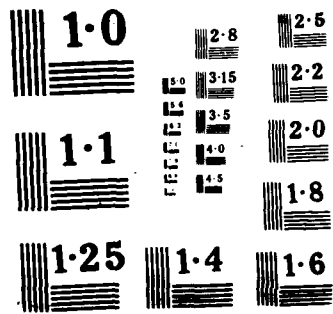


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Photophysics of Polyurethanes Based on  
1,5-Naphthalene Diisocyanate in Solution and Film

by  
C. E. Hoyle and K. J. Kim

Prepared for Publication in the  
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Department of Polymer Science  
University of Southern Mississippi  
Southern Station Box 10076  
Hattiesburg, MS 39406-0076

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Photophysics of 1,5-Naphthalene Diisocyanate  
Based Polyurethanes

by

Charles E. Hoyle and Kyu-Jun Kim

Department of Polymer Science

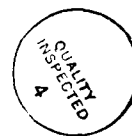
University of Southern Mississippi

Southern Station Box 10076

Hattiesburg, MS 39406-0076

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ABSTRACT



Using both steady-state and transient fluorescence decay spectroscopy, the formation of intramolecular excimers in dilute solutions of a naphthalene diisocyanate based polyurethane is identified. Investigation of an appropriate model compound leads to the conclusion that hydrogen bonding is a key factor in stabilizing excimers formed from naphthyl carbamates. While the decay kinetics of the model naphthyl carbamate are described by a typical Birks excimer scheme involving a single excited monomer species in dynamic equilibrium with the excimer, the polymer decay kinetics can be adequately interpreted by an "isolated monomer" scheme involving both an interactive (excimer forming) and non-interactive excited naphthyl carbamate monomer. The extent of excimer formation is dependent on the ability of the solvent to solvate the polyurethane, i. e., excimer formation is increased in poor solvents. In addition, excimer formation in solid polyurethane films is quite high where hydrogen bonding, as

identified by the shift in the carbonyl stretching frequency, is prevalent.

## INTRODUCTION

Excimers, which are simply excited state complexes formed from equivalent chemical species one of which is excited prior to complexation, were first reported in small molecule systems. However, during the past 20 years one of the more vigorous research areas in photophysics has been the investigation of excimers formed in polymers<sup>1</sup>. In most of the cases reported to date, the excimer studies in polymer systems have been conducted on polymers bearing pendant polycyclic aromatic chromophores. Only a few papers have been published on excimers formed from polymers with the excimer forming groups in the backbone<sup>2-5</sup>. Herein, we report on intramolecular excimers between naphthyl carbamate groups spaced periodically in polyurethanes made from 1,5-naphthalene diisocyanate. It is found that even in very dilute solutions, well below the concentrations required for intermolecular interaction, excimer emission can be quite strong depending on the nature of the solvating system employed. The driving mechanism for excimer formation of the naphthyl carbamate groups is shown to be based, at least in part, on hydrogen bonding.

## EXPERIMENTAL SECTION

### Materials

Dichloromethane, dimethylformamide (DMF), and benzene were obtained from Burdick & Jackson and used without further purification. 2,3-Butanediol and 1-butanol (Aldrich) were used as received. Propyl benzene (Aldrich) was distilled before use. Deionized water was used.

### Equipment

Emission spectra and absorption spectra were recorded on a Perkin-Elmer 650-10S Fluorescence Spectrophotometer and a Perkin-Elmer 320 UV spectrophotometer, respectively. Fluorescence decay data were obtained on a single-photon-counting apparatus from Photochemical Research Associates. The samples were bubbled with nitrogen for the steady-state fluorescence spectroscopy and the fluorescence decay measurement. The data were analyzed by a software package obtained from PRA based on the iterative convolution method.  $^{13}\text{C}$  NMR spectra were obtained on a JEOL FX90Q and FTIR spectra were recorded on a Nicolet 5DX. The elemental analyses were conducted by M-H-W Laboratories of Phoenix, AZ.

### Synthesis of Model Compounds

1,5-Naphthalene diisocyanate (NDI) To a stirring solution of p-dioxane (50ml) containing the 1,5-diaminonaphthalene (Fluka, 5.1g) was added trichloromethyl chloroformate (Fluka, 17g) in p-dioxane (15ml) through an addition funnel under a nitrogen stream. The white precipitate was immediately observed. After addition, the temperature was increased to reflux. The forming HCl was removed by passing through water. After 1 hour, the

solution turned clear and was allowed to react for another 3 hours. The p-dioxane was evaporated under reduced pressure and the resulting solid was vacuum sublimed twice to give the colorless crystals in 71% yield: mp 126-128 ° (lit<sup>6</sup>. mp 129.5-131 °C); IR 3022, 2300, 1600, 1500 cm<sup>-1</sup>; <sup>13</sup>C NMR 130.9, 128.7, 127.7, 124.2, 122.2 ppm (benzene); Anal. C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> Calc. C, 68.57; H, 2.88; N, 13.33; Found C, 68.62; H, 2.91; N, 13.32.

Propyl 1-(N-naphthyl) carbamate(PNC) Into 50ml of an ethylacetate (distilled and dried) solution of 1-naphthyl isocyanate (Aldrich, distilled, 10g) was added 1-propanol (Baker, distilled and dried, 7.1g) through an addition funnel. The temperature was increased to the reflux temperature of ethylacetate and the mixture was allowed to react for 8 hours under a nitrogen stream. The precipitates were removed by filtration and ethylacetate was evaporated under reduced pressure. The forming product was purified by recrystallization from CH<sub>3</sub>CN: mp 72°C; IR 3325, 2950, 1675, 1600, 1540, 1500 cm<sup>-1</sup>; <sup>13</sup>C NMR 156.1, 135.3, 129.1, 126.8, 126.6, 125.5, 123.4, 120.9, 67.1, 23.2, 10.9 ppm (DMF); Anal. C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub> Calc. C, 75.24; H, 6.59; N, 6.11; Found C, 75.36; H, 6.51; N, 6.18.

Propyl N-methyl N-(1-naphthyl) carbamate(PNMNC) For the preparation of this compound, all reaction were carried out in an ice bath. NaH (Alfa, 50% in oil, 1.2g) was dispersed in DMF (Burdick & Jackson, dried, 5ml) and the solution was cooled in an ice bath. The propyl 1-(N-naphthyl) carbamate (3.3g) in DMF (15ml) was added into a reactor through an addition funnel dropwise under a nitrogen stream. Immediately, hydrogen was generated and the reaction mixture turned to green. The stirring



was continued for 1.5 hours. The  $\text{CH}_3\text{I}$  (Aldrich, distilled, 4.0g) in DMF (10ml) was added dropwise and the reaction mixture turned colorless. The solution was allowed to react for 2 hours. When the reaction was complete, the precipitates were removed by filtration and DMF was evaporated under reduced pressure. The residue was redissolved in diethylether and the insoluble were removed by filtration. After evaporation of solvent, the resulting liquid was vacuum distilled. The colorless liquid was obtained; bp 120-125°C at 0.5 mmHg; IR 3060, 2950, 1700, 1600, 1500  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  NMR 158.6, 142.9, 137.4, 133.3, 131.2, 130.4, 129.3, 128.9, 128.5, 127.7, 125.5, 69.5, 40.7, 25.0, 12.7 ppm (neat); Anal.  $\text{C}_{15}\text{H}_{19}\text{NO}_2$  Calc. C, 74.05; H, 7.04; N, 5.75; Found C, 74.16; H, 6.95; N, 5.69.

Dipropyl N-(1,5-naphthyl) biscarbamate(DNB) To a p-dioxane solution containing 1-propanol (1.71g) and dibutyltin dilaurate (Polysciences, 0.2g) was added 1,5-naphthalene diisocyanate (1.5g) at once. The reaction mixture was heated to 80 °C and allowed to react for 4 hours with stirring under a nitrogen stream. After evaporation of p-dioxane, the forming product was purified by recrystallization from  $\text{CH}_3\text{CN}/\text{DMF}$  (50/50); mp 203°C; IR 3290, 3000, 1685, 1540, 1500  $\text{cm}^{-1}$ ; Anal.  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$  Calc. C, 65.44; H, 6.71; N, 8.48; Found C, 65.38; H, 6.63; N, 8.59.

#### Synthesis of NDI-Polyurethane (NDI-650)

To 20ml of tetrachloroethane (Baker, distilled and dried) containing polytetraethylene ether glycol (Polysciences, MW 650, 2.17g), dibutyltin dilaurate (Polysciences, 0.11g), and Dabco (Aldrich, 0.08g) was added 1,5-naphthalene diisocyanate (0.7g) at

once. The mixture was heated to 100°C and allowed to polymerize for 2.5 hours with stirring under a nitrogen stream. The tetrachloroethane was evaporated under reduced pressure and the products were dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> solution was poured dropwise into 500 ml of cyclohexane. The precipitated polymers were collected and dried; IR 3310, 2930, 1740, 1695, 1540, 1500 cm<sup>-1</sup>; <sup>13</sup>C NMR 157.2, 136.2, 130.4, 128.4, 122.3, 120.3, 73.1, 67.9, 29.1, 28.6 ppm (CH<sub>2</sub>Cl<sub>2</sub>); Anal. Calc. C, 65.71; H, 9.15; N, 3.26; Found C, 65.99 H, 9.32 ; N, 3.29. The molecular weight of NDI-650 and NDI-2000 were 51,000 and 63,000 respectively by GPC.

## RESULTS AND DISCUSSION

The results of our studies will be presented in three sections. The first deals with the fluorescence properties of model naphthyl carbamates. This section is particularly important in providing the background necessary to interpret the results in the next two sections which are concerned with the fluorescence of naphthalene diisocyanate (NDI) based polyurethanes in solution and film.

