CHAPTER - 5

RESULT AND DISCUSSION

In this chapter luminescence spectra have been presented for discussions. The six specimens undertaken for the study are 5,7 - dihydroxy - 4 - methyl coumarin and five of its polyesters. The specimens under investigation are

1)	5,7 - OH - 4 - Me - Coumarin	M
2)	Copolymer of 5,7 - OH - 4 - Me - Coumarin with Maleic acid	P_1
3)	Copolymer of 5,7 - OH - 4 - Me -Coumarin with Sebacic acid	P_2
4)	Copolymer of 5,7 - OH - 4 - Me - Coumarin with Phthalic acid	P_3
5)	Copolymer of 5,7 - OH - 4 - Me - Coumarin with Isophthalic acid	P_4
6)	Copolymer of 5,7 - OH - 4 - Me - Coumarin with Tetephthalic acid	P_5

Emission spectra have been presented for all the above specimens monomer M and Polymers P_1 through P_5 in as received condition and also when they are dissolved into the solvents. Here the solvents used are Dioxane (DO), Tetrahydrofuran (THF), Dimethylformamide (DMF), Acetonitrile (ACN) and Dimethylsulphoxide (DMSO); at two different concentrations (lower as well as higher concentration)

Figures 5.1 to 5.6 represent fluorescence spectra for the monomer specimen M and polymer specimens P_1 through P_5 , for the as received specimens. In as received monomer specimen, the emission peak is observed at 430 nm. However, this peak is observed to have shifted at 410 nm in all the polymer specimens P_1 through P_5. The intensity of the peak also found to increase in the specimens in an order M, P_2, P_1, P_3,P_4 and P_5. Another emission peak which occurs around 520 nm as a hump or a shoulder in all the above specimens has also been observed. It is known that non-substituted coumarin shows very less fluorescence. The less

fluorescence in coumarin can be explained as, it is suggested [1] that energy gap between the highest occupied and lowest unoccupied orbitals of carbonyl substituted molecule is smaller than the gap between the highest occupied and lowest unoccupied orbitals of unsubstituted coumarin molecule. Thus the carbonyl present at position 2 of the coumarin molecule attributes to non-fluorescent behaviour of it. In fact carbonyl group in the main ring enhances [2] the rate constant for intersystem crossing and decreases the fluorescence quantum yield. Substitution of different groups reduces intersystem crossing resulting in the increased fluorescence. Thus, the fluorescence efficiency of coumarin depends on nature and position of the substituents, and may get changed due to the change in surrounding media such as polarity, pH, concentration etc. Substituent groups also decide the intensity of fluorescence. Substituents enhancing electron mobility increases the fluorescence intensity and substituents which decrease the electron mobility decreases fluorescence intensity. The observed fluorescence in monomer is due to the substitution at 4^{th} , 5^{th} and 7^{th} position of coumarin, as these substitutions reduce intersystem crossing.

Monomer (M) shows fluorescence peak at 430 nm while polymers shows fluorescence peak at 410 nm. The peak at 520 nm appears as a shoulder. The observed shift of 430 nm to 400 nm can be attributed to esterification of hydroxyl group present at 5^{th} and 7^{th} position of coumarin.

The intensity of emission at 410 nm increases in specimens P_1 to P_5 compared to specimen M. An appreciable increase in number of molecules forming the chains of specimens P_1 to P_5 causes the intensity of this emission to increase. In polymers, P_1 and P_2, 5,7 - dihydroxy - 4 - methyl coumarins are connected by aliphatic group while in rest of the polymer specimens the connecting units are the aromatic groups. The intensity of specimen P_1 is much higher than that in the specimen P_2. This is due to the difference in repeating units of the polymers P_1 and P_2. In polymer P_1, the repeating unit consists of the aliphatic group - CH=CH -

while in polymer P_2, repeating unit consists of the aliphatic group - (CH_2)$_8$. The double bond in aliphatic group P_1 contributes to the increased polarizability of the molecule of P_1. This increased polarizability of P_1 contributes to the increased intensity of the fluorescence. In the polymer specimen P_2; two 5,7 - dihydroxy - 4 - methyl coumarin molecules are connected by a chain of eight methyl groups. This chain attributes to the decreased intensity of the fluorescence.

Comparison of the intensity for specimens P_1 and P_2 with the intensity of specimens P_3 to P_5 show that the latter specimens exhibit more intensity than the former. This can also been explained on the basis of the polarizability. The polarizability is larger in the specimen P_3 to P_5 because of the repeating units which consist of aromatic groups instead of aliphatic ones. The π - bond character of the aromatic nuclei will enhance the polarizability of polymer molecules P_3 to P_5

The enhanced polarizability reflected in increased intensity of emission band in the polymer specimen P_5 is considerably more than in P_4 and also than in P_3. Here the steric factors [3,4,5] play an important role in deciding the intensity of the emission. The steric hindrance decreases the intensity of fluorescence viz , the cyanine dyes show less intensity due to steric hindrance. The steric hindrance in P_5 is less than P_4 and in turn less than in P_3. The comparison of the structure of repeating units of P_5 with P_4 and P_3 show that repeating units of latter have higher steric hindrance due to 1-3 and 1-2 substitution on the benzene ring of the acid. The steric interaction will be maximum in the specimen P_3 due to the presence of phthalate group in the repeating units. Therefore,the intensity of fluorescence in P_3 is minimum among the polymer P_3,P_4 and P_5. The steric hindrance is least in P_5 due to presence of terephthalate group in repeating units. This, in turn, results in the higher intensity of emission in specimen P_5.

The second peak is observed in all the fluorescence spectra around 520 nm. This band can be attributed to the prescence of heteroatom in the pyrole ring of the coumarin. The non bonding electron present on the oxygen can be held mainly responsible for this peak. It is observed that the position of this emission peak in the monomer M as well as in the polymer specimens P_1 to P_5 is same.

This is an expected phenomena since structure of the pyrole ring remains same in the monomer specimen M and also in the polymer specimens P_1 to P_5. This has not been the case as in the benzene ring; conjugated to the pyrole ring. The 5^{th} and 7^{th} position of monomer is occupied by the hydroxyl group, however, this position is occupied by the ester group in all the polymers. Therefore, no shift in the energy band is expected. Hence, it has been expected to be the reason for the peak not getting shifted in the polymer specimens.

The monomer and polymer specimen P_1 to P_5 are then dissolved in the solvents, such as Dioxane (DO), Tetrahydrofuran (THF), Dimethylformamide (DMF), Acetonitrile (ACN) and Dimethylsulphoxide (DMSO). Their fluorescence spectra in the above specimens are reported in figures 5.7 to 5.12. Figure 5.7 shows the record of fluorescence spectra for the monomer specimen in all the above solvents while figure 5.8 to 5.12 show fluorescence curves for the polymer specimens P_1, P_2,P_3,P_4 and P_5 in the solvents respectively. It can be seen from the figures that as polarity of solvent increases, the fluorescence peak shifts towards higher wavelength, that means the red shift or bathochromic shift is observed. It is also seen that the intensity of the fluorescence peak depends on the polarity of the solvents. As polarity increases, the intensity of the peak is also increases.

Luminescence spectra for the monomer specimen M and polymer P_1 through P_5 in different solvents are shown in figure 5.7 to 5.12. The different solvents used are Dioxane (DO), Tetrahydrofuran (THF), Dimethylformamide (DMF), Acetonitrile (ACN) and Dimethylsulphoxide (DMSO).

Figure 5.7 represents the fluorescence spectra for the monomer M, while figure 5.8 to 5. 12 are the curves of fluorescence for the polymer specimen P_1,P_2,P_3,P_4 and P_5 respectively. By observing the figure it is seen that as polarity increases fluorescence peak shift towards longer wavelength. The extent of the shift is not specific but depends on the specimen and the solvent. For all the specimens; transitions [6] involved are $\pi \rightarrow \pi^*$.

When a specimen is mixed in solvent, an interaction takes place. This interaction can be similar to the polarity induced interaction results in perturbing the position of energy level. Due to this perturbation, position of energy level changes, they are shifted in such a way that energy gap between them is reduced i.e. energy gap between highest occupied level and lowest unoccupied level decreases. The explanation for lowering the value of energy gap can be given as

The unpaired electron present on the oxygen atom delocalises the energy throughout the system (intramolecular charge transfer). As polarity increases, more energy is delocalised, reducing the gap between energy levels i.e. energy in $\pi^* \rightarrow \pi$ transition reduce, resulting in observed red shift or bathochromic shift. The magnitude of shift depends on the polarity, as the shift is the result of polarity induced interaction. It is also seen that intensity of peak increases with the polarity of the solvent. For solvent with low polarity, the $\pi^* \rightarrow \pi$ triplet state may be close to the first excited singlet state. This closeness of energy level allows intersystem crossing in large amount resulting in the reduction of solute molecule. However in highly polar solvents, the energy levels are so perturbed that the $\pi^* \rightarrow \pi$ triplet state and first excited singlet are separated by large energy gap thereby reducing the polarizability of intersystem crossing hence the increased intensity.

The figures 5.13 to 5.18 shows the fluorescence spectra for specimens M, P_1, P_2, P_3, P_4 and P_5 respectively for the solutions of high concentration. It can be seen from the graph at higher concentration the intensity of peak is less as compared to intensity of peak for lower concentration. At higher concentration, due to low fluorescence yield, the intensity of peak is less. Concentration quenching is responsible for low fluorescence yield In high concentrated solution collision between solvent and solute more, hence loss of energy is more; thereby intensity of the peak is less. The position of emission peak doesn't shift, clearly indicates that change in concentration do not perturb the position of ground state and fist excited singlet state. For confirmation of above conclusions more work is needed in the study of luminescence in solvents at various concentrations. This is presently done at our laboratory by other workers.

