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Photochemistry of Bisphenol-A-Based Polycarbonate: The Effect of the Matrix and Early Detection of Photo-Fries Product Formation

by

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by

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ABSTRACT

The effect of polymer matrices on a photo-induced rearrangement process has been shown to be dependent upon whether the photoreactive group is attached to a polymer backbone, or free. If diphenylcarbonate is simply embedded in a polymer matrix, the rearrangement process is independent of whether the host film is above or below its glass transition. However, if the diphenylcarbonate group is incorporated as part of a polycarbonate backbone, the Fries rearrangement process is significantly reduced for photolyses conducted at temperatures well below the glass transition of polycarbonate. The utility of fluorescence spectroscopy in identification of the initial salicylate type photo-Fries type rearrangement product of polycarbonate is also demonstrated. The broad, structureless fluorescence spectrum with peak maximum at 470 nm produced by photolysis of polycarbonate films for short time periods is assigned to emission from phenyl salicylate type photoproducts.

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INTRODUCTION

During the past three decades there have been a large number of papers written describing the photochemical decomposition of bisphenol A (BPA) based polycarbonate (1-19). From a review of the most recent literature published during the last 10 years, it is readily apparent that there are indeed a number of pathways which comprise the composite photodegradation process of polycarbonate. It is important to note that the decomposition pathway actually followed may in fact be dictated by the wavelength of the excitation light source (15, 17, 9). One of the problems in attempting to follow the photolysis process is to be able to detect the appearance of products at the point that they first begin to form. A second, and perhaps even more fundamental consideration is the effect of matrix constraints on product formation. In this paper, we will address both of these fundamental questions concerning the decomposition of BPA polycarbonate. It is expected that the results will provide a sound, fundamental basis for continuing studies of polycarbonate photochemistry.

Before presenting our results, it is worth reviewing the basics of the photochemistry of polycarbonate reported in the literature. The primary decomposition pathway for photolysis of polycarbonate when wavelengths of less than 300 nm are employed is reported to be due to an alpha cleavage process between the carbonyl carbon and the oxygen in the carbonate linkage, and a subsequent rearrangement to give the ortho-photo-Fries product (see Scheme I). Other possible pathways for photo induced decomposition which have been mentioned in the literature, but are not depicted in Scheme I, range from a side-chain photooxidation process to a radical ring-attack

reaction. In addition, when wavelengths of light greater than 300 nm are used to induce the photodecomposition, there are a number of additional oxidation pathways, some of which are probably due to the presence of impurities, which are no doubt operative (13, 15-18). The paper by Factor et al. (10) describes the various possibilites. It is our intention in this paper to center on the primary cleavage process. Subsequent paper will focus on the photodecomposition of polycarbonate due to other mechanisms.

EXPERIMENTAL

Diphenyl carbonate (99% Polyscience) was recrystallized from methanol. Polycarbonate was obtained from GE and reprecipitated in acetone. Polymethyl methacrylate (Aldrich, medium molecular weight) and polyhexyl methacrylate (Polyscience 20 wt% solutions in toluene) were used as obtained. Spectra grade dichloromethane (DCM) from Burdick and Jackson was used. Films for photolysis of the diphenyl carbonate in a polymer matrix were cast from a solution containing 0.1 gram of diphenyl carbonate, 1 gram of the matrix polymer (PMMA or PHMA) and 10 mL of dichloromethane. Polycarbonate films were cast from approximately 20 wt% solutions on glass plates. UV spectra were obtained on a Perkin-Elmer Lambda 6 UV-Vis spectrophotometer and IR Spectra were obtained on a Perkin-Elmer PE-1600 series FTIR Spectrometer. Fluorescence spectra were obtained on a SPEX Fluorolog-2.

Photolysis was either carried out using low pressure phosphorus coated mercury lamp (302 nm maximum, Model XX-15B from Spectronics Corporation) or in a Rayonet Reactor with lamps having a maximum of about 300 nm.

RESULTS AND DISCUSSION

The results section will be divided into two parts in order to facilitate the presentation of the data. The first section will deal with the photolysis of polycarbonate in both solution and solid phase. As well, model compounds will be utilized in order to provide a rationale for the effect of a restricted environment on the cleavage/rearrangement process inherent to the formation of photo-Fries products. Second, fluorescence spectroscopy will be used to monitor the photolysis of both model compounds and polycarbonate in order to analyze the initial stages of the photodegradation process. As will become obvious as the discussion proceeds, fluorescence is capable of detecting the decomposition in very early stages compared to other methods.

Flexibility and Mobility

Figures 1 and 2 show the absorption spectra of diphenyl carbonate (DPC) and bisphenol-A based polycarbonate (PC) before and after exposure to the output of a low pressure phospor-coated mercury lamp which emits with a maximum at 302 nm. Two points are noted. First, the vibrational spectrum of unphotolyzed DPC is somewhat less well defined than for PC. Despite this small difference, however, upon photolysis the formation of new absorption bands above 300 nm, attributable in part to ortho phenyl salicylate type photo-Fries (maxima near 311 nm) products and subsequently derived

dihydroxy benzophenone type products (absorption maxima near 350 nm), appear. Second, the amount of product formed is essentially independent of the substitution on the diphenyl carbonate moiety, i.e., the PC photolysis and the DPC photolysis produce approximately the same absorption spectra for a given exposure period. This establishes a baseline from which to draw conclusions concerning the photolysis of the diaryl carbonate moiety in restricted environments. Figure 3 shows a plot of the absorbances at 311 nm and 345 nm for the photolyzed DPC and PC solutions as a function of photolysis time. The similarity in the build up of absorbance at 311 nm (A_{311}) and 345 nm (A_{345}) is indicative of the lack of any significant effect of the polymer backbone on the photo-induced rearrangement process, at least in solution.

In order to probe the effect of a solid state matrix on the photo-induced rearrangement process, it is necessary to conduct the photolysis in a restricted environment. This is accomplished in two ways. First, the DPC is dissolved uniformly in inert polymer films of differing flexibility. Second, films of polycarbonate are cast from solvent followed by subsequent photolysis. In the latter case, the central aryl carbonate moiety is attached to a polymer chain which may be somewhat restrictive in the solid state compared to solution. Figures 4 and 5 show the changes in the absorption spectra of DPC in polyhexylmethacrylate (PHMA) and polymethylmethacrylate (PMMA) upon exposure to the output of the 302 nm lamps. It is interesting to note that PMMA and PHMA are in difference states at about 32 °C, the temperature during UV exposure: PMMA is a glass at 32 °C while PHMA is about 40 °C above its T_g. Despite this, there is little difference in the absorbance changes in the photolyzed films for a given photolysis

period. This reflects the lack of effect of a glassy matrix on photo-Fries rearrangements and is in agreement with previous reports from our lab (20) as well as others (21-22).

Our results for DPC in PMMA and PHMA thus provide additional evidence for the absence of a significant retarding effect of a glassy matrix (PMMA) on simple rearrangement processes. In fact, our results for the solution photolysis versus photolysis in PMMA and PHMA suggest that indeed there are little differences in the rearrangement process in solution versus a glassy (below T_g) or rubbery (above T_g) matrix. This point has been demonstrated both by Guillet (21), Moore (22) and Hoyle (20) in detailed product yield studies of rearrangements in restrictive inert polymer environments. However, when a reactive chromophore is placed in the backbone of a polymer matrix, it might be expected (see reference 20 for an example of this phenomena) that the restrictive nature of the polymer backbone might be important in retarding the mobility required for rearrangement processes to occur efficiently.

Figure 6 shows results for the photolysis of a PC film which has been adjusted to give the same initial optical density as the PMMA and PHMA films with the DPC. The contrast between the results for the photolysis of PC and DPC in PMMA and PHMA is remarkable. In accordance with a previous report (20) from our lab on carbamate moieties in the backbone of polyurethanes which also undergo a photo-Fries reaction, we find that there is a marked effect on the efficiency of the rearrangement process when the reaction center is attached to the main polymer backbone and the polymer is in the solid state, i.e. a film. This is perhaps more vividly illustrated in the present case by plotting the change in the absorbance of the polycarbonate film at 311 nm and 345 nm, wavelengths

where the phenyl salicylate type product and the dihydroxybenxophenone type product have their maxima (Figure 7). Results are also plotted for DPC (taken from Figures 4 and 5) in PMMA and PHMA for comparison. The difference between DPC in either PMMA or PHMA and PC itself is obvious. Since both PC and PMMA are glasses at 32 °C, the difference between the results for DPC in the PMMA matrix and PC films must be a direct result of the incorporation of the aryl carbonate group into the polymer backbone.

Fluorescence Analysis of PC and DPC

One of the most difficult problems associated with assessing the photodegradation of any polymer film is to be able to detect spectroscopic changes upon exposure to light for very short periods of time. Of course in the case of polycarbonate there have been a large number of papers which have been written over the years using spectroscopic evaluation to monitor the progress of the photodecomposition (1, 4, 8, 10, 11, 13, 15-19). However, relatively long photolysis times are required to measure significant changes in the absorption spectrum. As an example, Figure 8 shows FT-IR spectra of a polycarbonate film before and after photolysis for 1 and 6 hours. Instead of attempting to define the disappearance/appearance of structural features with photolysis time, we simply wish to demonstrate that only after longer photolyses times can significant changes be detected. There are ample references dealing with interpretation of IR spectral changes upon photolysis of polycarbonate (15-17).

We turn in this paper, to what we feel is an extremely sensitive means of detecting the formation of photoproducts, in particular the ortho-photo Fries rearrangement product

in polycarbonate. We demonstrate the technique for the DPC model first. Figure 9 shows the fluorescence spectra of a DPC solution in dichloromethane before and after photolysis of times up to 3 minutes. The absence of fluorescence upon excitation at 310 nm prior to photolysis is expected since DPC has no absorbance above 300 nm. Photolysis results in the appearance of new absorption bands with wavelengths greater than 300 nm, and a distinct fluorescence when exciting from 300-350 nm with an emission maximum at 470 nm. The excitation spectra (Figure 10) of the 470 nm emission have maxima at about 310 nm: hence the choice of 310 nm as the excitation wavelength for the solutions in Figure 9. Since the primary photoproduct from photolysis of DPC is expected to be phenyl salicylate (phenol is the other) its fluorescence spectra in dichloromethane is recorded in Figure 11. An excitation spectrum is also presented. Comparison of the results in Figure 11 with Figures 9 and 10 suggests that the emission maxima upon excitation at 310 nm for the photolyzed DPC solution at 470 nm corresponds to the maximum of the fluorescence of phenyl salicylate.