Fluorescence of Naphthyl Carbamate Models Two model compounds (shown below) based on carbamate substituted naphthalene will be considered as models for the naphthalene diisocyanate based polyurethanes under investigation in this paper. The propyl N-(1-naphthyl) carbamate (PNC) and dipropyl N-(1,5-naphthyl) biscarbamate (DNB) model compounds were made by reacting the requisite mono- or diisocyanate with 1-propanol.

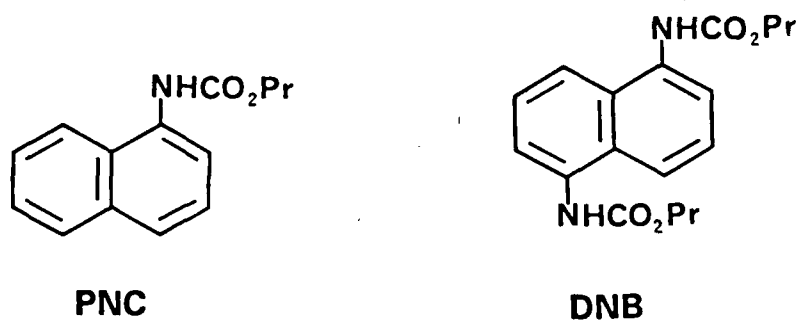
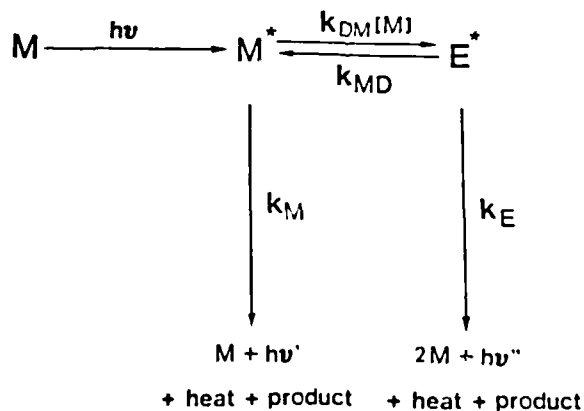


Figure 1 shows the fluorescence spectra of dilute solutions of PNC (0.1g/l) and DNB (0.05g/l) in dichloromethane. Each exhibits a single exponential decay ( $\tau_1$  in Table I) with the biscarbamate DNB having the shortest lifetime (1.84 nsec). (In each case, the decay curves were single exponential and invariant when measured at any emission wavelength from 330nm to 400nm). Unfortunately, DNB is only sparingly soluble in most organic solvents and attempts to obtain concentrated solutions were limited to PNC. As the concentration of PNC increases (Figure 2), a new red-shifted emission appears. The red-shifted emission spectra are characteristic of naphthalene substituted compounds and, in keeping with traditional interpretation of such phenomena, are assigned to excimers between naphthyl carbamate molecules. In accordance with this interpretation, the fluorescence decay curves were recorded in concentrated solutions for PNC at a series of wavelengths spanning the range from 330nm to 500nm. Figure 3 shows the decay curve for PNC (1.5M) recorded at a representative wavelength in the monomer emission region at 330nm. The 330nm decay curve is readily fit to a double exponential decay function with decay parameters of 0.3 nsec ( $\tau_2$ ) and 15.3 nsec ( $\tau_3$ ). By monitoring at 480nm in the excimer region and fitting the long-lived portion of the decay curve to a single

exponential decay function, a lifetime of 15.4 nsec (Table I) was recorded. Comparison of the short-lived component (0.3 nsec-- $\tau_2$ ) of the monomer decay in the concentrated solution with the lifetime (3.5 nsec-- $\tau_3$ ) in the dilute solution leads to the conclusion that the monomer emission in the concentrated solution is significantly quenched. Both the large decrease of the fluorescence lifetime of the monomer naphthyl carbamate and the presence of the long-lived component in the monomer emission region suggests that the monomer exists in a dynamic equilibrium with the excimer as represented by the classical scheme (Scheme I) for excimer kinetics where the value for  $k_{MD}$  has a finite value which makes the dissociation process of the excimer  $E^*$  into its component species  $M$  and  $M^*$  a viable process.

At this point, it is appropriate to consider the factors which may enter in to stabilization of the excimer in the PNC solutions.

Scheme I



where,

$k_M$  = non-radiative plus radiative rate constant for  
excited PNC monomer  $M^*$ .

$k_{DM}$  = rate constant for excimer formation between M and  
 $M^*$ .

$k_{MD}$  = rate constant for dissociation of excimer E into  
component species M and  $M^*$ .

$k_E$  = non radiative plus radiative rate constant for  
excimer  $E^*$ .

M = ground state PNC.

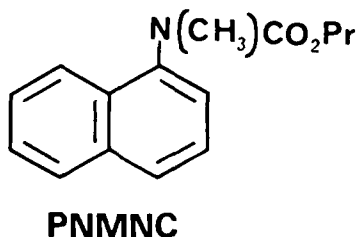
$M^*$  = excited state PNC.

$E^*$  = PNC excimer.

First, it is worthy noting that at least some excimer formation, as monitored by recording fluorescence decay curves in the monomer region, occurs at concentrations of PNC as little as 0.005M in organic solvents. However, it is only above 0.5M that appreciable build up of excimer emission is recorded.

It has long been recognized that polyurethanes, which contain carbamate chromophores, are characterized by hydrogen bonding, for example between the hydrogen attached to the nitrogen of the carbamate group and the carbamate carbonyl group, which contributes to the unique physical properties of polyurethanes. The PNC model system also shows appreciable hydrogen bonding between carbamate chromophores which is quite prevalent at higher concentrations. This is illustrated in Figure 4 by the IR spectra of PNC recorded at two concentrations. In the dilute solution (0.2M) the IR shows a single peak in the N-H

stretching region. This peak at  $3416\text{ cm}^{-1}$  results from a non-bonded (or free) N-H stretching in the carbamate moiety. At the higher concentration (2.0M) a new band due to a hydrogen-bonded N-H stretching appears at  $3320\text{ cm}^{-1}$ . It is in this concentration region that the higher degree of excimer formation is recorded in Figure 2. Thus, it is reasonable to assume that hydrogen bonding between the PNC molecules contributes to the stabilization of the excimer. In support of this supposition, propyl N-methyl N-(1-naphthyl) carbamate (PNMNC) with a methyl group substituted on the nitrogen carbamate was synthesized.



The methyl group prohibits hydrogen bonding. Figure 5 shows that little or no excimer emission is recorded for NMPNC up to concentration of 3M in dichloromethane. Only at concentrations above 10M can any excimer emission be observed. Consequently, it can be concluded that hydrogen bonding is indeed an important factor in the excimer formation of PNC.

#### Photophysics of an 1,5-Naphthalene Disocyanate Based Polyurethane in Solution

Having established the basic features of excimer formation in naphthyl carbamates and realizing that hydrogen bonding plays a significant role in excimer formation, we turn to consideration

of a 1,5-naphthalene diisocyanate (NDI) based polyurethane which has the naphthyl carbamate groups periodically spaced as an integral part of the polymer backbone. The polymer, designated as NDI-650, is based on NDI and polytetramethylene ether glycol (average molecular weight of 650) and has a molecular weight of 51,000. The steady state fluorescence spectrum of a very dilute dichloromethane solution of NDI-650 is shown in Figure 6. Although the basic structure of the fluorescence spectrum of NDI-650 is similar to the fluorescence of biscarbamate DNB in Figure 1 (curve a), there is a distinctive red-shifted tail above 400nm. Consistent with the red shift in the fluorescence spectra of NDI-650 is the fact that the fluorescence decay curves in dilute solution (monitored at any wavelength from 330nm to 500nm) cannot be fit to a single exponential decay function. These results indicate intramolecular excimer formation in the NDI-650 solutions.

To establish the nature of the excimer formation, either intramolecular or intermolecular, an extremely dilute solution solution ( $1 \times 10^{-3}$ g/l) of NDI-650 was prepared. Even in this ultra-dilute solution excimer emission was present. Figure 7 shows a plot of the excimer (430nm) to monomer (350nm) intensity ratio as a function of polymer concentration. Not until a concentration of 1.0g/dl is reached does intermolecular excimer formation between naphthyl carbamate groups on different polymer backbones become important.

To identify the nature of the absorbing chromophore in NDI-650 which leads to the emission spectra recorded in Figure 6, excitation spectra were recorded at a variety of emission

wavelength settings. The excitation spectrum in Figure 8 is exemplary of the curves recorded. Also included in Figure 8 is the absorption spectrum of NDI-650 for comparison. Except for minor differences due to recording on two instruments (the fluorescence spectra are uncorrected for wavelength response) the excitation spectrum is identical to the absorption spectrum. Although not shown, the absorption and excitation spectra of the model DNB are identical to those for NDI-650. In general, it can be safely concluded that the species responsible for the initial absorption of light leading to excimer formation in dilute solution is a single ground state naphthyl biscarbamate moiety in the backbone of NDI-650.

In the discussion of the fluorescence spectra of NDI-650, it was noted that the emission decay curves are not single exponential. Additionally, unlike for concentrated solutions of PNC, the decay curves recorded in the monomer emission region (anywhere from 330nm to about 370nm) could not be fit to a double exponential decay function. However, the decay curve (monitored at 330nm in the monomer emission region) obtained experimentally (Figure 9) could be fit to a triple exponential decay function with decay parameters of 1.20 nsec, 2.04 nsec, and 19.2 nsec. In addition, fitting the long-lived component of the decay curves monitored at 480nm to a single exponential decay function gave a value of 21.4 nsec for NDI-650, very similar to the value for the long-lived component of the monomer decay. This data is summarized in Table I along with the lifetime data previously obtained for PNC and DNB.

