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**FEASIBILITY STUDY : MONODISPERSE POLYMER PARTICLES
CONTAINING LASER-EXCITABLE DYES**

Final Report

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1. INTRODUCTION

The optical properties associated with small particles , which include aerosols , hydrosols and solid microspheres have an impact on several areas of science and engineering . Since the advent of high-speed computers and lasers , the interaction of light with matter in the form of small particles with a discontinuous optical boundary relative to the surroundings has been much better understood .

Various nonlinear optical effects have been observed involving interaction of a laser beam with both solid microspheres and liquid microdroplets [1-5] . These include observation of second and third harmonic generation , four wave mixing , optical bistability , two photon absorption , observation of stimulated emission and lasing , and Stimulated Raman Scattering . Many of these effects are observed with laser intensities which are orders of magnitude less than that required by threshold condition for interactions in macroscopic bulk medium . The primary reason for this is twofold . The front surface of the microsphere acts as a thick lens to enhance the internal intensity of the input laser radiation , and the spherical shape of the droplet acts as an optical cavity to provide feedback at specific wavelengths corresponding to the whispering gallery modes or the morphology dependent resonances (MDR's) .

The most interesting and significant recent finding in this field is undoubtedly the existence of resonance peaks in linear and nonlinear optical spectra . Such resonance peaks are only dependent on the particle morphology , which means the size , shape and refractive index of the particle . Because of the simultaneous presence of these resonances , they have been referred to by many names , including structural resonances , whispering modes or whispering gallery modes , creeping waves , circumferential waves , surfaces modes , and virtual modes . All of these names refer to the same phenomena , i.e. morphology dependent resonances (MDR's) which has already been described and

predicted precisely by electromagnetic theory and Loentz-Mie theory since 1908 . MDR's can become important when the particle size (radius a) approaches and exceeds the wavelength of the electromagnetic wave (λ) and the refractive index of the particle is greater than that of the surrounding medium . Such resonances are easiest to observe from a single particle with high symmetry , such as a sphere , spheroid , or cylinder . MDR's correspond to solutions of the characteristic equations of the electromagnetic fields in the presence of a sphere.

In a recent work , Kwok et-al . [6] observed lasing in laser-dye-doped ethanol droplets after two-photon absorption by dye molecules . The two-photon-pumped lasing emission by the droplets is at a higher frequency than the input laser . Thus Fig. 1 shows the two photon absorbed pumped lasing of 10^{-2} M coumarin 460 dye in ethanol droplets with an input laser at 629.6 nm . This figure clearly shows the MDR's with the spacing between them corresponding to the mode spacing of a 50 μm radius microdroplet laser . Like in all lasers , even for microdroplet lasers there is a threshold of population inversion below which gain is not enough for lasing . This can be see in Fig . 2 where the onset of lasing in microspheres is clearly seen by the growth of MDR's as the intensity of pump laser is increased . Bulk of the research in this area has been conducted with liquid microdroplets for reasons of ease with which these microdroplets can be generated with easily adjustable radius as well as the dye dopants . For practical applications , however , solid materials are necessary . Relatively less work has been done in this area . Laser oscillation has been observed in large solid spheres with diameters of several millimeters . In a recent work , lasing behavior and photon induced quenching of dye doped polystyrene microspheres with diameters ranging from 10 μm to 92 μm was observed [7] . In a preliminary work with dye doped 2.6 μm polystyrene spheres , we ourselves have observed enhanced emission or lasing action at certain wavelengths which correspond to

the whispering gallery modes of microspheres [8] , very similar to the resonances observed in Ref . 6 . More details of this work are presented later on . The advantage of organic materials like polystyrene is their plasticity so that they can be made into any shape . Polystyrene has a rather large refractive index of 1.58 and can be easily doped with the required laser dye and also made into spheres of required size . Benner et . al [7] observed MDR's in the fluorescence spectrum of dye doped polystyrene spheres . Thus polystyrene is suitable for the study of optical MDR's . The Q value of these microspherical laser cavities depends sensitively on the perfectness of the geometry . This work thus is naturally of interest from the prospect of fabricating highly monodisperse microspheres under conditions of microgravity . In this write up we describe some of the work we have carried out in this direction with 2.6 μm polystyrene microspheres doped with Bis-MSB laser dye . This was done in collaboration with the research workers at the Lehigh University , Bethlehem , Pennsylvania and the NASA Marshall Flight Center , Huntsville , Alabama .

2. STATEMENT OF THE PROBLEM STUDIED

The work was carried out in two stages :

I . Fabrication of microspheres

This was basically accomplished by the scientists at Lehigh University under the direction of Professor Vanderhoff . These microspheres were supplied to us at the Alabama A & M University for characterization . The microspheres were generally supplied as a colloidal suspension in organic solvent . These spheres of various diameters were made of a variety of polymers and doped with varying concentrations of laser dyes . This is shown in Table 1 . All of these samples were subjected to nonlinear optical studies .

Table 1

LIST OF MICROSPHERICAL SAMPLES INVESTIGATED

(Supplied by Lehigh University)

A . Nature of Host Material : Polymethyl Methacrylate (PMMA)

Sample # 1:

Classification : PMMA-S8 (contains no dye)

Size : 0.3-0.6 mm (300-600 μ m) diameter

Sample # 2:

Classification : PMMA-S9 (contains Bis-MSB dye)

Size : 0.3-0.6 mm (300-600 μ m) diameter

Dye Concentration : 0.050% (0.05 g dye/100 g of latex)

Mixture : Sample is supplied as 17.8% of solids as spheres in water .

B . Nature of Host Material : Polystyrene

Sample #3 :

Classification : PS-D (contains Bis-MSB)

Size : 2.6 μm diameter

Dye Concentration : 6.2×10^{-3} g dye/g polymer

Mixture : Sample is supplied as 10.6% of solids as spheres in dioxane and water.

Sample #4 :

Classification : PS-DD (contains Bis-MSB dye)

Size : 2.6 μm diameter

Dye Concentration : 6.2×10^{-3} g dye/g polymer

Mixture : Sample is supplied as 10.6% of solids as spheres in 25% dioxane and 64.4% water.

Sample # 5:

Classification : PSD-E1 (contains α -NPO)

Size : 274 nm diameter

Coefficient of Variation : 18.5%

Dye Concentration : 1.587×10^{-3} g dye/g latex

Mixture : Sample is supplied as 17.8 % solid as spheres in water

Sample # 6:

Classification : PSD-E2 (contains Bis-MSB)

Size : 230 nm diameter

Dye concentration : 1.0×10^{-3} g dye/g latex

Mixture : Sample supplied as 16% solid as spheres in water

Sample # 7:

Classification : PSD-E3 (contains PPO)

Size : 71 nm

Coefficient of Variation : 25.4%

Dye Concentration : 0.989×10^{-3} g/g latex

Mixture : Sample Supplied as 5.3% solid as spheres in water

II. Characterization of the Dye-Doped Microspheres Supplied to us for their Fluorescence and Lasing Properties .

The plan in these experiments was to irradiate the dye-doped microspheres in thin film form and look for the emitted light with a suitable monochrometer . As the laser light intensity is increased beyond the threshold of lasing , one should be able to observe the transition from a broad low-spectral density fluorescence to the sharp resonances or MDR's associated with the high Q microsphere . The goal was to look for resonances that can be ascribed to one of the MDR's .

