. The naphthalene emission has occurred in a wide range i.e. UV as well as violet region of the spectrum. It is also seen that as the concentration of naphthalene increases the emission band observed in UV region gets quenched in comparison to the bands observed in the visible region. At higher concentration of naphthalene 4.531 wt % the emission band in UV region is completely quenched and bands observed in the visible region become prominent.

The mirror image relationship observed between excitation and fluorescence spectra further indicates the monomeric emission from naphthalene in polystyrene matrix. Thus when polystyrene film doped by naphthalene is

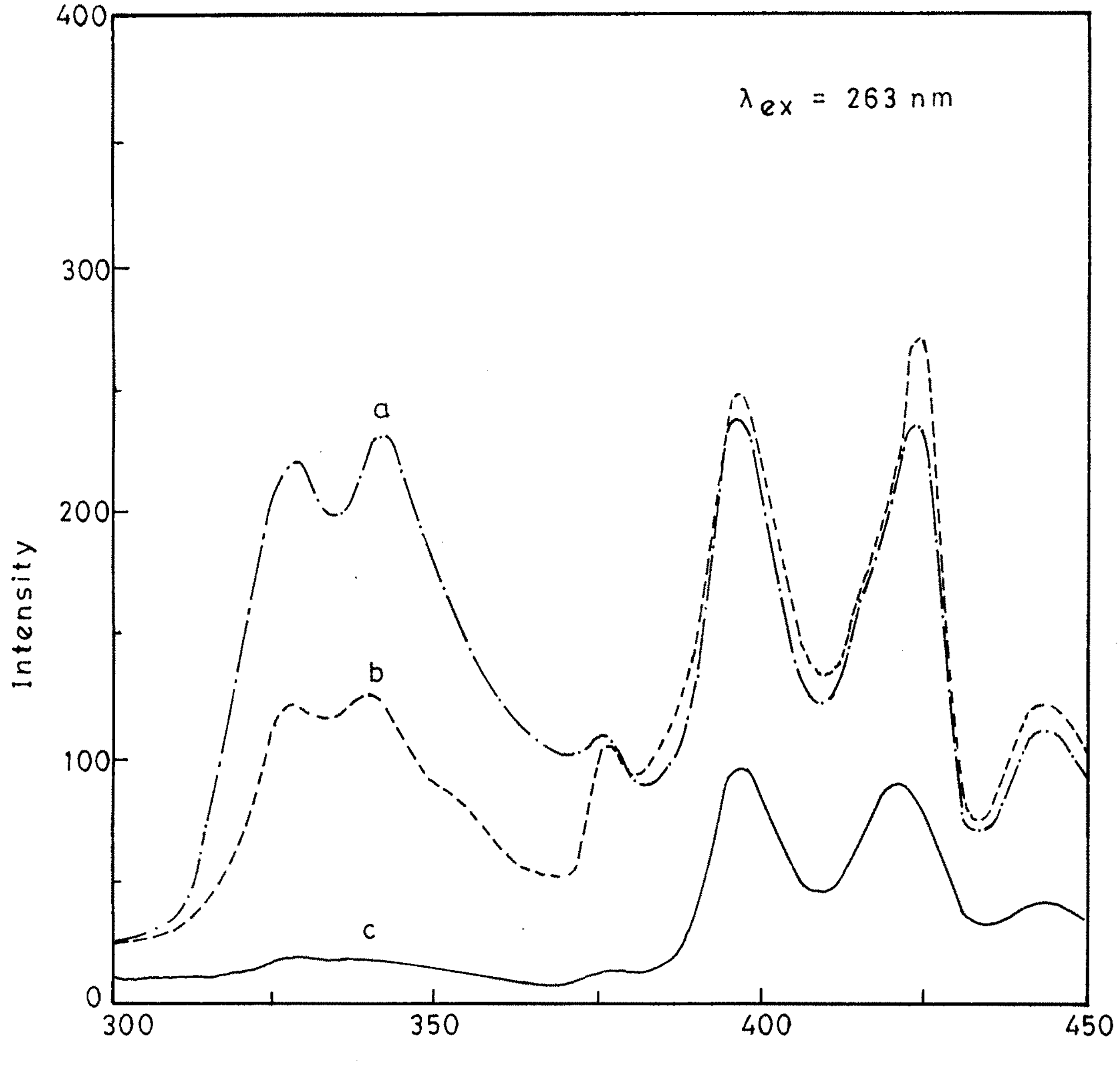


Fig. 3·16 – The fluorescence spectra of PS films containing varying wt % of Naphthalene

a) (1·1327 wt %) Naphthalene

b) (0·02266 wt %) Naphthalene

c) (4·531 wt %) Naphthalene

excited by long wave UV radiation (314 nm), the naphthalene is excited to its first excited singlet level. The excitation radiation (314 nm) corresponds to excitation energy of naphthalene and therefore from the polystyrene film only naphthalene is excited, as excitation of polystyrene requires radiation having wavelength below 250 nm.

The first singlet excited naphthalene deactivates after its life time and gives monomeric emission from single naphthalene molecule. The spectrum of naphthalene in polystyrene even at higher wt % is not modified spectrally. This suggests that the aggregation of naphthalene molecule in polystyrene is not possible. The mechanism of fluorescence emission is explained stepwise as given below

Presentation	Process
$NP_{(So)} + h\nu \longrightarrow NP^{*}_{(S1)}$	excitation
$NP^{*}_{(S1)} \longrightarrow NP_{(So)} + h\nu_f$	naphthalene monomer emission

3.7 Solute-Solute interaction in polymer matrix : Naphthalene –Pyrene doped PS films

Naphthalene doped polymer films are emitting in the region 300-400 nm. Pyrene has strong absorption in this region.[80] Therefore, it is believed that pyrene present with naphthalene could trap its excitation energy and may exhibit its monomer or excimer fluorescence which could be more intense than films without naphthalene. The pyrene and naphthalene doped polystyrene films were excited by the radiation corresponding to excitation energy of naphthalene i.e. long wave UV radiation (314 nm). Fig.3.17 shows fluorescence spectra of naphthalene doped PS(1), Pyrene doped PS(2) and pyrene and naphthalene doped PS (3). From the figure it is seen that the spectrum of pyrene and naphthalene doped PS films show

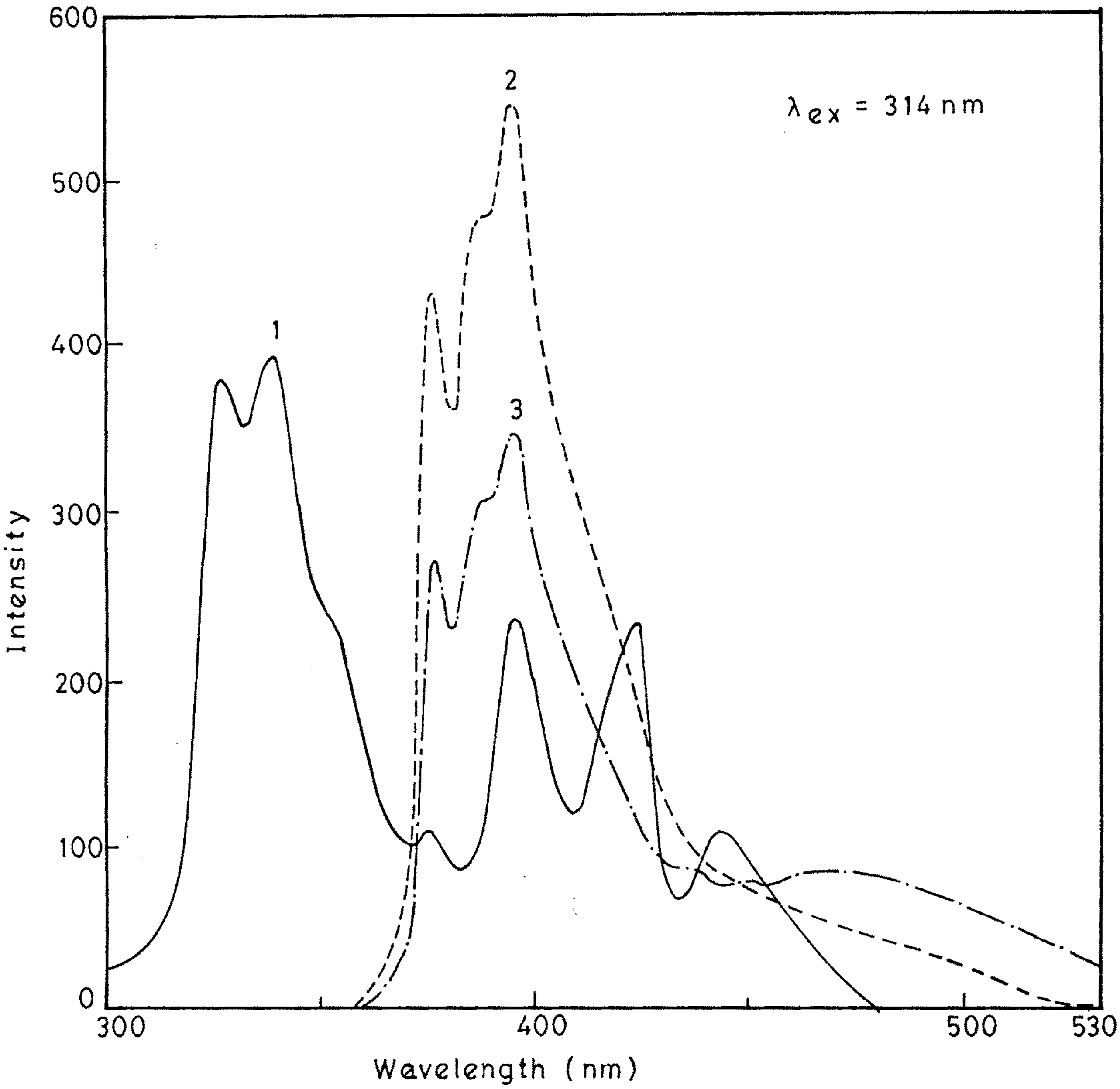


Fig. 3·17 Fluorescence spectrum of Polystyrene doped by Naphthalene (1) doped by Pyrene (2) and doped by Pyrene and Naphthalene (3).

structured manomer fluorescence of pyrene and a broad, featureless tail towards longer wavelength side. The fluorescence of naphthalene is not seen in the spectrum 3. When pyrene was excited without naphthalene at 314 nm its fluorescence found very weak and the concentration 0.17275 wt % gives pyrene manomer fluorescene.

Fluorescence spectra of polystyrene doped by pyrene (0.17275 wt %) and varying amounts of naphthalene are shown in Fig.3.18. Naphthalene concentration is varied in the range 0.04531 wt % to 1.813 wt %. The concentration of pyrene is kept constant to a value 0.17275 wt % in polystyrene which corresponds to its monomer emission. The variation in naphthalene concentration has quenched pyrene monomer fluorescence. The spectrum 'b' containing 0.04531 wt % naphthalene quenches pyrene monomer fluorescence from 540 iu to 350 iu and a tail appears towards red. The gradual increase in naphthalene concentration quenches pyrene fluorescence and intensity of broad, featureless band increases. The film containing 1.813 wt % naphthalene shows a more pronounced broad band with maximum emission at 480 nm. This band does not correspond with excimer of pyrene having maximum emission at 470 nm. Hence, this band is attributed to as arising due to exciplex formed between NP and pyrene by energy transfer process.