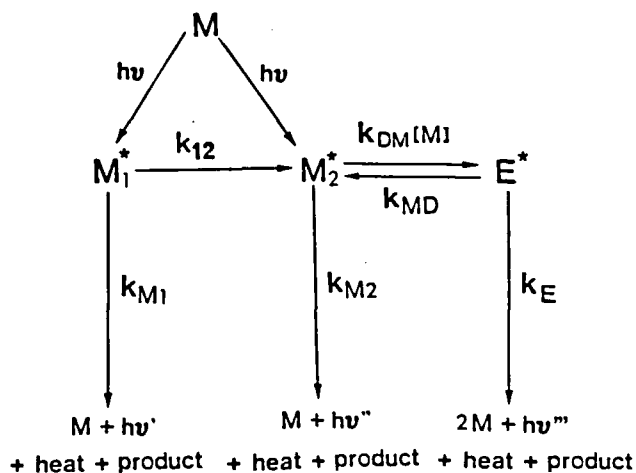
From analyzing the results from the decay curves compiled in



Table I, one can infer from the long lived decay of the monomer emission ( $\lambda_{em} = 330\text{nm}$ ) that the excimer is reversibly formed and exists in a dynamic equilibrium with an excited state monomer species. This is in reasonable agreement with the reported<sup>7,8</sup> reversibly formed excimers between naphthyl chromophores in poly (vinyl naphthalenes). The two short lived components are attributed (after Phillips et. al. <sup>7,8</sup>) to monomeric species, one which is quenched and in a dynamic equilibrium with the excimer and another which is an "isolated monomer" unquenched by interaction to form an excimer. The longer lived component ( $\tau_1 = 2.04$  nsec) of the two fast components corresponds to the lifetime of the model biscarbamate DNB (1.84 nsec), and probably results from the isolated monomer. The shorter lifetime ( $\tau_2 = 1.20$  nsec) can be assigned to the quenched monomer emission in equilibrium with the excimer. The "isolated monomer" concept, as recently reported by Phillips et. al.<sup>7,8</sup> and Holden et. al.<sup>9</sup> to account for the excimer kinetics in polymers with pendant naphthalene groups, adequately accounts for the excimer kinetics of dilute solutions of NDI-650 in dichloromethane. The basic mechanism for the "isolated monomer" is given in Scheme II with the parameters as defined.

In the case of NDI-650, since the 2.04 nsec lifetime ( $\tau_1$ ) for the "isolated monomer" is essentially identical, within our error limits, to the DNB lifetime of 1.84 nsec, we conclude that the rate constant  $k_{12}$  for conversion of the excited isolated monomer  $M_2^*$  is low compared to the rate constant  $k_{M1}$  for deactivation of  $M_1^*$ .

Scheme II



where,

$k_{M1}$  = non-radiative plus radiative rate constant for excited isolated naphthyl monomer  $M_1^*$ .

$k_{M2}$  = non-radiative plus radiative rate constant for excited excimer forming naphthyl monomer  $M_2^*$ .

$k_{DM}$  = rate constant for excimer formation between  $M_2^*$  and  $M$ .

$k_{MD}$  = rate constant for dissociation of excimer  $E^*$  into component species  $M_2^*$  and  $M$ .

$k_E$  = non-radiative rate constant for excimer  $E^*$ .

$k_{12}$  = rate constant for formation of excited excimer forming naphthyl monomer  $M_2^*$  from the excited isolated naphthyl monomer  $M_1^*$ .

$M$  = ground state naphthyl monomer.

$M_1^*$  = excited isolated naphthyl monomer.

$M_2^*$  = excited excimer forming naphthyl monomer.

A similar conclusion was reached by Holden et. al.<sup>9</sup> who also postulated that  $k_{12}$  was low compared to  $k_{M1}$  for polymers with naphthyl chromophores separated by greater than three carbon atoms. The naphthyl groups in the backbone of NDI-650 are certainly separated by more than three carbon atoms and thus our results are quite consistent with those of Holden et. al.<sup>9</sup>.

To provide confirming evidence for existence of the isolated monomer, the fluorescence decay curves were analyzed for DNB and NDI-650 in a second solvent system (1-butanol) in which the DNB lifetime increased to 2.48 nsec. As shown in Table I, the decay parameter for the triple exponential fit to the decay curve of NDI-650 in benzene lead to the same conclusion as the results in dichloromethane. Particularly important to note is the virtual agreement between  $\tau_1$  for DNB (dilute) in benzene and  $\tau_1$  obtained for NDI-650 in benzene. In short, the  $\tau_1$  value is altered by the solvent both for the DNB small molecule model and NDI-650. The correlation between the  $\tau_1$  values in the two solvents provides additional evidence for the "isolated monomer" scheme. Similar results to those in dichloromethane and 1-butanol in Table I have been obtained for over 10 solvent systems<sup>10</sup>. In each case, despite the variation of the DNB model lifetime with solvent, there is excellent agreement between the  $\tau_1$  values calculated for DNB and NDI-650.

Having established the existence of the excimer emission of NDI based polyurethanes in solution, and realizing that the

intramolecular excimer forming naphthyl carbamate groups are located on the backbone of the polymer, it becomes apparent that an excellent opportunity exists for chain conformational studies as a function of solvent. Figure 10 shows the steady-state fluorescence spectra of NDI-650 in four solvents with distinctively different solvating power. In each case (curves a-d) both monomer and excimer emission is observed; however, the ratios of excimer to monomer emission reflect conformation differences of the NDI-650 polymer in the solvent employed. The excimer to monomer intensity ratio ( $I_{ex}/I_m$ ) recorded at 430nm ( $I_{ex}$ ) and 355nm ( $I_m$ ) in Table II for the four pure solvent systems under consideration shows an increase in the order:  $I_{ex}/I_m$  (2,3-butanediol) <  $I_{ex}/I_m$  (dichloromethane) <  $I_{ex}/I_m$  (benzene) <  $I_{ex}/I_m$  (propyl benzene). This parallels the decrease in solubility parameters for each solvent and reflects the ability of the solvent to effectively solvate the polyurethane chain. In other words, propyl benzene is a fairly "poor" solvent for NDI-650 and results in a more compact polymer chain with higher degree of intramolecular excimer formation than benzene, dichloromethane, and 2,3-butanediol. The ratio of  $I_{ex}/I_m$  parallels the decrease in the solubility parameter (Table II). If indeed our supposition concerning the relationship between the solubility parameter and  $I_{ex}/I_m$  is true, then we should be able to find a solvent system with an extremely high solubility parameter which also has a large value for  $I_{ex}/I_m$ . In order to attain such a solvent system with a very high solubility parameter, DMF and water were mixed in 70/30 ratio (vol %) and the photophysical parameters were recorded (Table II). For the

DMF/water (70/30) system, the  $I_{ex}/I_m$  ratio is quite high indicating a very compact coil with a high degree of intramolecular excimer formation. Apparently, from the data in Table II, both propyl benzene with a low solubility parameter and the DMF/water (70/30) solvent system with a high solubility parameter are relatively "poor" solvents for the NDI-650 polymer with dichloromethane and 2,3-butanediol being relatively "good" solvents. This would most likely place the NDI-650 solubility parameter somewhere between 20 and 25  $(J/m^3)^{1/2} \times 10^{-3}$ . A detailed analysis<sup>10</sup> shows the solubility parameter to be approximately 23  $(J/m^3)^{1/2} \times 10^{-3}$ .

Photophysics of NDI-650 and NDI-2000 polyurethane Films. The fluorescence spectrum of an NDI-650 polyurethane film ( $\lambda_{ex} = 300nm$ ) is dominated by excimer emission (Figure 11). A preliminary multiexponential analysis of the excimer and monomer emission decay curves indicates a complicated photophysical system. However, it can be reported that the long-lived component of the excimer decay curve (taken at 500nm) does yield a lifetime of ~22 nsec for excimer emission, close to that obtained in  $CH_2Cl_2$ .

In contrast to the results for the NDI-650 polyurethane, the fluorescence spectrum of a polyurethane film of NDI-2000 [based on NDI and poly (tetramethylene ether glycol) with average molecular weight of 2,000] shows appreciable emission from the monomer component (Figure 11). Although the excimer and monomer decay curves are complex and difficult to analyze, the long-lived component of the excimer decay curve (recorded at 500nm) is about

21 nsec, in close agreement with the lifetime obtained for the NDI-650 film.

In contrasting the results for the NDI-650 and NDI-2000 films, it is apparent that the extent of excimer formation is greater for the NDI-650 film. It may be argued that the increased relative concentration of naphthyl carbamate chromophores in the NDI-650 film leads to increased excimer formation. It should, however, be pointed out that there is a distinct and perhaps critical structural difference between the NDI-650 and NDI-2000 polyurethane films which may manifest itself in increased excimer formation. In the NDI-650 polyurethane film, there is a significant degree of hydrogen bonding to the carbonyl on the urethane moiety. This is exemplified by the infrared spectra of the NDI-650 and NDI-2000 films given in Figure 12. The NDI-650 has primarily hydrogen bonded carbonyls ( $1695\text{ cm}^{-1}$ ) while the NDI-2000 films have a high content of non-bonded carbonyls ( $1740\text{ cm}^{-1}$ ). Employing the same arguments used to describe hydrogen bonding effects in the PNC model compounds in solution (See Figure 4), it can be reasoned that the hydrogen bonding in the NDI-650 film locks in or stabilizing the excimer site geometry and provides for an increased degree of excimer, relative to monomer, fluorescence.

#### CONCLUSION

Both steady-state and transient fluorescence spectroscopy indicate the existence of intramolecular excimer formation in naphthalene diisocyanate based polyurethanes. In solution, the

extent of excimer formation is directly related to the "poorness" of the solvent. In solution, a preliminary kinetic analysis indicates that the excimer is reversibly formed, both for the polyurethane and an appropriate model monocarbamate of naphthalene isocyanate. The excimer formation of model compounds in solution correlates with the degree of hydrogen bonding between chromophores. In the case of the polymer, the fluorescence decay results are interpreted by an "isolated monomer" scheme. For NDI based polyurethane films, steady-state fluorescence shows a distinct difference in the excimer to monomer intensity ratio which depends on the length of the polyol segment. This difference is probably due to hydrogen bonding of carbonyls in the urethane moiety.