FIGURE 5.1 Fluorescence spectra for As received M specimen monomer

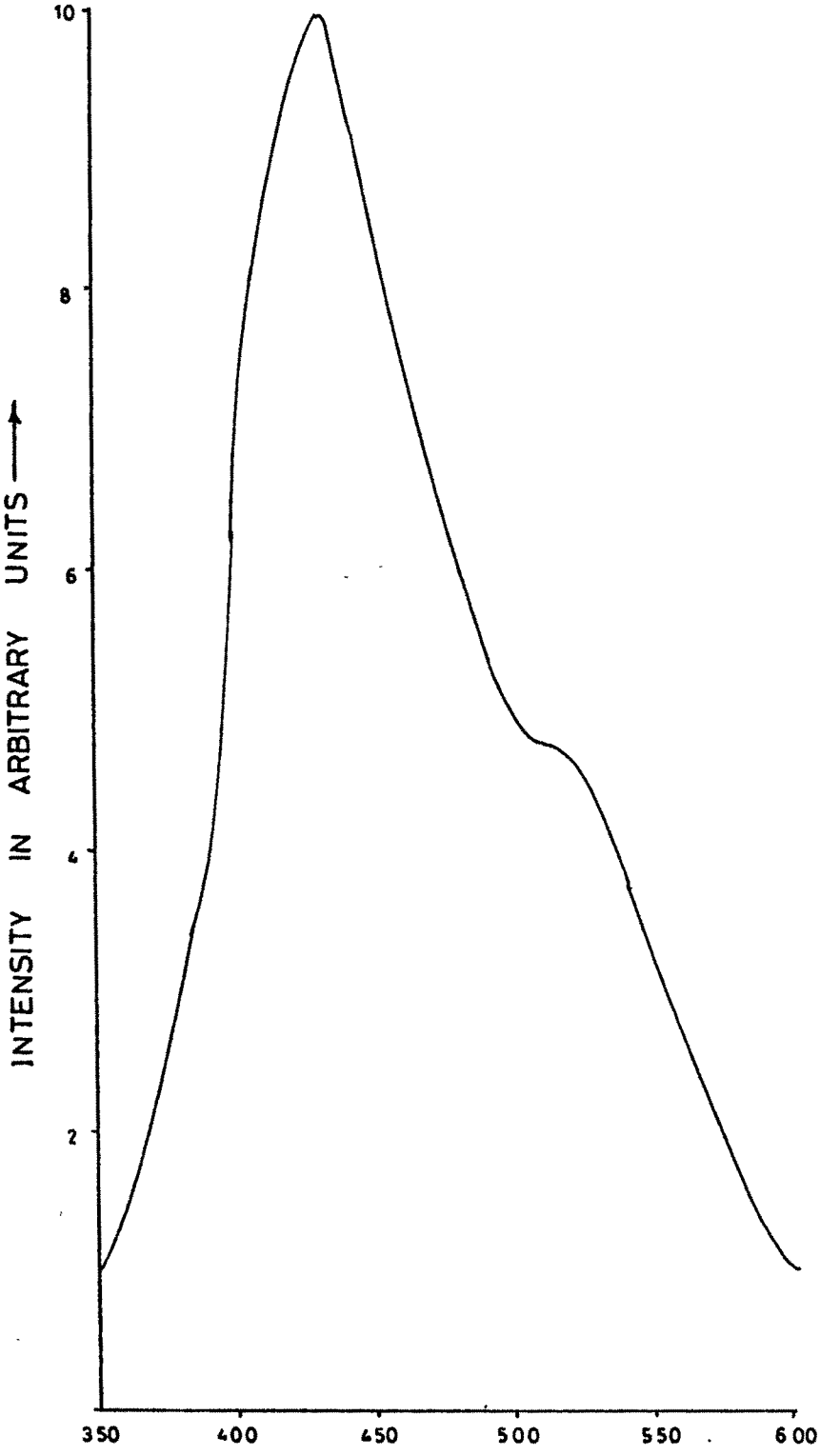
10
8
6
4
2
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.1

FIGURE 5.2 Fluorescence spectra for As received P_1 specimen polymer

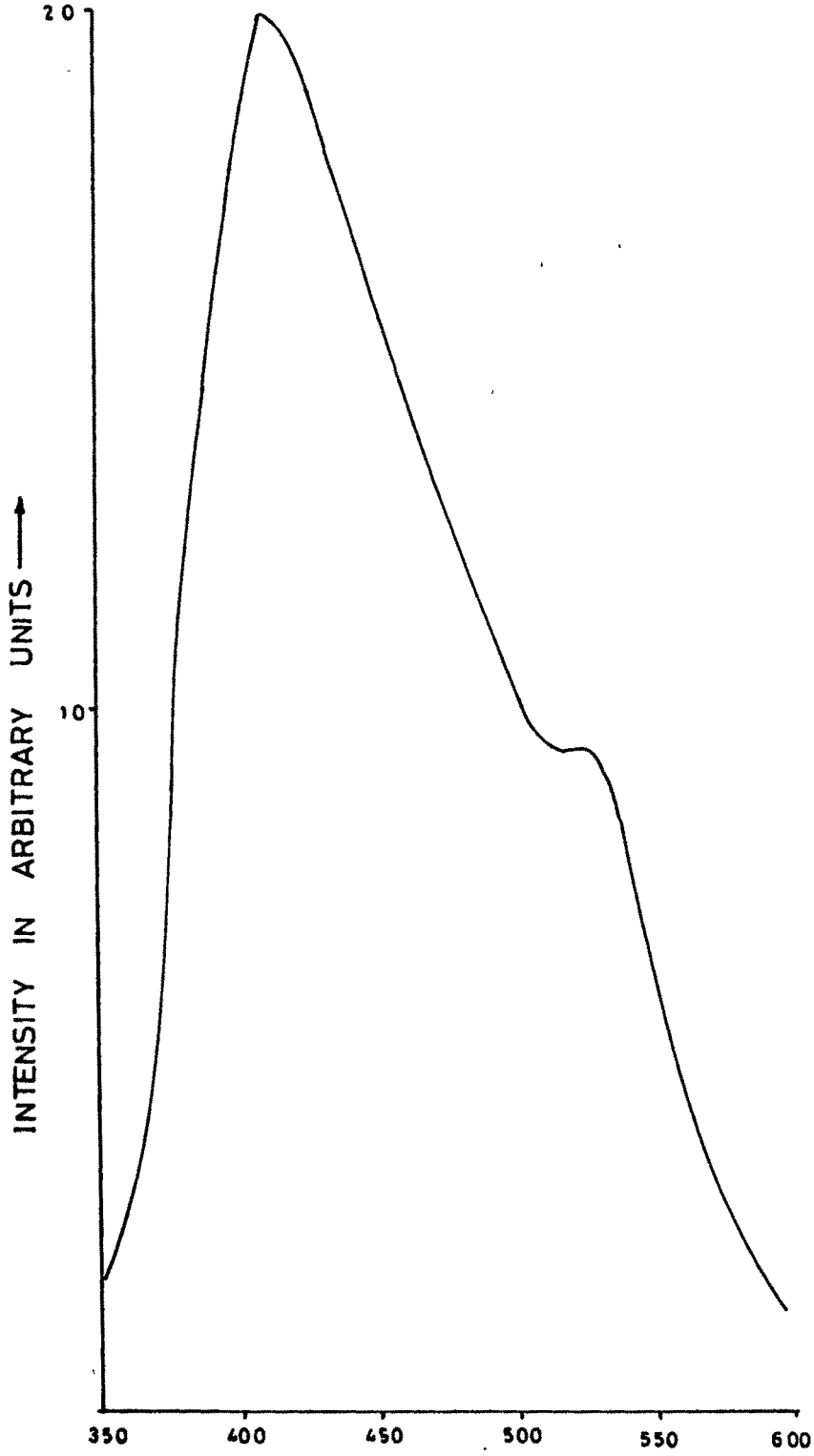
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm
FIGURE: 5.2

FIGURE 5.3 **Fluorescence spectra for As received P_2 specimen polymer**

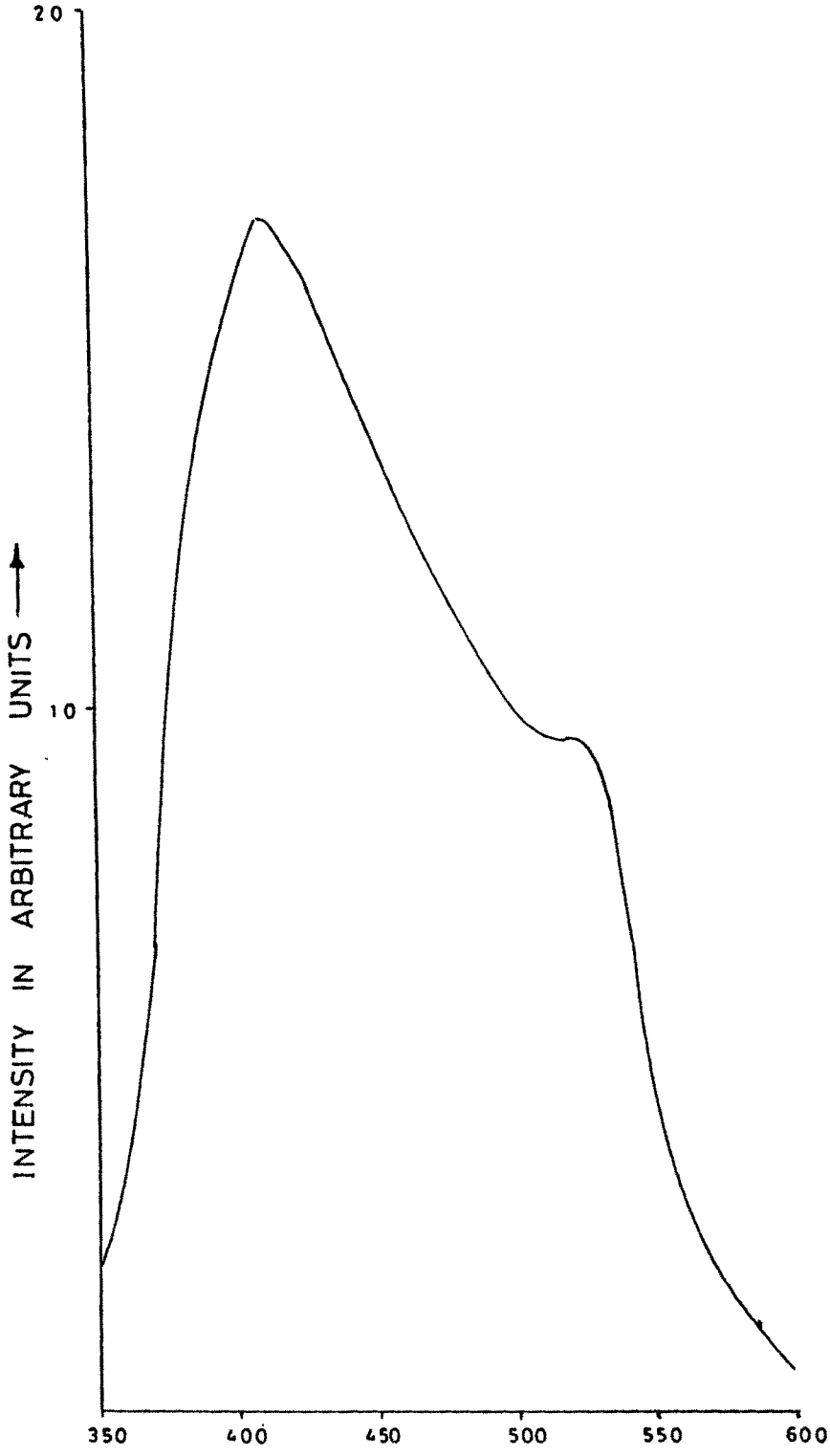
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.3