Attempts have been made to enhance the exciplex emission band by increasing concentration of naphthalene as well as pyrene. It is found that keeping naphthalene wt % constant and varying that of pyrene in polystyrene films, the exciplex emission remain unchanged. However, when concentration of naphthalene is increased, the exciplex emission band is enhanced as shown in figure 3.19. This observation suggests that naphthalene forms exciplex with pyrene and observed emission is not of pyrene excimer, expected to occur at

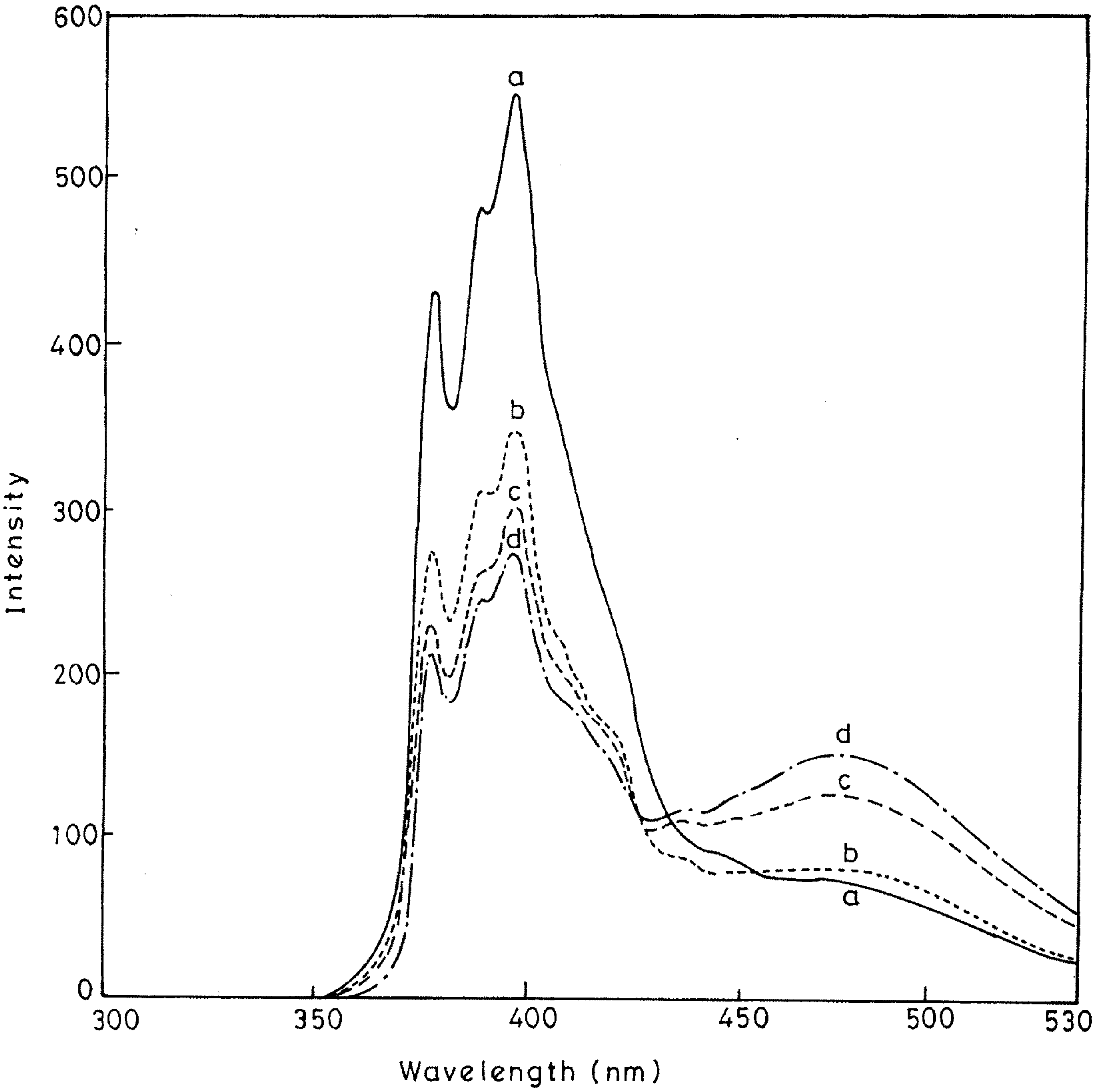


Fig. 3·18 – Fluorescence spectra of PS films doped by Pyrene (0·17275 wt %) and varying wt % of Naphthalene.

a) (0·17275 wt %) Pyrene.
b) (0·17275 wt %) Pyrene + (0·04531 wt %) Naphthalene.
c) (0·17275 wt %) Pyrene + (1·1327 wt %) Naphthalene.
d) (0·17275 wt %) Pyrene + (1·813 wt %) Naphthalene.

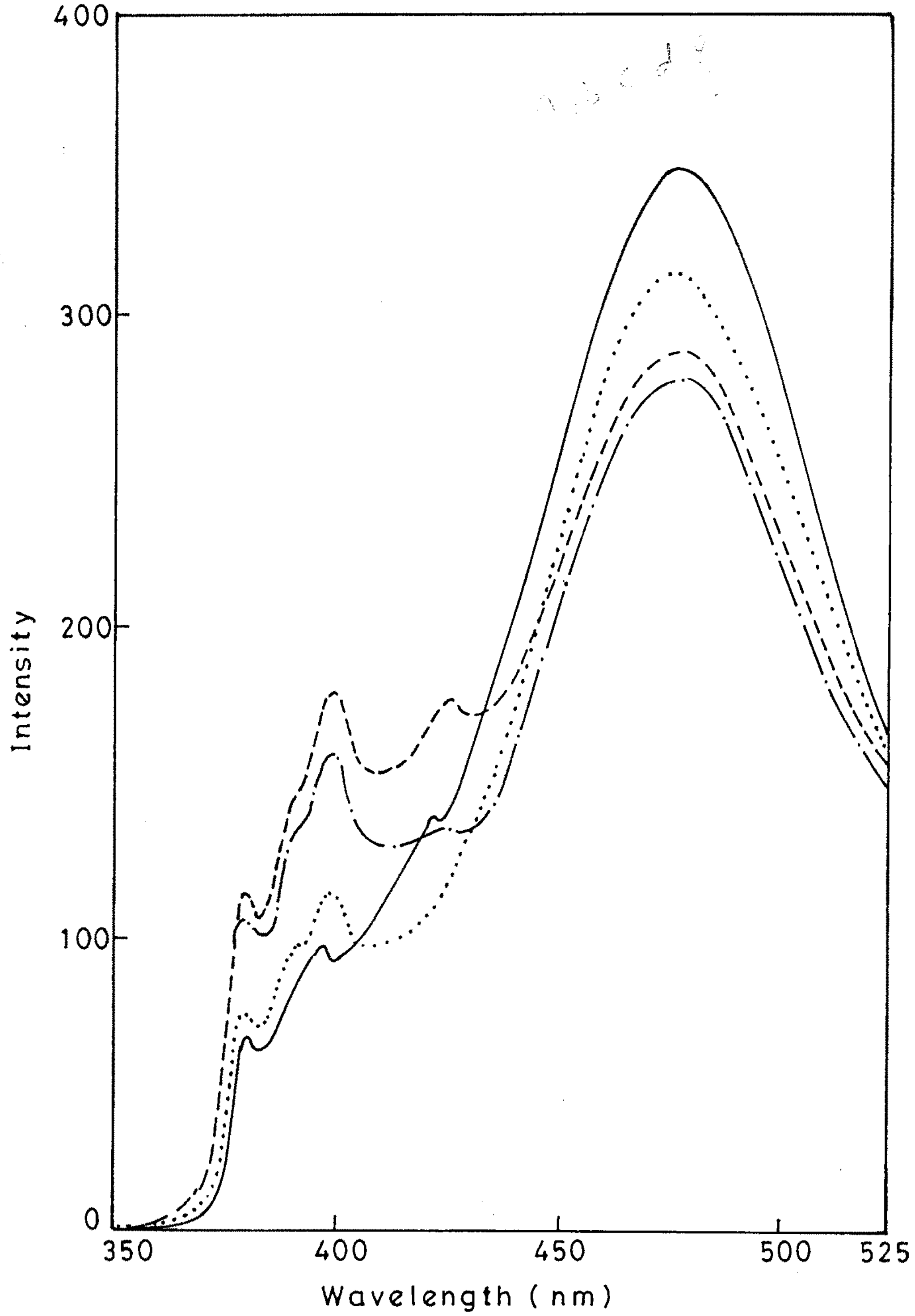


Fig. 3·19 - Fluorescence spectra of PS films containing 0·1728 wt % Pyrene and varying wt % of Naphthalene.
a) (4·531 wt %) b) (2·2655 wt %)
c) (1·813 wt %) d) (1·359 wt %)

479 nm. Naphthalene is also known to serve as efficient donor of energy in condensed system[118] and results of fluorescence studies on naphthalene in polystyrene films have exhibited its capacity to form exciplex by π-orbital overlapping between adjacent molecules.

The observed exciplex emission is further confirmed by excitation and absorption spectroscopy. Figure 3.20 shows UV-visible absorption spectra of naphthalene doped polystyrene film (a) and polystyrene film doped by Np and Py (b) The structured spectrum of Np in film is not modified in presence of Py as is seen in spectrum 'b' which reveals characteristic absorption bands of both Py and Np. The modification in the form of red or blue shifted bands and band broadening generally indicates association or complex formation in the ground state between solute molecules. The absence of modification in UV-visible absorption spectrum indicates that ground state heterodimeric species formation is not probable in the film environment. This observation is further supported by excitation spectra of above films are containing only Np and other containing both Np and Py. shown in fig 3.21 The excitation spectrum Np doped film is bonded. However, in presence of pyrene these bands appear to be quenched and broad band with maximum at ≃ 400 nm is seen in the spectrum 'b'. The broad band is an indication of formation of heterodimeric species in the excited state between pyrene and naphthalene.

3.8 Mechanism of Exciplex Formation and Emission.

The polystyrene film of pyrene and naphthalene was excited by using excitation wavelength corresponding to Naphthalene excitation energy as was determined from excitation spectrum of PS doped by naphthalene (fig. 3.15). From Fig. 3.20 it is seen that absorption region of naphthalene and pyrene are separated. Hence in presence of pyrene the naphthalene can be selectively excited

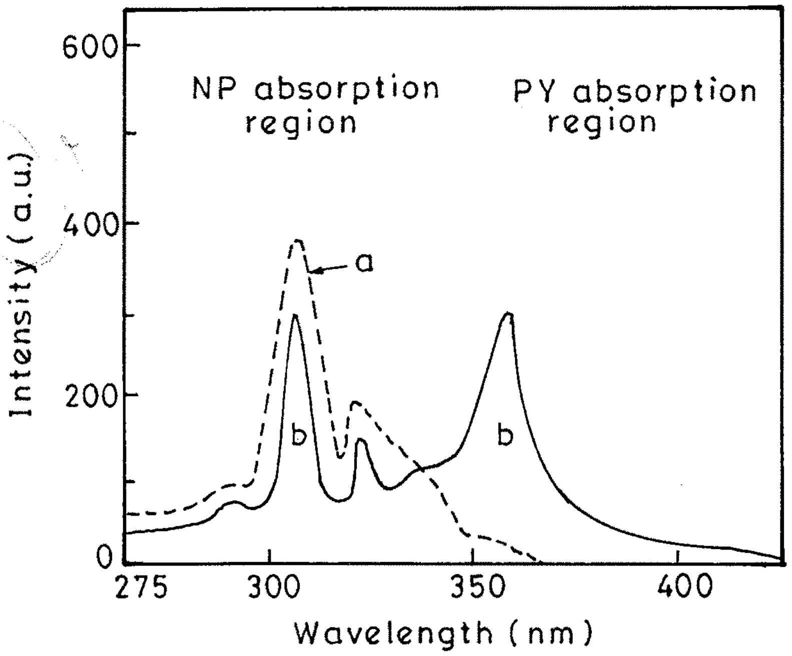


Fig. 3·20 - Absorption spectra of Naphthalene doped PS films (a) and PS doped by Naphthalene and Pyrene (b).

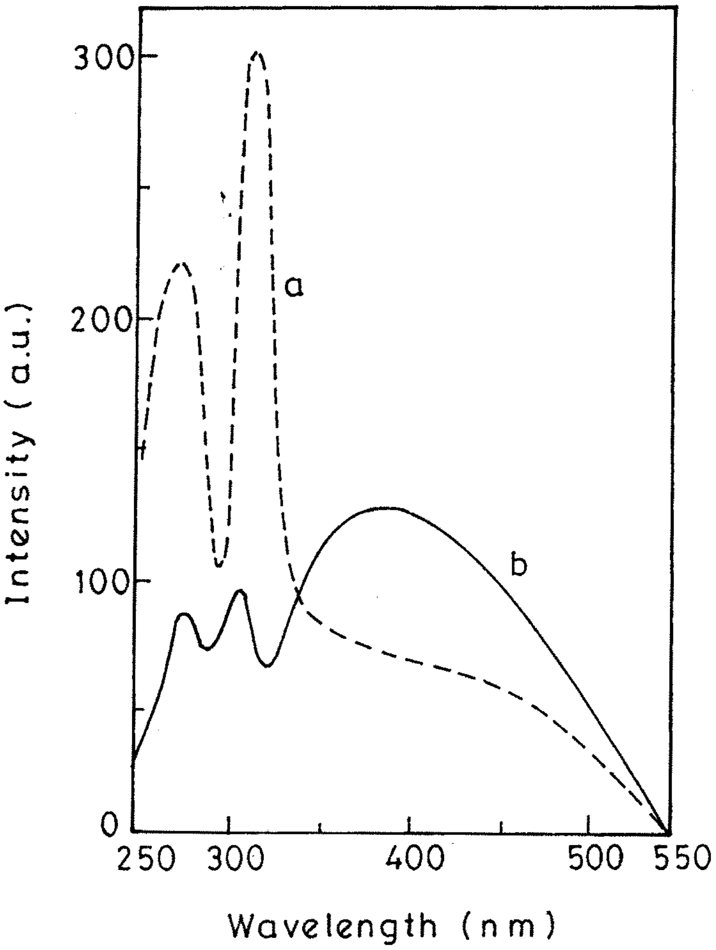


Fig. 3·21 – Excitation spectra of Naphthalene in PS film (a) and of Naphthalene and Pyrene in PS film (b).

to its singlet level. The fig. 3.17 has indicated naphthalene fluorescnec quenching and appearance of pyrene monomer emission. The observed quenching suggests EET from excited Np to Py molecule. The appearance of pyrene monomer emission band indicate that some of the excited pyrene molecules thus formed by accepting energy of Np deactivates radiatively as Py monomer emission has appeared. However, increase in wt. % of Np in the film has decreased Py monomer emission and appearance of red shifted broad band in the spectrum of doubly doped Ps films led us to conclude that some of excited py molecules must aggregating with Np to form an exciplex. Further the intensity of broad band increases as concentration of naphthalene increases which supports the exciplex formation when concentration of Np is higher. The possibility of occurrence of pyrene excimer is ignored as the concentration of Py used in Ps films corresponds to monomer emission.