3. REPORT OF THE WORK ACCOMPLISHED :

Work has been carried out in our laboratory to look for lasing in various microspheres doped with laser dyes . These samples are listed in Table 1 . The goal was to look for morphology dependent resonances in the fluorescence excited by a suitable pump laser . If the pump power is above the threshold of lasing , the dye doped droplet behaves like a tiny microspherical laser cavity with the mode spacing between longitudinal modes given by

$$\Delta\nu = \frac{f}{\pi D} \dots\dots\dots (1)$$

$\Delta\nu$ is the mode spacing in cm^{-1} , D is the diameter of the spherical droplet and f is factor which depends on the refractive index m of the sphere .

$$f = \frac{\tan^{-1}(m^2 - 1)^{\frac{1}{2}}}{(m^2 - 1)^{\frac{1}{2}}} \dots\dots\dots (2)$$

As an example for refractive index $m=1.58$ for polystyrene and a diameter $D=2.6 \mu\text{m}$, $\Delta\nu \approx 880 \text{ cm}^{-1}$.

As described in table 1 , the polystyrene and PMMA spheres are doped with a variety of dyes like Bis-MSB , α -NPO and PPO . Of all the samples studied , the best results in terms of lasing in dye doped microspheres were obtained for $2.6 \mu\text{m}$ diameter polystyrene spheres doped with Bis-MSB dye (Samples 3 and 4) . Sample 1 of course is without any laser dye in the microspheres . In sample 2 , the diameter of the Bis-MSB doped PMMA is $0.3\text{-}0.6 \text{ mm}$. For 0.3 mm diameter spheres , the mode spacing between the longitudinal modes of the microspherical cavity is 7 cm^{-1} where as for 0.6 mm diameter spheres , the mode spacing is 3.5 cm^{-1} . Not only are these mode spacings too small to observe clearly , but the presence of all sizes of spheres between $0.3\text{-}0.6 \text{ mm}$

diameter will wash out any anticipated MDR's . Samples 5 , 6 and 7 consist of microspheres with diameters of 247 nm , 230 nm and 71 nm respectively . The essential condition for observing MDR's or lasing in microspheres is that the lasing wavelength must be smaller than the radius of the spheres . Thus none of the spheres in samples 5 , 6 and 7 are expected to show MDR's . This is also borne out by our experimental observation . The only samples which might be expected to show lasing and the presence of well resolved morphology dependent resonances are Sample #3 and #4 which consist of 2.6 μm diameter microspheres doped with Bis-MSB dye . Indeed , our experimental results verify this clearly .

The samples of microspheres are supplied as a colloidal mixture in dioxane and water . This is spin coated on a glass substrate . After dioxane and water evaporate , a thin film of microspheres is left on the glass substrate . Laser induced fluorescence from various such thin films is observed using an excimer laser source , giving about 100 mJ pulses at 308 nm . The experimental setup for observing MDR's is shown in Fig . 3 . This wavelength is especially suitable for spheres doped with Bis-MSB dye as can be seen from the absorption spectrum of Bis-MSB dye (Fig . 4). The peak of absorption for this dye is around 308 nm [9] . The emission spectrum of Bis-MSB is in a region 395-500 nm . This can be seen in Fig . 5 for Bis-MSB dissolved in Toluene . The absorption spectra of α -NPO and PPO dyes is shown in Figures 6 and 7 respectively [9] . The fluorescence spectrum of 230 nm Bis-MSB dye-doped microspheres using an excimer laser is shown in Fig . 8 . The concentration of dye is 1.0×10^{-3} g dye/g polymer . The fluorescence extends from 330-580 nm . The region 325-520 nm shows a coarse structure with maximum being around 428 nm . The fluorescence obtained in the present experiments may be compared with the one obtained by Venkateswarlu and his collaborators (Fig . 5) from Bis-MSB dye in toluene . The above experiment is repeated with 2.6 μm

polystyrene spheres doped with Bis-MSB dye . The fluorescence spectrum obtained on excitation with the Excimer laser is shown in Fig . 9 . This shows interesting sharp structure in the 350-490 nm region along with a sharp maximum at 591 nm . Though the spectral region is similar to that of Fig . 8 , there is a difference in details between the two . The one in Fig . 9 is clearer and shows very clear and largely equidistant structure . The discrete maxima are marked in the Fig . 9 . The interesting structure of fluorescence in the 325-520 nm region appears to give evidence for lasing in the dye doped microsphere . Calculation with the help of the formula (1) shows that mode spacing in Fig . 9 which is around 780 cm^{-1} yields a droplet diameter of $2.8 \text{ }\mu\text{m}$ taking the value refractive index m as 1.58 . This is remarkably close to diameter of the microsphere ($2.6 \text{ }\mu\text{m}$) as measured at the time of preparing these samples at Lehigh University . Fig . 9 shows a structure which resembles the modes of the microdroplet laser as repeated by Kwok et.al. [6] in Fig . 2 . Further work is to be done to find out the concentration dependence and sphere size dependence of the lasing efficiency . Laser excited fluorescence of undoped PMMA (0.5 mm in diameter) has been recorded as well as of PMMA spheres doped with the laser dye Bis-MSB . The fluorescence spectra of these two samples excited by an excimer laser (308 nm) are shown in Fig . 10 and Fig . 11 . The fluorescence has shifted to shorter wavelength at 365 nm while that in the undoped spheres is at 425 nm . This large shift is interesting , but strange . Therefore , we intend to study this with different samples to confirm the observation and then to understand the reason for this shift . Size of the spheres is $0.3\text{-}0.6 \text{ mm}$ ($300\text{-}600 \text{ }\mu\text{m}$) , with a dye concentration of $0.05 \text{ g dye}/100 \text{ g latex}$. The spectrum of the laser excited fluorescence of polystyrene spheres doped with α -NPO is shown in Fig . 12 . The fluorescence extends from 320 nm to 600 nm . this may be compared with the fluorescence spectrum of α -NPO in toluene obtained by Venkateswarlu and his collaborators shown in Fig . 13 . Here the fluorescence is from

360 nm to 510 nm with maximum at 401 nm and subsidiary maxima at 420.3 nm and 395 nm . The size of the spheres is 274 nm with a dye concentration of 1.587×10^{-3} g dye/g latex . A mixture of 17.8% solids with 82.4% water was used to prepare the film on a glass slide .

The laser excited fluorescence spectrum of polystyrene spheres doped with PPO is shown in Fig . 14 . It is spread from 330 nm to 600 nm with a maximum at 390 nm . This may be compared with the fluorescence of PPO in ethanol by Venkateswarlu and his collaborators shown in Fig . 11 where the spread is from 350 nm to 479 nm with maxima at 384.1 nm and 368.3 nm . There is again no fluorescence in the region from 470 nm to 600 nm as in Fig . 12 . One has to see whether the fluorescence in the region from 510 nm to 600 nm in Fig . 12 is due to the undoped polystyrene sample itself . Size of the spheres here is 71 nm in diameter . Dye concentration is 0.989×10^{-3} g dye/g latex . The solids (5.6%) were placed in water (94.4%) and the mixture was spun on a glass slide which gives a non-uniform thin layer .

4. CONCLUSIONS :

We have observed laser induced fluorescence in all the samples mentioned in Table 1. Of these , as predicted by the theory we have observed lasing (MDR's) in 2.6 μ m microspheres doped with Bis-MSB dye . Further work needs to be done to characterize the lasing process in microspheres with respect to their sizes as well as the concentration and nature of the laser dyes with which these microspheres are doped . This work is in progress now .