FIGURE 5.4 Fluorescence spectra for As received P_3 specimen polymer

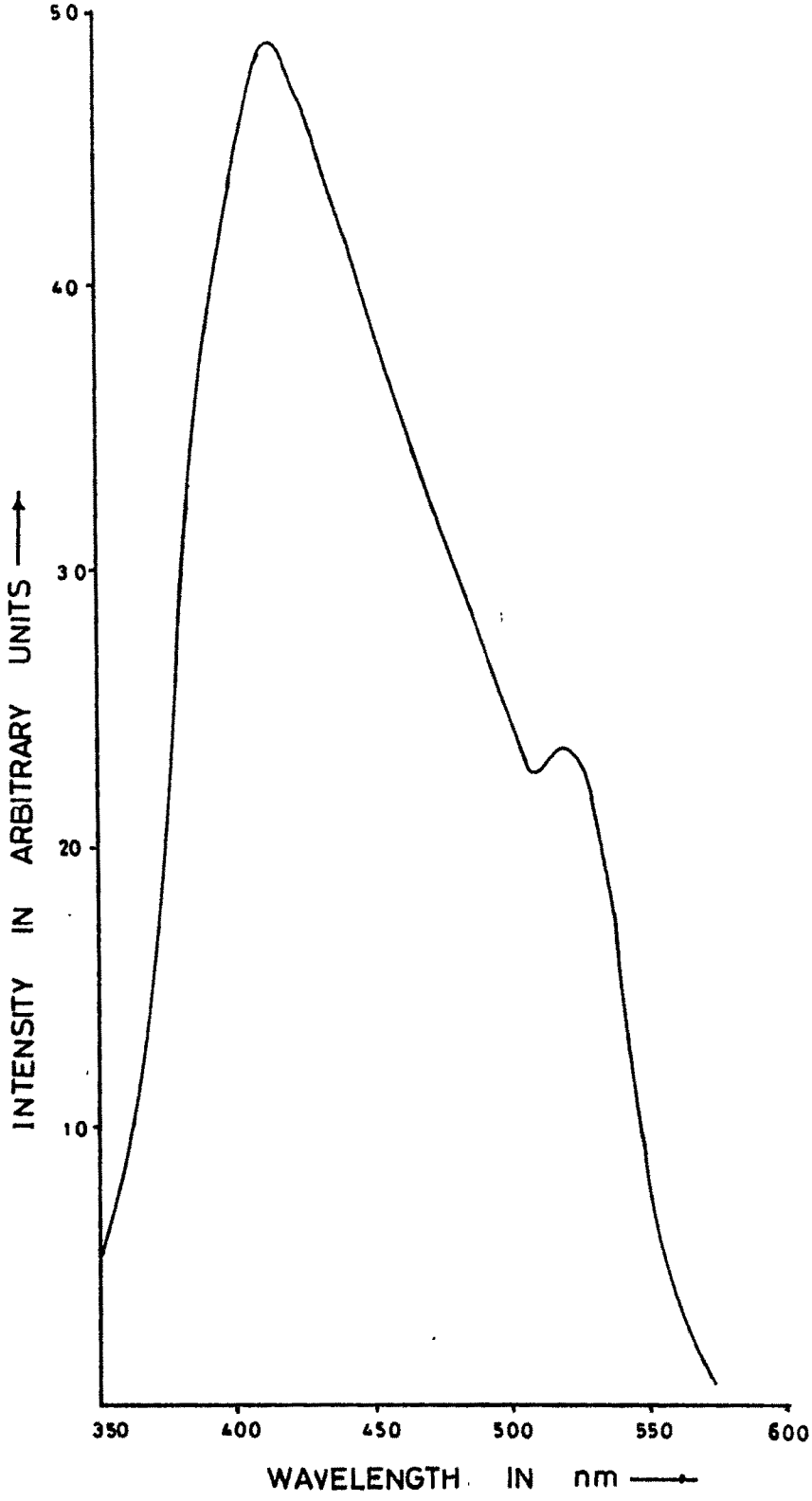
50
40
30
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.4

FIGURE 5.5 Fluorescence spectra for As received P4 specimen polymer

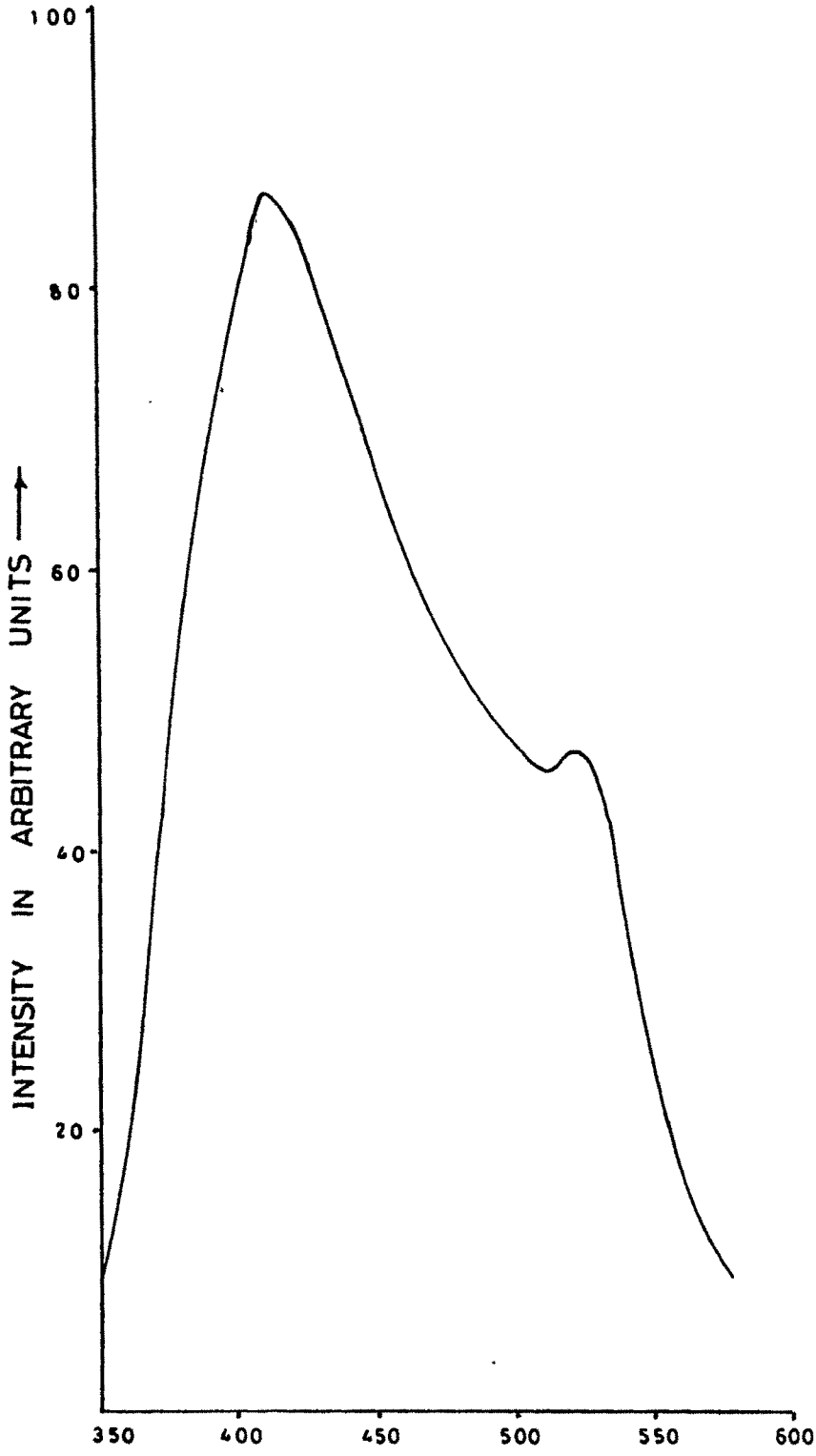
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS ⟶
350
400
450
500
550
600
WAVELENGTH IN nm ⟶