Presentation	Process
$NP_{(So)} + h\nu \longrightarrow NP^{*}_{(S1)}$	NP(s_1) excitation.
$NP^{*}_{(S1)} + Py_{(So)} \longrightarrow NP_{(So)} + Py^{*}_{(S1)}$	EET
$Py^{*}_{(S1)} + Np \longrightarrow [\,Np - Py\,]^{*}$ exciplex	Energetic interaction (heterodimer)
$[Np - Py]^{*} \longrightarrow NP_{(So)} + Py_{(So)} + h\nu_f$	Exciplex emission.

3.9 Fluorescence Studies of Biphenyl Doped Polystyrene Films :

Biphenyl is an aromatic hydrocarbon in which two phenyl rings are joined by C-C linkage. The phenyl rings may randomly oriented or may be coplanar because of the possible C-C, rotations. Biphenyl is known to exhibit a broad, structureless absorption spectrum in solution not due to association of molecules to form dimer but due to random orientation of phenyl rings. The fluorescence spectrum of biphenyl solution is structured and is believed to be due to the fact that the phenyl rings in excited state becomes coplanar. We believe that the coplanar orientation of biphenyl rings may form eximer in the rigid matrix or an exiplex with other impurity such as pyrene present in the matrix. The fluorescence behaviour of biphenyl in polymer matrix is not yet been studied as such studies need to explore the possibility of energetic interaction with in polymere martrix. With this view the biphenyl was doped in polystyrene films and its fluorescence behaviour was studied in the rigid polymer matrix first without pyrene and then in presence of pyrene.

Biphenyl is soluble in benzene and hence polystyrene films doped by varying amounts of biphenyl were prepared. Fig. 3.22 shows fluorescence spectra of these films. It is seen that the spectrum of the film containing lower wt % of biphenyl (0.001756 wt %) is a broad band peaking at 325 nm. The fluorescence spectra of the film containing higher wt % shows additional emission bands in the region 375-425 nm. The bands are appeared at wavelength 325, 375, 400 and a weak band at 425 nm. Therefore, it seems that as wt % of biphenyl in the film increases the spectra become structured. This concentration dependence nature of the fluorescence spectra is explained on the basis of orientation of phenyl rings about C-C bond. The broad band appeared in the spectrum of the film containing lower wt % of biphenyl is due to random orientation of phenyl rings in the rigid polymer. However, as amount of biphenyl increases the phenyl rings become more coplanar and spectrum becomes structured. this conclusion is further confirmed by excitation spectra of the films containing lower and higher wt. % of biphenyl. Fig. 3.23 shows excitation spectra of biphenyl doped polystyrene. Spectrum ‘a’ is a broad band peaking at 277 nm and is of the film containing low wt. %, of biphenyl

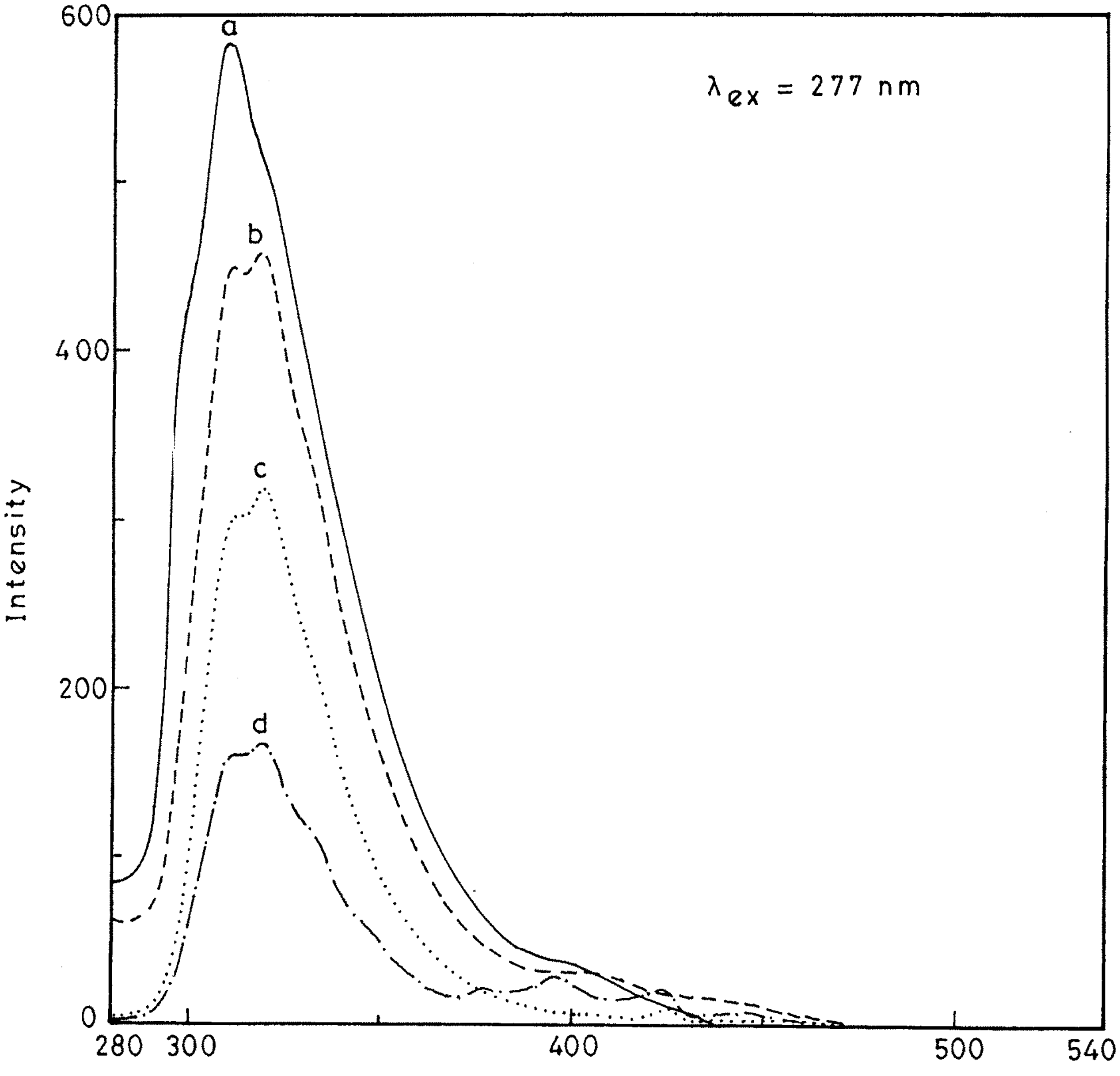


Fig.3·22 - Fluorescence spectra of PS films doped by biphenyl
a) 0·001756 wt % b) 0·01756 wt %
c) 0·1756 wt % d) 1·756 wt %

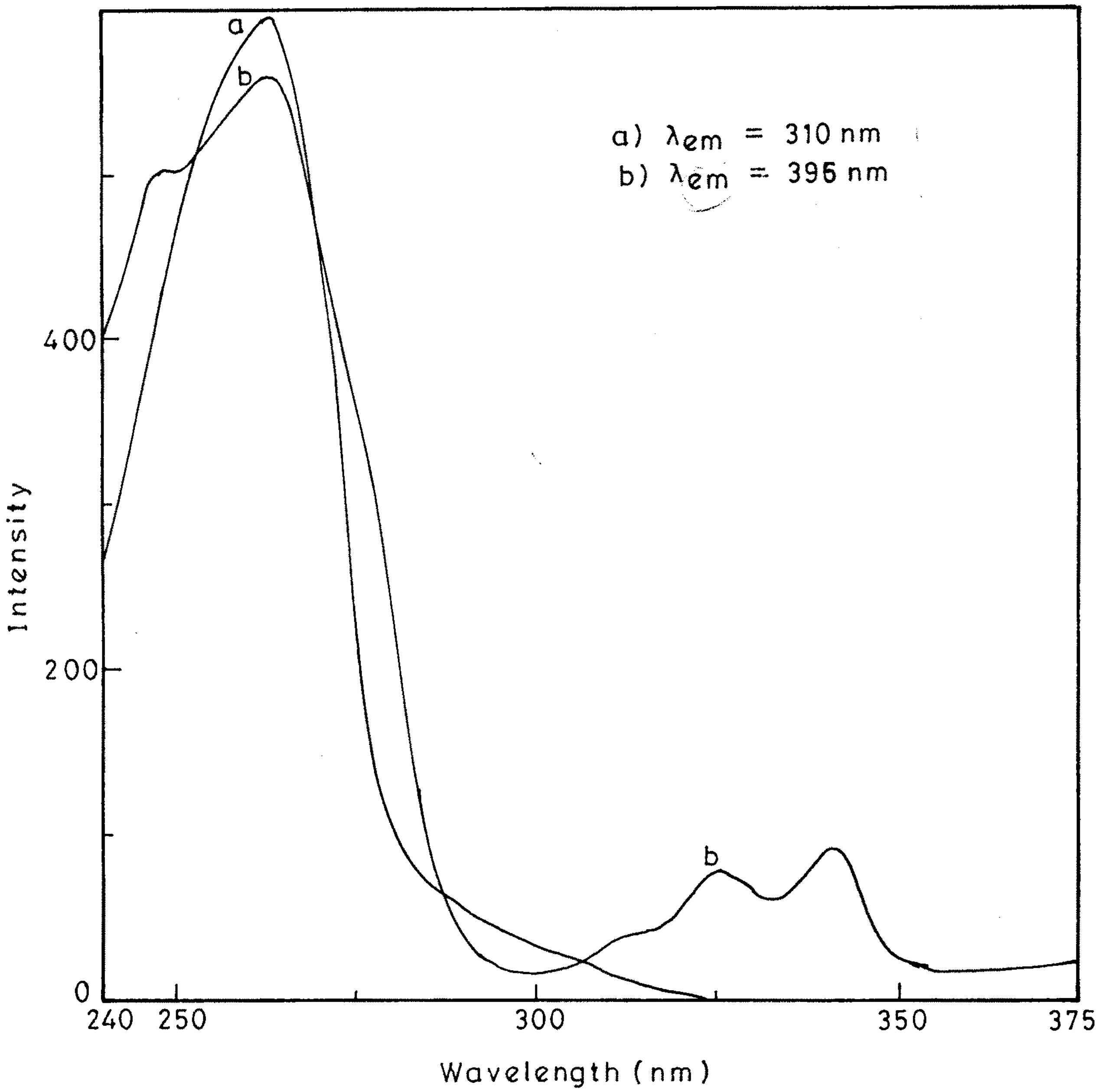


Fig. 3·23 - Excitation spectra of PS films doped by biphenyl.
a) 0·001756 wt % b) 1·756 wt %

(0.001756 wt %). The spectrum 'b' is structured with bands at 277, 325 and 345 nm. This excitation spectrum of film containing higher wt.% of biphenyl (1.756 wt %) is also a mirror image of the fluorescence spectrum of the same film. Therefore, in the film containing higher wt. %, the biphenyl rings are oriented more co-planerly.

The energy level diagram constructed on the basis of available information[119] is presented in the fig. 3.24. The figure shows first excited singlet level (S_1), triplet level (T_1) and ground state level. The biphenyl molecule in the ground state absorb energy from excitation radiation of wavelength 277 nm and promoted to first excited singlet level as shown in figure. The deactivation of excited biphenyl emits fluorescence. In the excited state the phenyl rings are lying in the same plane and becomes more coplanar and hence the fluorescence spectrum shows more vibrational structure as compared to its absorption and excitation spectrum. The origin of biphenyl fluorescence from film is represented as below.

Presentation	Process
$Bi_{(S0)} + h\nu \longrightarrow Bi^{*}_{(S1)}$	Biphenyl excitation
$Bi^{*}_{(S1)} \longrightarrow Bi_{(S0)} + h\nu_f$	Biphenyl fluorescence.

3.10 Fluorescence of Polystyrene Films Doped by Biphenyl and Pyrene

Fig. 3.25 shows fluorescence of polystyrene films doped by 1.2769 wt % biphenyl and 0.23033 wt % pyrene. For the purpose of comparison the fluorescence spectra of film containing individual components are also shown in the same figure. The spectrum reveals three different features in the regions 300-360 nm; 360-440 nm and 440-530 nm. The regions might be respectively biphenyl, pyrene monomer and pyrene excimer or exciplex emission regions.