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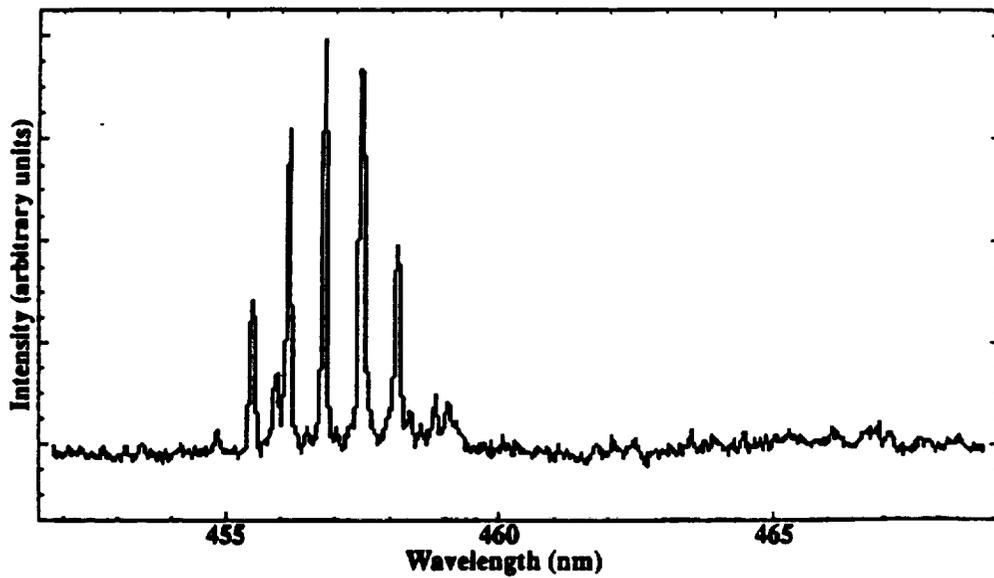


Fig. 1. TPA-pumped lasing spectrum of 10^{-2} M Coumarin 460 in ethanol droplets with an input laser at 629.6 nm and an input intensity I_{in} of 1 GW/cm^2 . The periodic peaks correspond to the MDR's of the droplet.

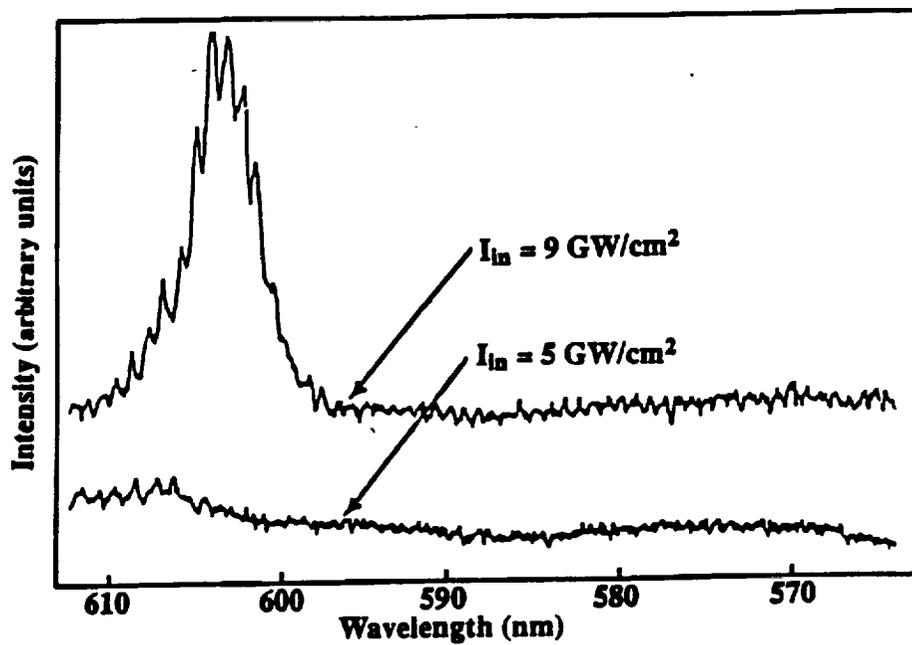


Fig. 2. TPA-pumped fluorescence and lasing spectrum of 2.5×10^{-4} M Rhodamine 6G in ethanol droplets with input laser at 1064 nm. At 5 GW/cm^2 , only fluorescence is detected. At 9 GW/cm^2 , MDR-related lasing peaks can be observed.

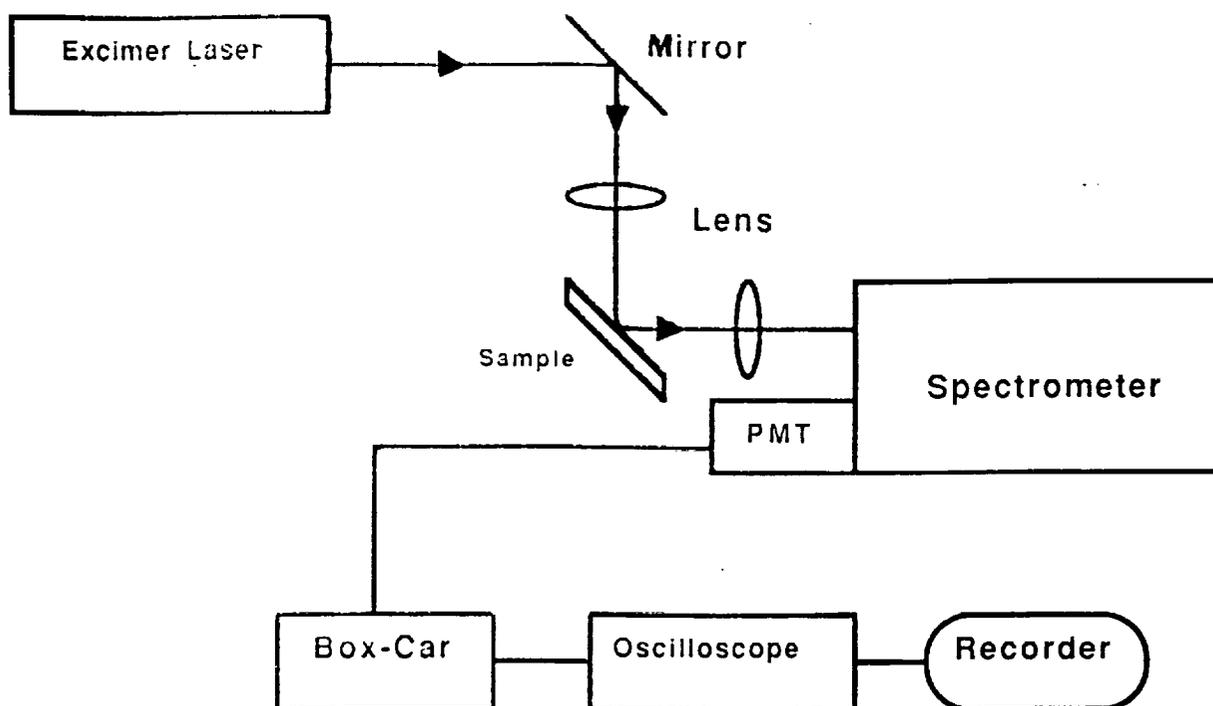
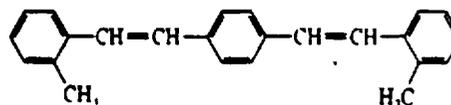