FIGURE: 5.5

FIGURE 5.6 **Fluorescence spectra for As received P_5 specimen polymer**

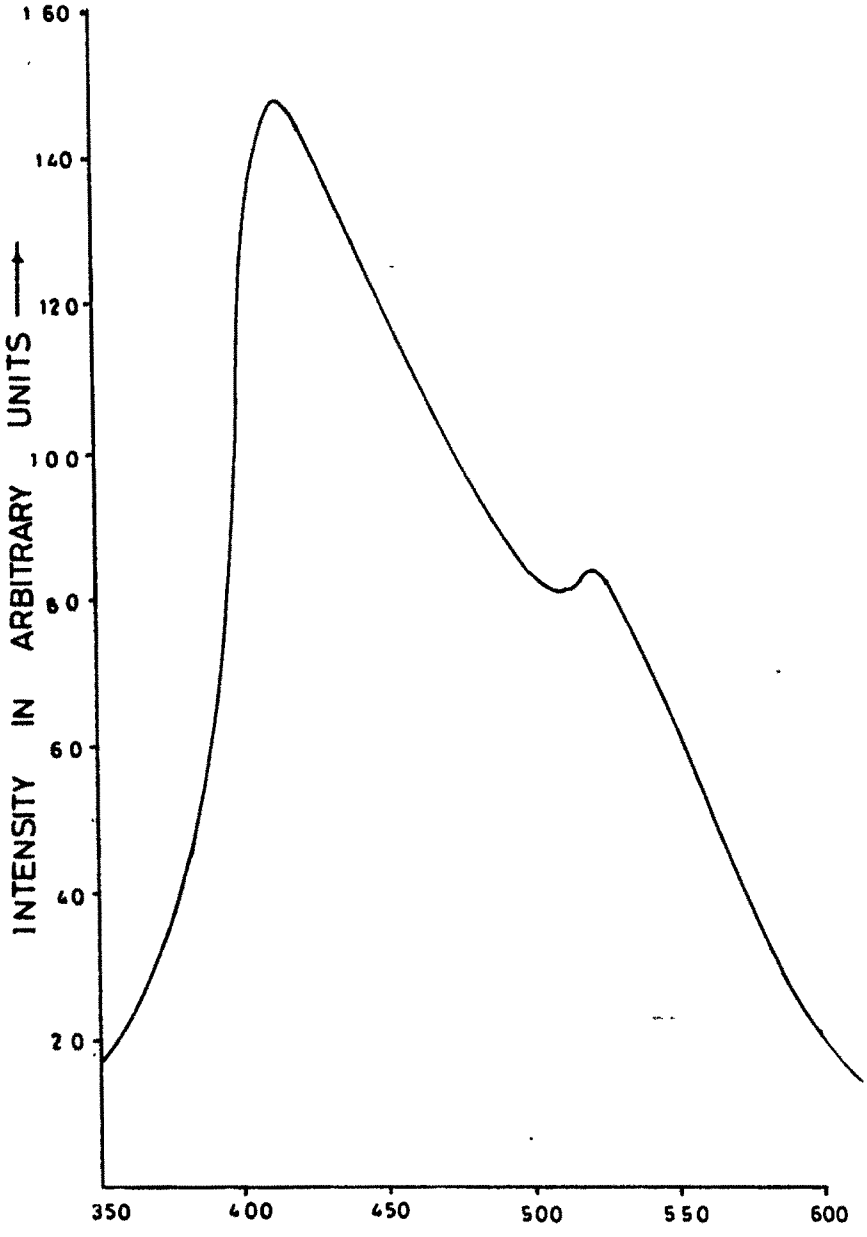
160
140
120
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.6

FIGURE 5.7 **Fluorescence spectra for monomer M dissolved indifferent solvents for Low concentration**

1. **Dioxane** ————
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

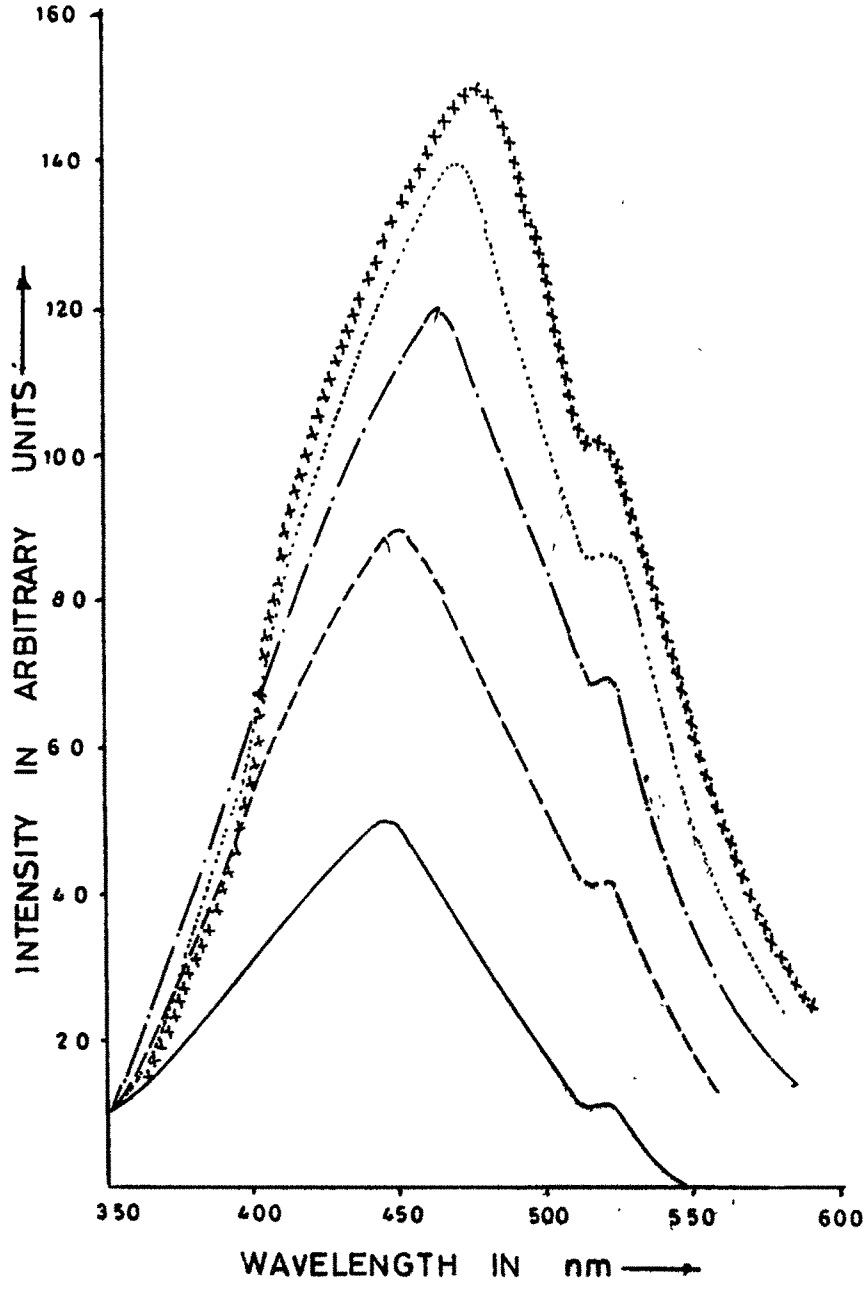
160
140
120
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.7

FIGURE 5.8 Fluorescence spectra for polymer P_1 dissolved indifferent solvents for Low concentration

1. Dioxane ————
2. Teterahydrofuran - - - - -
3. Dimethylformamide -.-.-.
4. Acetonitrile . . . .
5. Dimethylsulphoxide x x x x

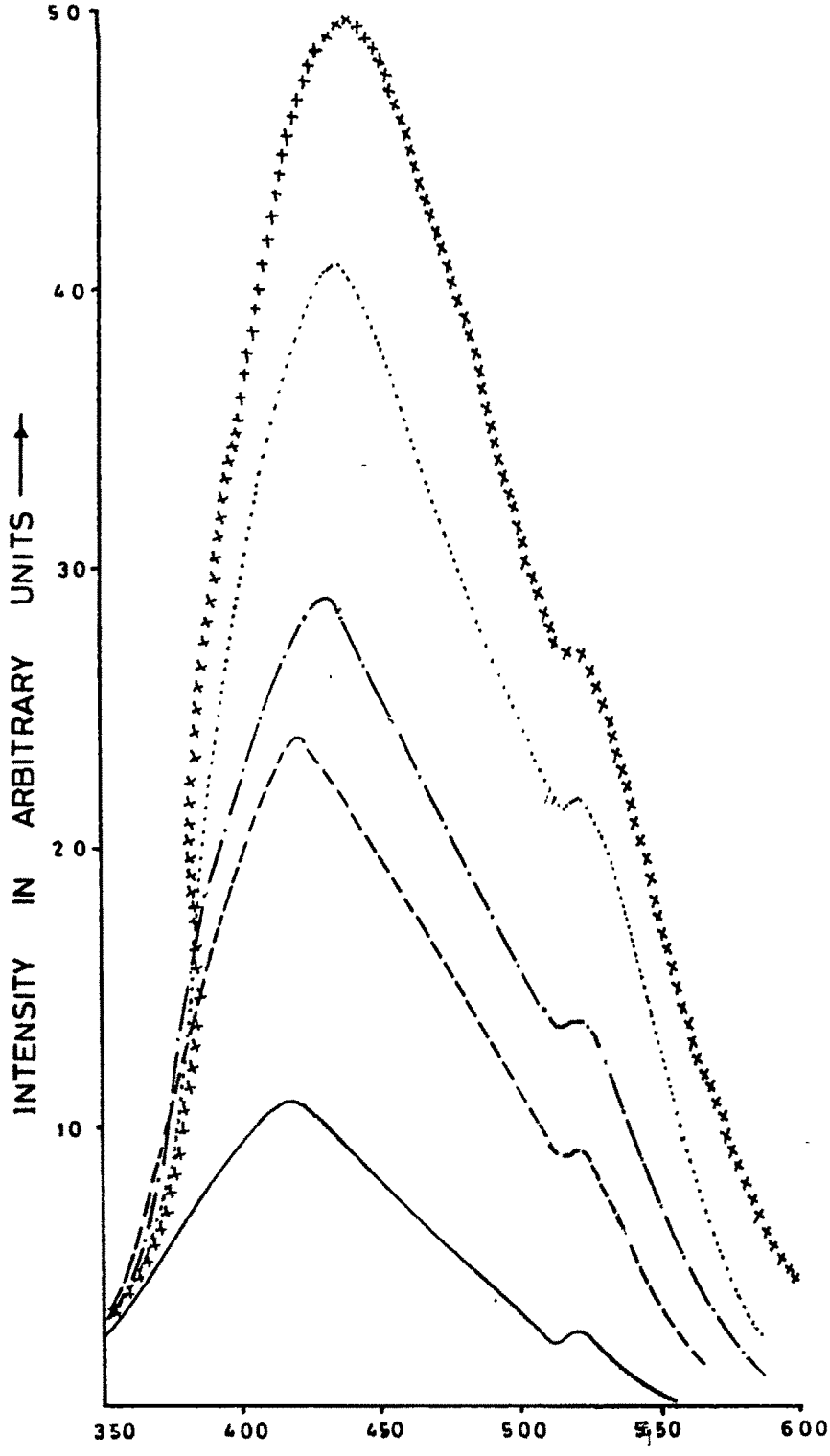
50
40
30
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.8