In order to extend these results a dichloromethane solution of polycarbonate was photolyzed for time periods of up to 3 minutes with the 300 nm lamps of the Rayonet Reactor. Emission (λ_{ex} =310 nm) and excitation spectra (λ_{em} =470 nm) in Figures 12 and 13 suggest that photolysis of PC in dichloromethane results in generation of the same species responsible for the fluorescence in the photolyzed DPC solutions. The emission with peak maximum at 470 nm and the corresponding excitation spectra are consistent with the fluorescence of phenyl salicylate in Figure 11. The emission spectra of a photolyzed thin polycarbonate film cast from a solution of dichloromethane is shown in

Figure 14. The peak maxima of the 470 nm emission of the photolyzed polycarbonate is almost identical to that recorded for the DPC and PC solution photolysis, indicating rapid formation of the photoproduct with emission maximum at 470 nm. The excitation spectra of the photolyzed polycarbonate films (monitored at 470 nm) in Figure 15 are essentially identical to that of phenyl salicylate in Figure 11, again suggesting that the fluorescence with peak maximum at 470 nm results, at least in large part, to a phenyl salicylate type product in the photolyzed polycarbonate film. The results in Figures 9-15 are consistent, as already stated, with the formation of phenyl salicylate in the case of DPC, or a phenyl salicylate type rearrangement product in the case of polycarbonate solutions or films. It might be argued that UV spectroscopy offers a means of evaluation of photo-Fries type rearrangement products, i.e., phenyl salicylates. However, the broad structureless absorption bands require longer photolysis times to generate any perceptible structural features, and then the resolution is somewhat lacking. Our results indicate that fluorescence spectroscopy is a useful method for early detection and identification, at least within the limits of the technique, of photoproduct formation. Finally, we also note that the fluorescence spectra of Figures 9, 12, and 14 all begin to exhibit the broad-band emission with peak maximum at 470 nm at very short photolysis times: certainly at much shorter photolysis times than significant structural changes are observed in the IR spectra of Figure 8 and the UV spectra of models or polycarbonate in solution or films.

CONCLUSIONS

In this paper, we have shown that the polymer backbone can have a profound effect on the photochemical rearrangement processes of a diaryl carbonate moiety. When the reactive group is incorporated into the polymer backbone, there is a marked decrease of photo-Fries product formation. As in earlier reports, we find that photoinduced rearrangements of small molecules doped into polymer films proceed with the same efficiency in either glassy or rubbery (above T_g) matrices. In addition to the product studies, we have shown that fluorescence spectroscopy can be a very effective tool for detection of photo-Fries (aryl salicylate) product formation in the early states of polycarbonate degradation and as such is an extremely sensitive measure of product formation. The results obtained when polycarbonate films are subjected to extensive long time photolysis will be the subject of a future investigation. For the present, we have clearly demonstrated the technique as an effective tool for detecting chemical changes in polycarbonate film after very short exposure times.

ACKNOWLEDGEMENT

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REFERENCES

1. Humphrey, J.S., Jr., Shultz, A.R. and Jaquiss, D.B.G., *Macromolecules*, 6 (1973) pp. 305-14.
2. Gupta, A., Liang, R., Moacanin, J. and Goldbeck, R., *Macromolecules*, 13 (1980) pp 262-7.
3. Moore, J.E., *ACS Symp. Ser.*, 151 (1981) pp. 97-107.
4. Pryde, C.A., *Polymer Stabilization and Degradation*, (Klemchuk, P.P., ed.) American Chemical Society Symposium Series No. 280 (1985) pp. 329-351.
5. Gupta, M.C. and Tahilyani, G.V. *Colloid Polym. Sci*, 266 (1988) pp. 620-3.
6. Gupta, M.C. and Pandey, R.R., *Makromol. Chem., Macromol. Symp.*, 27, (1989) pp. 245-54.
7. Webb, J.D. and Czanderna, A.W., *Macromolecules*, 19 (1986) pp. 2810-25.
8. Gupta, A., Rembaum, A. and Moacanin, J., *Macromolecules*, 11 (1978) pp. 1285-8.
9. Factor, A. and Chu, M.L., *Polym. Degradation Stab.*, 2 (1980) pp. 203-23.
10. Factor, A., Ligon, W.V. and May, R.J., *Macromolecules*, 20 (1987) pp. 2461-8.
11. Bellus, D., Hrdlovic, P. and Manasek, Z., *Polymer Letters*, 4 (1966) pp. 1-5.
12. Factor, A., Lynch, J.C. and Greenberg, F.H., *J. Polym. Sci.: Part A: Polymer Chemistry*, 25 (1987) pp. 3413-22.
13. Mullen, P.A. and Searle, N.Z., *J. Appl. Polym. Sci.*, 14 (1970) pp. 765-76.
14. Abbas, K.B., *J. Appl. Polym. Sci: Appl. Polym. Symp.*, 35 (1979) pp. 345-60.
15. Rivaton, A., Sallet, D. and Lemaire, J., *Polym. Photochem.*, 3 (1983) pp. 463-81.

16. Clark, D.T. and Munro, H.S., *Polym. Degrad. Stab.*, 4 (1982) pp. 441-57.

17. Rivaton, A., Sallet, D. and Lemaire, J., *Polym. Degrad. Stab.*, 14 (1986) pp. 1-22.

18. Rivaton, A. Sallet, D. and Lemaire, J., *Polym Degrad. Stab.*, 14 (1986) pp. 23-40.

19. Lemaire, J., Gardette, J.L., Rivaton, A. and Roger, A., *Polym. Degrad. Stab.*, 15 (1986) pp. 1-13.

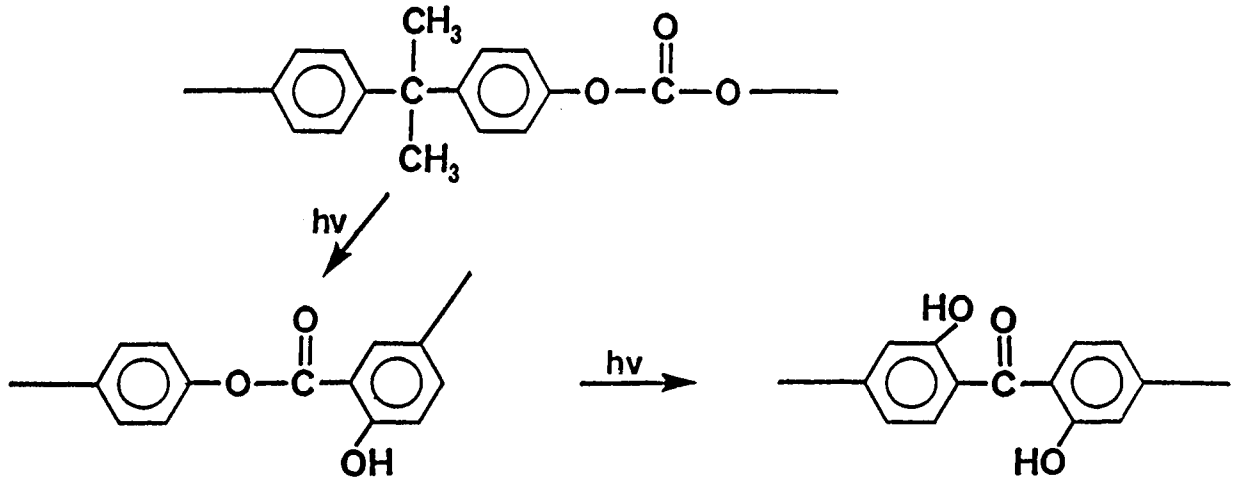
20. Hoyle, C.E., Chawla, C.P. and Kim, K.J., *Journal of Polymer Science: Part A: Polymer Chemistry*, 26, (1988) pp. 1295-1306.

21. Li, S.K.L. and Guillet, J.E., *Macromolecules*, 10 (1977) pp. 840-44.

22. Moore, J.W., Ph.D. Dissertation, University of Toronto, (1987).

SCHEME I

PHOTO-FRIES REARRANGEMENT



PHENYL SALICYLATE TYPE

2,2'-DIHYDROXYBENZOPHENONE TYPE

FIGURE CAPTIONS

Figure 1. UV of DPC (0.00088 M) in DCM photolyzed with 302 nm tabletop lamp.

Figure 2. UV of PC (0.0004 M) in DCM photolyzed with 302 nm tabletop lamp.

Figure 3. (a) A_{311} and (b) A_{345} for: (o) DPC in DCM and (□) PC in DCM.

Figure 4. UV of DPC in PHMA as a function of photolysis time with 302 nm tabletop lamp.

Figure 5. UV of DPC in PMMA as a function of photolysis time with 302 nm tabletop lamp.

Figure 6. UV of PC film as a function of photolysis time with 302 nm tabletop lamp.

Figure 7. (a) A_{311} and (b) A_{345} for: (○) DPC in PHMA, (□) DPC in PMMA, (Δ) PC film.

Figure 8. IR spectra of PC film photolyzed for 0,1, and 6, hours with 300 nm Rayonet Reactor Lamps.

Figure 9. Emission spectra (λ_{ex}=310 nm) of DPC (0.0045 M) in DCM for 0, 1, and 3 min. photolysis in Rayonet Reactor with 300 nm lamps.

Figure 10. Excitation spectra (λ_{em}=470 nm) of DPC (0.0045 M) in DCM for 0, 1, and 3 min. photolysis in Rayonet Reactor with 300 nm lamps.

Figure 11. Emission spectrum (λ_{ex}=310 nm) and excitation spectrum (λ_{em}=470 nm) of phenyl salicylate in DCM.

Figure 12. Emission spectra (λ_{ex} = 310 nm) of PC (0.00065 M) in DCM after photolysis for 0, 1, and 3 min. in Rayonet Reactor with 300 nm lamps.