Future work will concentrate on the relationship between the photophysics of polyurethane systems based on naphthalene diisocyanate and the corresponding photochemical processes. In particular, the effect of excimer formation on the photodegradation process will be investigated. In addition, a more detailed photophysical study will be conducted to determine the extent, if any, of preformed excimers due to the hydrogen bonding effect.

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## REFERENCES

1. J. E. Guillet, Polymer Photophysics and Photochemistry: An Introduction to the Study of Photoprocesses in Macromolecules, Cambridge, Cambridge University Press, 391 (1985).
2. J. A. Ibemsi, J. B. Kimssinger, and M. Ashraf El-Bayoumi, J. Polym. Sci., Chem. Ed., 879 (1970).
3. N. S. Allen and J. F. McKellar, Makromol. Chem., 179, 523 (1978).
4. N. S. Allen and J. F. McKellar, J. Appl. Polym. Sci., 22, 2085 (1978).
5. M. Graley, A. Reiser, A. J. Roberts, and D. Phillips, Macromolecules, 14, 1752 (1981).
6. A. Barbalata, A. A. Caraculacu, and V. Iurea, Eur. Poly. J., 14, 427 (1978).
7. D. Phillips, A. J. Roberts, and I. Soutar, Eur. Poly. J., 17, 101 (1981).
8. D. Phillips and G. Rumbles, Polymer Photochemistry, 5, 153 (1984).



9. D. A. Holden, P. Y. K. Wang, and J. E. Guillet.  
Macromolecules, 13, 295 (1980).

10. C. E. Hoyle and K. J. Kim, Macromolecules, manuscript in  
preparation.

Table I. Lifetime data for model and polymer systems  
(in CH<sub>2</sub>Cl<sub>2</sub> and 1-butanol).

| Compound                        | $\tau_1^f$ (nsec) | $\tau_2^g$ (nsec) | $\tau_3^h$ (nsec)        |
|---------------------------------|-------------------|-------------------|--------------------------|
| DNB (dilute) <sup>a</sup>       | 1.84              | ----              | ----                     |
| DNB (dilute) <sup>b</sup>       | 2.48              | ----              | ----                     |
| PNC (dilute) <sup>c</sup>       | 3.53              | ----              | ----                     |
| PNC (concentrated) <sup>d</sup> | ---               | 0.33              | 15.3 (15.4) <sup>i</sup> |
| NDI-650 (dilute) <sup>e</sup>   | 2.04              | 1.20              | 19.2 (21.4) <sup>i</sup> |
| NDI-650 (dilute) <sup>j</sup>   | 2.41              | 1.22              | 22.9 (22.3) <sup>i</sup> |

a.  $3.0 \times 10^{-4}$  M in CH<sub>2</sub>Cl<sub>2</sub>

b.  $3.0 \times 10^{-4}$  M in 1-butanol

c.  $4.4 \times 10^{-4}$  M in CH<sub>2</sub>Cl<sub>2</sub>

d. 1.5 M in CH<sub>2</sub>Cl<sub>2</sub>

e. 0.1g/l in CH<sub>2</sub>Cl<sub>2</sub>

f. unquenched monomer lifetime

g. quenched monomer lifetime

h. excimer lifetime

i. lifetime of long-lived component monitored at 480nm

j. 0.1g/l in 1-butanol

Table II. Excimer to monomer intensity ratios for NDI-650 in several solvents

| <u>Solvent</u>              | $I_{430}/I_{355}$ | Solubility Parameter<br>$(\text{J}/\text{m}^3)^{1/2} \times 10^{-3}$ |
|-----------------------------|-------------------|--|
| Propyl benzene              | 0.55              | 17.6   |
| Benzene                     | 0.35              | 18.8   |
| Dichloromethane             | 0.21              | 19.8   |
| 2,3-Butanediol              | 0.11              | 22.7   |
| DMF/H <sub>2</sub> O(70/30) | 0.91              | 31.7   |

### Figure Captions

Figure 1. Steady state fluorescence spectra ( $\lambda_{ex} = 300\text{nm}$ ) of DNB (curve a, 0.05g/l) and PNC (curve b, 0.1g/l) in dichloromethane.

Figure 2. Steady state fluorescence spectra ( $\lambda_{ex} = 300\text{nm}$ ) of PNC in dichloromethane at concentrations of  $4.4 \times 10^{-4}\text{M}$  (curve a) and 3.6M (curve b).

Figure 3. Fluorescence decay curve ( $\lambda_{ex} = 300\text{nm}$ ,  $\lambda_{em} = 330\text{nm}$ ) of PNC (1.5M) in dichloromethane.

Figure 4. Infrared spectra of PNC at concentration of 0.2M (curve a) and 2.0M (curve b) in dichloromethane.

Figure 5. Steady state fluorescence spectra ( $\lambda_{ex} = 300\text{nm}$ ) of PNMNC at concentration of  $4.1 \times 10^{-4}\text{M}$  (——), 3.7M (.....) and 9.25M (— · —).

Figure 6. Steady state fluorescence spectrum of NDI-650 (0.1g/l) in dichloromethane. ( $\lambda_{ex} = 310\text{nm}$ )

Figure 7. Ratio of excimer ( $I_{ex}$ ) to monomer ( $I_m$ ) fluorescence intensity ( $\lambda_{ex} = 310\text{nm}$ ) as a function of NDI-650 concentration in dichloromethane.

Figure 8. Absorption (curve a, 0.1g/l) and excitation

spectrum (curve b,  $\lambda_{em} = 460\text{nm}$ ,  $0.01\text{g/l}$ ) of NDI-650 in dichloromethane.

Figure 9. Fluorescence decay curve ( $\lambda_{ex} = 310\text{nm}$ ,  $\lambda_{em} = 330\text{nm}$ ) of NDI-650 ( $0.1\text{g/l}$ ) in dichloromethane.

Figure 10. Steady state fluorescence spectra ( $\lambda_{ex} = 310\text{nm}$ ) of NDI-650 in 2,3-butanediol (curve a,  $< 0.05\text{g/l}$ ), dichloromethane (curve b,  $0.1\text{g/l}$ ), benzene (curve c,  $0.1\text{g/l}$ ) and propyl benzene (curve d,  $0.05\text{g/l}$ ).

Figure 11. Steady state fluorescence spectra of NDI-2000 (curve a) and NDI-650 (curve b) films.

Figure 12. Infrared spectra of NDI-2000 (curve a) and NDI-650 (curve b) films.