FIGURE 5.9 **Fluorescence spectra for polymer P_2 dissolved indifferent solvents for Low concentration**

1. **Dioxane** ————
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

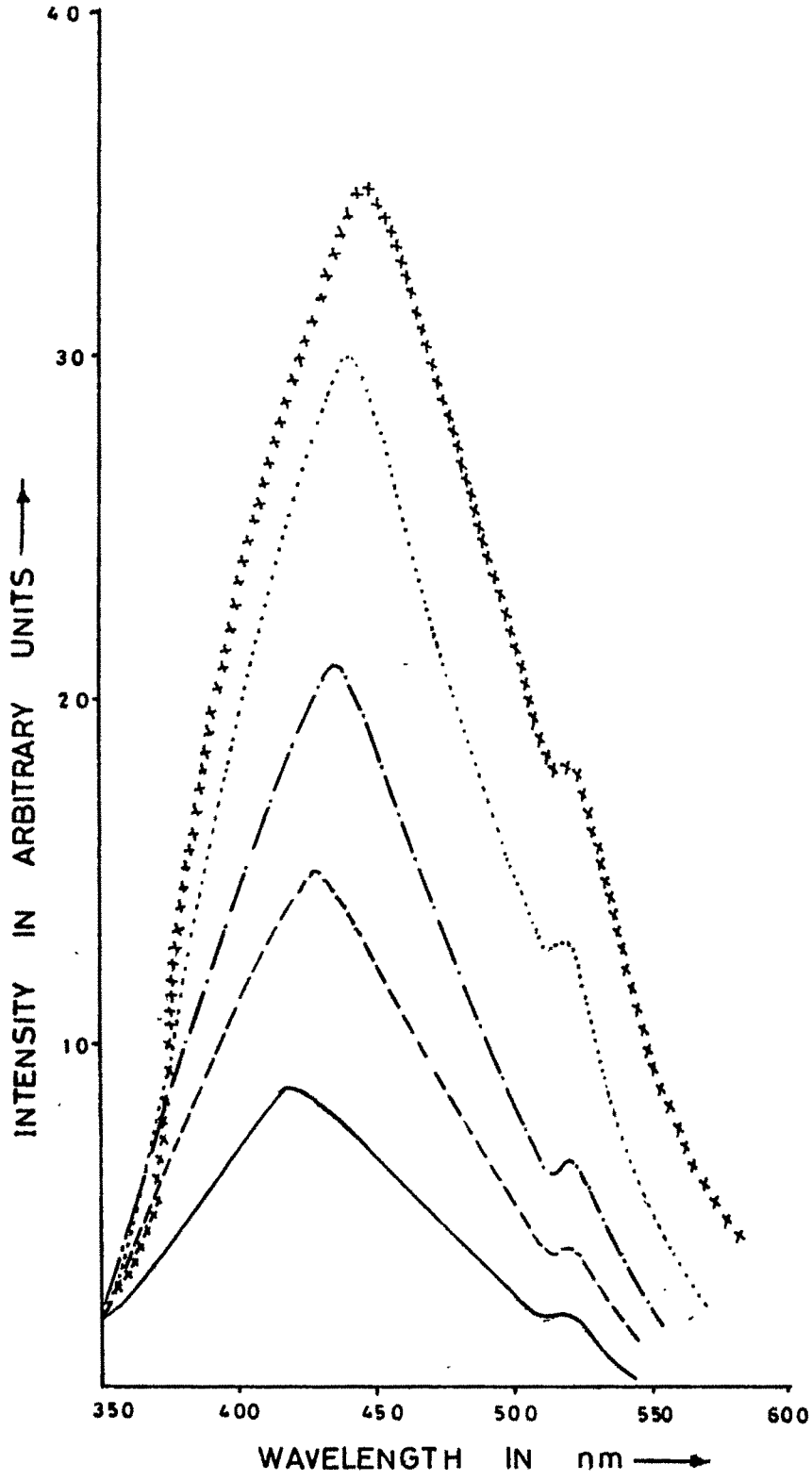
40
30
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE : 5.9

FIGURE 5.10 **Fluorescence spectra for polymer P_3 dissolved indifferent solvents for Low concentration**

1. **Dioxane** ———
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

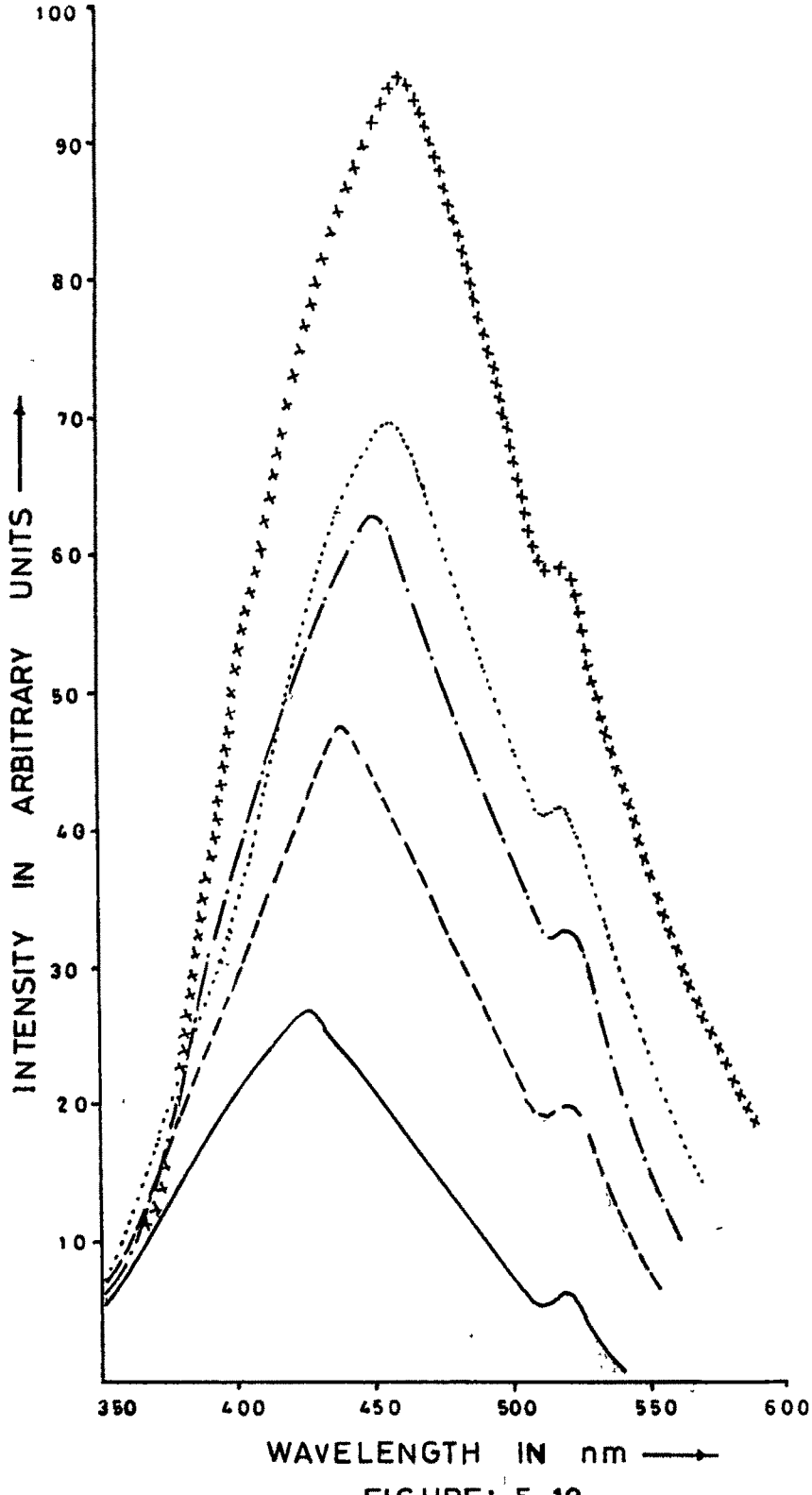
100
90
80
70
60
50
40
30
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.10

FIGURE 5.12 **Fluorescence spectra for polymer P_5 dissolved indifferent solvents for Low concentration**