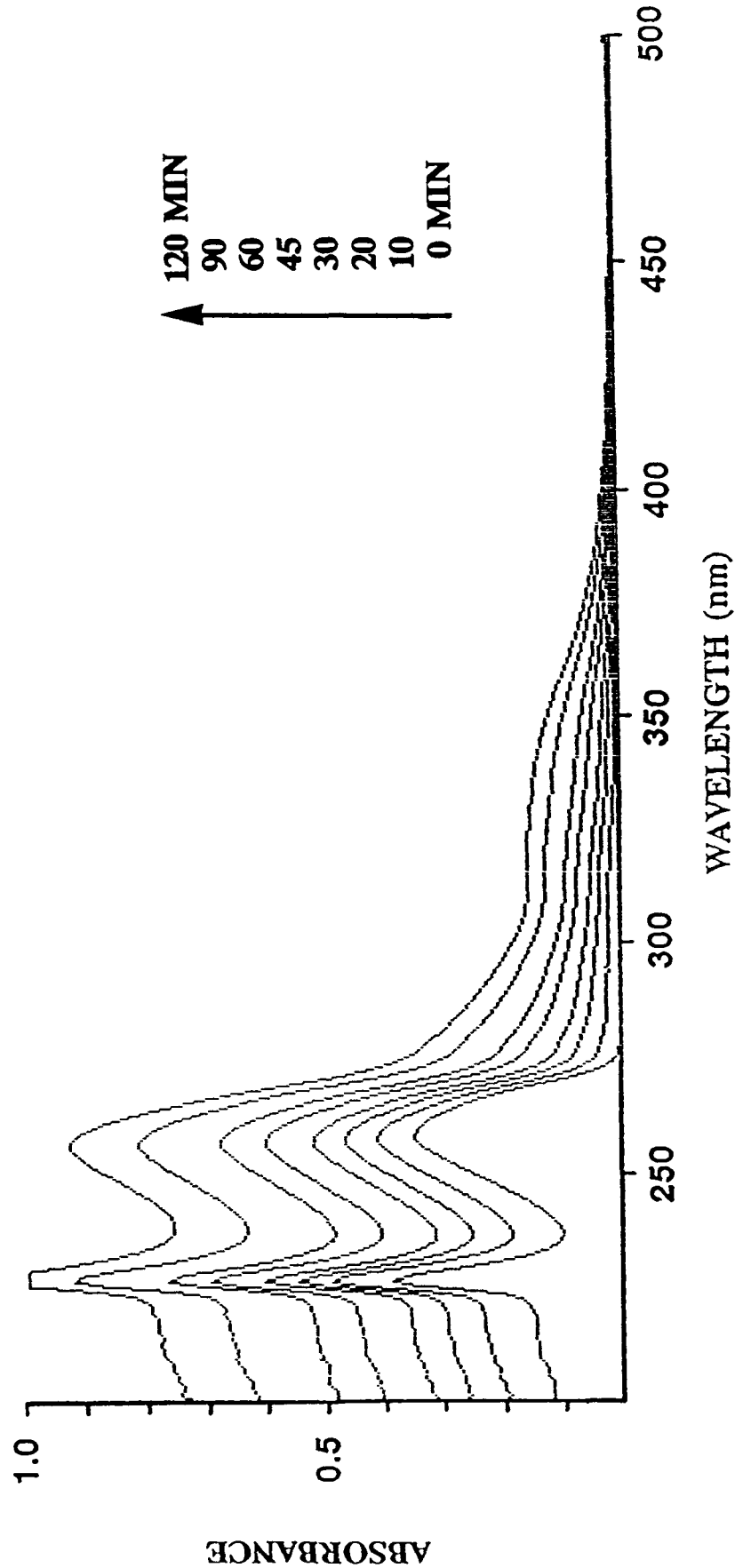
Figure 13. Excitation spectra (λ_{em} = 470 nm) of PC (0.00065 M) in DCM film after photolysis for 0, 1, and 3 min. in Rayonet Reactor with 300 nm lamps.

Figure 13. Excitation spectra (λ_{em} = 470 nm) of PC (0.00065 M) in DCM after photolysis for 0, 1, and 3 min. in Rayonet Reactor with 300 nm lamps.

Figure 14. Emission spectra (λ_{ex} = 310 nm) of PC film after photolysis for 0, 15, 30, and 60 min. in Rayonet Reactor with 300 nm lamps.

Figure 15. Excitation spectra (λ_{em} =470 nm) of PC film photolyzed in Rayonet Reactor with 300 nm lamps for 0, 15, 30, and 60 min. Scatter peak around 310 nm was artificially removed.

Fig. 1


120 MIN
90
60
45
30
20
10
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ABSORBANCE
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0.5
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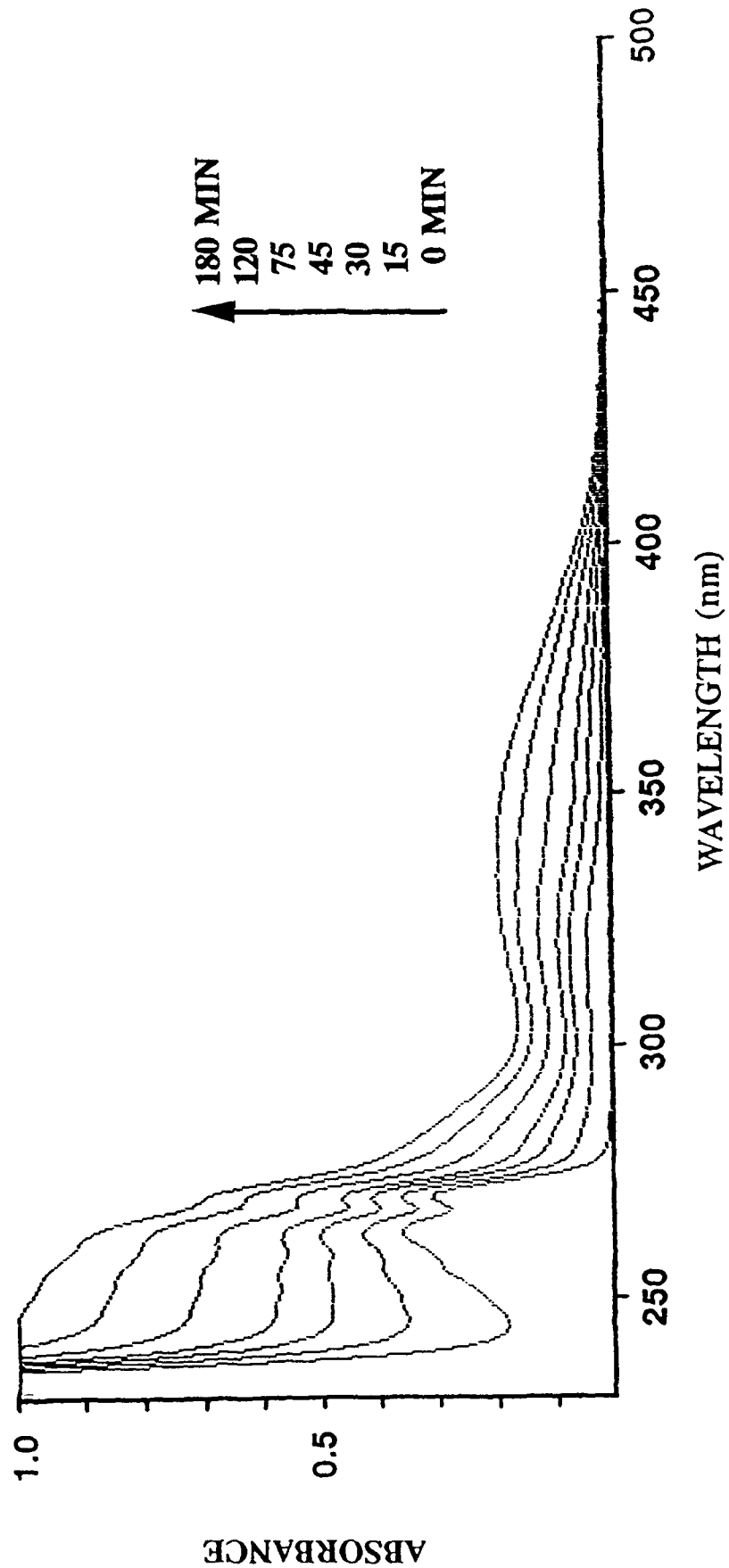
300
350
400
450
500
WAVELENGTH (nm)

Fig-2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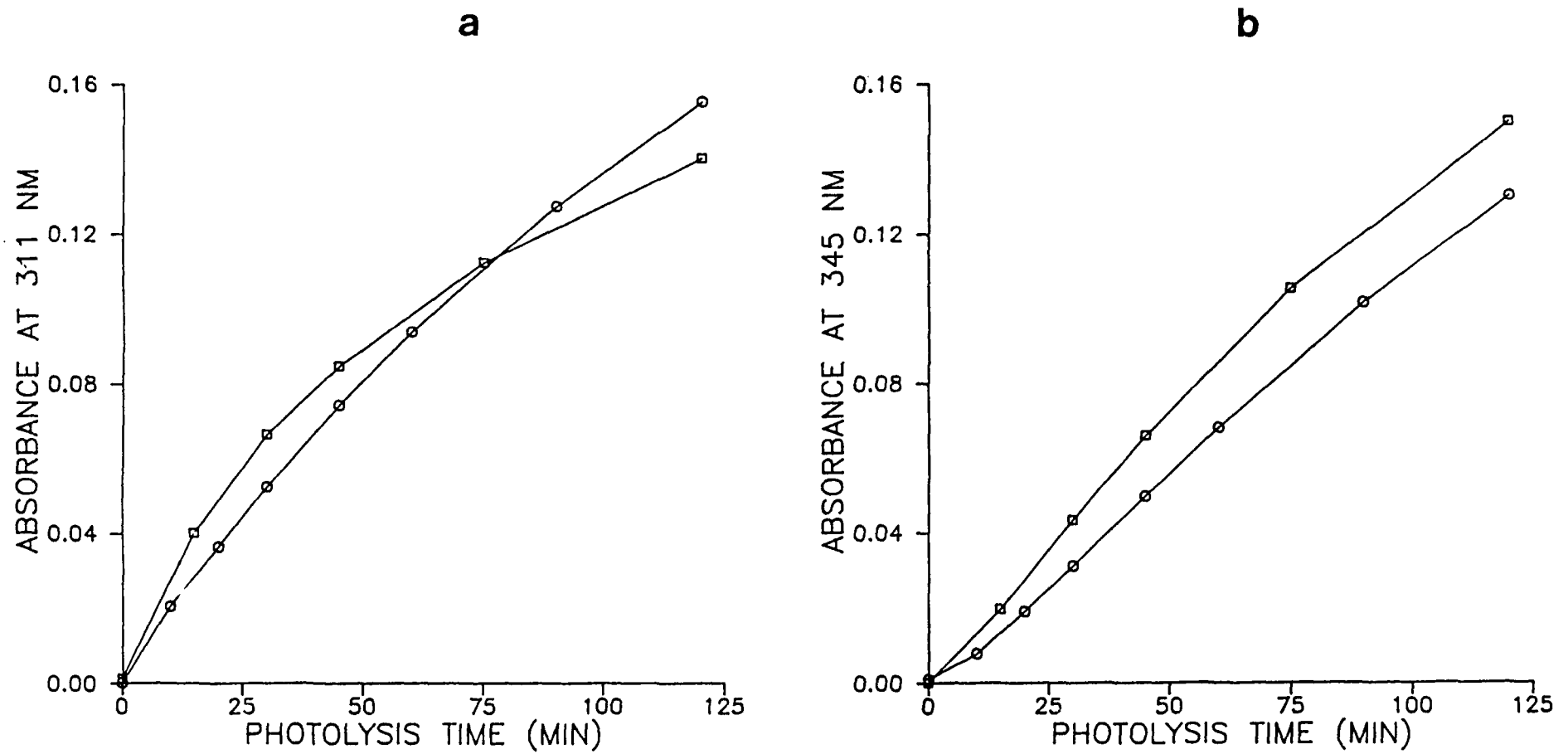
ABSORBANCE