Fig 1

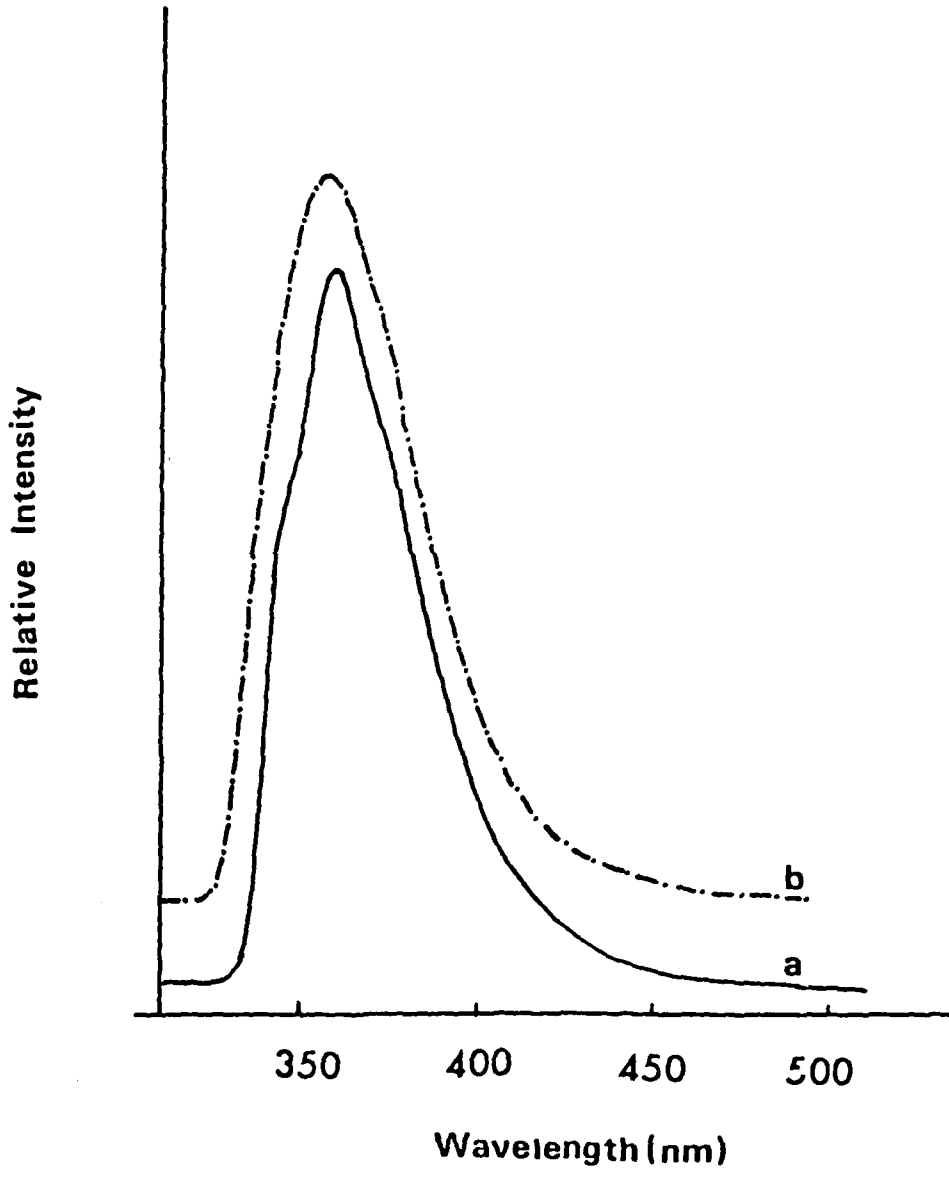


Fig 2

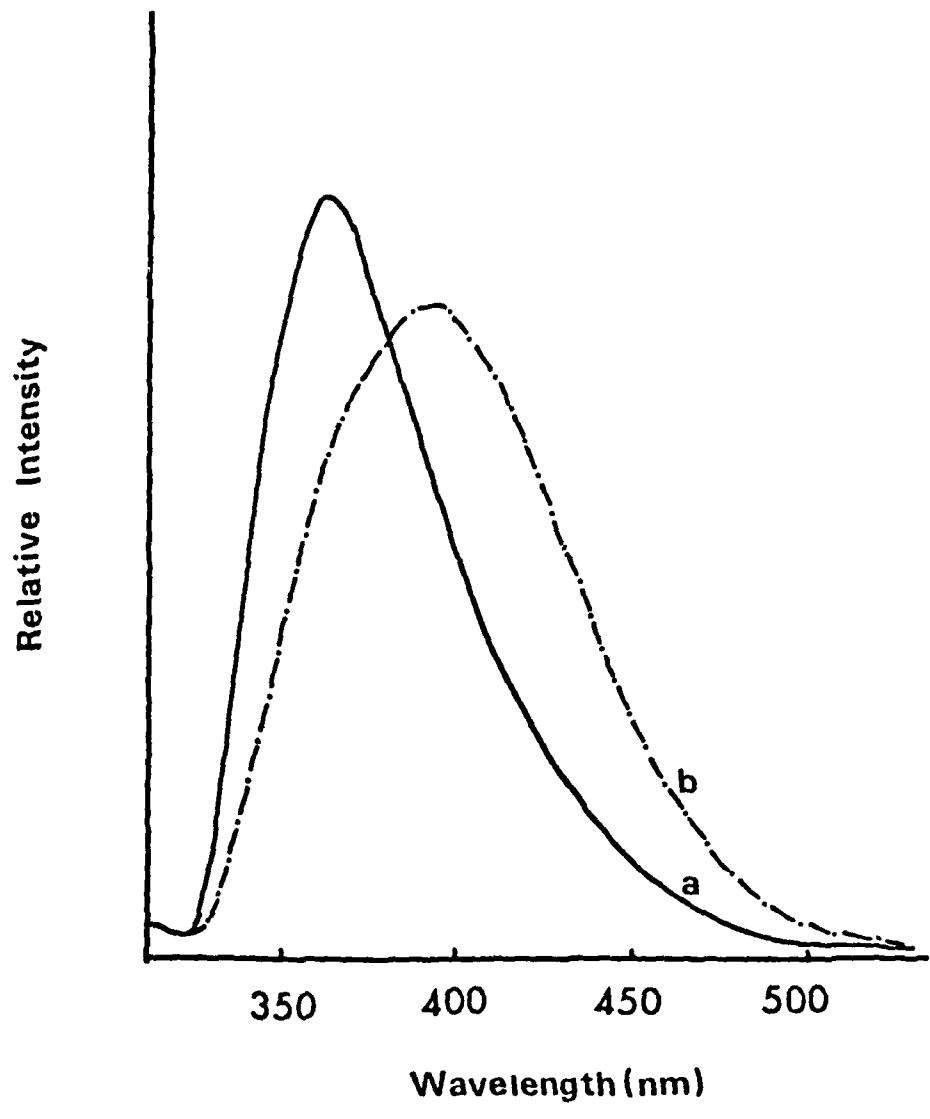


Fig 3

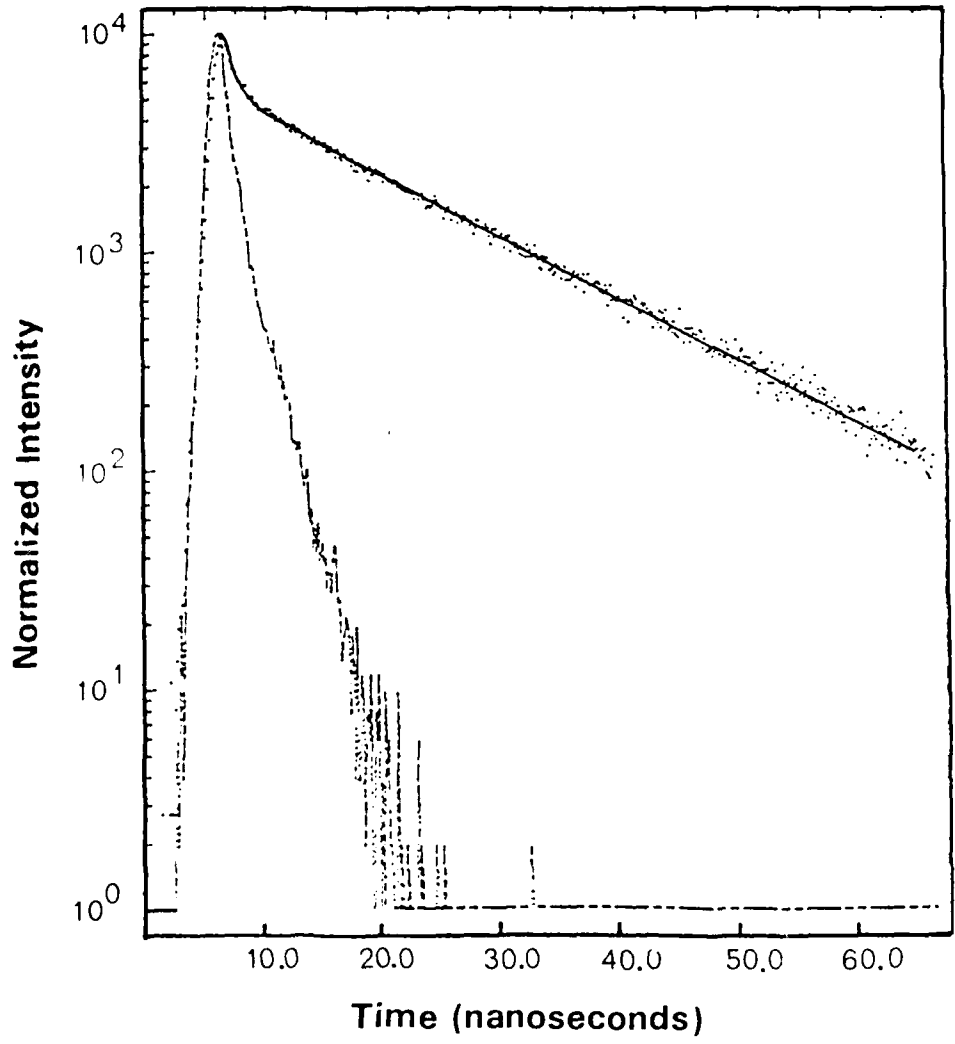




Fig 4