1. **Dioxane** ————
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

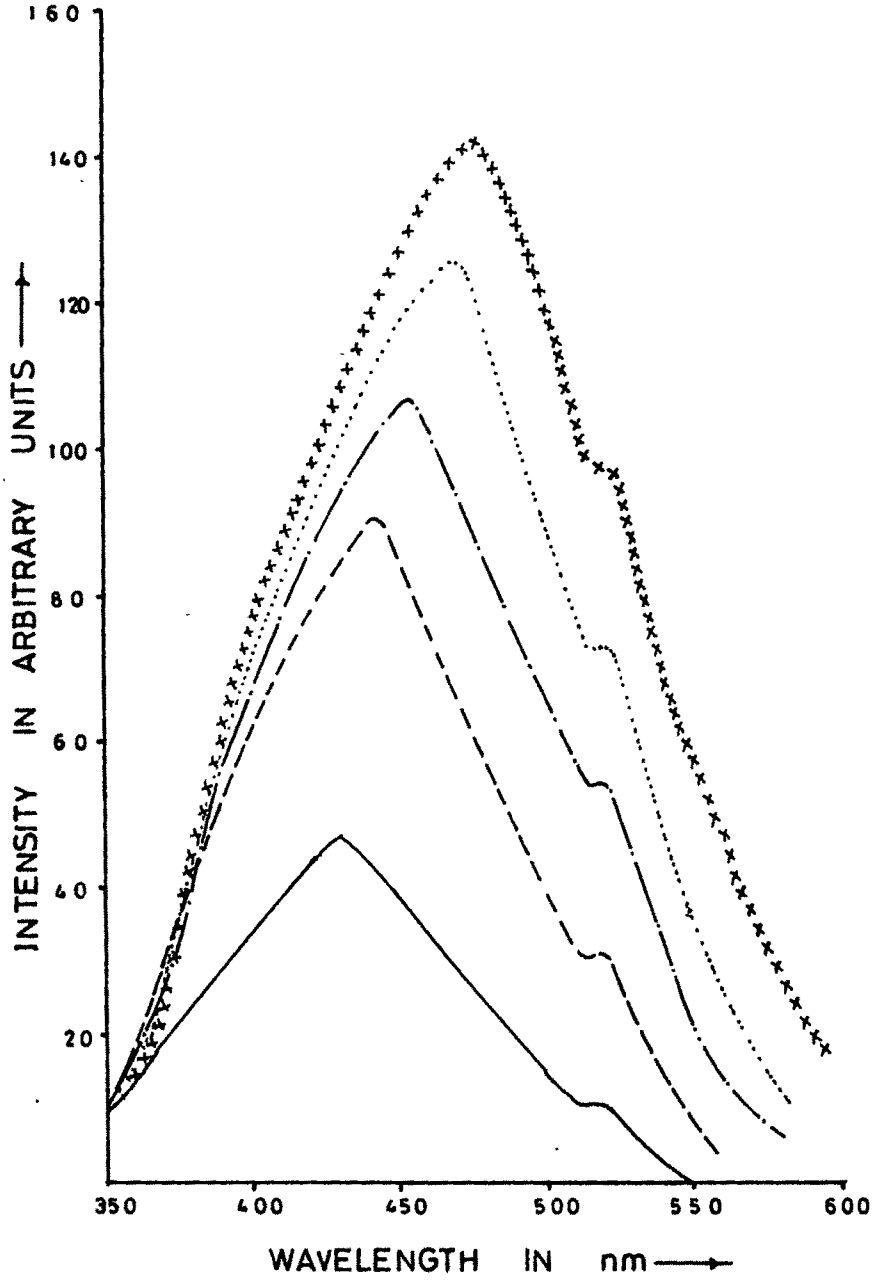
160
140
120
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5. 11

FIGURE 5.11 **Fluorescence spectra for polymer P_4 dissolved indifferent solvents for Low concentration**

1. **Dioxane** ———
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

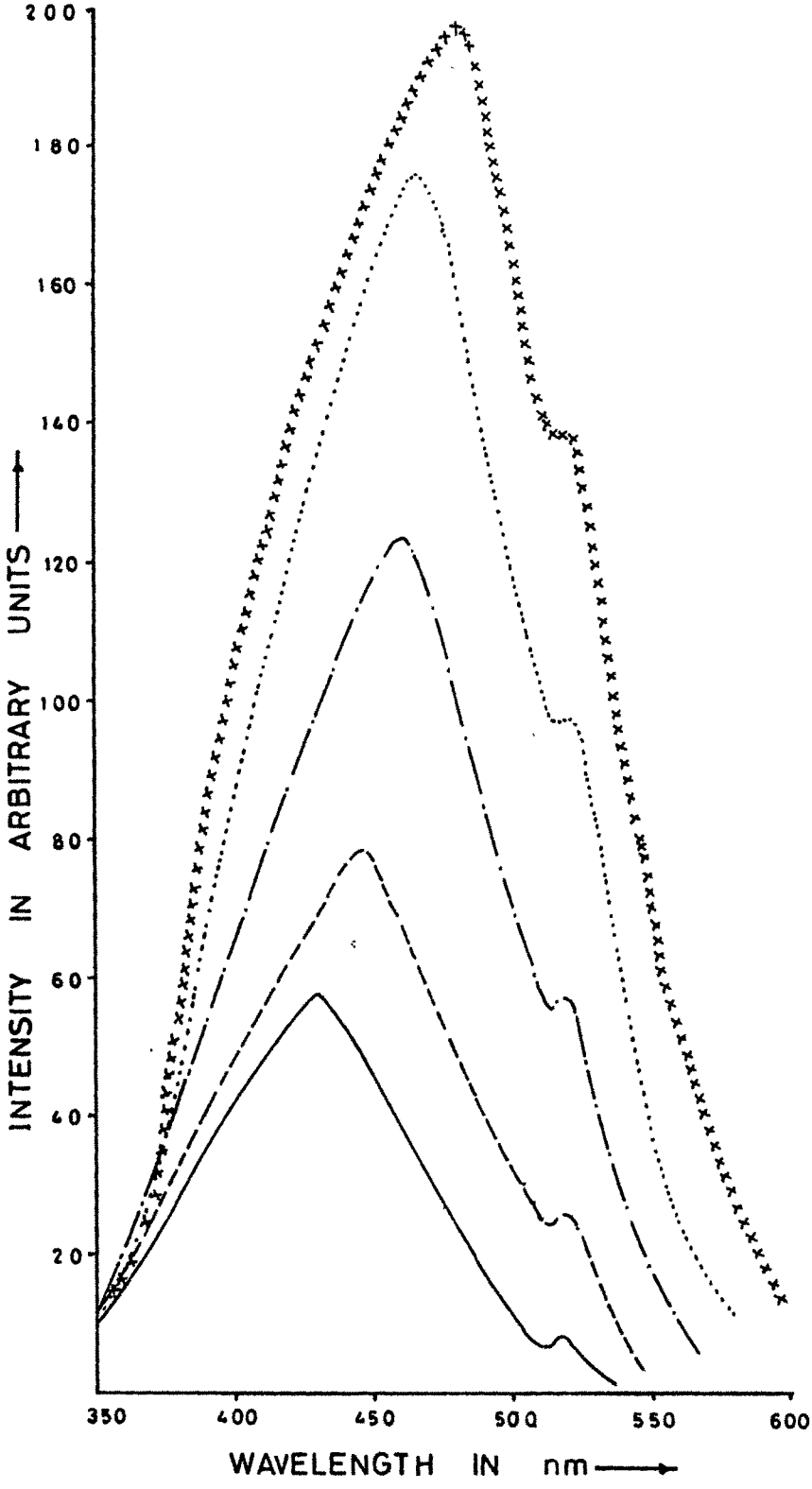
200
180
160
140
120
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.12

FIGURE 5.13 **Fluorescence spectra for monomer M dissolved indifferent solvents for High concentration**

1. **Dioxane** ———
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

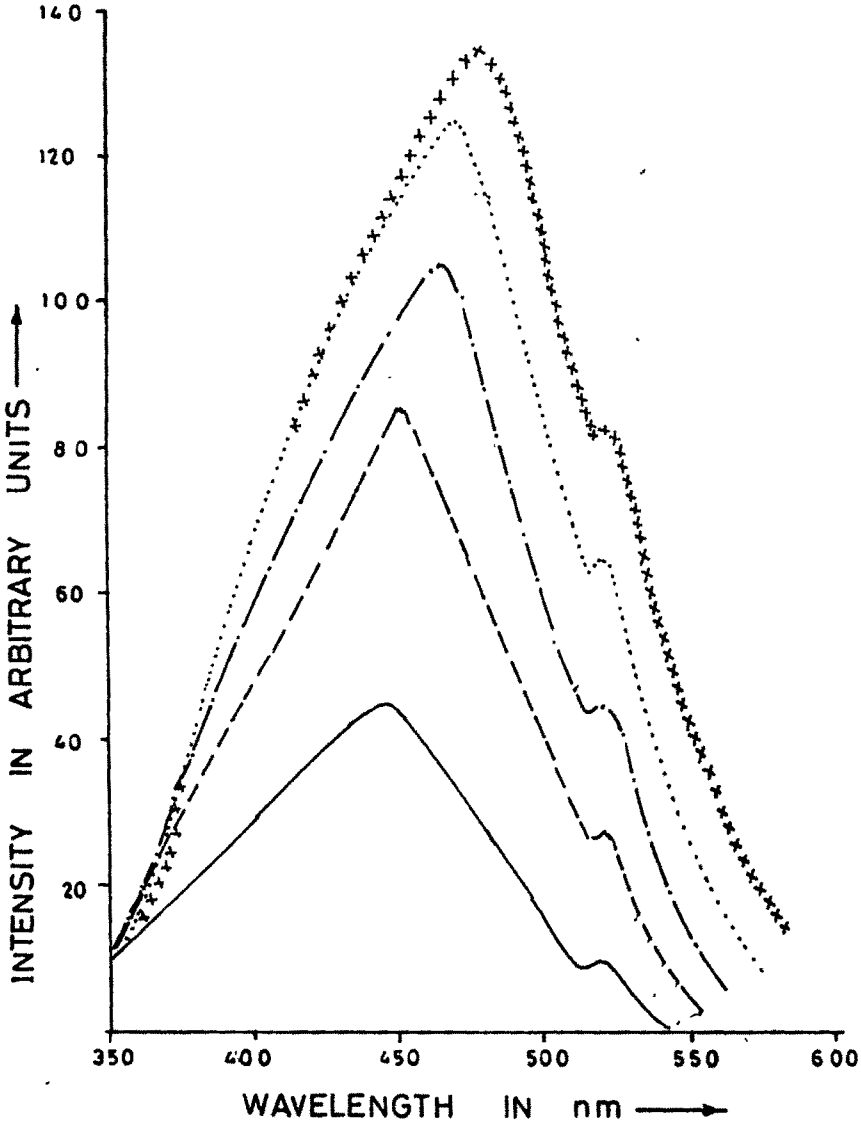
140
120
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.13