a
b
ABSORBANCE AT 311 NM
ABSORBANCE AT 345 NM
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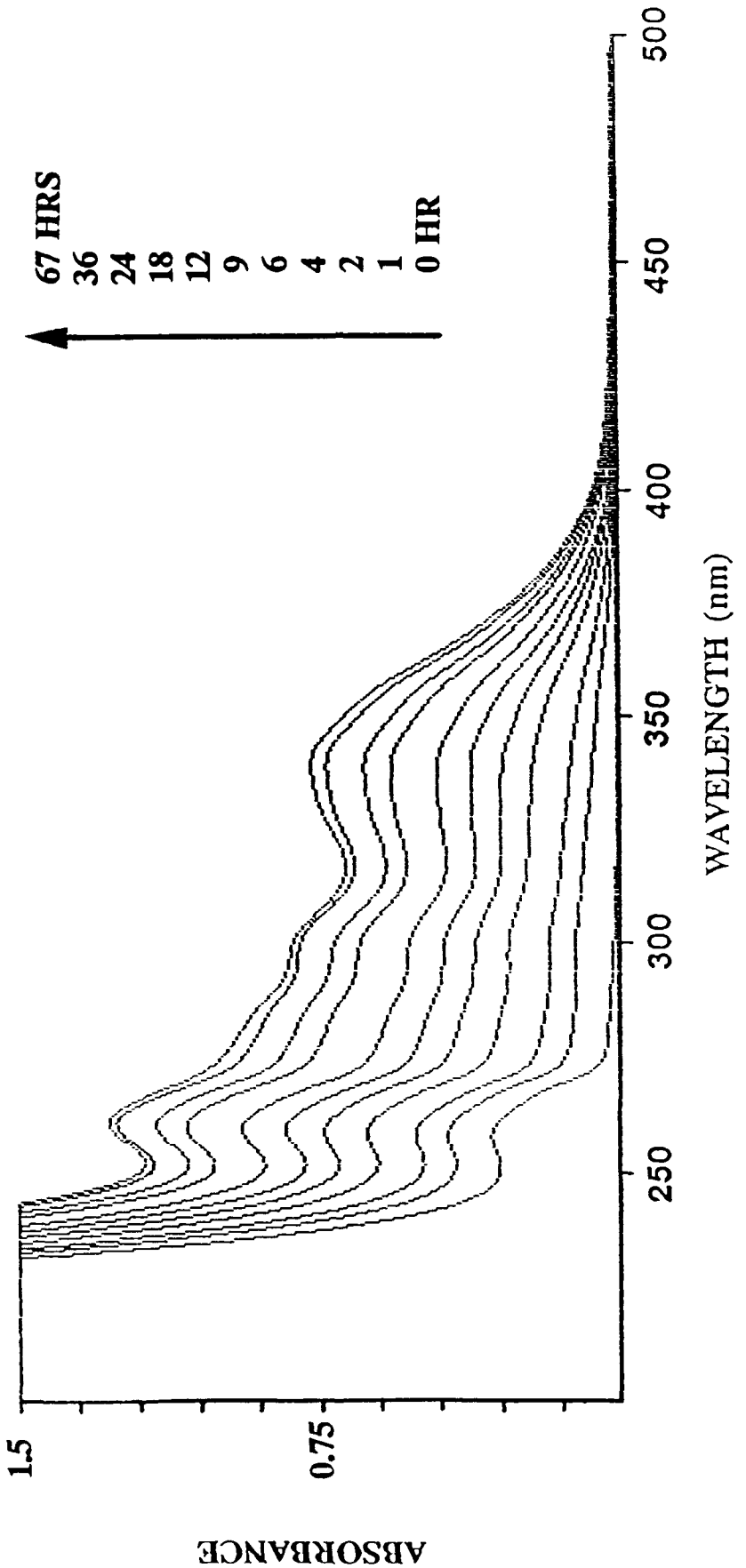
75
100
125
PHOTOLYSIS TIME (MIN)

Fig. 3

Fig. 4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24
18
12
9
6
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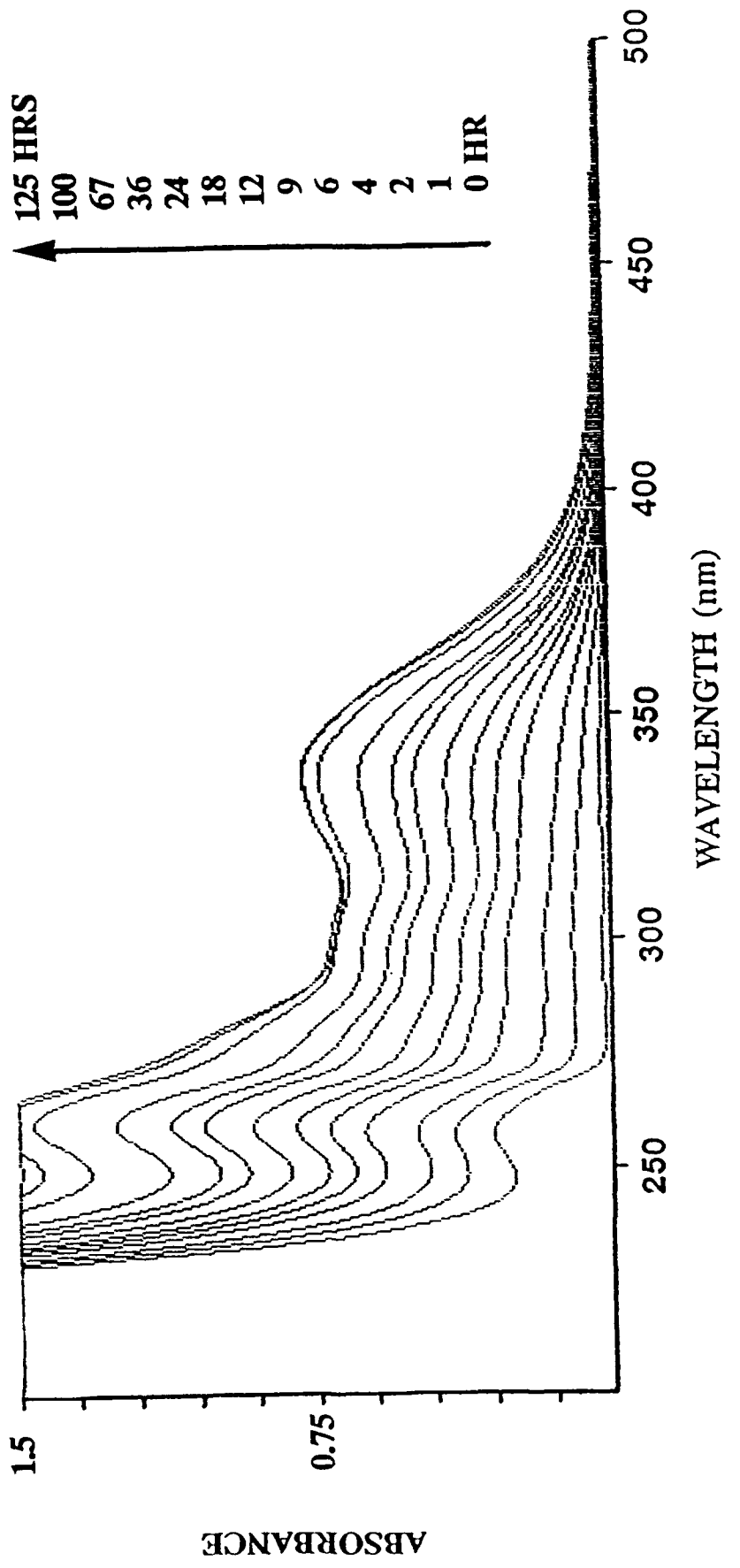
350
400
450
500
WAVELENGTH (nm)