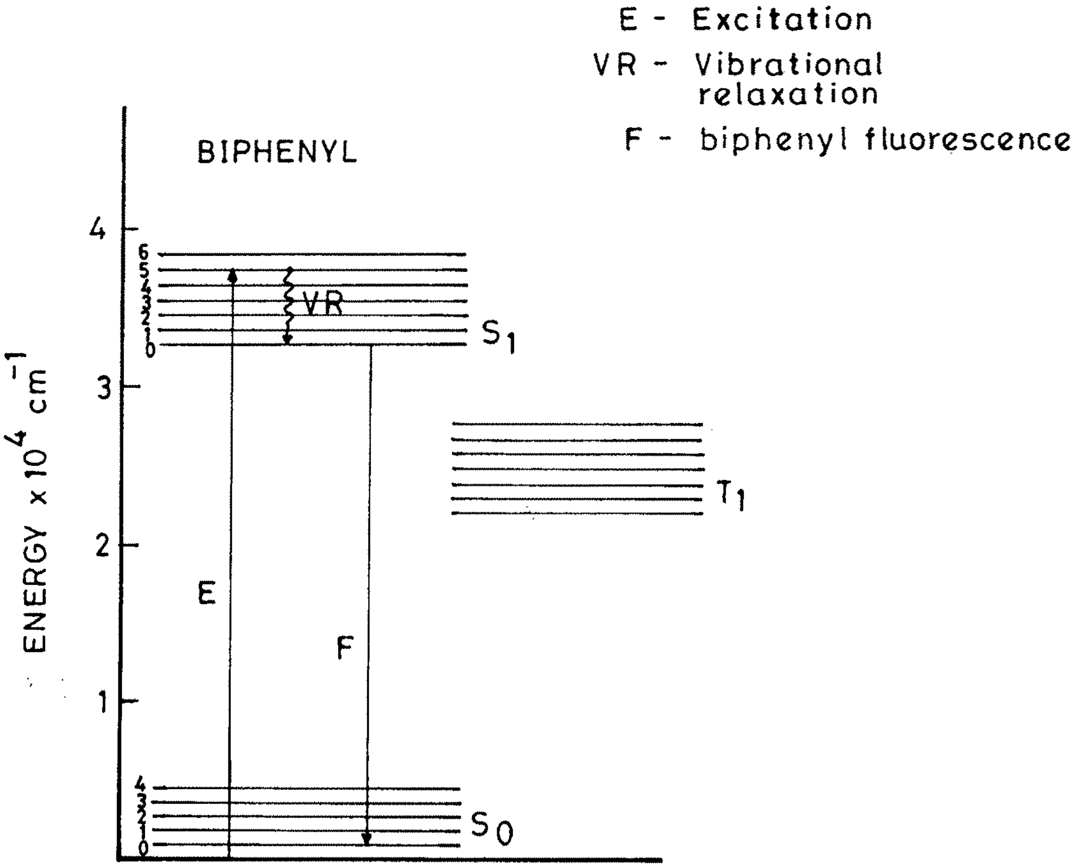


Fig. 3·24 - Molecular energy level diagram of biphenyl.

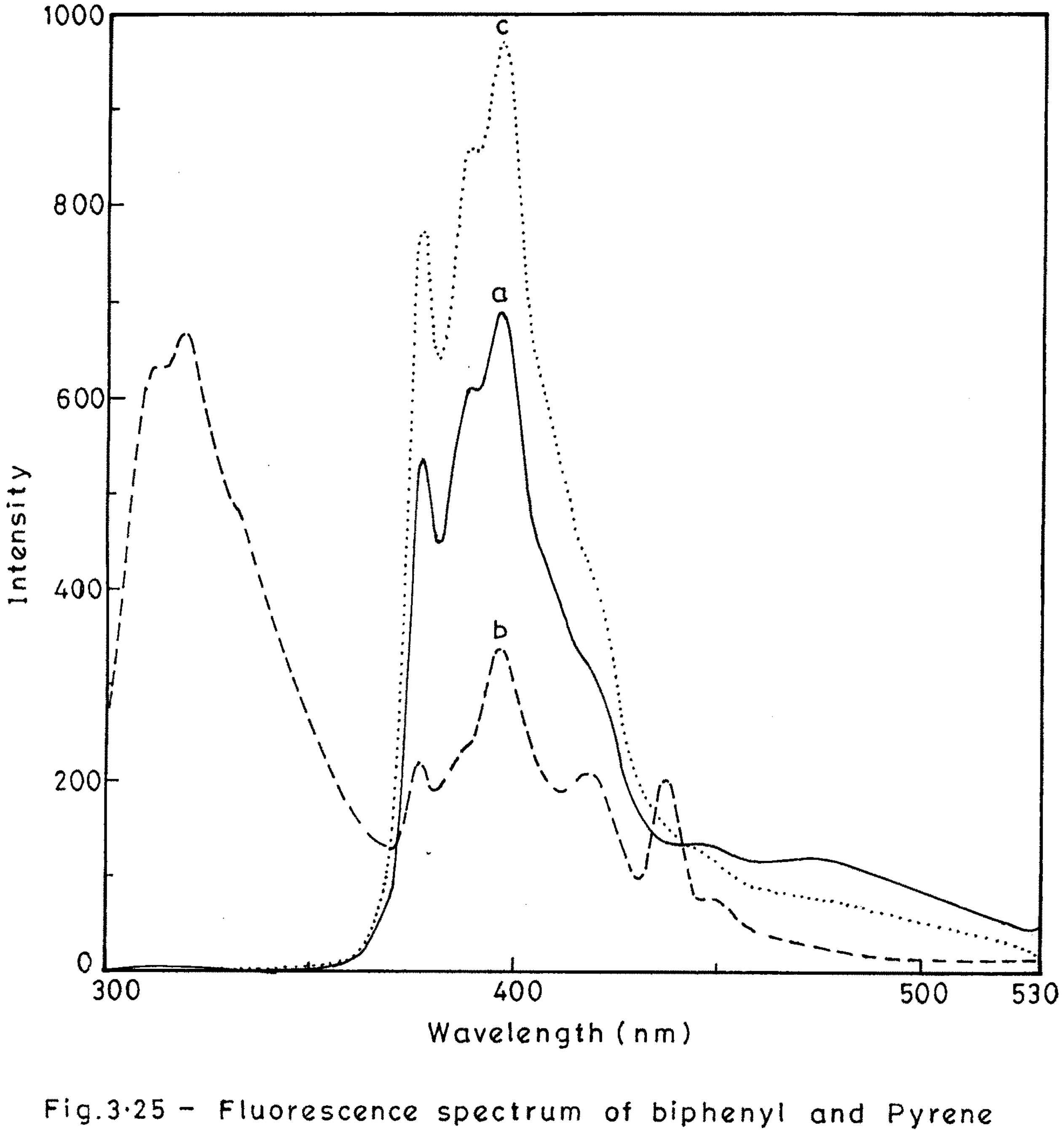


Fig.3·25 – Fluorescence spectrum of biphenyl and Pyrene doped PS film (a) biphenyl doped PS film (b) and Pyrene doped PS film (c).

Correct assignment of these regions are made by comparing the spectrum with the emission spectrum of polystyrene film doped by individual components i.e. 1.2769 wt % biphenyl and polystyrene films doped by pyrene exhibiting its monomer fluorescence spectrum as shown in fig. 3.25.

It is seen that the first band in the region 300-360 matches with biphenyl emission, which in presence of pyrene seems to be quenched. The structured bands in region 360-440 nm corresponds with monomer fluorescence of pyrene. In this region biphenyl has also emission but in presence of pyrene it is masked. The broad featureless band does not match with well known excimer pyrene emission expected to occur at λ_{max} 470 nm . Hence it may be an exciplex emission band of biphenyl and pyrene as is reported in the condensed system.[119] The concentration dependence of film fluorescence with biphenyl variation helped to make correct assignment of this band.

3.11 Concentration Dependence of Fluorescence of PS Films Doped by Pyrene and Varying Amounts of Biphenyl.

Fig.3.26 shows fluorescence spectra of PS films doped by 0.1728 wt % (spectrum No.1) and other spectra No.2 to 9 containing 0.1728 wt % Pyrene and varying amounts of biphenyl. The spectrum No.1 is structured in the region 350-400 nm due to pyrene monomer emission. However, other spectra of pyrene have shown interesting modification in presence of biphenyl as new structureless emission band towards red. It is also observed that as concentration of biphenyl in the film increases the pyrene monomer emission intensity decreases and that of broad band seems to increased at its maximum emission wavelength 458 nm. Figure reveals isoemissive point clearly at 400 nm which is an indication of formation of dimeric species due to either charge transfer (CT) or due to lateral orbital coupling between two solutes in the excited state.

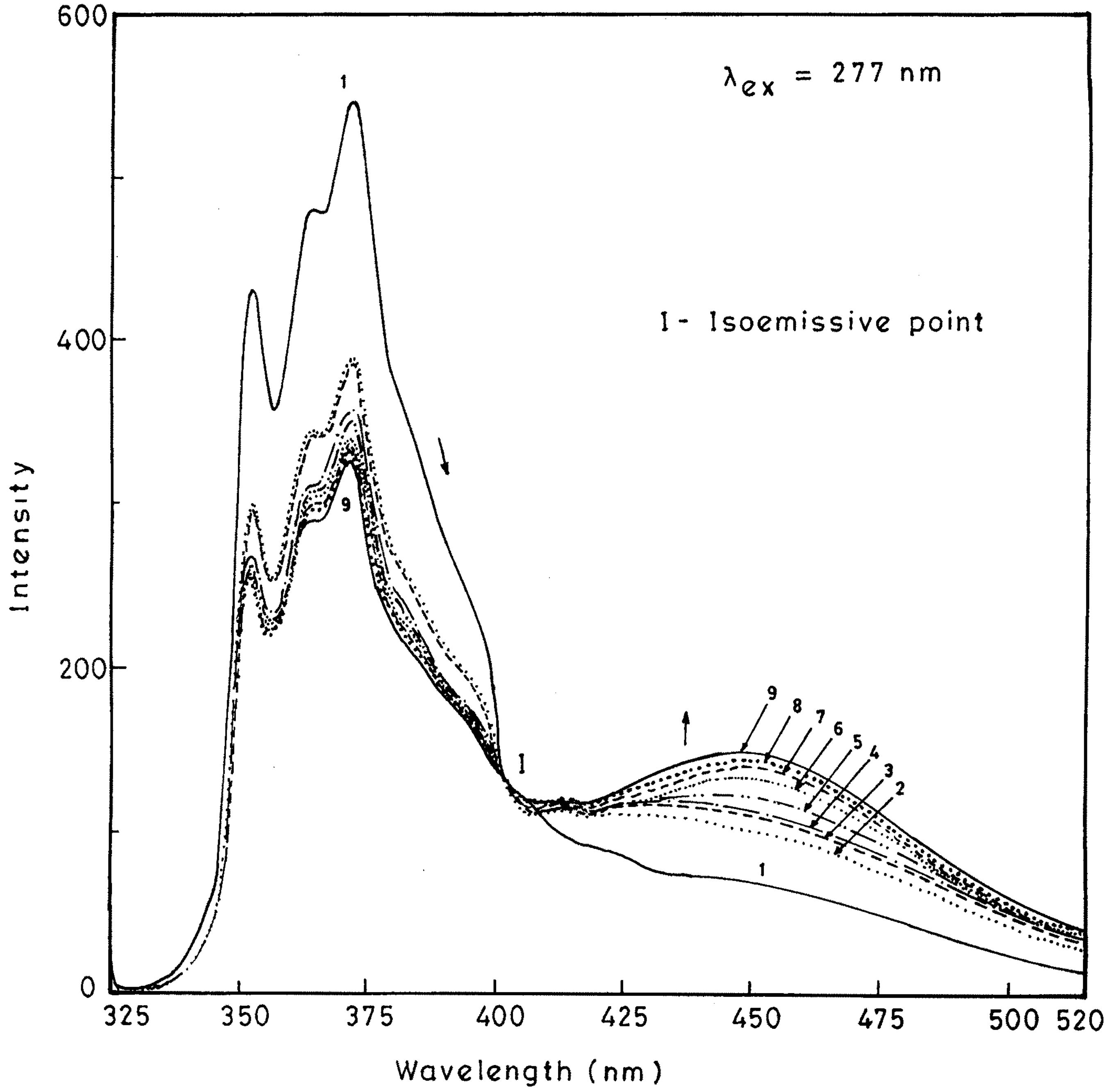


Fig. 3·26 - Effect of biphenyl concentration on fluorescence of Pyrene in PS matrix.

1) 0·1728 wt % Pyrene (without biphenyl) and

2-9) Spectra containing 0·1728 wt % Pyrene and varying amounts of biphenyl.