FIGURE 5.14 Fluorescence spectra for polymer P_1 dissolved indifferent solvents for High concentration

1. Dioxane ———
2. Teterahydrofuran - - - - -
3. Dimethylformamide -.-.-.
4. Acetonitrile . . . .
5. Dimethylsulphoxide x x x x

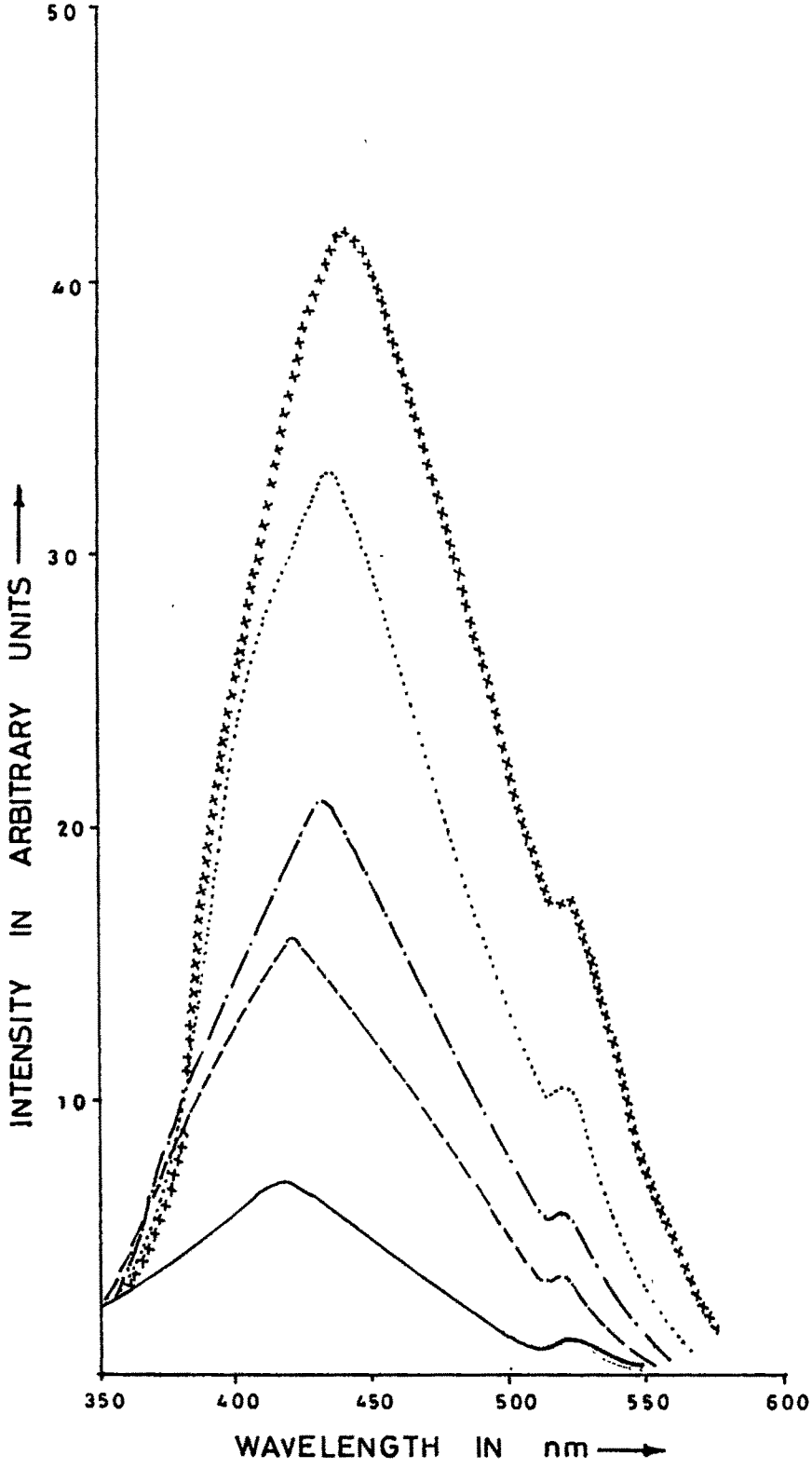
50
40
30
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.14

FIGURE 5.15 **Fluorescence spectra for polymer P_2 dissolved indifferent solvents for High concentration**

1. **Dioxane** ———
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

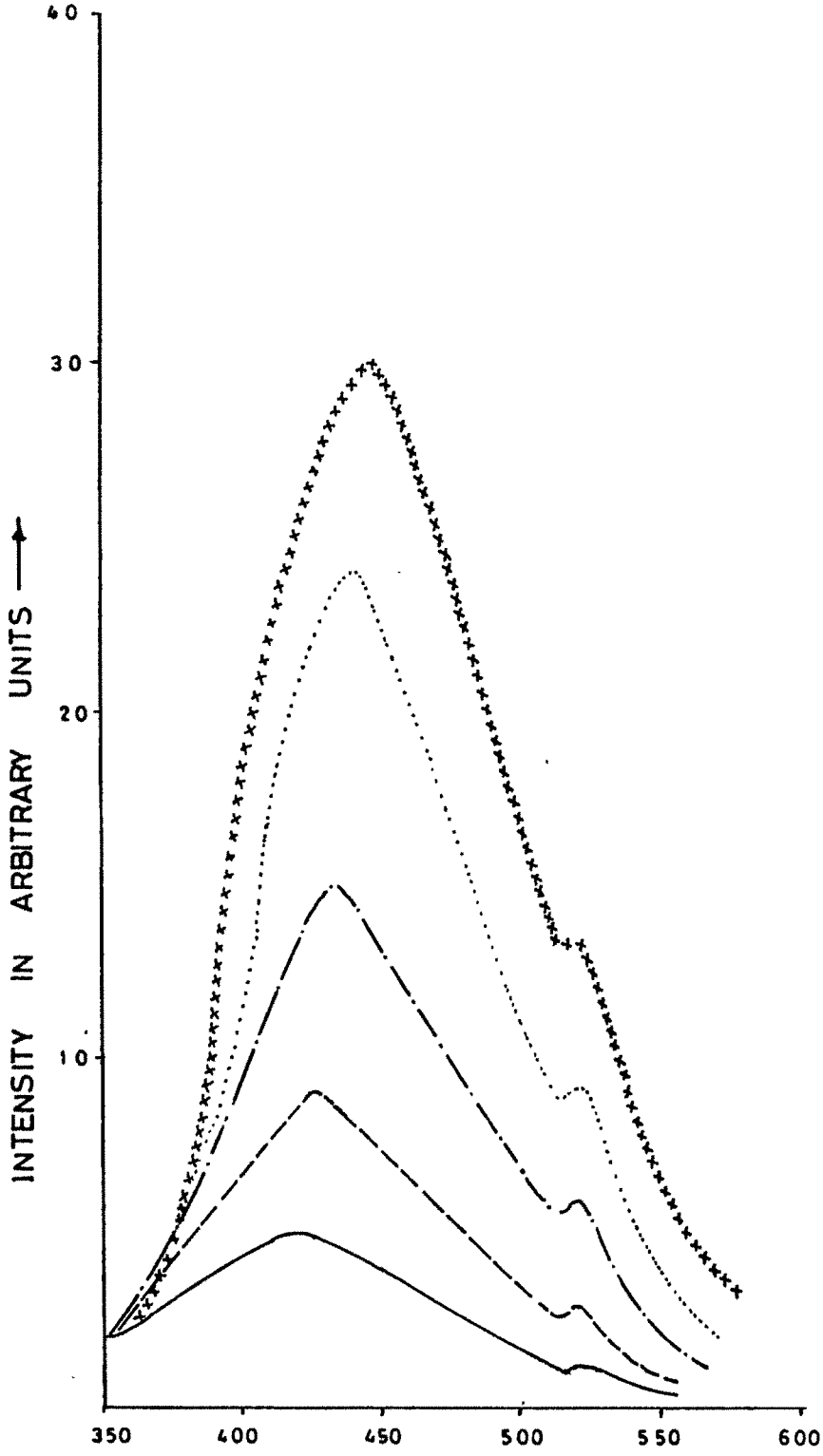
40
30
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.15

FIGURE 5.16 **Fluorescence spectra for polymer P_3 dissolved indifferent solvents for High concentration**