Fig. 5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WAVELENGTH (nm)
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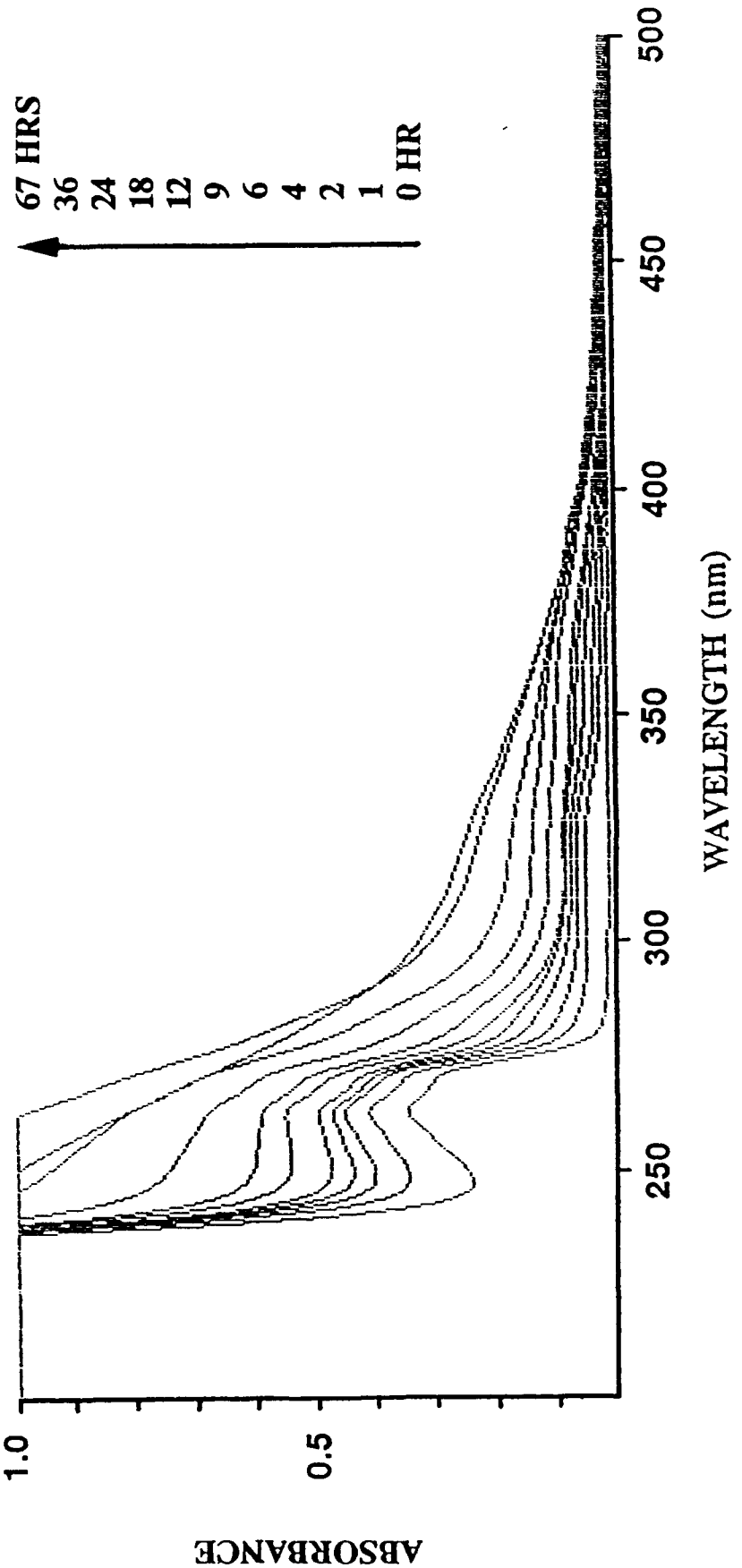
0.75
ABSORBANCE

Fig. 6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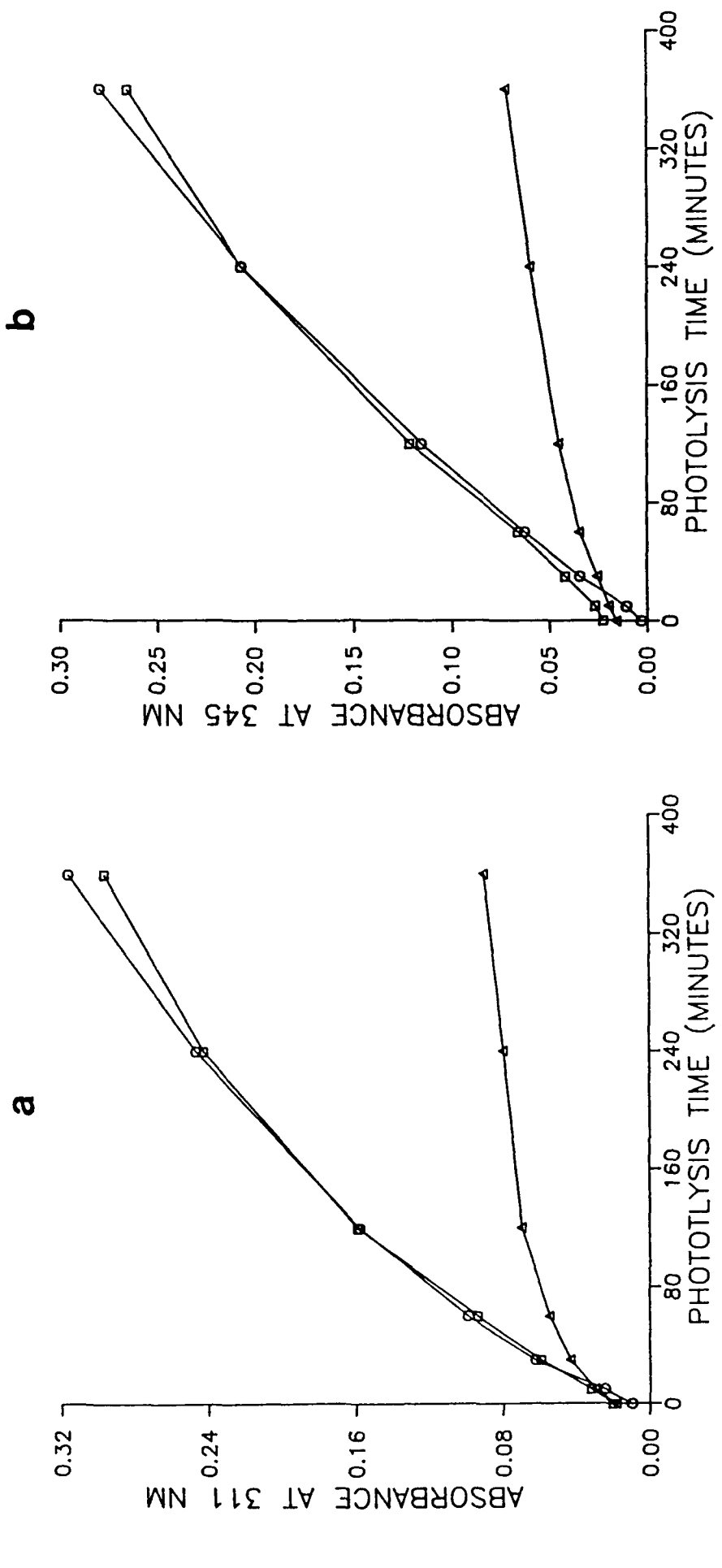
WAVELENGTH (nm)

Fig. 7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ABSORBANCE AT 311 NM
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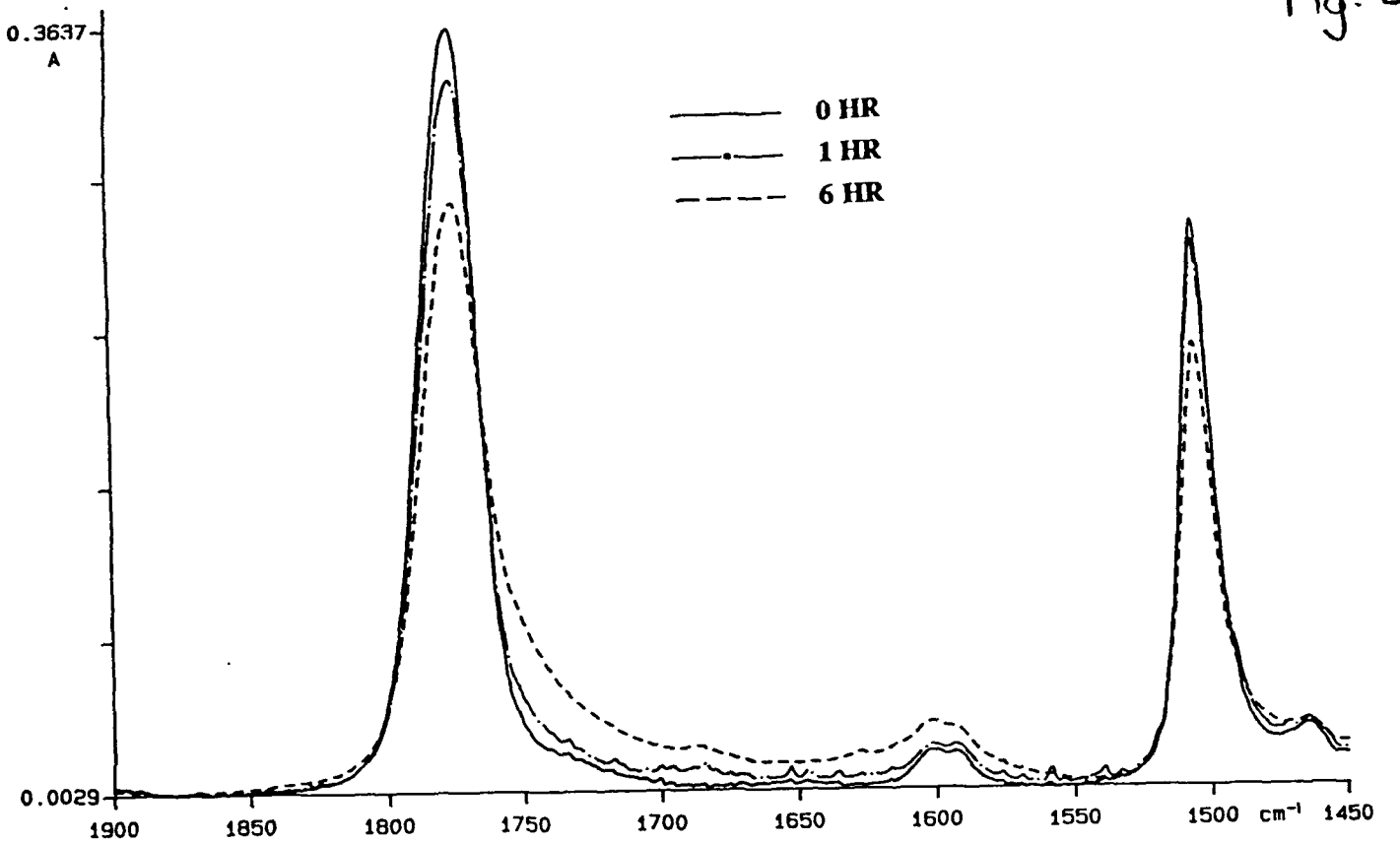
0.08
0.16
0.24
0.32
0
80
160
240
320
400
PHOTOLYSIS TIME (MINUTES)
b
ABSORBANCE AT 345 NM
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0
80
160
240
320
400
PHOTOLYSIS TIME (MINUTES)