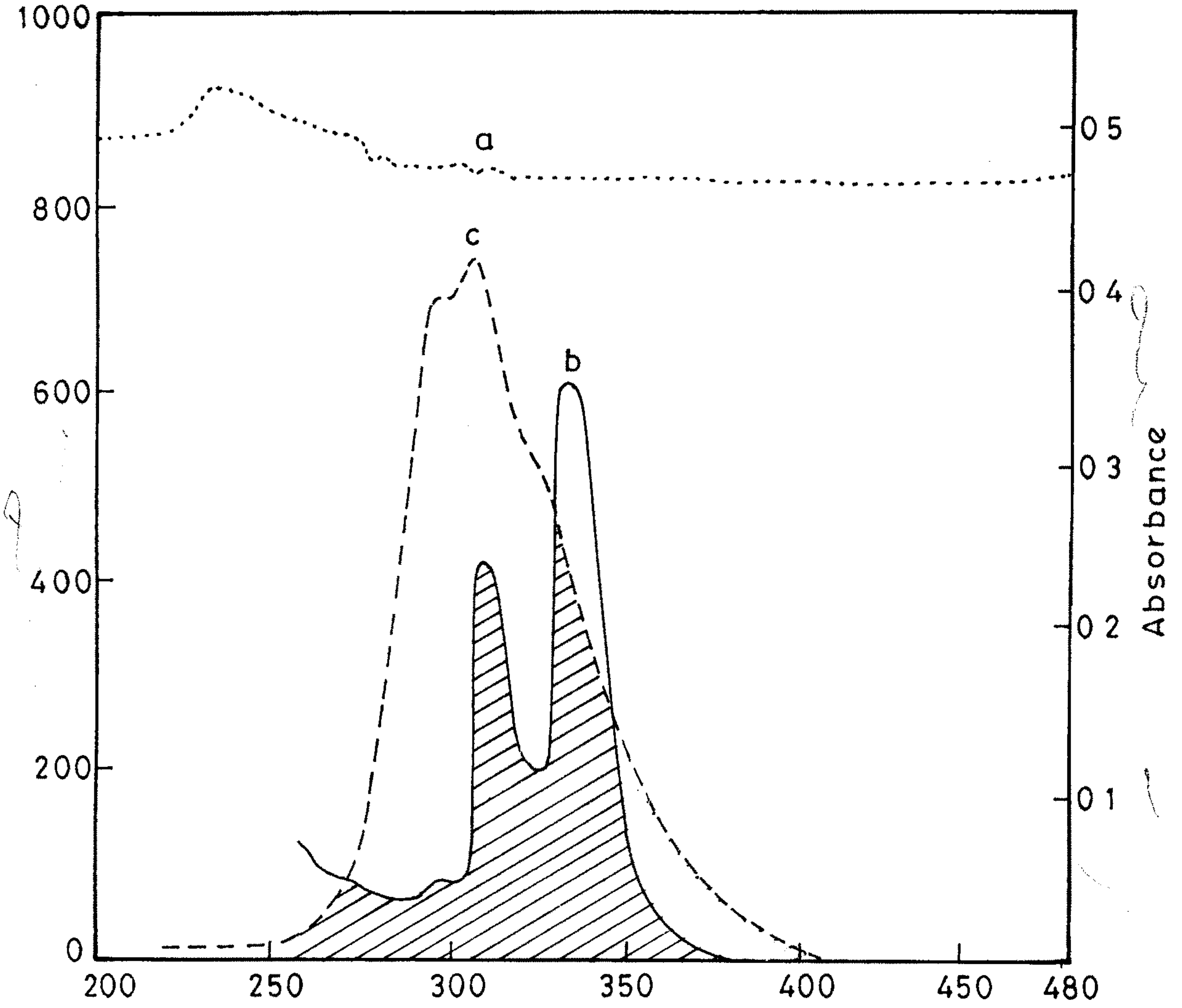
2) 0·00365 wt % 3) 0·01837wt % 4) 0·0365 wt %

5) 0·1840 wt % 6) 0·368 wt % 7) 1·1039 wt %

8) 1·189 wt % 9) 1·472 wt %

Biphenyl is sensitive to excitation radiation of 277 nm, while pyrene absorbs strongly in the region 310-360 nm as is indicated by its absorption spectrum. The biphenyl and pyrene are widely separated in terms of their absorption wavelength. Hence selective excitation of one component in presence of other is possible. One of the objectives of present work is to prepare photosensitive films which absorb short wave uv radiation and transform them into visible radiation. Hence the polystyrene films containing biphenyl and pyrene were excited by radiation of wavelength 277 nm. This wavelength is obtained from the excitation spectrum of biphenyl film. Hence, in presence of pyrene, biphenyl is selectively excited to its first singlet level. The absorption spectra of pure biphenyl and that of pyrene are shown in fig. 3.27. Figure also shows emission spectrum (c) of biphenyl film. Figure reveals that the emission spectrum of biphenyl and absorption spectrum of pyrene has a very good overlap. This overlap indicates that the excitation energy of biphenyl could be trapped by pyrene molecules. The fact of excitation energy transfer from biphenyl to pyrene is further supported by the energy level diagram presented in fig. 3.28. Figure shows singlet and triplet energy levels of biphenyl and pyrene.

It is seen that the singlet-singlet energy transfer from biphenyl to pyrene is probable as singlet level of pyrene (26,802 cm^{-1}) lie below the corresponding level of biphenyl (32,480 cm^{-1}). Thus the EET results into formation of first excited singlet molecules of pyrene. The observed quenching of biphenyl fluorescence in presence of pyrene (fig. 3.26) also supports that the excitation energy of biphenyl is trapped by pyrene molecules. The excited pyrene thus formed deactivates to ground state either by giving its monomeric emission or may undergo association with ground state biphenyl molecule to form exiplex. The formation of excimer



Absorption spectra

Fig. 3·27 - Absorbance ~~spectram~~ of individual components biphenyl (a) Pyrene (b) in PS films and emission spectrum of biphenyl film (c).

Region of overlap shown by sheded lines.

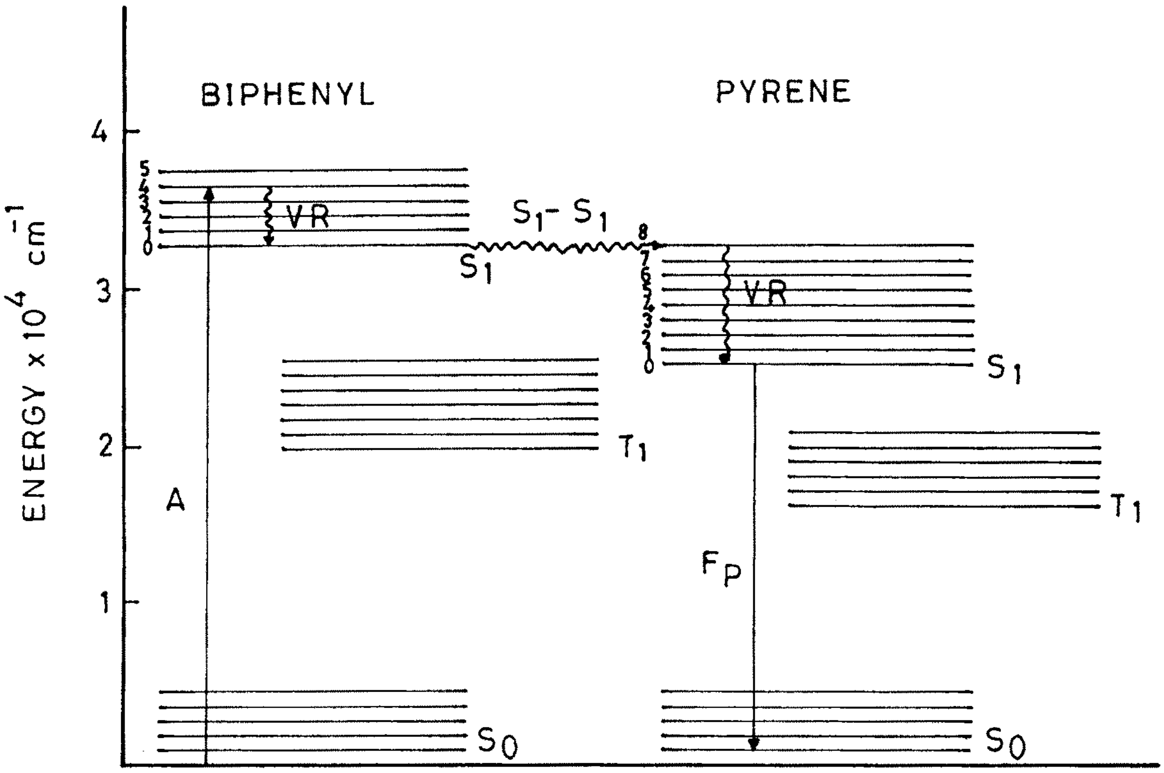


Fig. 3·28 - Molecular energy level diagram of biphenyl and pyrene.

A - Absorption ; VR - Vibrational relaxation ;
S_1-S_1 - Singlet - Singlet energy transfer ;
Fp - Pyrene monomer fluorescence .

of pyrene is improbable as concentration of pyrene in the film corresponds to its monomer emission.

From Fig. 3.26 it is observed that the pyrene monomer emission quenches as wt. % of biphenyl increases and at the same time the intensity of broad band appeared at 458 nm increases. These observations led us to conclude that the excited pyrene undergo association with ground state pyrene to form their exciplex. The exciplex emission is characterized by the broad, featureless band as seen in fig. 3.26. The mechanism of exciplex formation and its emission is represented as below :

Presentation			Process
$Bi_{(S0)}$ + hν	$\longrightarrow$	$Bi^{*}_{(S1)}$	Biphenyl excitation.
$Bi^{*}_{(S1)}$ + $Py_{(S0)}$	$\longrightarrow$	$Bi_{(S0)} + Py^{*}_{(S1)}$	singlet-singlet energy transfer.
$Py^{*}_{(S1)}$ + $Bi_{(S0)}$	$\longrightarrow$	$(PyBi)^{*}$ Exciplex	exciplex formation
$(PyBi)^{*}$	$\longrightarrow$	$Py_{(S0)} + Bi_{(S0)}$ + $h\nu_f$	exciplex emission.

The molecular ordering in the film between biphenyl and pyrene molecules favour parallel alignment of chromophore unit. Therefore formation of exciplex is more probable in the polystyrene film rather than in condensed system. In film the molecules forming an exciplex are brought so close that the intermolecular distance between the components decreases.

3.12 Fluorescence of 9ACA Doped Polymer Films

9-Anthracene carboxylic acid is a well known crystalline aromatic acid and known to exhibit characteristic dual fluorescence in crystalline and in solutions prepared in different protic and aprotic solvents.[120-123] The fluorescence shows a pronounced concentration dependence and exhibit anthracene line sharp structure as well as broad, structureless and largely stokes shifted bands. With a hope to obtain such interesting solution fluorescence of 9ACA suitable for use in solid state devices in microelectronics industry, 9-anthracene carboxylic acid doped polymer films were prepared. The polymeric environment affect the association of aromatic hydrocarbon.[124] The complicated nature of the aggregation of 9ACA in different solid matrices revealed excimer like and anthracene like emission in different polymers. The properties exhibited by 9ACA in alcohol, alcohol-water and in benzene are different.[122-126] Hence polymer films have been prepared by using these solvents and suitable polymers soluble in these solvents. Polystyrene soluble in benzene and polyvinylalcohol soluble in water and water-alcohol system were used to prepare thin polymer films doped by 9ACA.

3.13 9ACA – Doped Polystyrene Films Prepared from Benzene Solution :

Polystyrene films containing varying amounts of 9ACA were prepared from benzene solution. Concentration of polystyrene in solution was kept constant to a value 4%. Fig.3.29 shows fluorescence spectra of polystyrene films doped by 9ACA and monitored at excitation wavelength 368 nm. Fluorescence spectra of the films containing lower amounts of 9ACA eg.0·009122 wt % and 0·0009122 wt % show single band peaking at 412 nm. As concentration increases this single band disappears and a broad intense band appears in the region 425 to 550 nm, with a maximum at 468 nm. The intensity of band is a function of concentration of 9ACA in the film. However, at higher concentration the rate of fluorescence enhancement decreases. The sharp band appeared at 412 nm from the film containing lower amounts of 9ACA is the monomer emission which is not identical with its sharp structured fluorescence of anthracene like emission reported from its dilute solution in ethanol.[122,124,125] This is due to aprotic benzene used in film preparation where – COOH of 9ACA remains undissociated in its