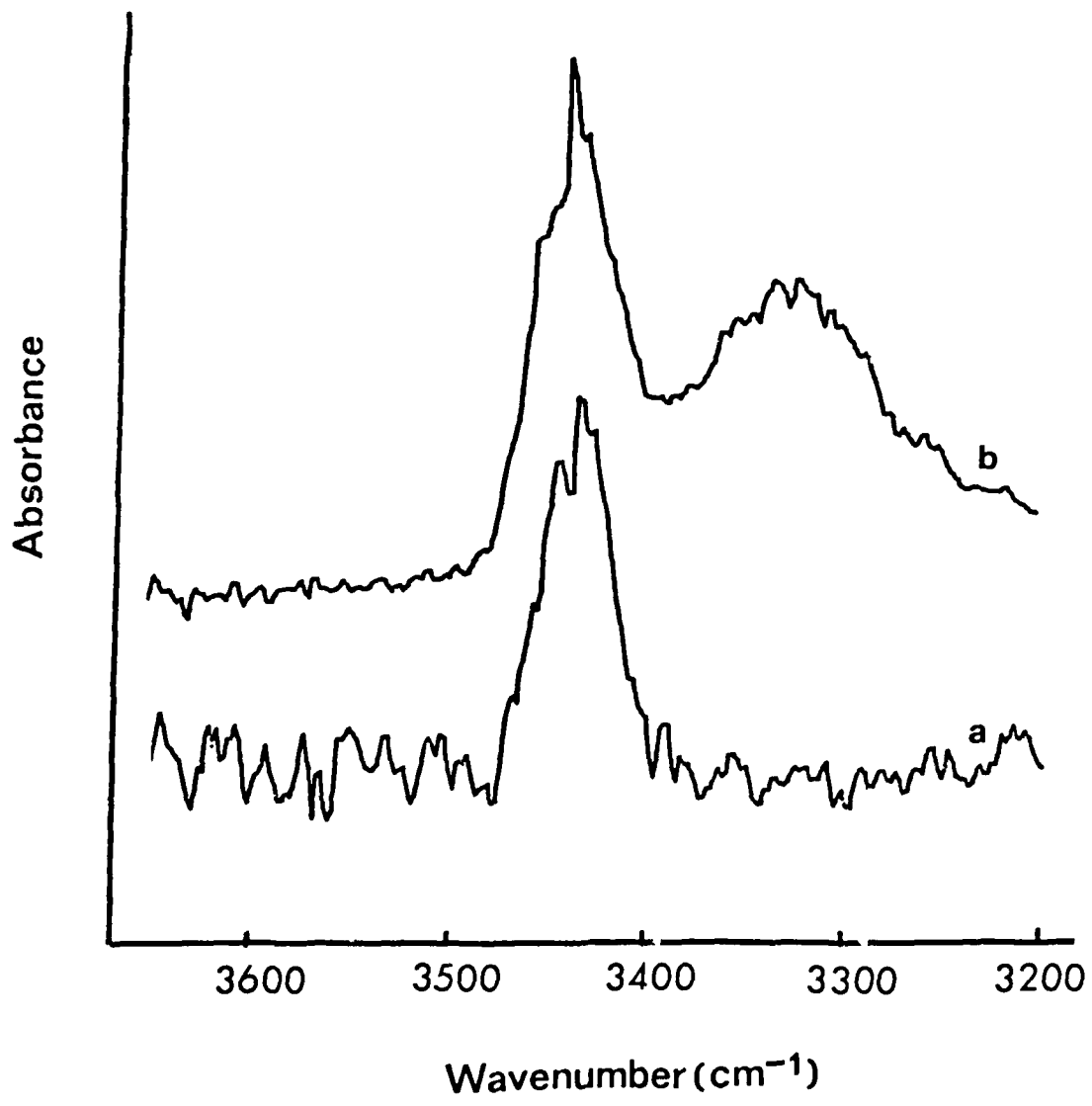


Fig 5

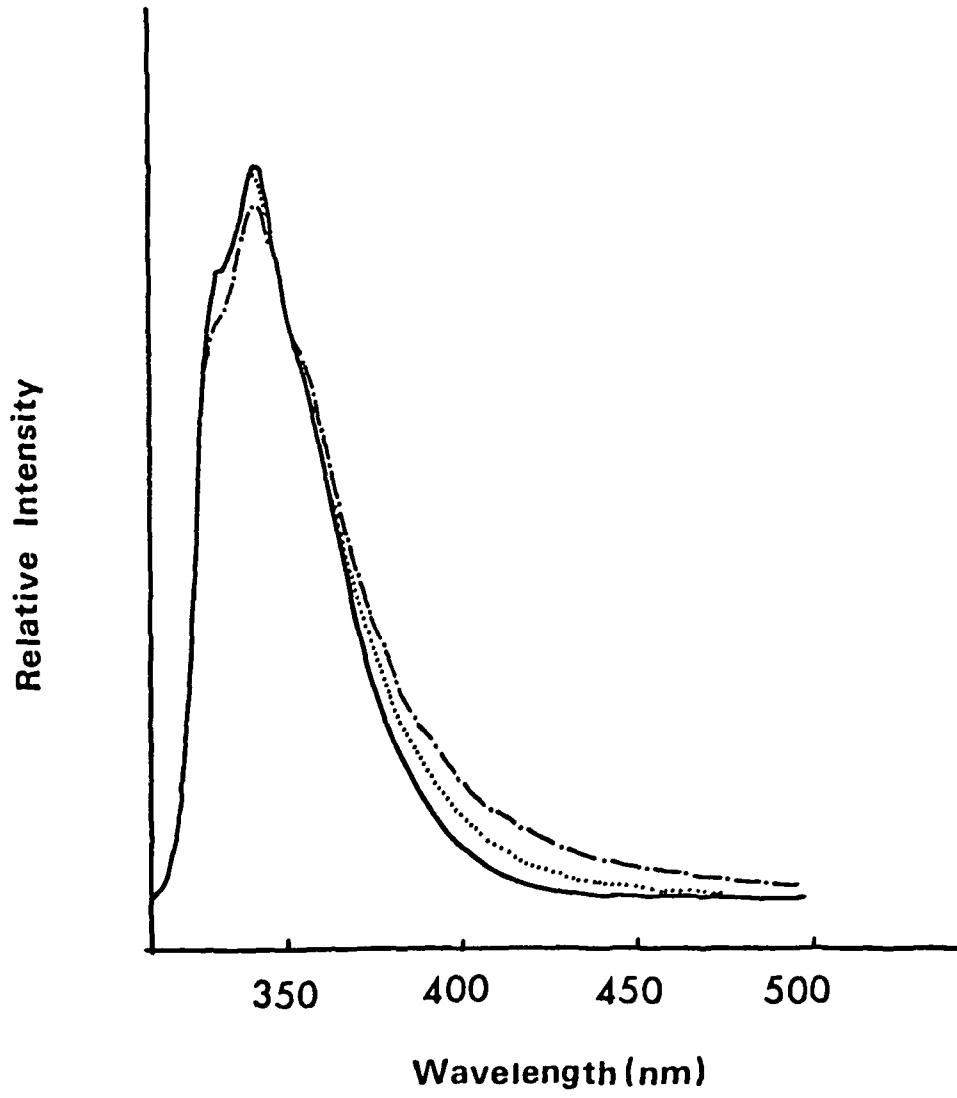


Fig 6

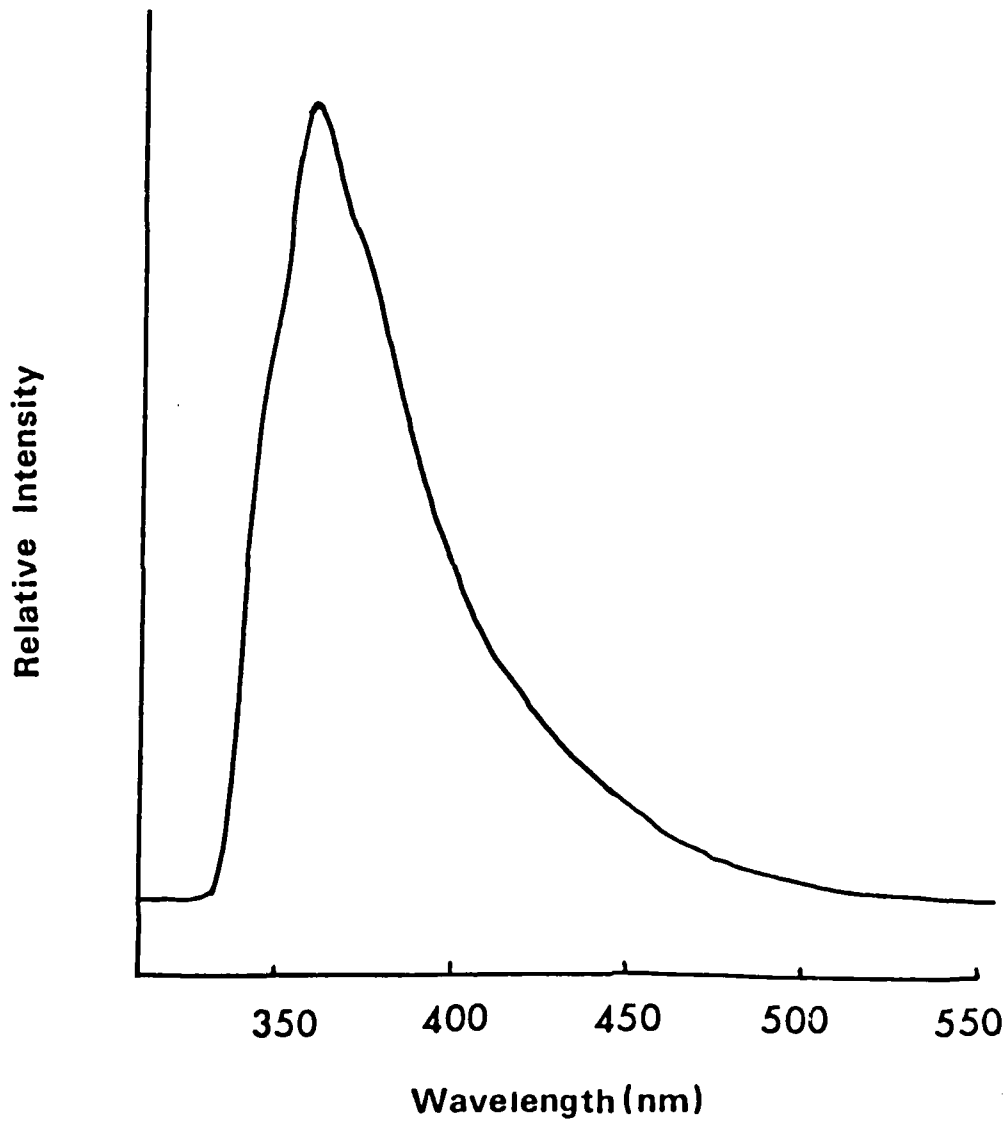


Fig 7

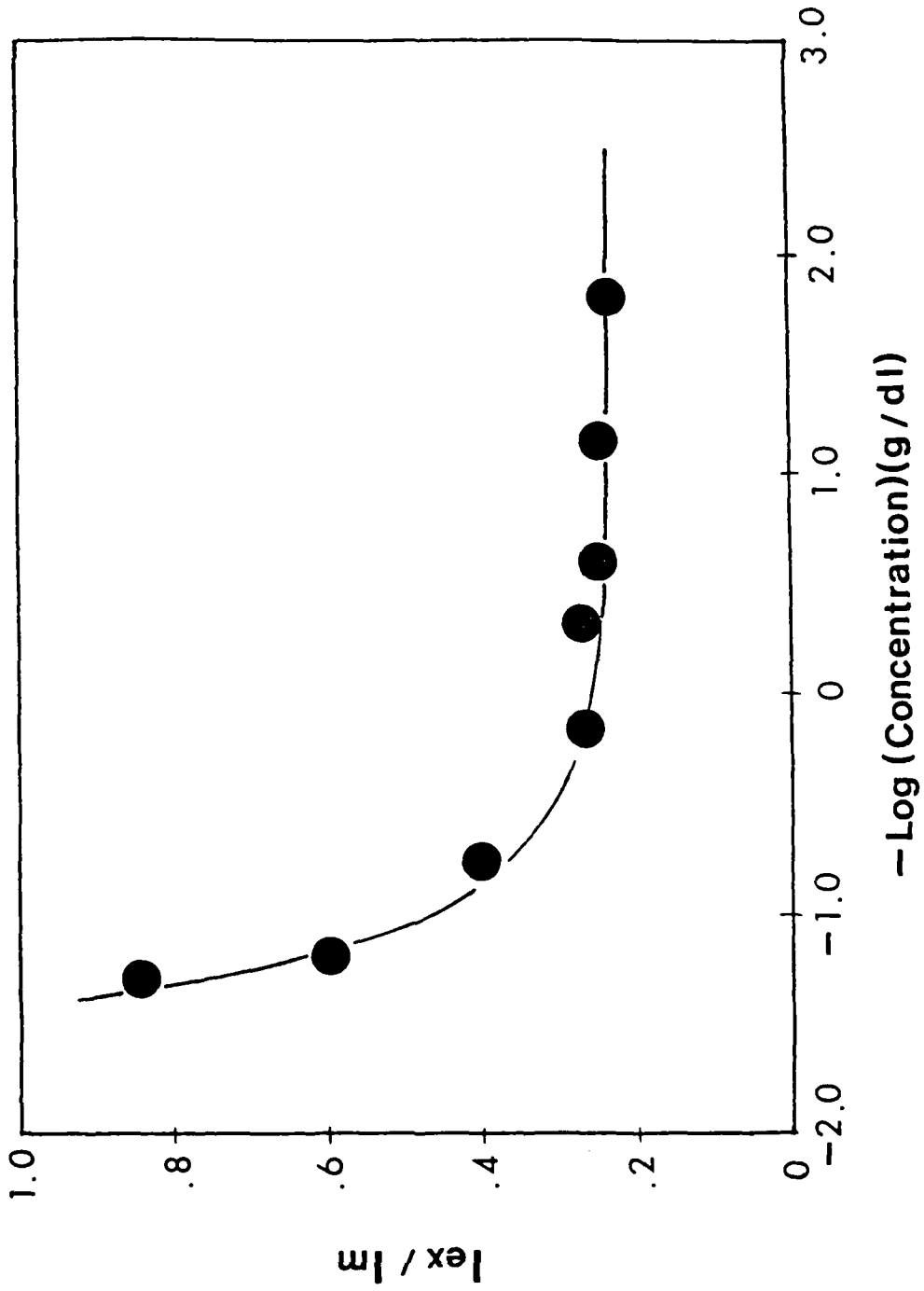