Fig. 8

a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1600
1550
1500
cm⁻¹
1450

b

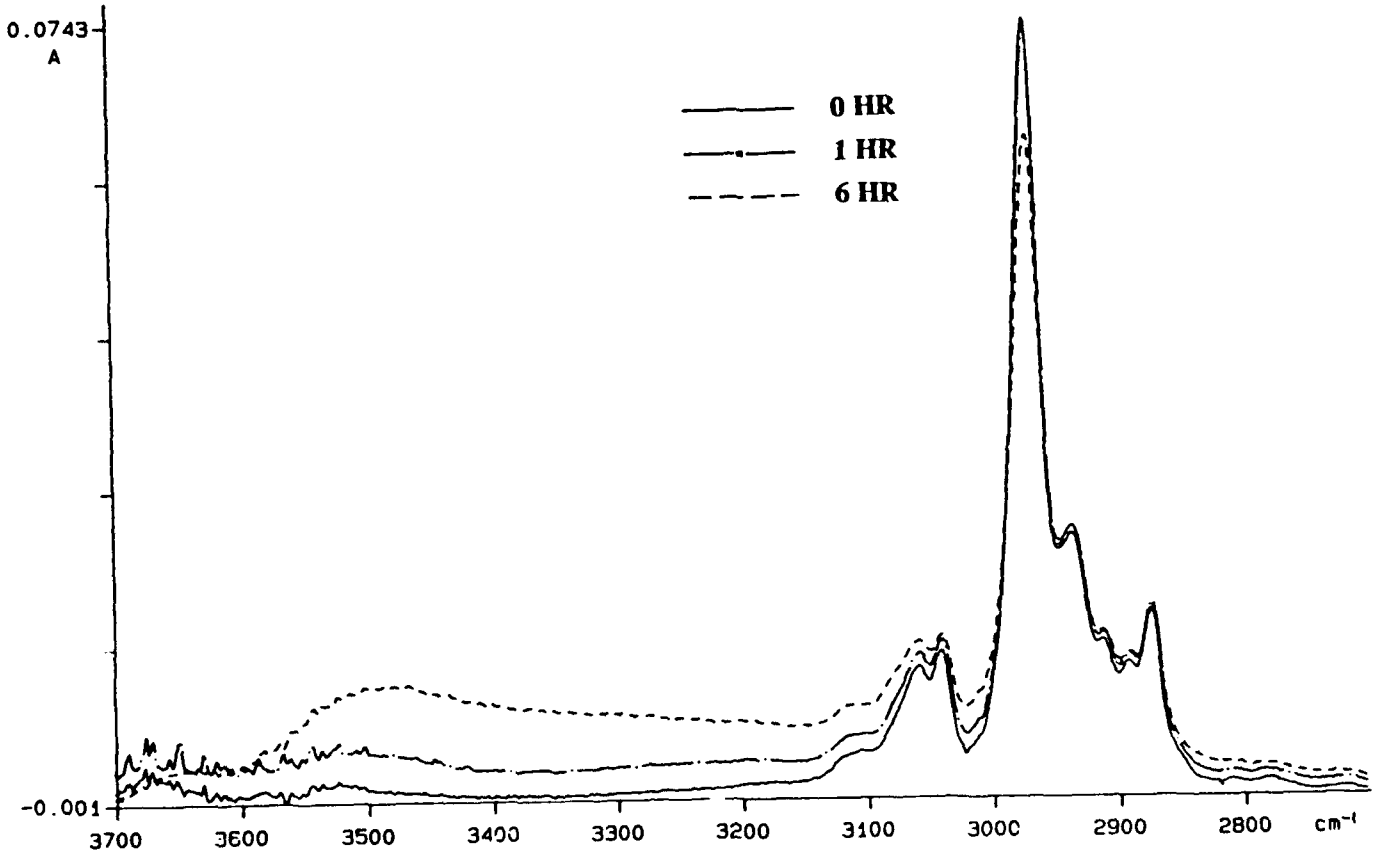

0.0743
A
0 HR
1 HR
6 HR
-0.001
3700
3600
3500
3400
3300
3200
3100
3000
2900
2800
cm⁻¹

Fig. 5

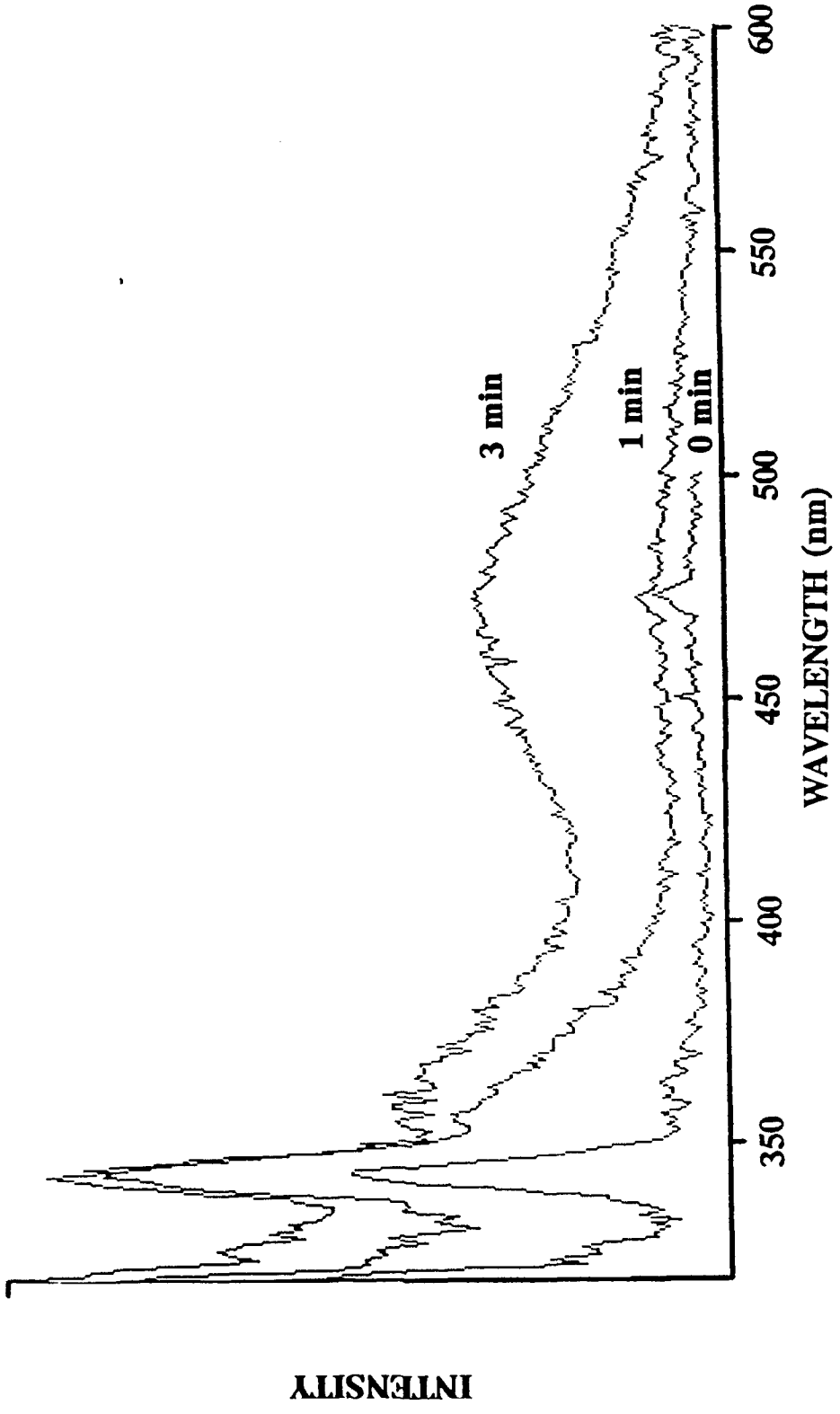

3 min
1 min
0 min
350