Fig . 3. Experimental Configuration for Recording Fluorescence Spectrum

BIS(MSB)

p-Bis(*o*-methylstyryl)benzene



Mol form.: C₂₄H₂₂

Mol wt: 310.44

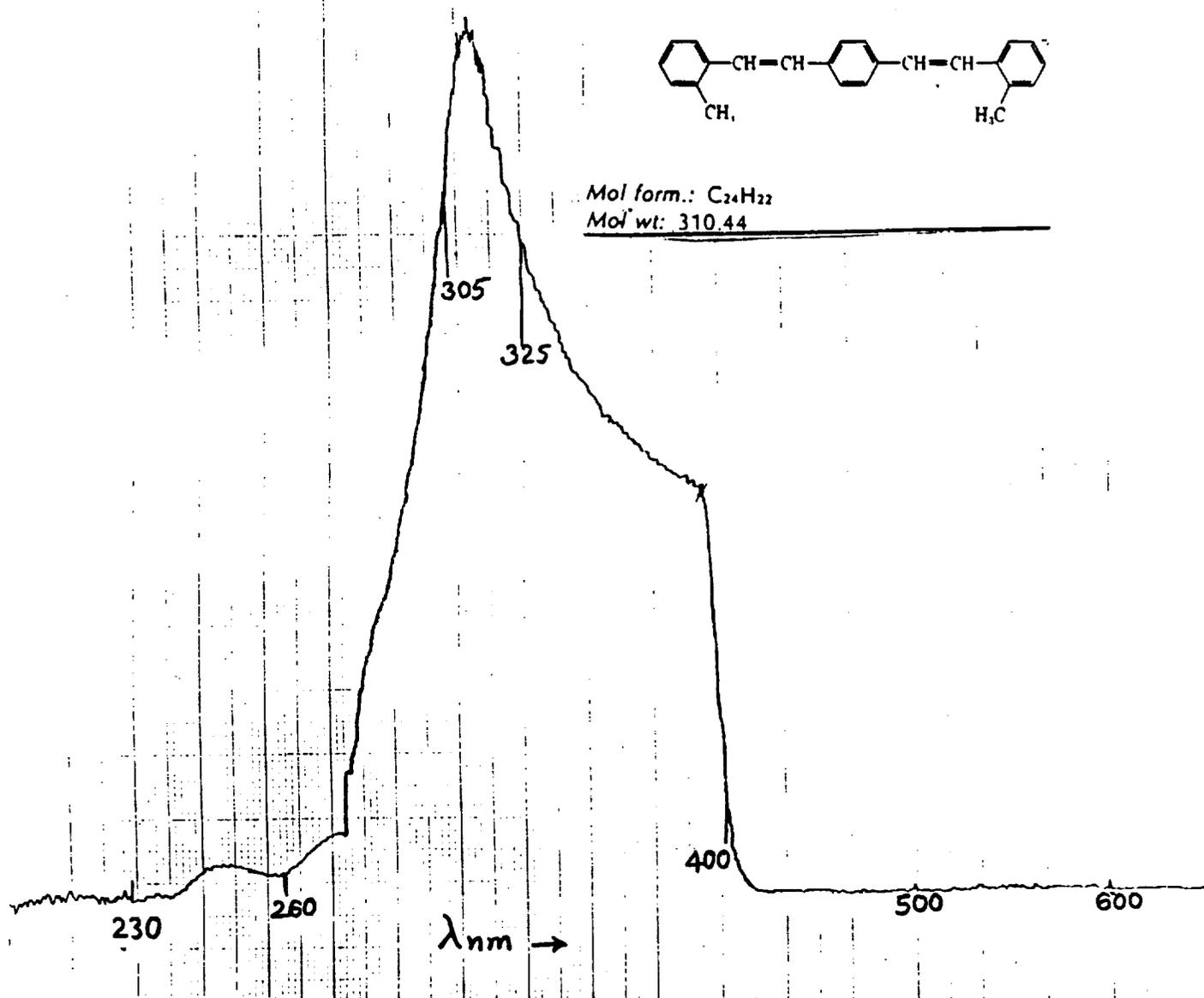


Fig. 4. Absorption spectrum of Bis-MSB in Toluene measured by Perkin-Elmer spectrophotometer.

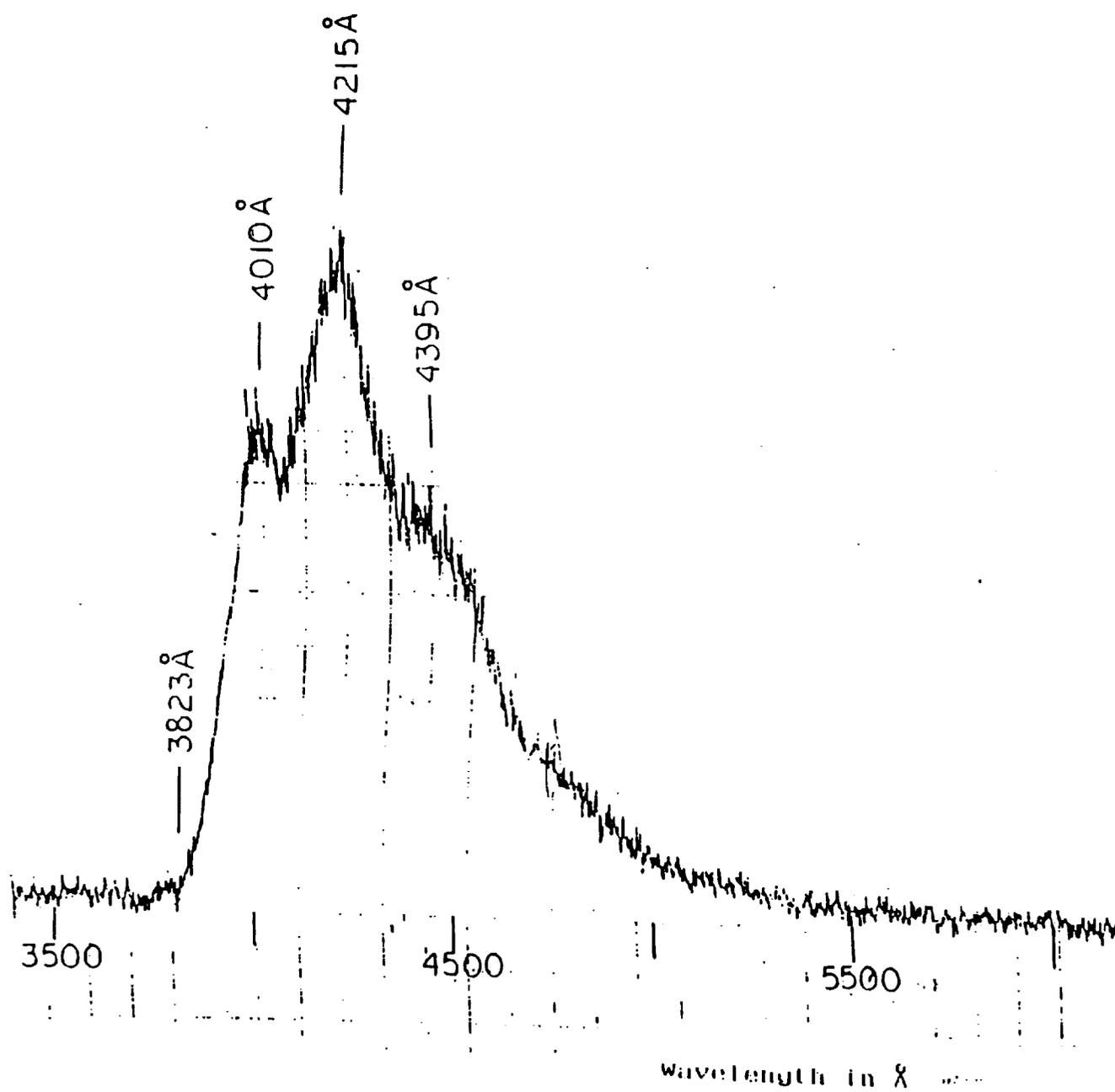


Fig. 5. Fluorescence spectrum of Bis-MSB in Toluene excited by a Nitrogen laser.