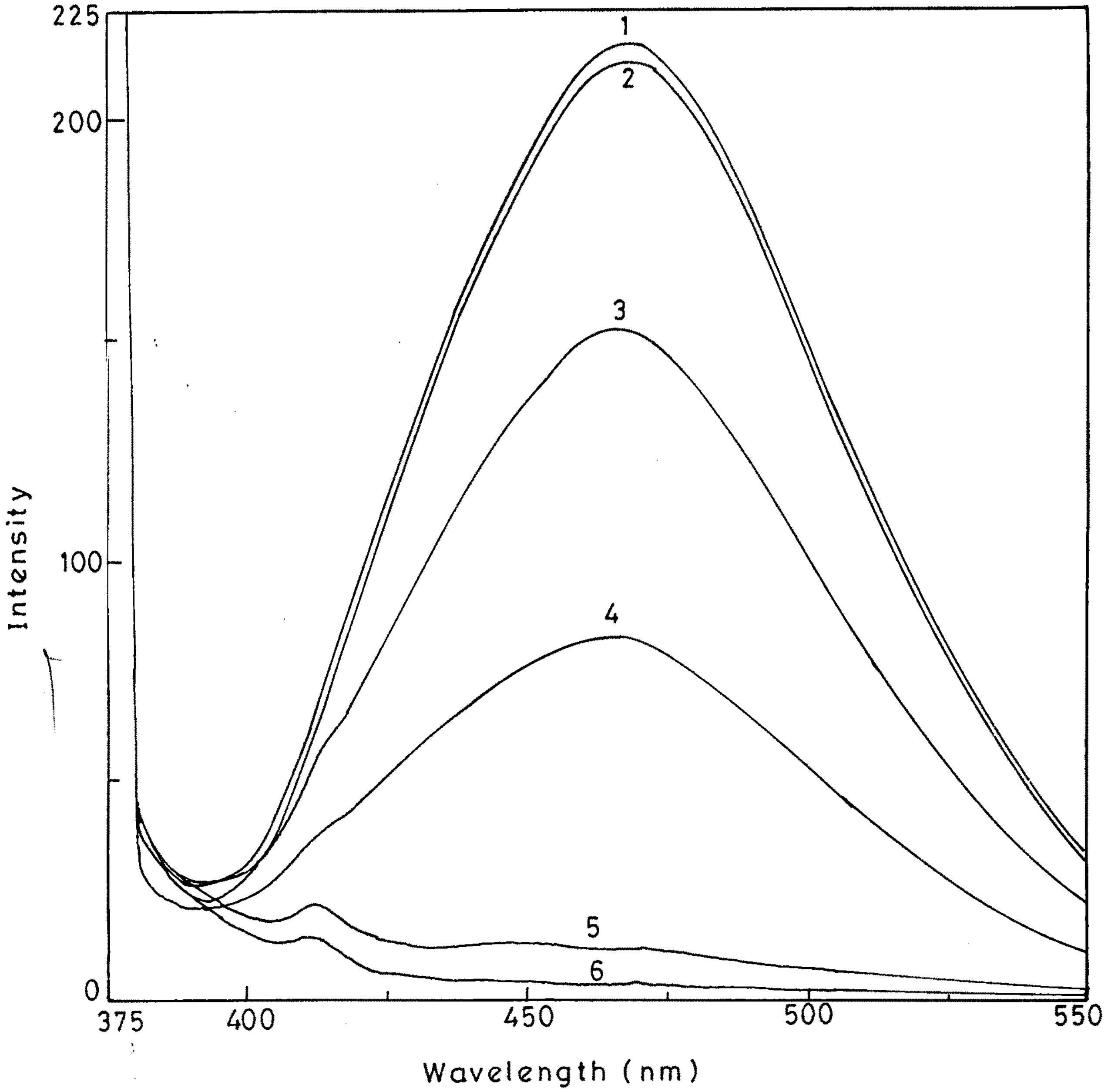


Fig. 3·29 - Fluorescence spectra of PS films doped by varying amounts of gACA (films were prepared from their solution in Benzene .

1) 0·06081 wt % gACA 2) 0·05473 wt % gACA
3) 0·03649 wt % gACA 4) 0·01824 wt % gACA
5) 0·009122 wt % gACA 6) 0·0009122 wt % gACA

monomer (A-COOH) form. The broad structureless emission peaking at 468 nm corresponds with the emission observed by Bazilevskaya and Cherkasov[121] from concentrated solution of 9ACA in solution studies. The broad bands are characteristics of either an excimer formed in the excited state or of a excited dimer produced due to excitation in ground state dimer. It is believed that broad structureless band at 468 nm must be originating from a coplanar (II) form of 9ACA resulting from the perpendicular ($\perp$) or twisted ground state.

3.14 9ACA-Doped Polystyrene Films Prepared from CCl_4 Solution.

The results observed in other nonpolar solvents such as carbon tetrachloride are similar. Fig.3.30 shows fluorescence spectra of 9ACA doped in polystyrene films prepared from CCl_4 solution. The fluorescence spectra are identical with that shown in fig.3.29.

3.15 9ACA-Doped Polyvinyl Alcohol Films Prepared from Ethyl Alcohol Solution.

Fig.3.31 shows fluorescence spectra of 9ACA doped PVA films prepared from ethyl alcohol solution. The fluorescence spectrum of film containing lower wt % 9ACA solute shows a single sharp band peaking at wavelength 412 nm. The increase in concentration of solute, quenches the intensity of this band and at higher wt % of 9ACA the broad bands peaking at 490 nm appears. At the concentration 1.3587 wt % broad band seems to shift towards red and has maximum emission at wavelength 507 nm. These results are completely different than those presented in Fig.3.29 and Fig. 3.30. It seems that 9ACA dissociates slightly to give $9ACOO^-$ in the alcohol phase. However at higher concentration the probability of dimer formation increases and monomer anion species are in equilibrium with the dimers formed in the film. Therefore the spectra of the films containing higher wt % of 9ACA shows sharp band corresponding to monomer

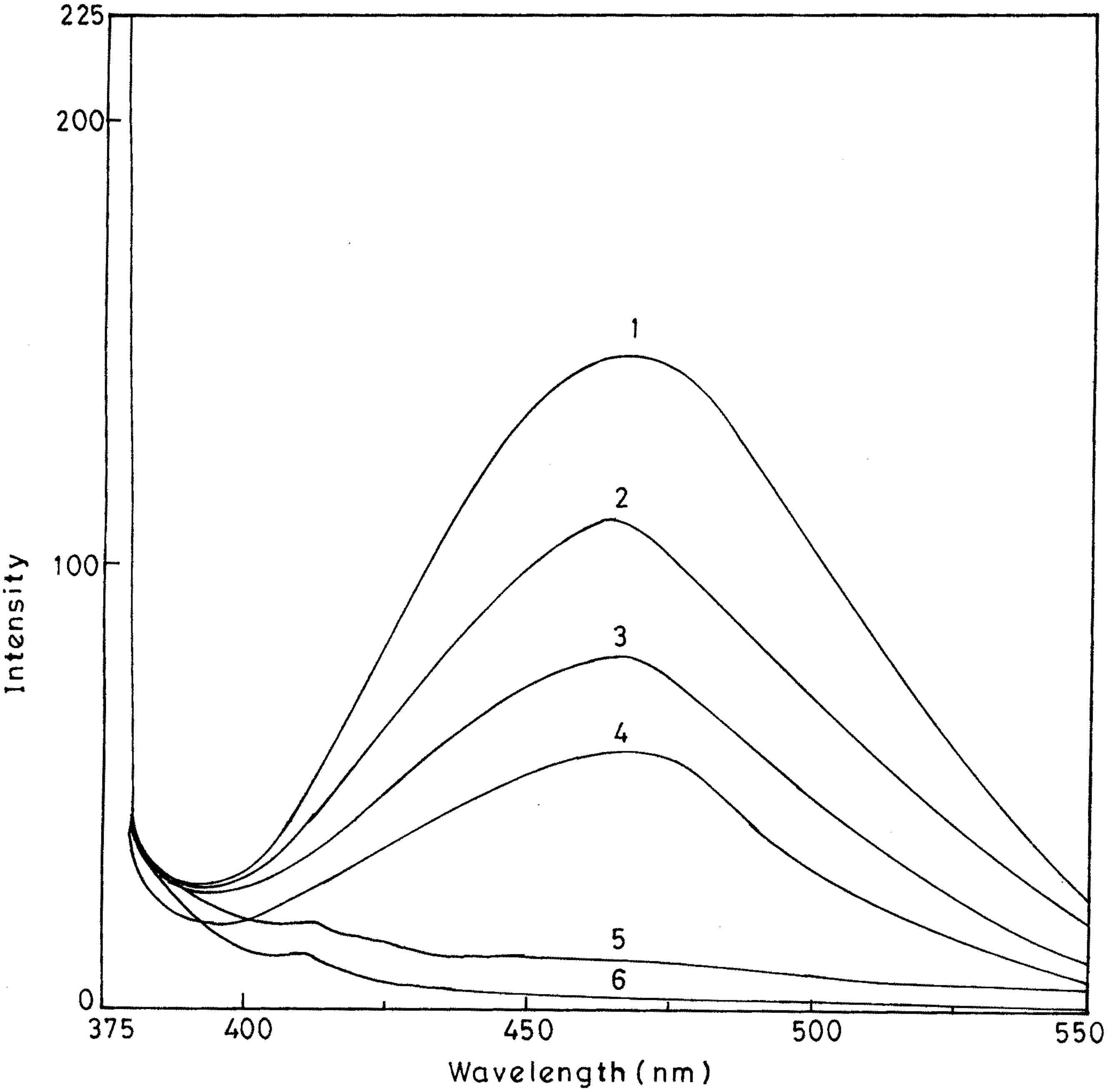


Fig.3·30 – Fluorescence spectra of PS films doped by varying amounts of gACA (films ware prepared from their solution in Carbontetrachloride)

1) 0·04886 wt % gACA 2) 0·03155 wt % gACA
3) 0·02010 wt % gACA 4) 0·01005 wt % gACA
5) 0·005026 wt % gACA 6) 0·0005026 wt % gACA

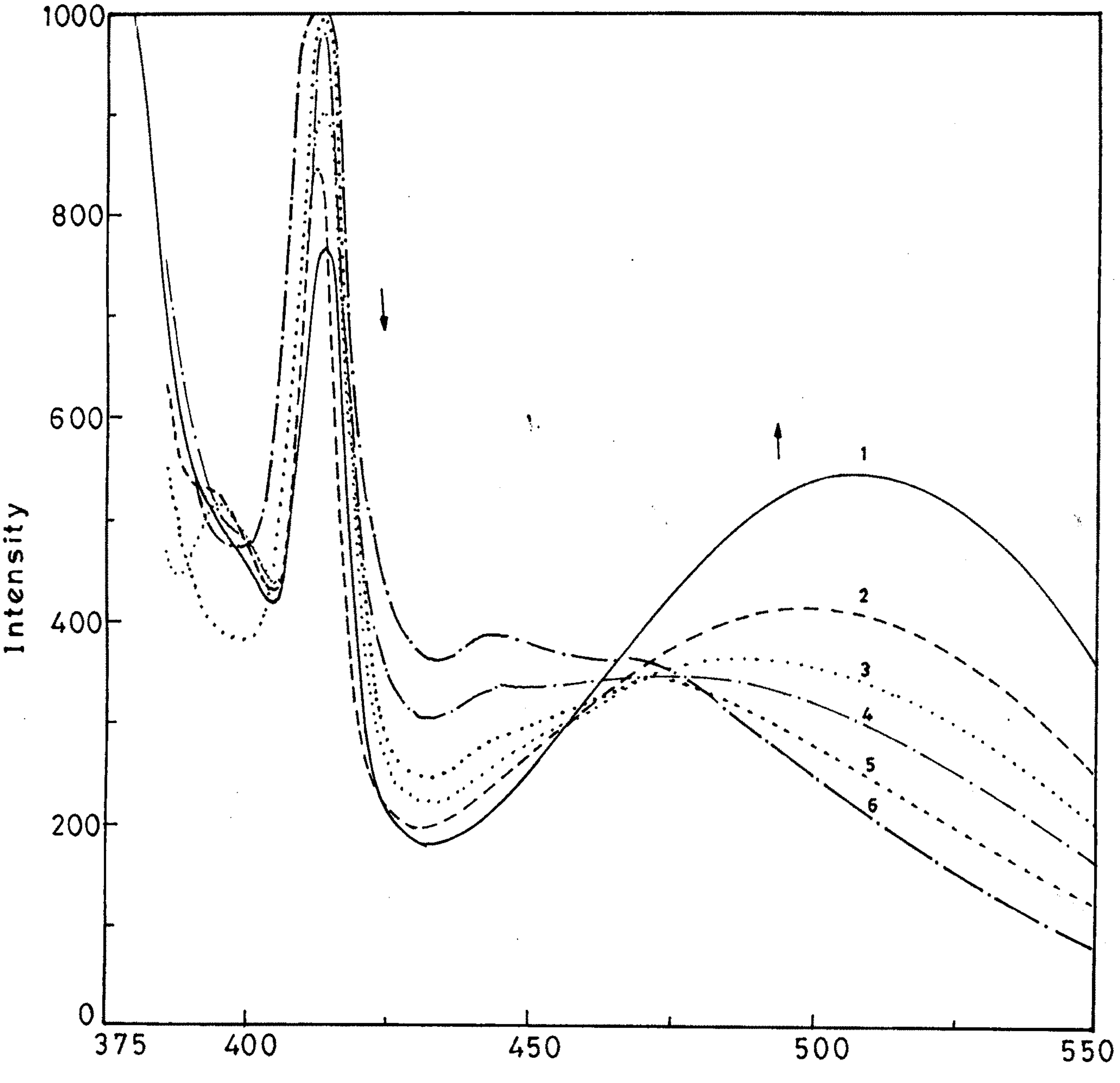


Fig.3·31 – Fluorescence spectrum of Polyvinyl alcohol (PVA) doped by varying amounts of g ACA (films were prepared from their solution in ethyl alcohol)

1) 1·3587 wt % gACA　2) 0·90861 wt % gACA
3) 0·78123 wt % gACA　4) 0·6369 wt % gACA
5) 0·46421 wt % gACA　6) 0·25475 wt % gACA

anion emission as well as broad excited dimer emission. The dimeric emission is observed due to overlapping of undissociated 9ACA molecules in the excited state. Thus the emission behaviour of the 9ACA in different polymer matrices is different. For sake of comparison the fluorescence spectra of the 9ACA solute embedded in PVA and polystyrene is shown in fig. 3.32. Figure shows that the broad bands are peaking at different emission wavelengths.