400
450
500
550
600
WAVELENGTH (nm)
INTENSITY

Fig. 10

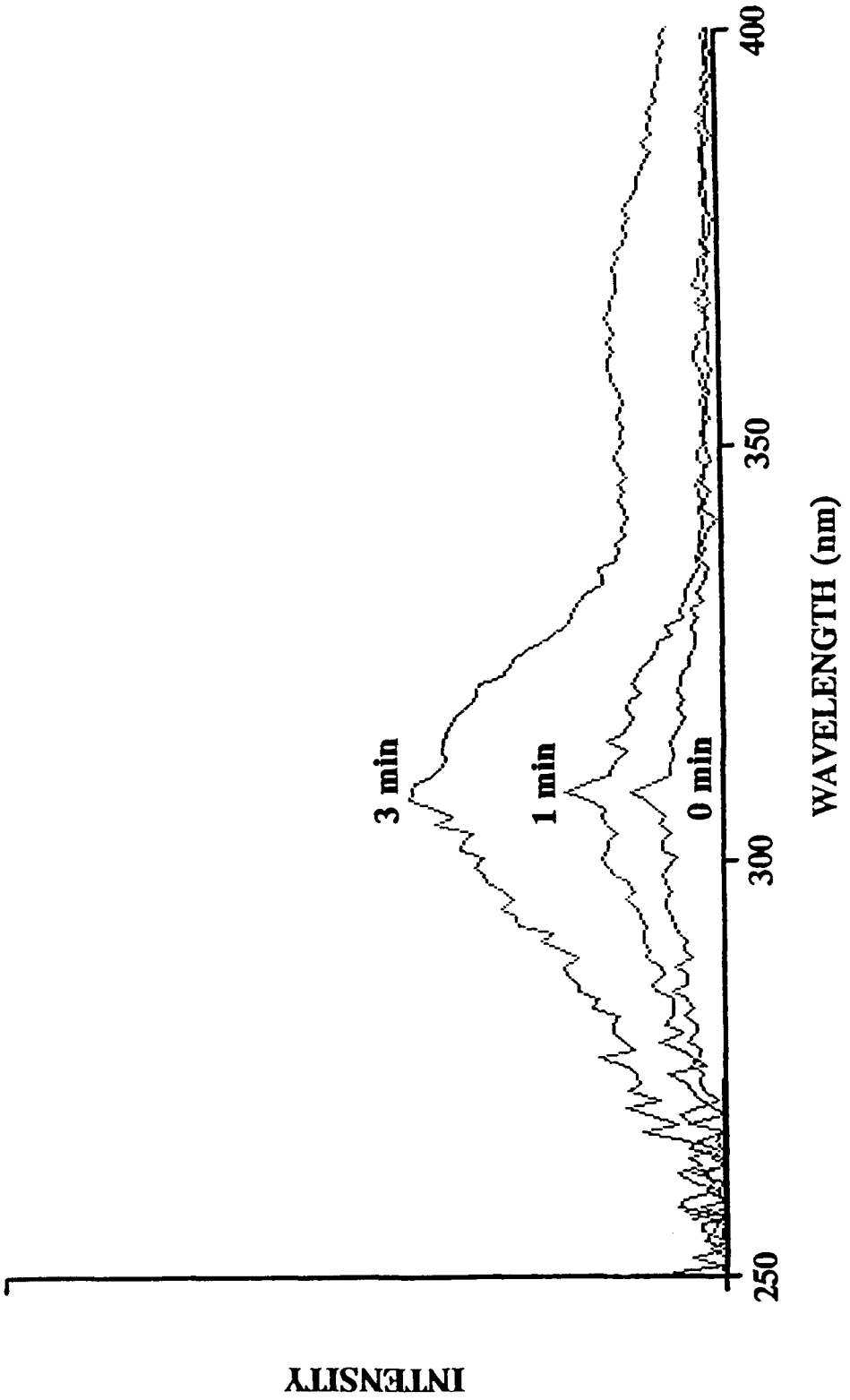


Fig. 11

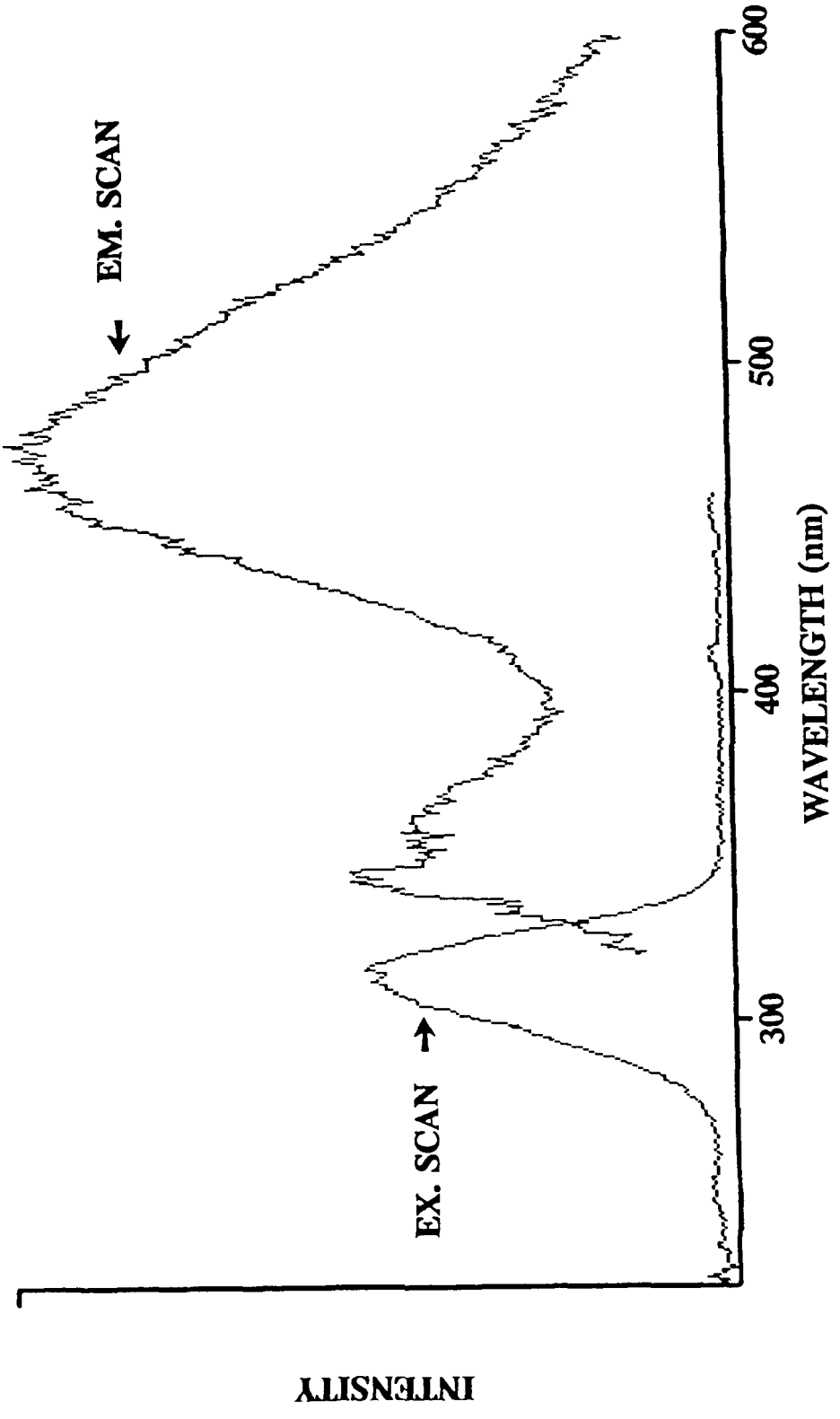


Fig. 12

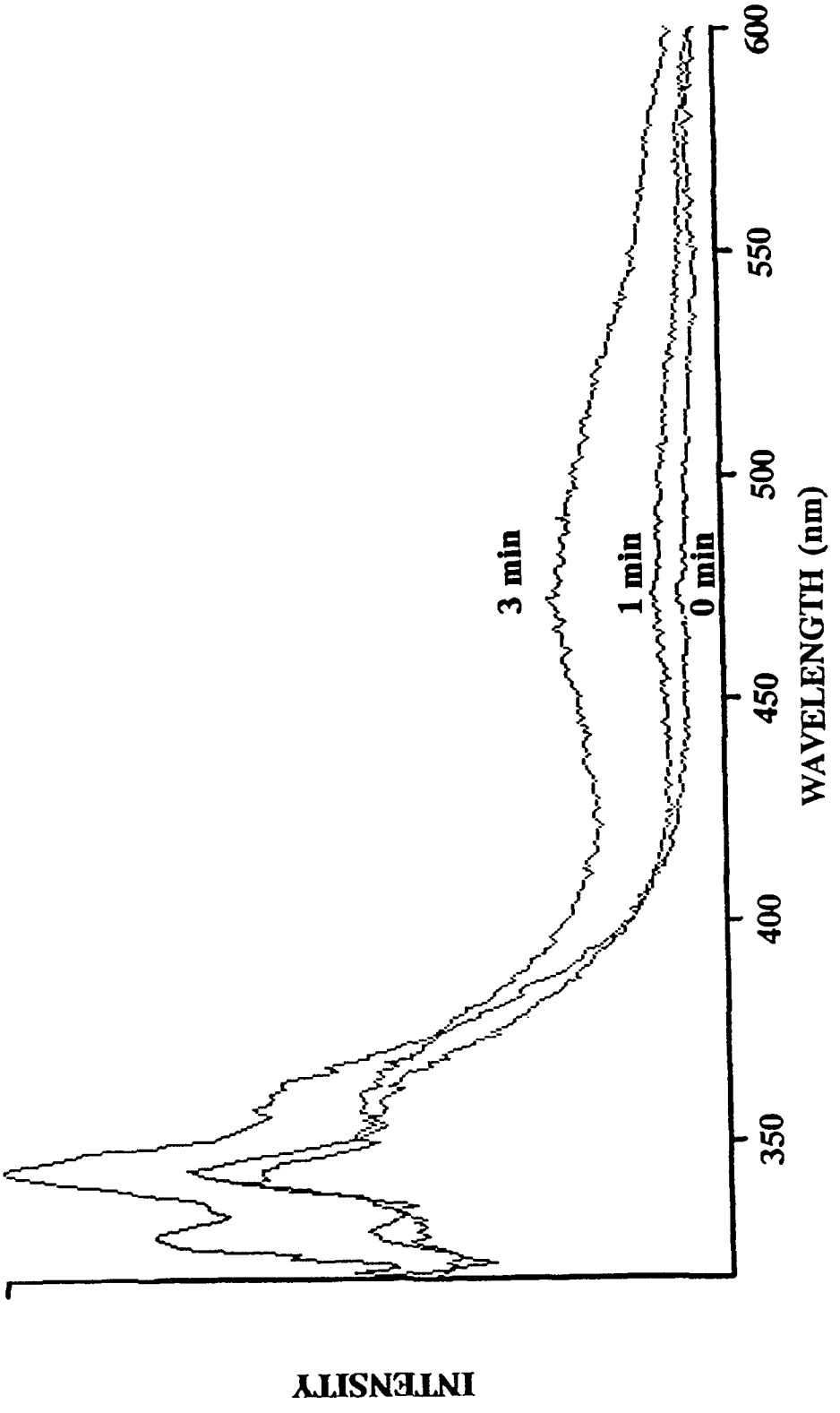

3 min
1 min
0 min
350
400
450
500
550
600
WAVELENGTH (nm)
INTENSITY

Fig. 15