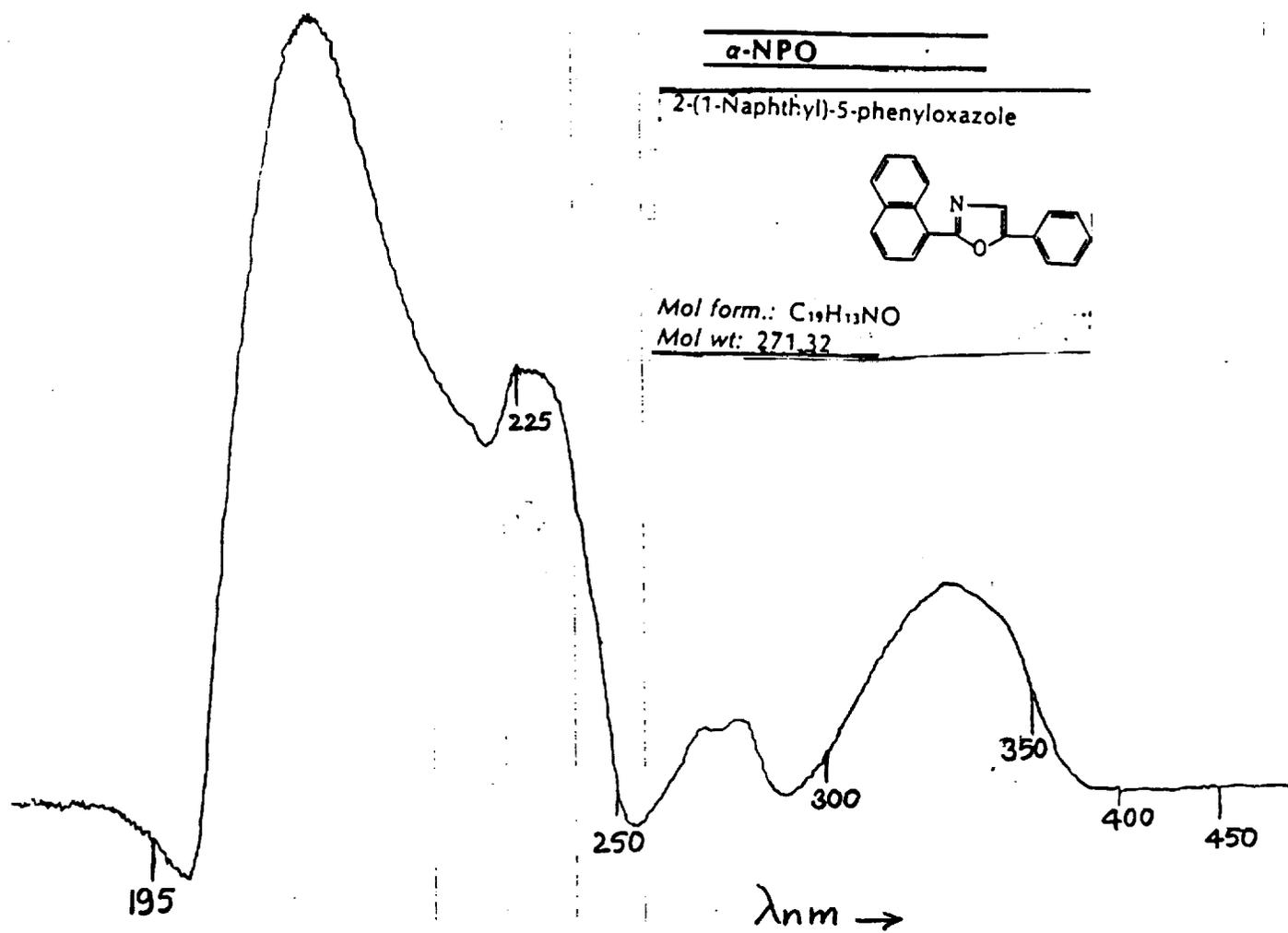
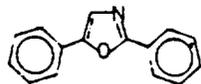


Fig.6. Absorption spectrum of α -NPO in Toluene

2.5 DIPHENYL OXAZOL

(PPO)