Fig 8

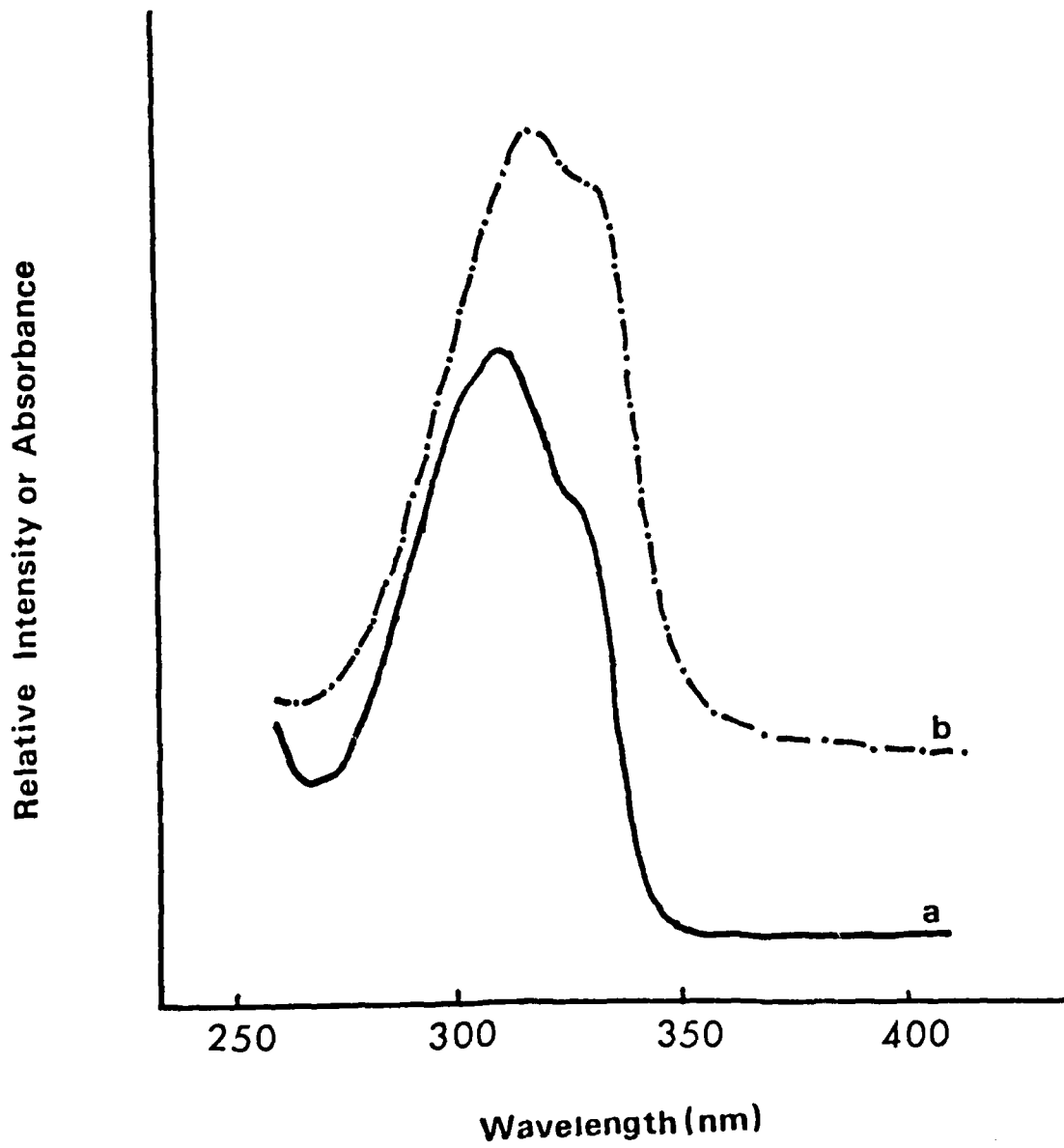


Fig 9

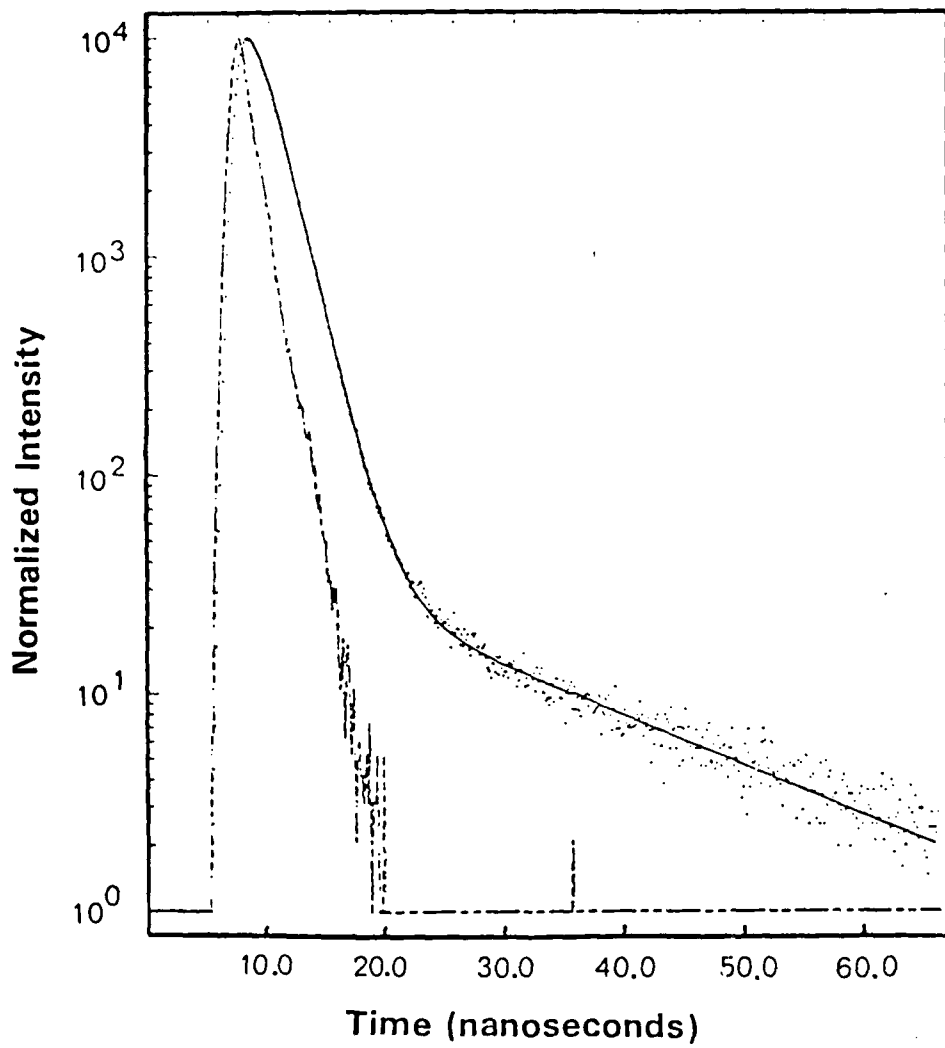


Fig 10

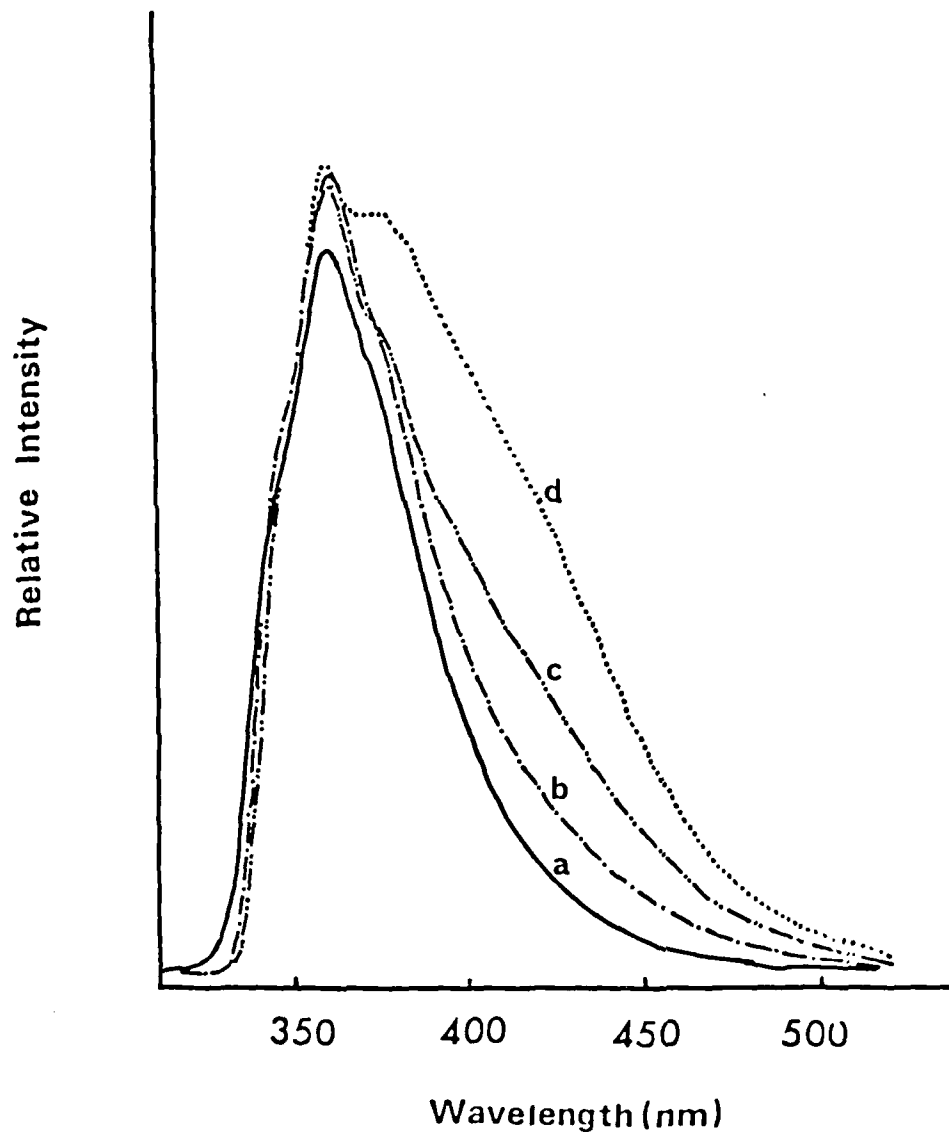