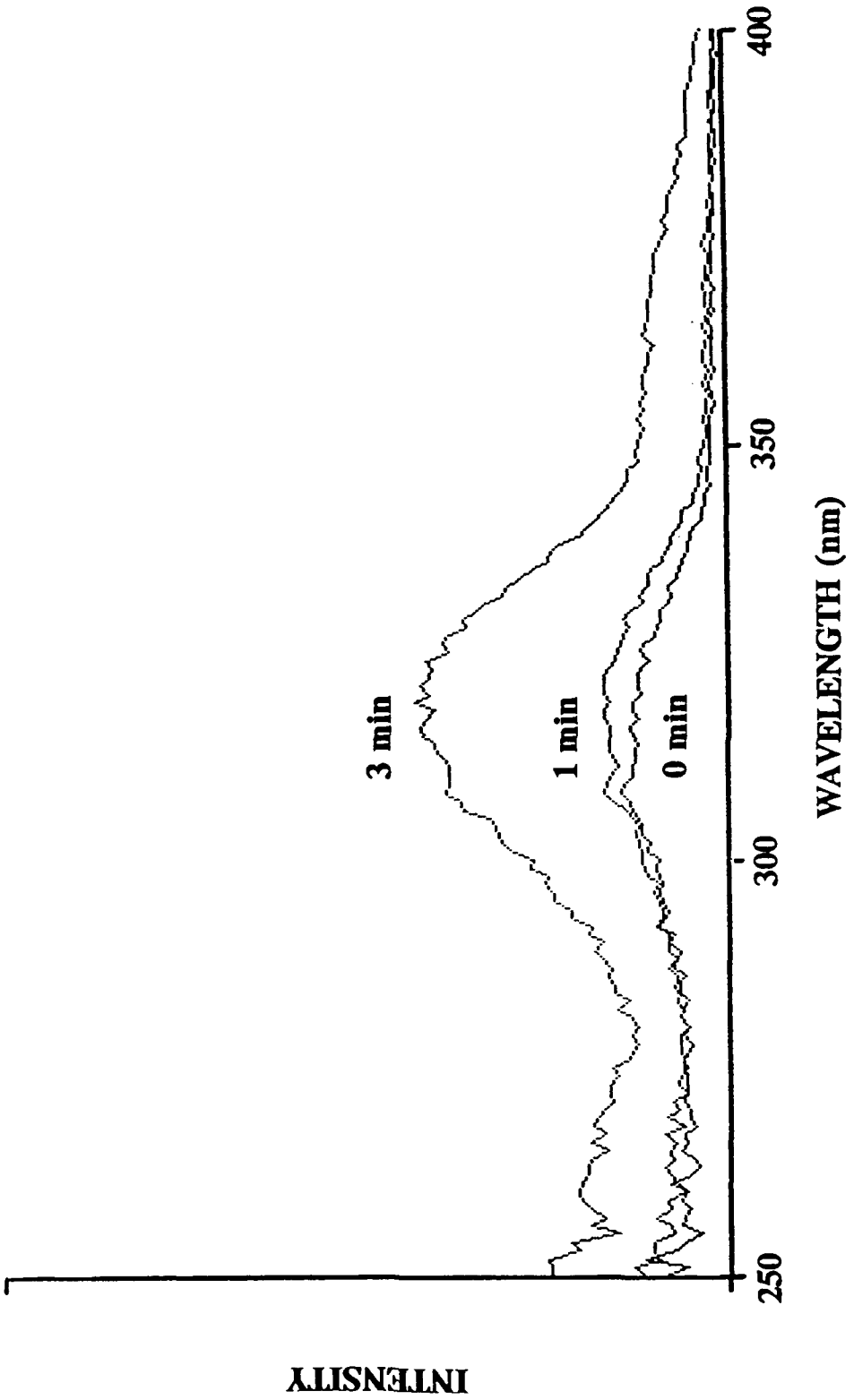


Fig. 4

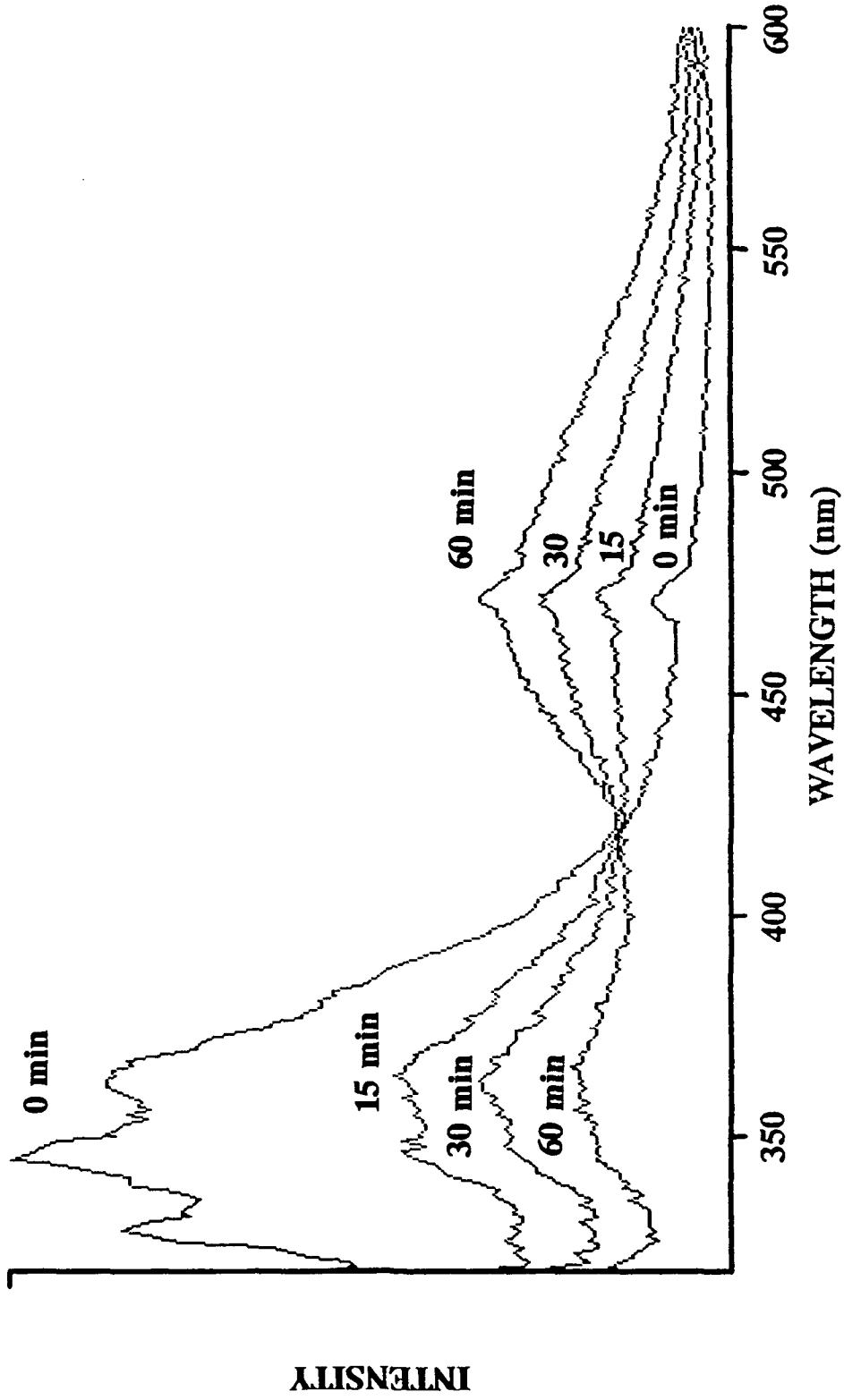
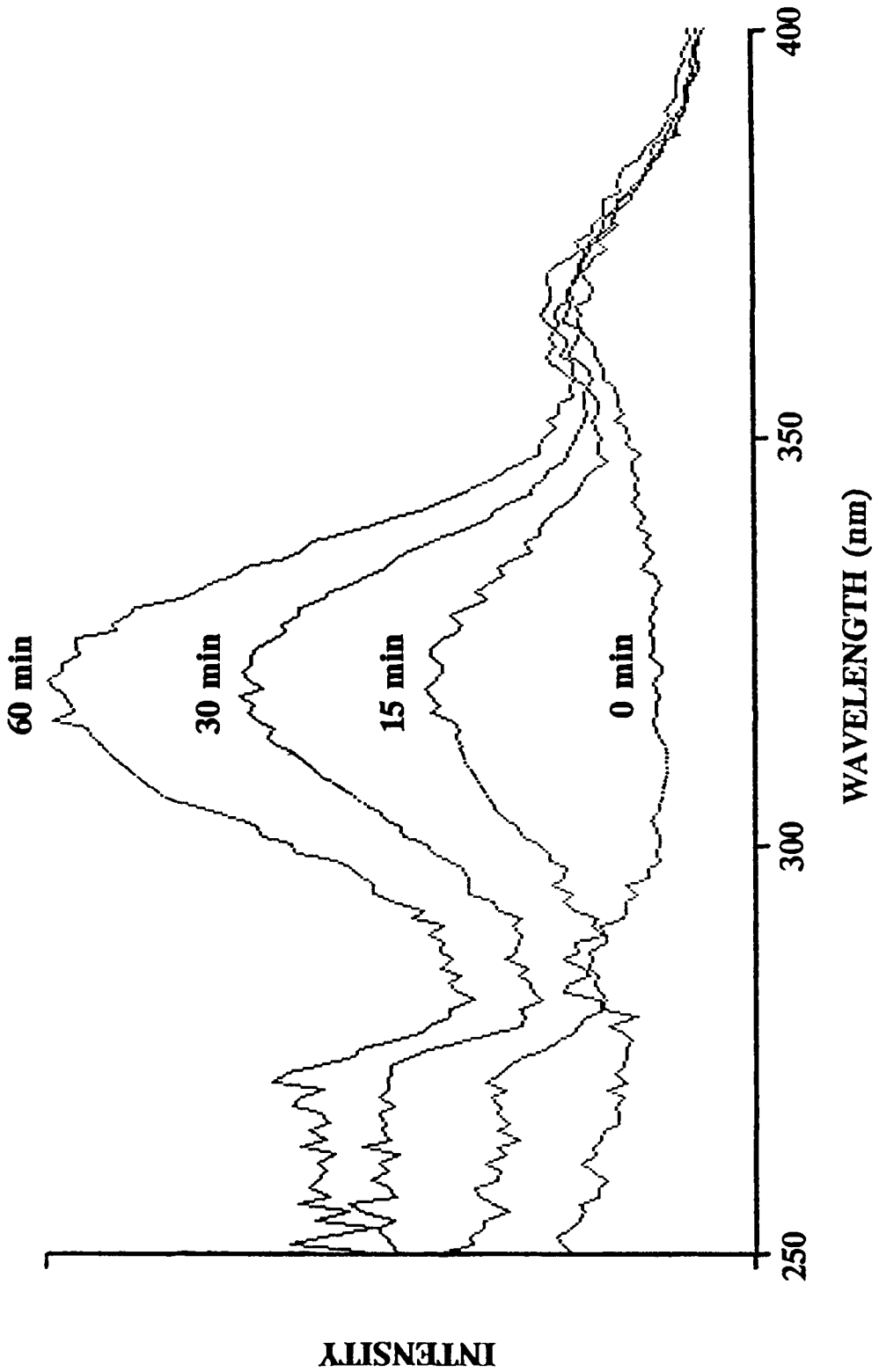

0 min
15 min
30 min
60 min
60 min
30
15
0 min
350
400
450
500
550
600
WAVELENGTH (nm)
INTENSITY

Fig. 15


60 min
30 min
15 min
0 min
250
300
350
400
WAVELENGTH (nm)
INTENSITY