MOL. FORM: $C_{15}H_{11}NO$

MOL. WT: 221.26

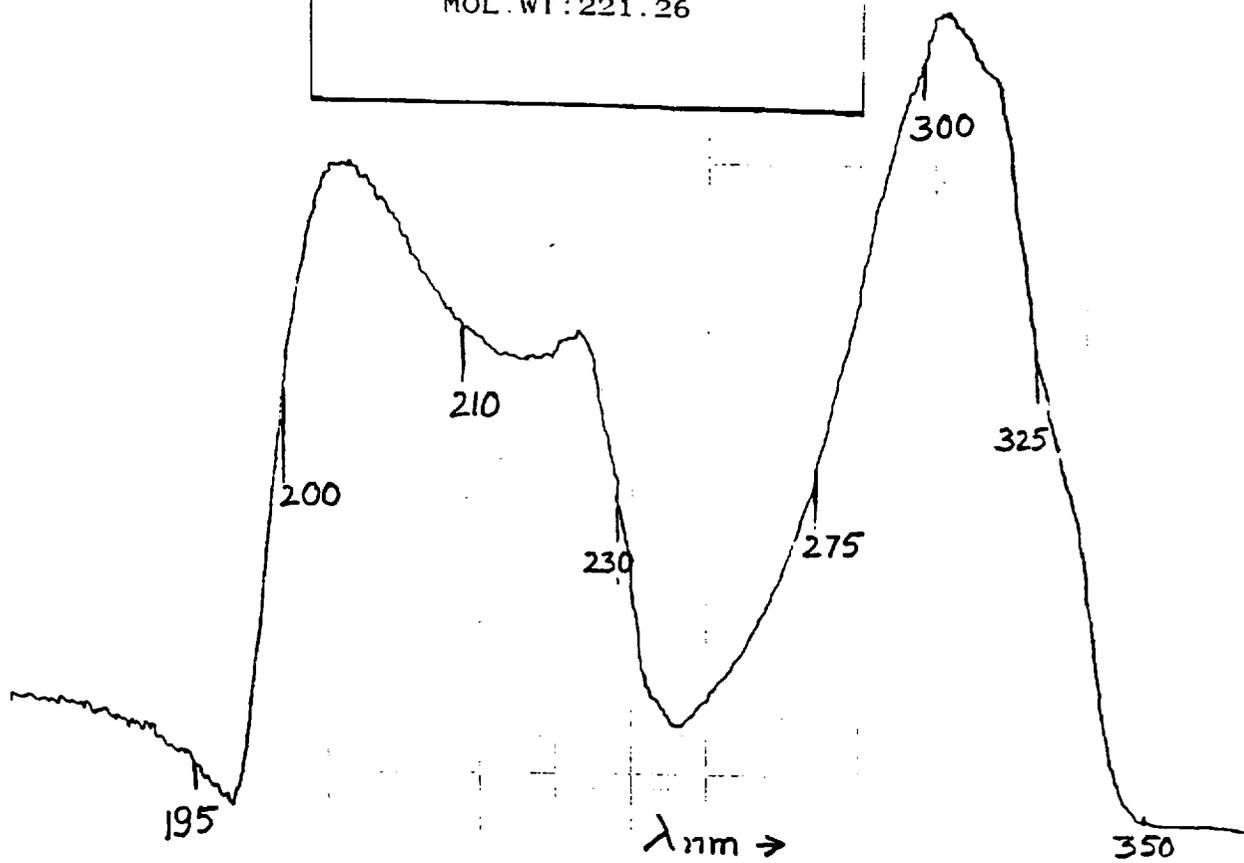


Fig. 7. Absorption spectrum of PPO in Ethanol

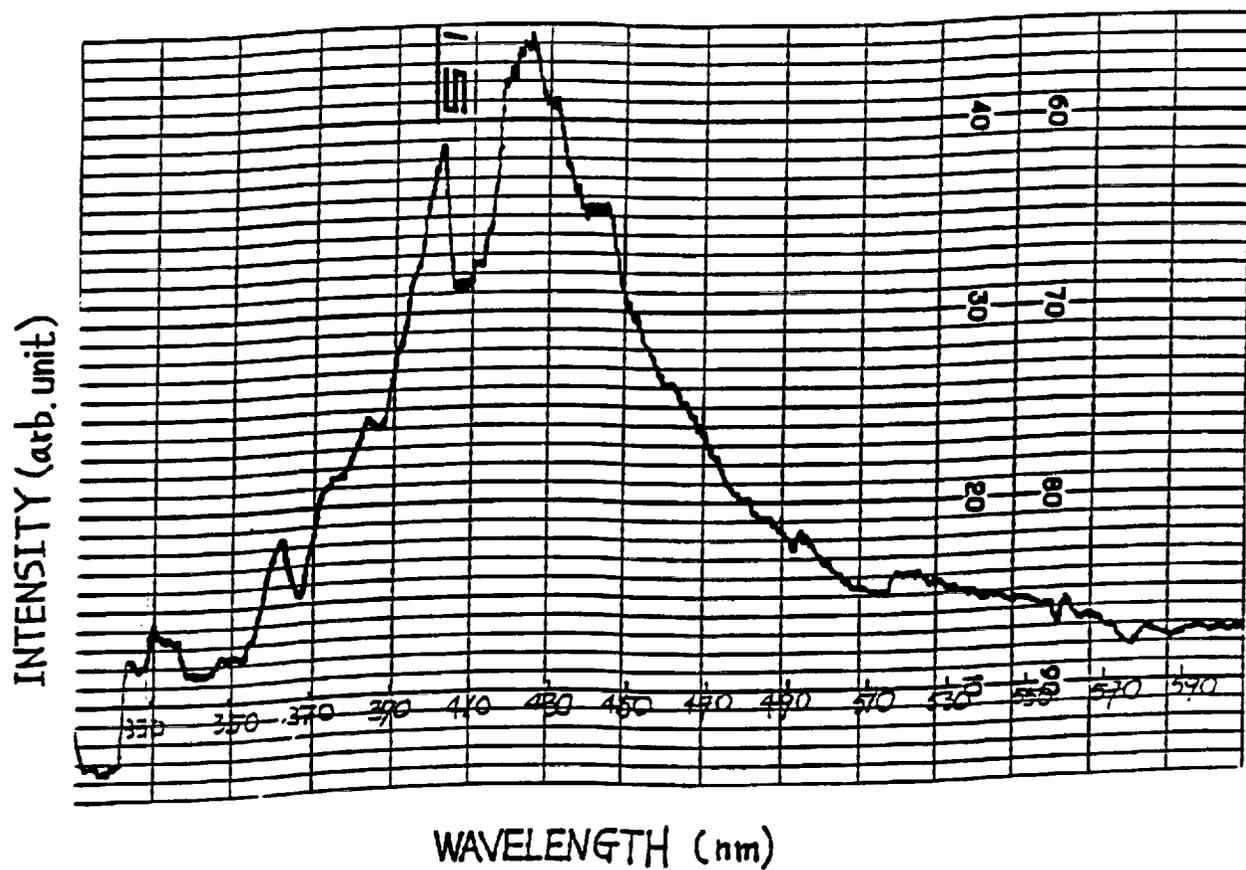


Fig. 8. Excimer laser (308 nm) excited fluorescence in Bis-MSB dye doped 230 nm polystyrene microspheres (PSD-E2).

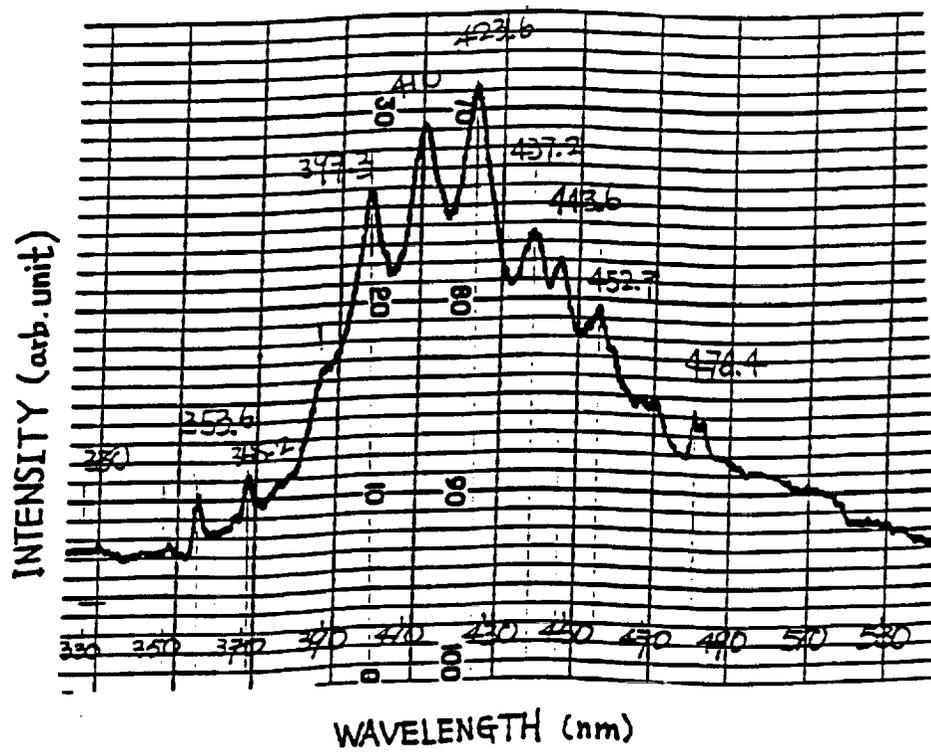


Fig. 9. Excimer laser (308 nm) excited fluorescence in Bis-MSB dye doped 2.6 μm polystyrene microspheres (PS-DD).