1. **Dioxane** ———
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

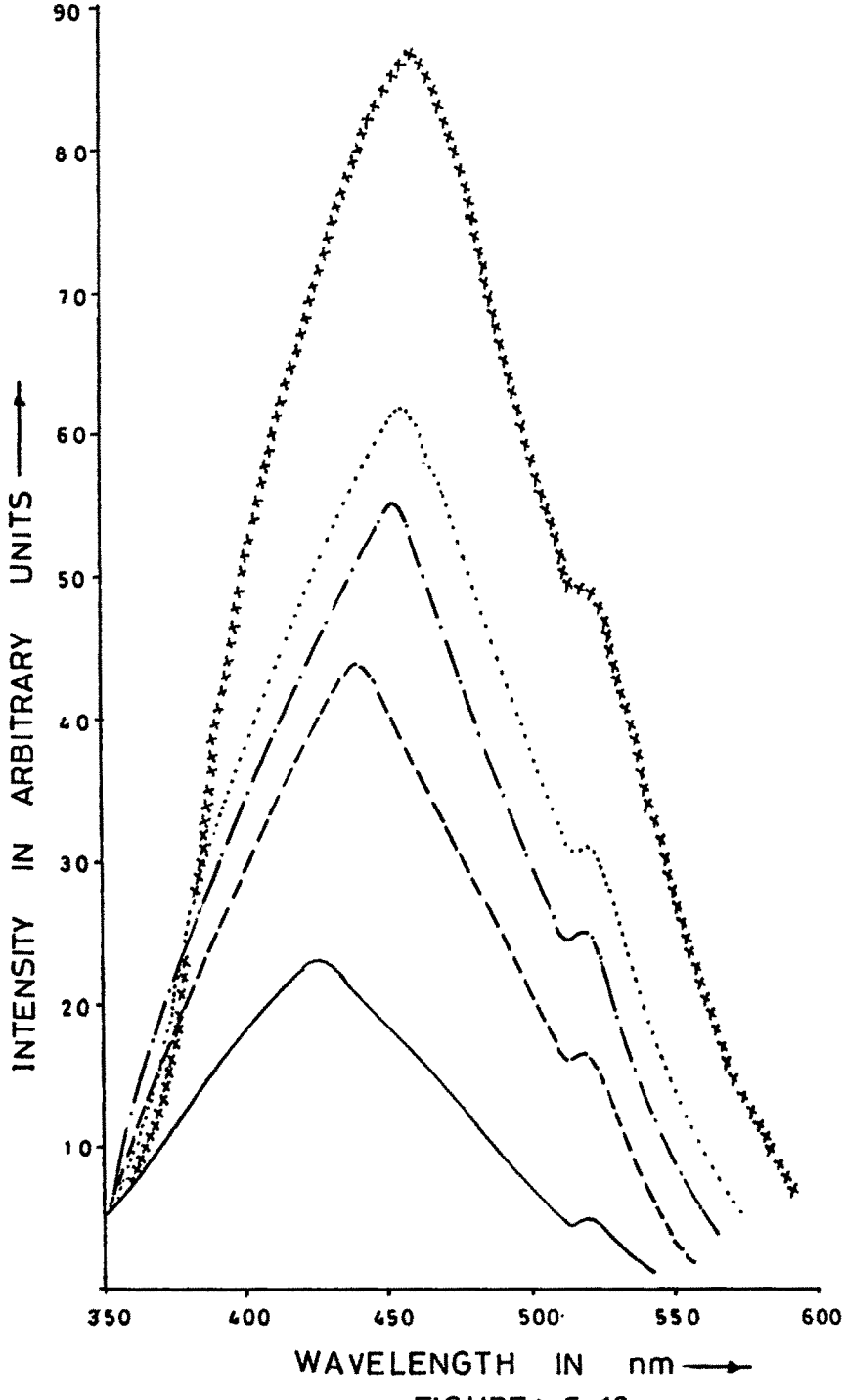
90
80
70
60
50
40
30
20
10
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5.16

FIGURE 5.17 **Fluorescence spectra for polymer P_4 dissolved indifferent solvents for High concentration**

1. **Dioxane** ————
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

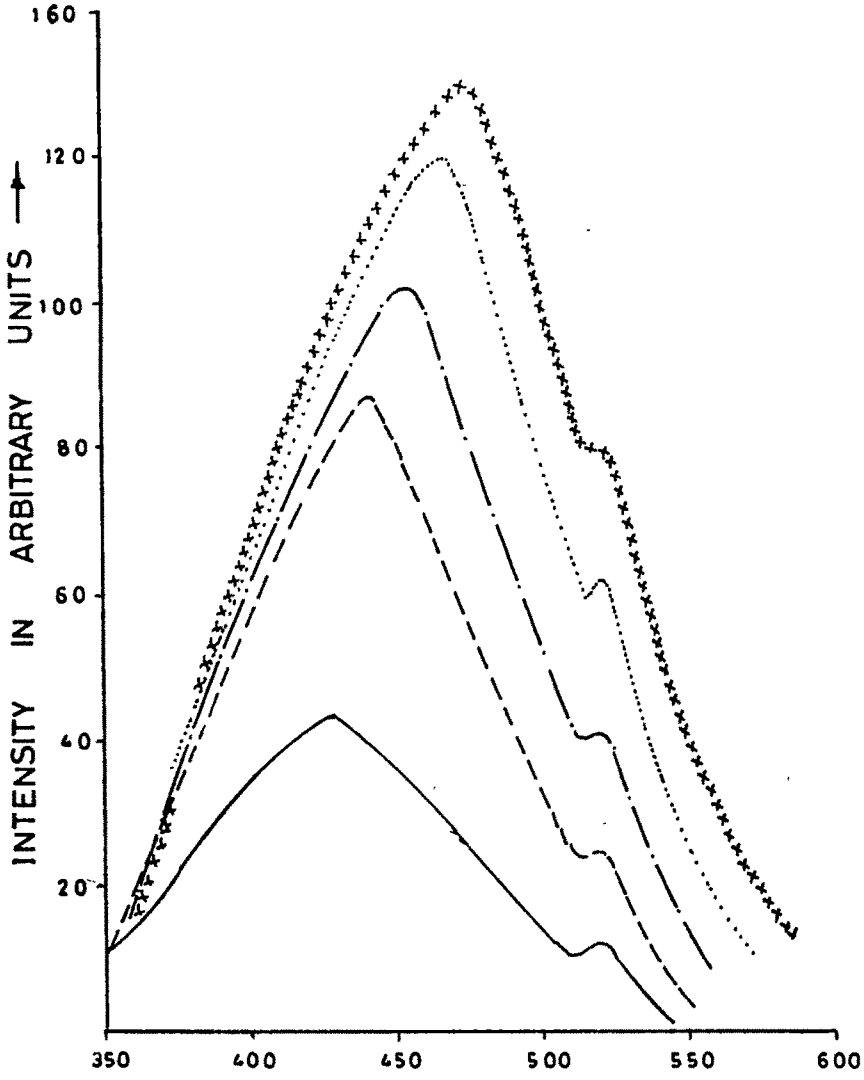
160
120
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5·17

FIGURE 5.18 **Fluorescence spectra for polymer P_5 dissolved indifferent solvents for High concentration**

1. **Dioxane** ————
2. **Teterahydrofuran** - - - - -
3. **Dimethylformamide** -.-.-.
4. **Acetonitrile** . . . .
5. **Dimethylsulphoxide** x x x x

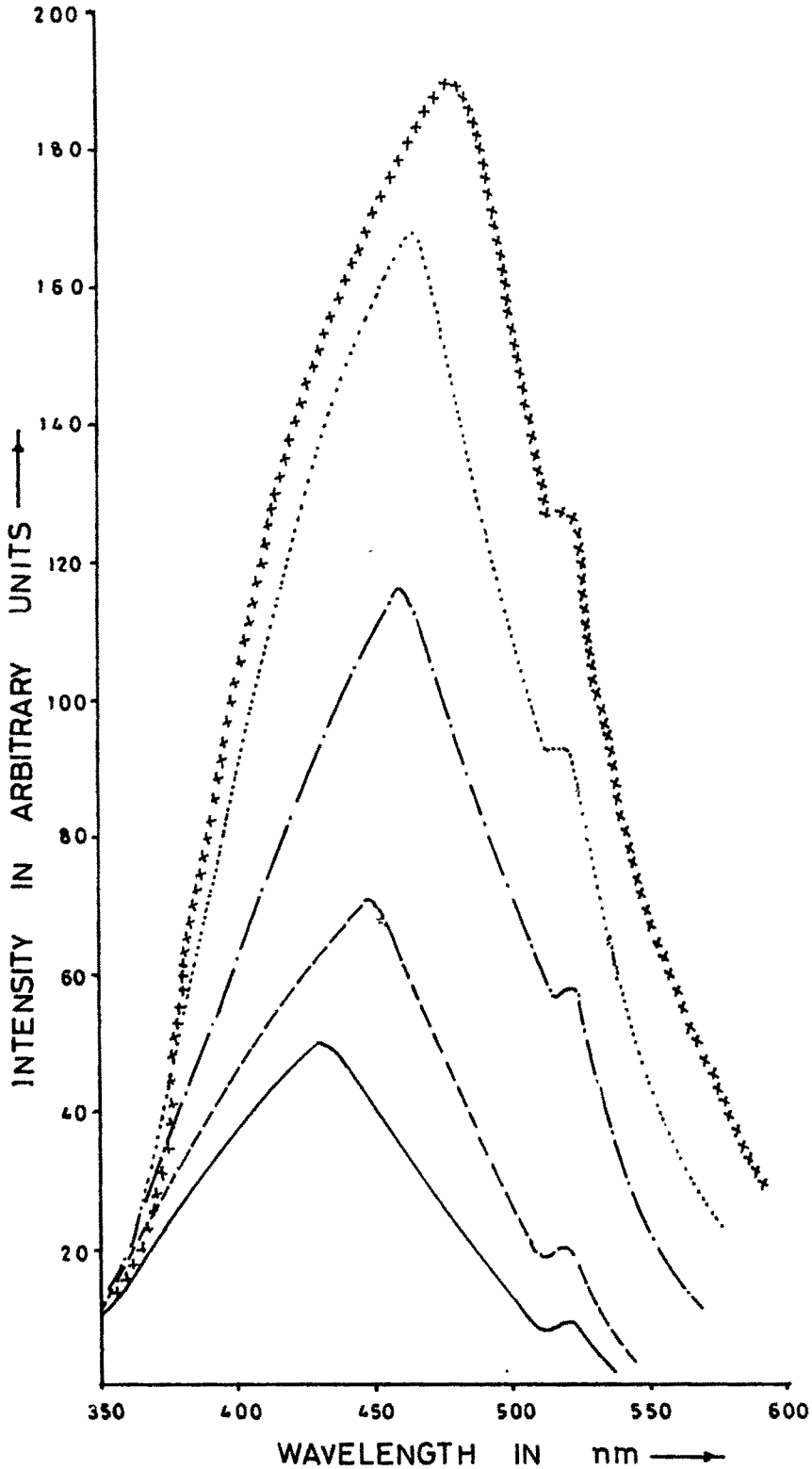
200
180
160
140
120
100
80
60
40
20
INTENSITY IN ARBITRARY UNITS
350
400
450
500
550
600
WAVELENGTH IN nm

FIGURE: 5·18

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