Fig 11

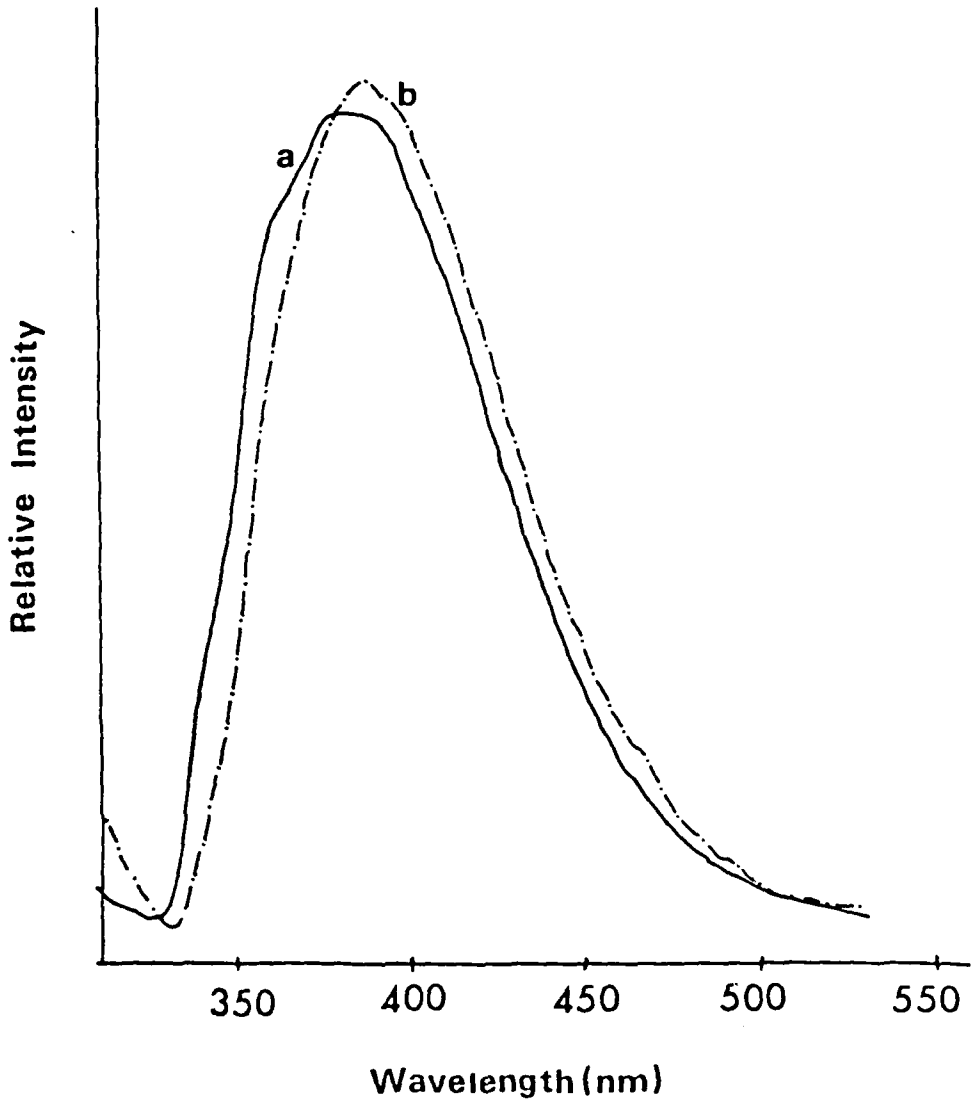
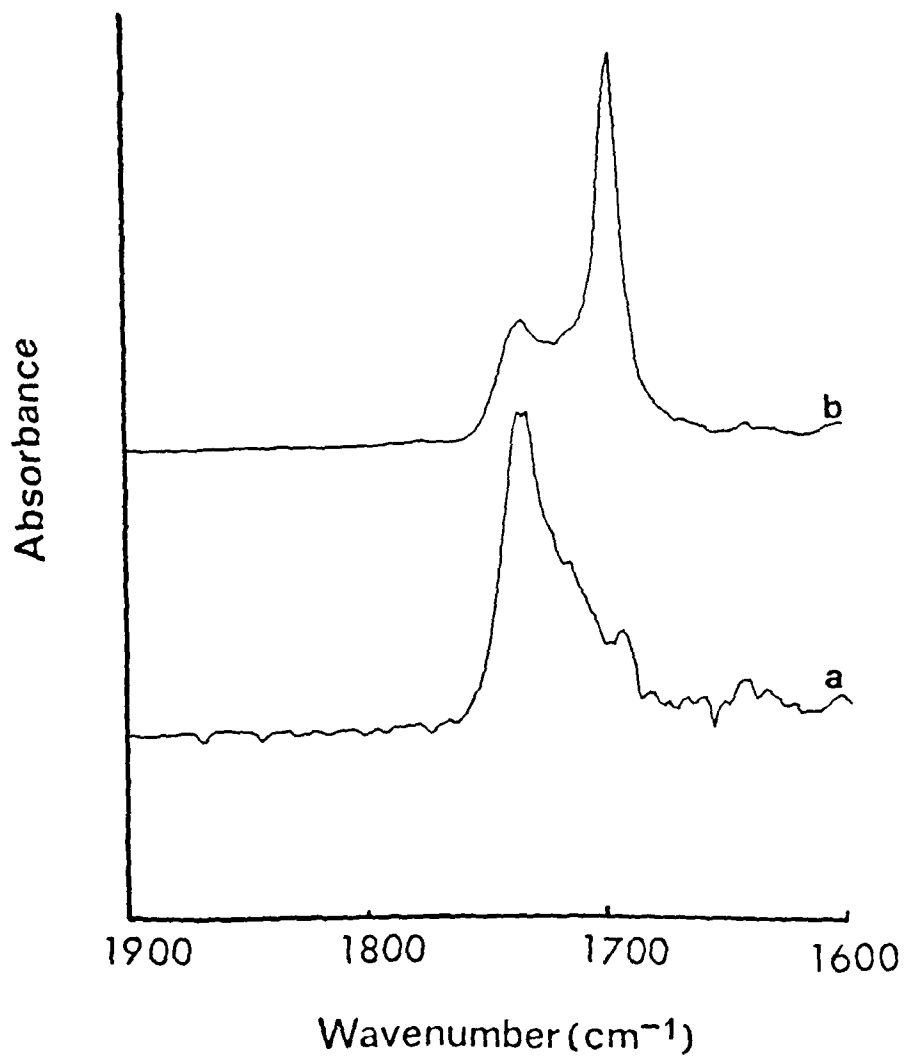




Fig 12



LMED  
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