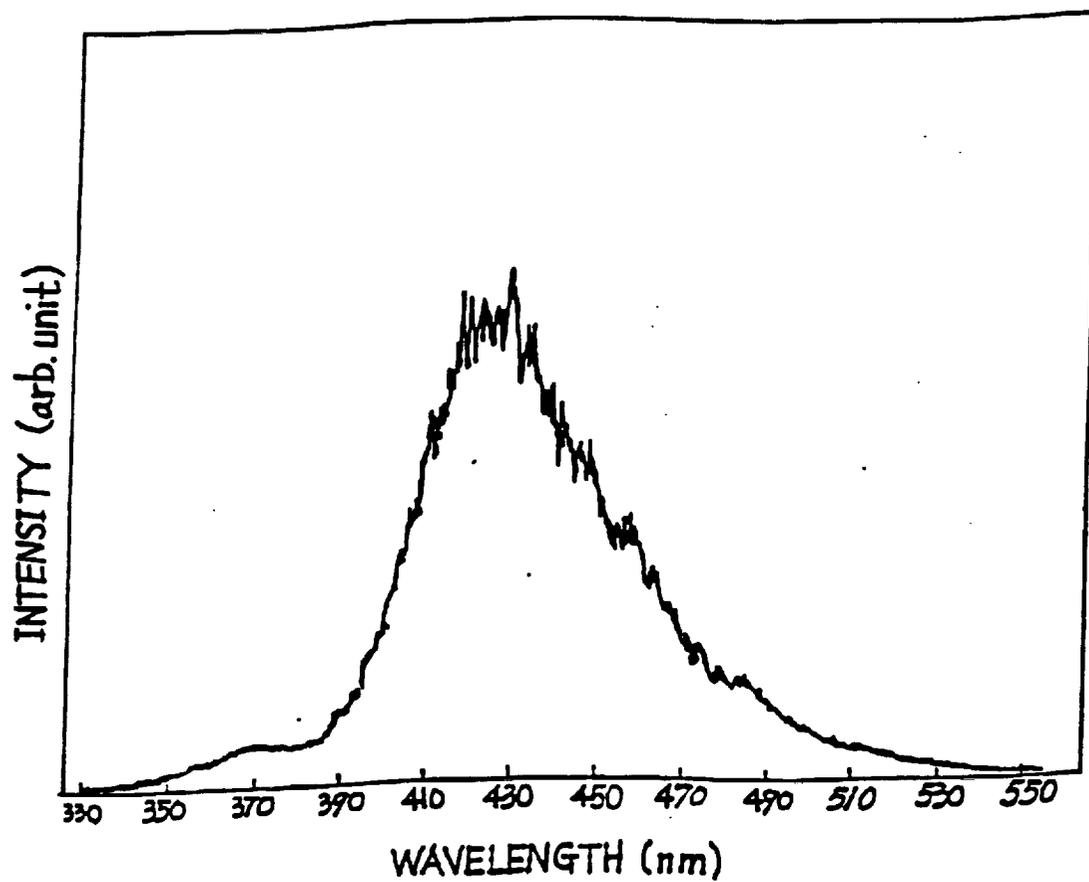


Fig. 10. Excimer laser (308 nm) excited fluorescence in polymethyl methacrylate microspheres (0.3-0.6 μm in diameter) containing no laser dye (PMMA-S8).

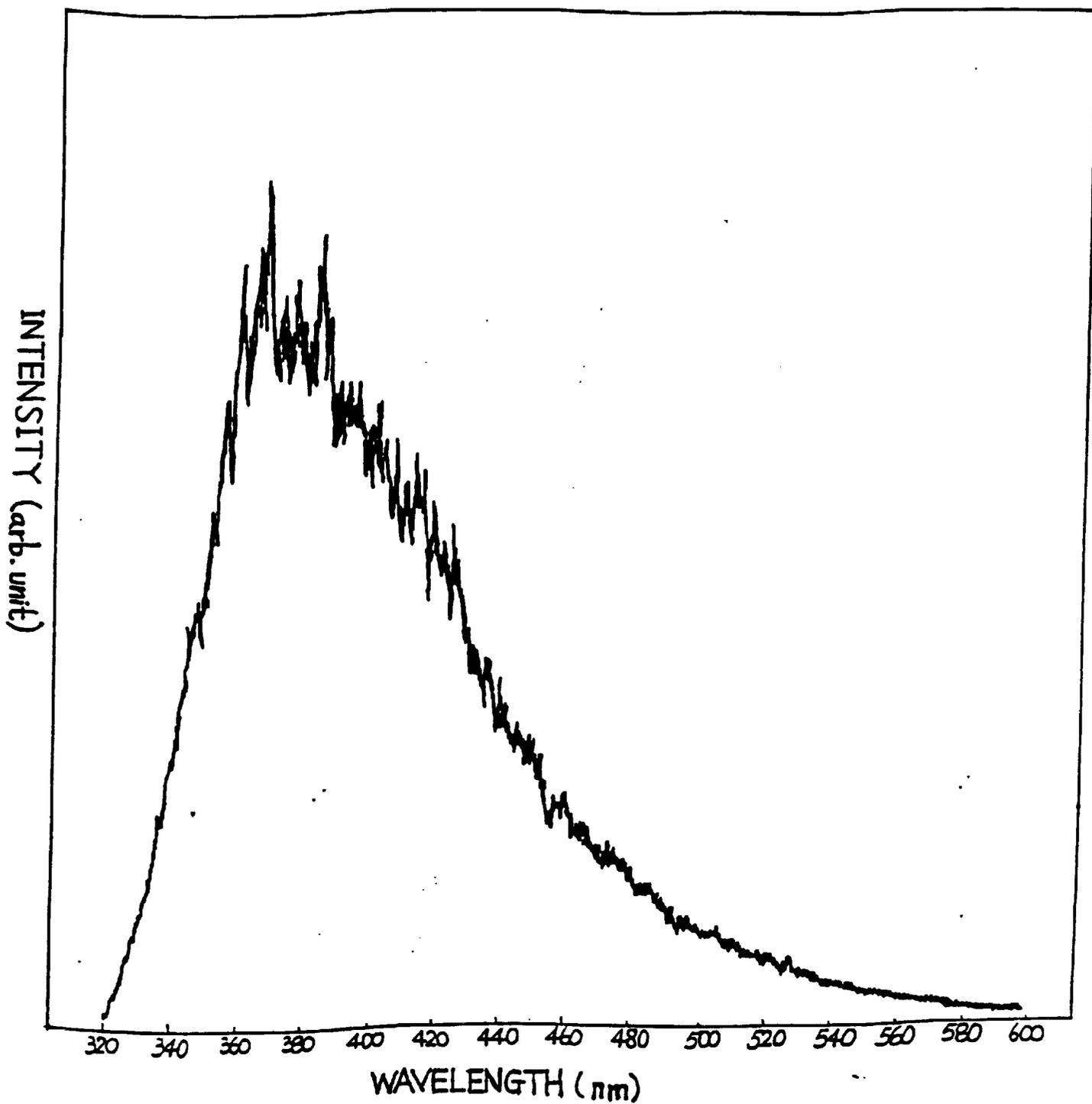


Fig. 11. Excimer laser (308 nm) excited fluorescence in Bis-MSB dye doped polymethyl methacrylate microspheres (0.3-0.6 μm in diameter). (PMMA-S9).