Fig. 3.33 represents fluorescence spectra of 9ACA doped PVA films prepared from its solution in ethyl alcohol and distilled water mixture. The fluorescence spectra have shown the concentration dependence. The spectra of film containing lower wt % of 9ACA shows a single band peaking at 412 nm which is similar to that observed in PVA films prepared from alcohol and benzene solution. However the films containing higher wt % of 9ACA shows structural anthracene like emission with emission bands peaking at 397, 412 and a shoulder at 447 nm. The broad bands corresponding to the excimer or hydrogen bonded dimer are not seen in the region 450-550 nm even in the films containing very high (0.21795 wt %) of 9ACA in PVA films. These observations led us to conclude that water-alcohol system has more pronounced solvation effect on aromatic acid by which emission of parent molecule anthracene dominates in the spectra. The water-alcohol also prevents the aggregation of molecules as excimeric bands are absent in the spectra.

The spectra of the PVA and polystyrene films monitored at emission wavelengths 412 nm and 468 nm respectively confirms the proposed monomer and excimer assignments. Fig.3.34 is the excitation spectra of PVA and polystyrene films. The excitation spectra of 9ACA doped PVA films shows bands at 331, 368 and 390 nm. These bands match with the bands reported in excitation spectrum of anthracene. The 9ACA would thus be considered to dissolve initially

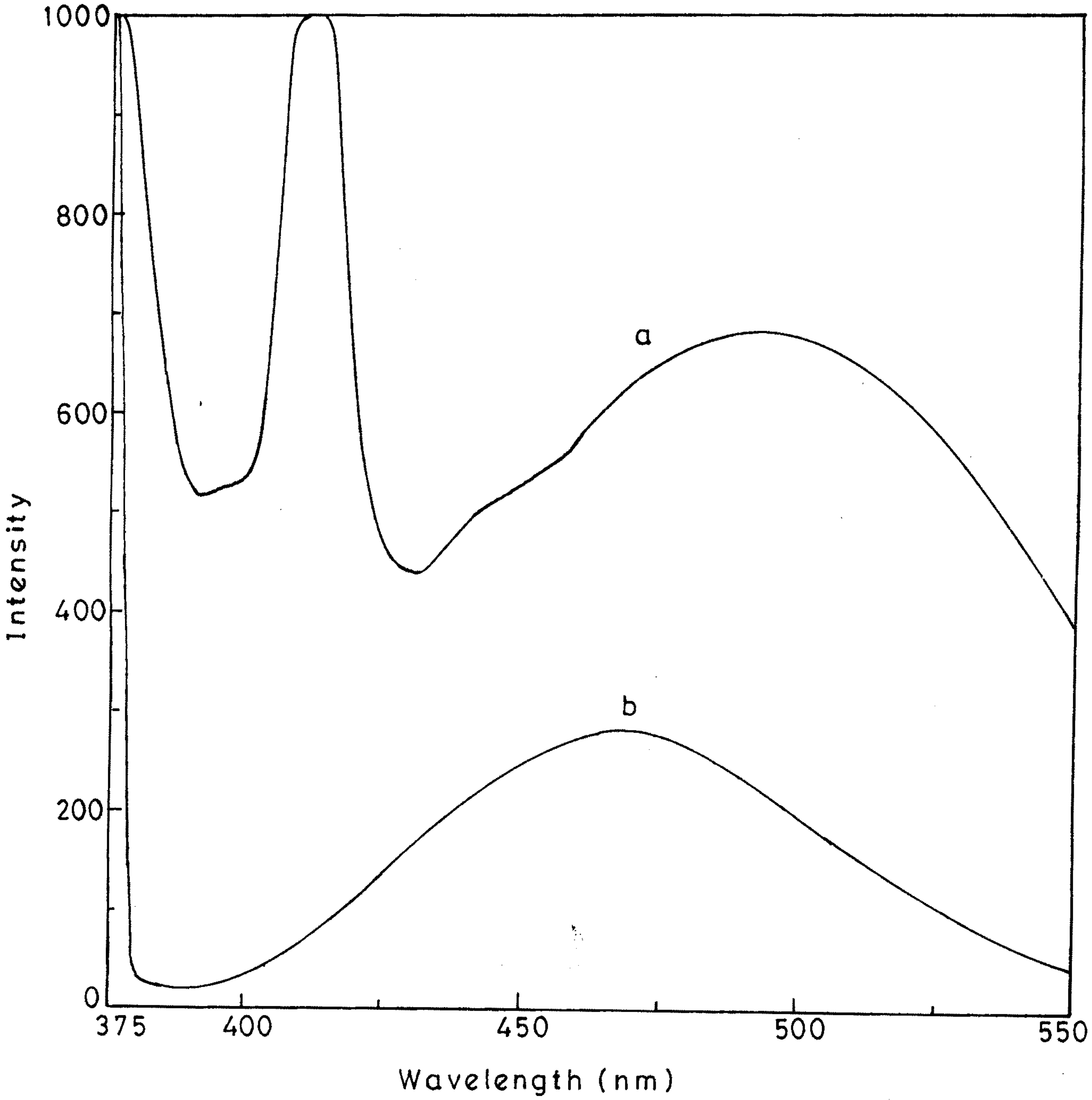


Fig. 3·32 - Comparison between spectral energy distribution of gACA in the films prepared from its solution in ethyl alcohol (a) and benzene (b)

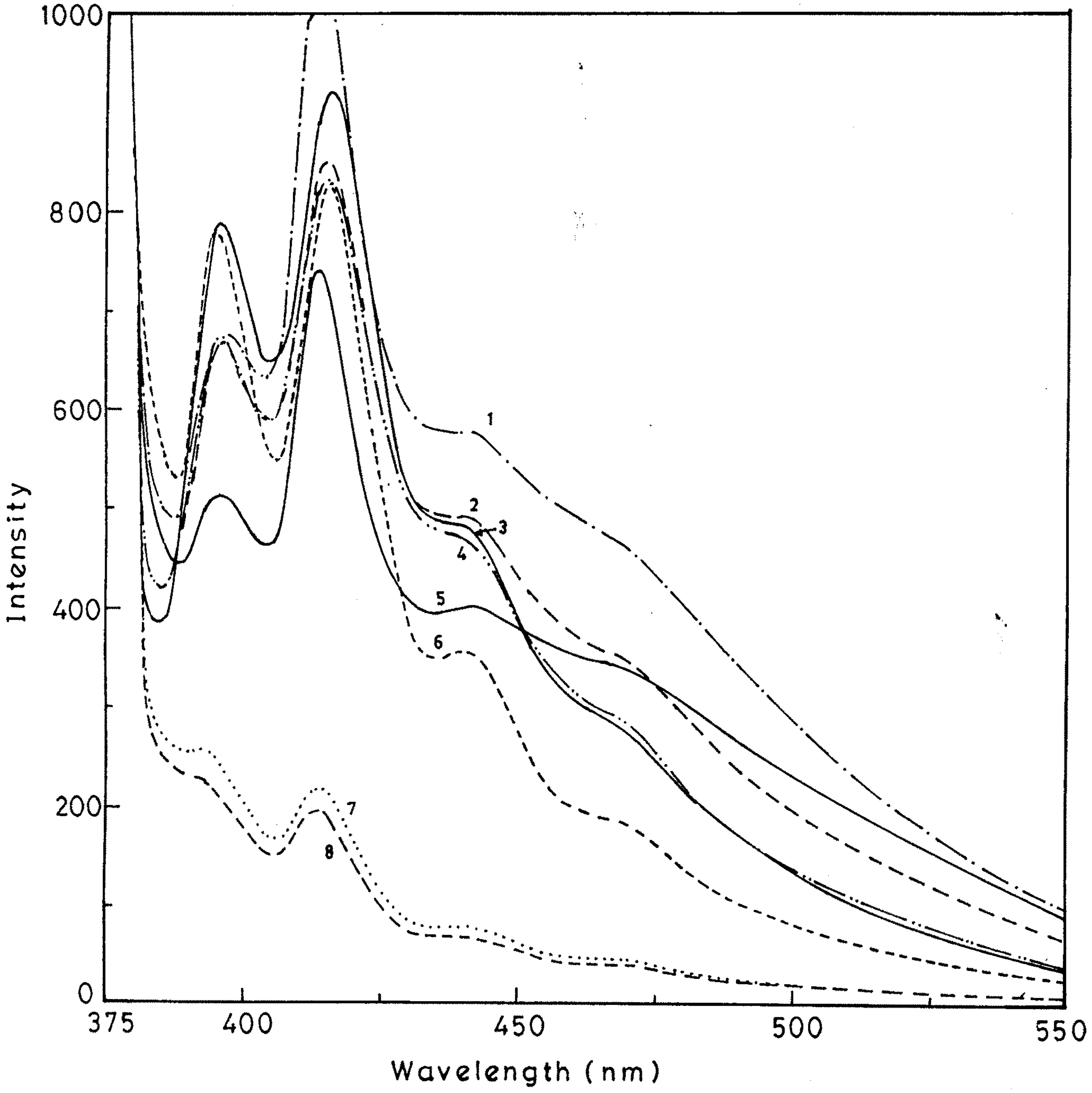


Fig. 3·33 - Spectral energy distribution of gACA in PVA films prepared from its solution in ethyl alcohol and distilled water mixture.

1) 0·2717 wt % gACA 2) 0·21795 wt % gACA
3) 0·1854 wt % gACA 4) 0·1090 wt % gACA
5) 0·05095 wt % gACA 6) 0·02548 wt % gACA
7) 0·005095 wt % gACA 8) 0·002548 wt % gACA

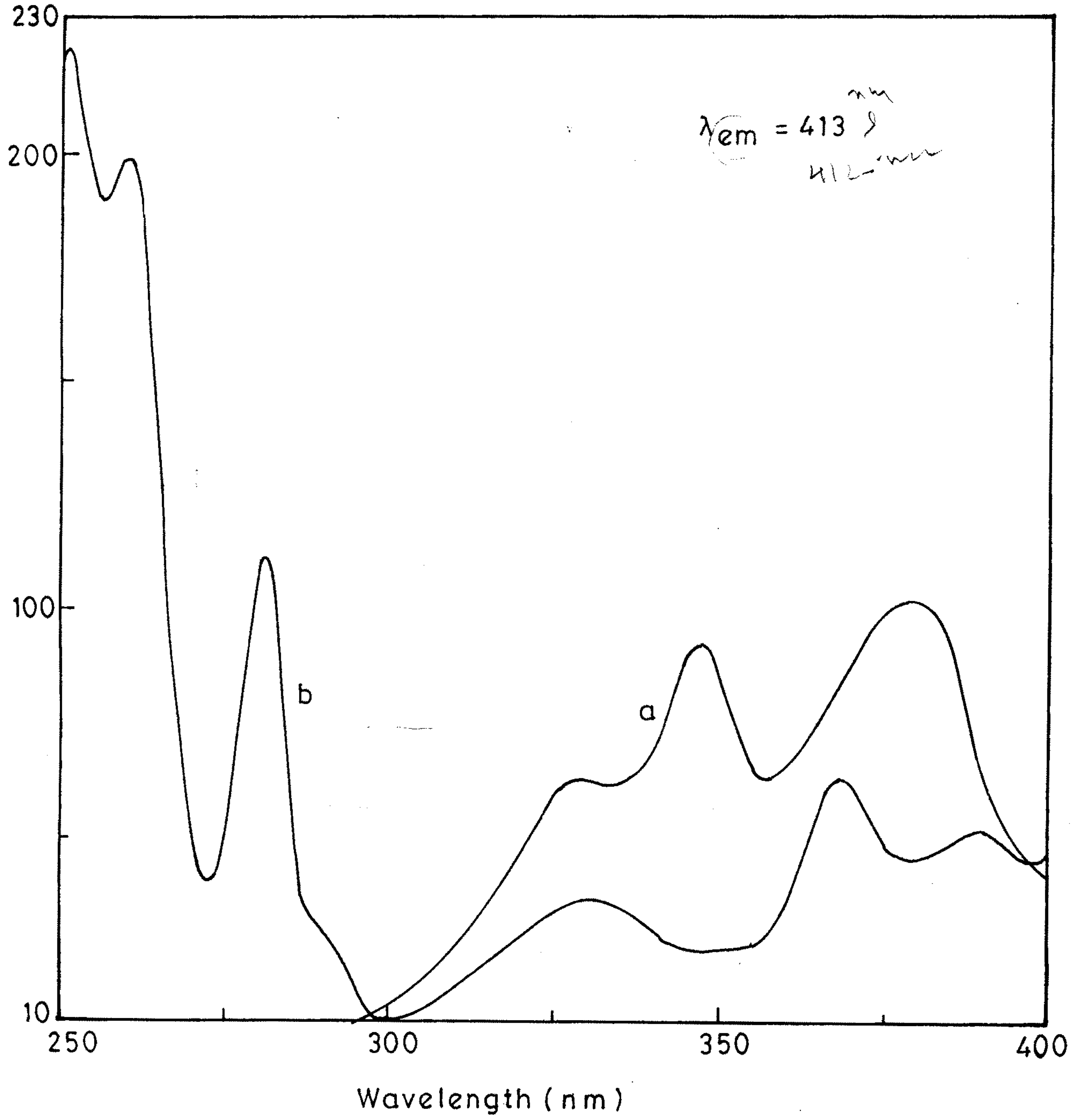


Fig. 3·34 – Excitation spectra of gACA in PS (a) and PVA (b) films.

as the anion in alcohol-water system. These anions deposited as such in PVA matrix would give anthracene like emission.