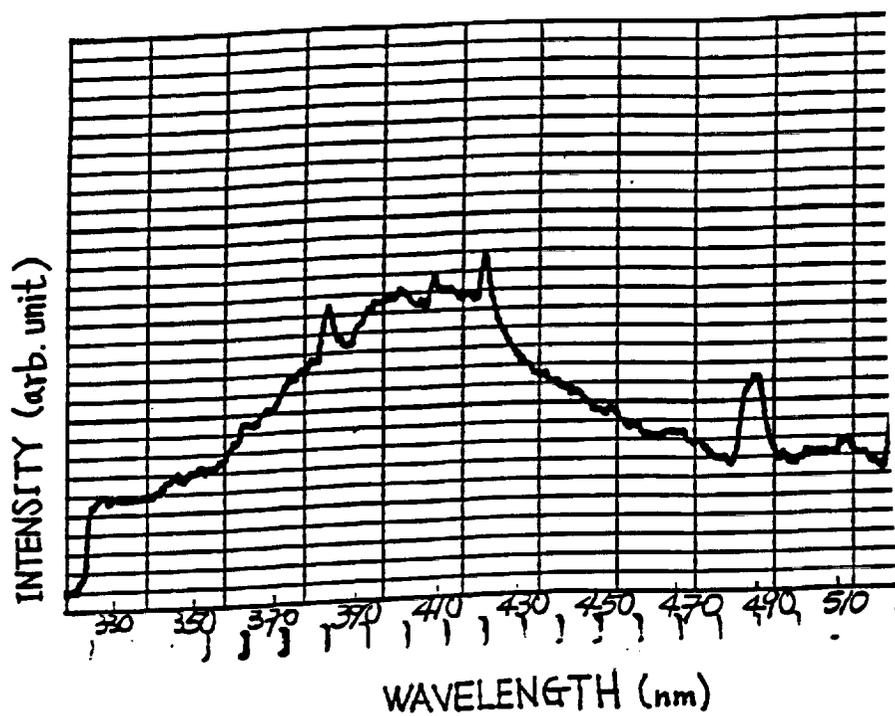


Fig .12. Excimer laser (308 nm) excited fluorescence in α -NPO dye doped 274 nm polystyrene microspheres (PSD-E1).

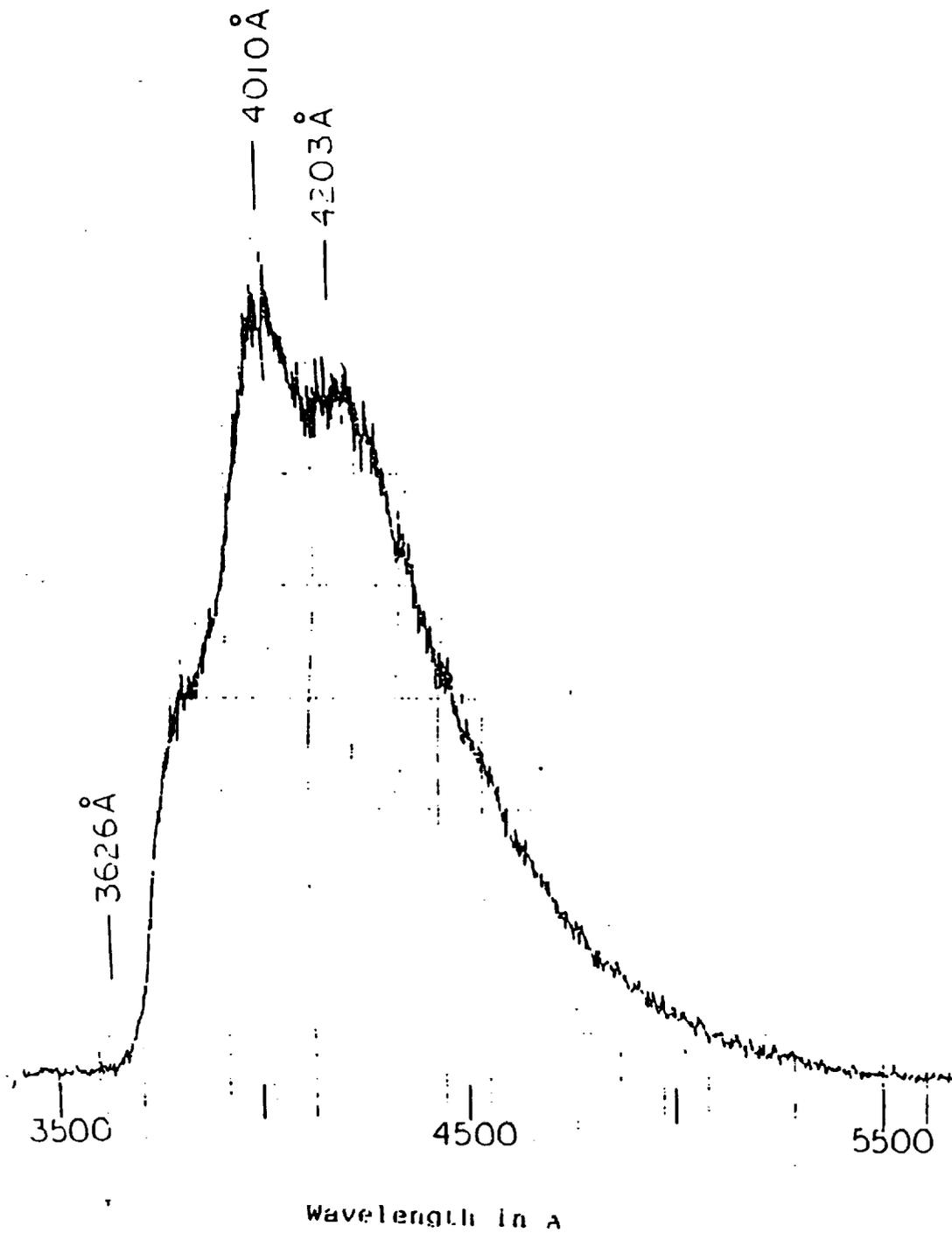


Fig. 13. Fluorescence spectrum of α -NFO in Toluene

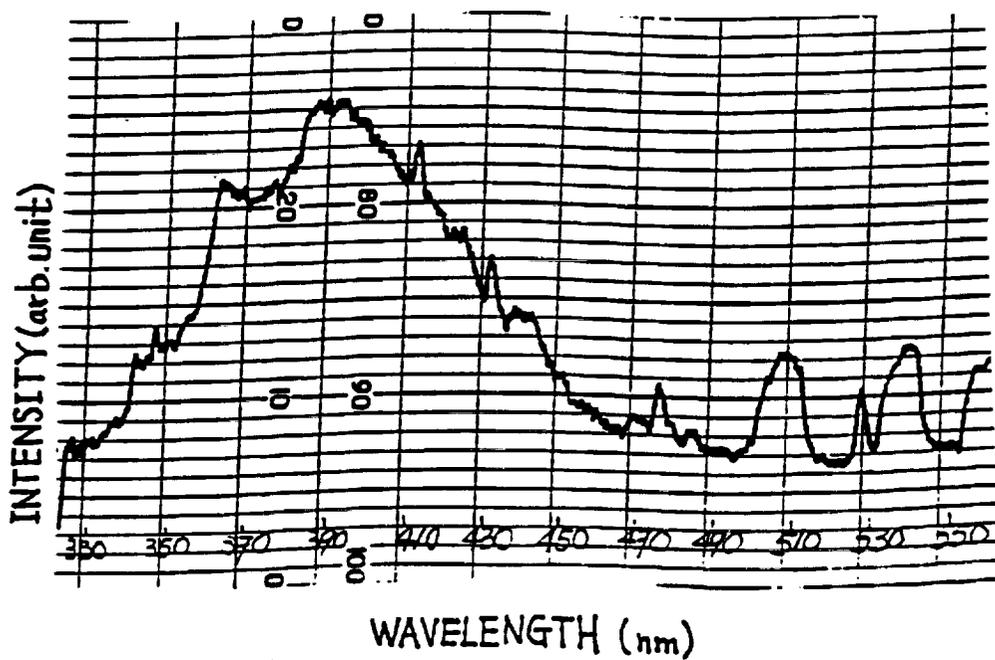


Fig. 14. Excimer laser (308 nm) excited fluorescence in PPO dye doped 71 nm polystyrene microspheres (PSD-E3).