The excitation spectra of polystyrene films monitored at 468 nm is broad band without vibronic structure. The lack of vibronic structure is an indication of aggregation of molecules and confirms the excimer formed between two 9ACA molecule in benzene and CCl_4 solvent which get deposited as such in the PS film and exhibits excimer emission band at 468 nm in the fluorescence spectrum.

Presentation Process
ACOOH $\leftrightarrows$ A $COO^- + H^+$ ionisation
anion cation

A $COO^- + h\nu \longrightarrow [A\ COO^-]^*$ excited monomer anion

$[A\ COO^-]^* \longrightarrow [A\ COO^-] + h\nu_f$ monomer fluorescence

Excimer

9A COOH + $h\nu \longrightarrow$ 9A $COOH^*$

9A $COOH^*$ + 9A COOH $\longrightarrow$ [2 9A $COOH]^*$
Excimer.

[2 9A $COOH]^*$ $\leftrightarrows$ 2 9A COOH + $h\nu_f$ Excimer fluorescence

3.16 Solute-Solute Interaction in Polymer Matrix : 9ACA – Pyrene Doped PS films.

9ACA exhibiting dual luminescence was dispersed in polystyrene matrix along with pyrene having 0.17275 wt % corresponding to its monomer emission. The concentration of pyrene was kept constant and wt percent of 9ACA in polymer was varied from 0.0009122 wt % to 0.06369 wt % during preparation of polystyrene films doped by pyrene and 9ACA. The films were prepared from a nonprotic benzene solutions. The fluorescence spectra of these films are shown in fig.3.35. The fluorescence spectra were recorded at 341 nm which corresponds to

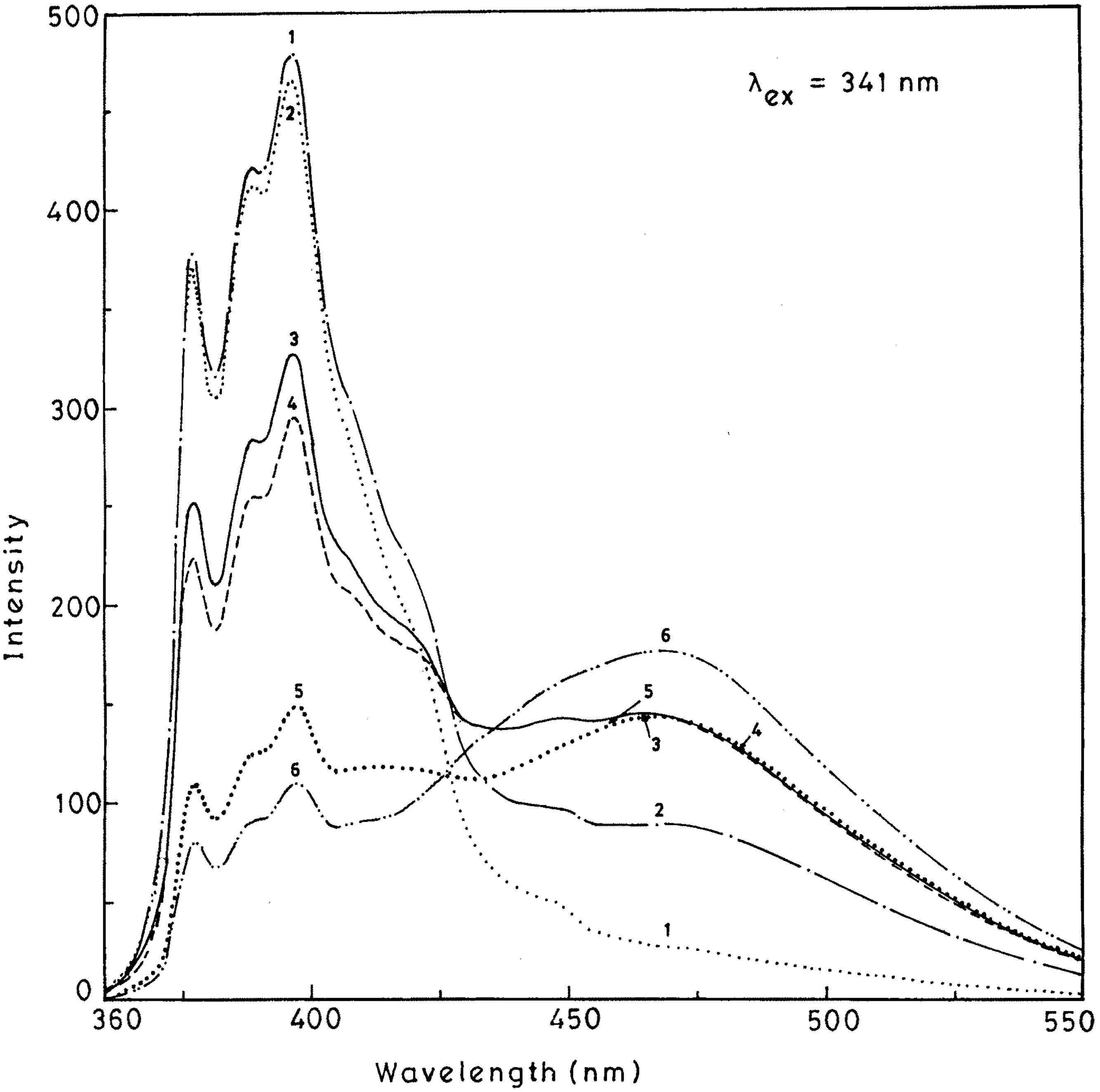


Fig. 3·35 - Fluorescence spectra of PS films doped by Pyrene and gACA.

1) Pyrene 0·1728 wt % (without gACA) in PS films and

2-6) Spectra containing 0·1728 wt % Pyrene and varying amounts of gACA.

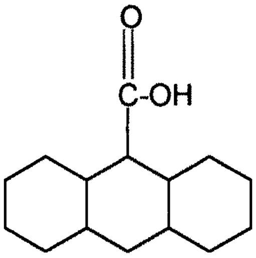
2) 0·0009122 wt % 3) 0·009122 wt % 4) 0·018244 wt %
5) 0·0365 wt % 6) 0·05727 wt %

excitation energy of pyrene. The spectrum of (0.17275 wt %) without 9ACA in PS film is also shown in the same figure (spectrum a). It is seen that the spectrum a exhibits structured emission of pyrene monomer in PS matrix. The spectra of films containing 9ACA show quenching of pyrene monomer emission. The quenching seems to depend upon the wt % of 9ACA. A 0.001019 wt % of 9ACA a red shifted broad emission band is observed peaking at about 467 nm. At 0.0736 wt % of 9ACA, this broad emission band becomes more prominent. 9ACA in PS films without pyrene have shown broad emission in the same region. Hence it is the excimer emission of 9ACA. The quenching of pyrene monomer emission in presence of 9ACA suggest the transfer of excitation energy from pyrene to 9ACA molecule.

Photophysics of organic molecules has indicated that the fluorescence always arised from the lowest excited state of each multiplicity. Manyfold. Exception to this is interesting and have been the subject of many investigation. Dual luminescence is one of such exception which consists two distinct fluorescence spectra from a single apparently homogenous sample. The best known case is monomer and excimer or exciplex emission due to aggregation between excited and ground state molecule.

Mataga N and Ottolenghi M, in Molecular Associations, Vol.2 ed. Foster R (Academic Press London) P.1 (1979).[78] In absence of such molecular association dual luminescene is attributed to different confirmers conformers of the excited molecule.

Reling W and Angew, Chem. 98, 968 (1987) dual luminescence has also been exhibited by 9-ACA molecules when dispersed in different matrices. In polymer matrices depending on nature of polymer it has shown emission in different region of visible spectrum. The structured emission of 9ACA observed in PVA matrix is monomer emission and broad structureless emission peaking at 467 nm is not to excimer but a broad. Structureless band develops on long wavelngth side when [9ACA] 0.02038 wt %. It was pointed out by Werner and Hercules that such b-emission band in solution from non-protic solvent such as benzene is originating from a coplanar(II) form of 9ACA resulting from the twisting of the carboxyl substituent from the perpendicular (⊥) or twisted ground state.



The intensity of 'b' emission band at 467 nm increases with 9ACA concentration.

The observed 'b' emission is further confirmed by excitation spectra of the film containing 0.17275 wt % pyrene and 0.05661. The excitation spectrum of the film monitored at emission wavelength 467 nm is shown in fig.3.36. The spectrum is appeared in region 300-400 nm and is structured. The band at 370 nm has maximum intensity. The structured emission band suggest that the excimer is not formed in the excited state. Hence 'b' emission must be due to some conformer of 9ACA molecule and not due to an excimer. The formation of excimer is indicated by the broad red shifted band towards red side of the visible spectrum.

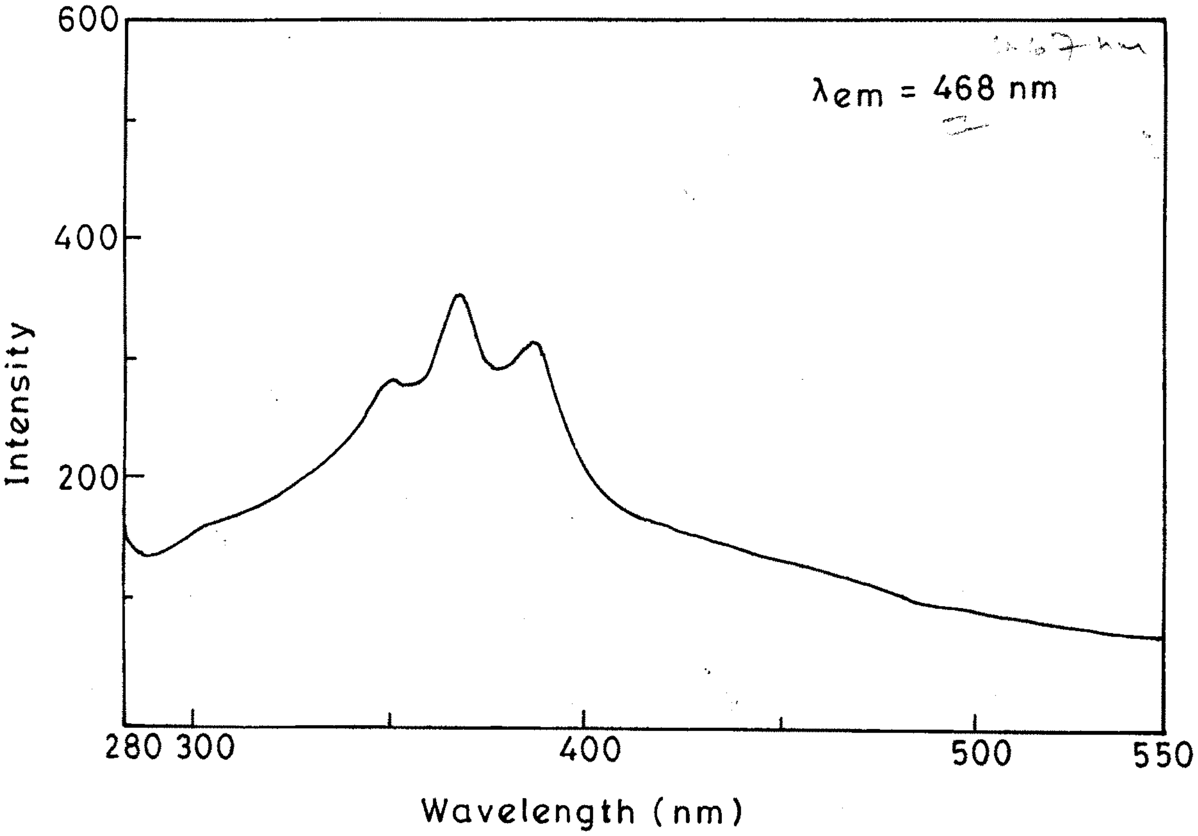


Fig.3·36- Excitation spectrum of gACA in PS film.