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Photodegradation of Polyimides. IV. Mechanism for the
Photooxidation Process Based on a Model Compound

by

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PHOTODEGRADATION OF POLYIMIDES. IV.
MECHANISM FOR THE PHOTOOXIDATION PROCESS
BASED ON A MODEL COMPOUND

by

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ABSTRACT

Based on analysis of the photochemistry of a model compound, N-phenylphthalimide, the photolysis of a polyimide derived from 4,4'-oxydianiline (ODA) and a diarylanhydride with a hexafluorinated isopropylidene bridging group (6F) is proposed to proceed via formation of a phthalic anhydride type photoproduct. The quantum yield for product formation of N-phenylphthalimide is quite low ($<10^{-3}$) indicating a rather inefficient first step in the overall oxidative degradation process. However, based on the efficiency of the photooxidation of the primary photoproducts, a process leading to the ultimate failure and complete ablation of the 6F-ODA films in air upon exposure to the unfiltered output of a mercury lamp is postulated.

INTRODUCTION

In previous papers in this series (1-4), we reported the effects of chemical structure, atmosphere and radiation source, and the processing conditions on the decomposition of polyimides derived from aromatic dianhydride and aromatic diamines. The primary results of our previous work demonstrate the marked effect of the hinge group in the general polyimide structure below on the photo-induced decomposition

I
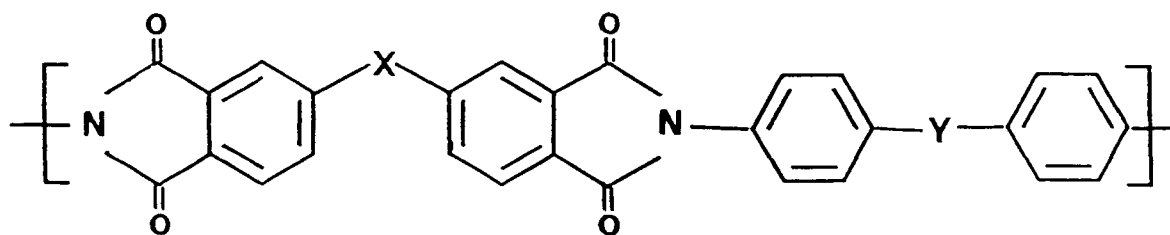
process in the presence of oxygen. Basically, when the prototypical dianhydride, pyromellitic dianhydride (PMDA), is replaced by dianhydrides in which the conjugation between two phenyl rings is limited by flexible bridging groups (x in polyimide structure I) such as a carbonyl, oxygen, or a hexafluoroisopropylidene (6F) moiety, the decomposition of the resultant polyimide film is accelerated. When the bridging groups between the two aniline rings in the diamine based part of the polyimide is changed from oxygen (oxydianiline-ODA) to a methylene group (methylenedianiline-MDA) there is a very modest, but detectable, difference in the resulting photostability in the presence of oxygen when photolysis is conducted via an unfiltered medium pressure mercury lamp.

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Probably the most striking feature of the photoinduced decomposition is exhibited by the 6F-ODA ($x = C(CF_3)_2$; $y = 0$) films in an air atmosphere. After 20 hours of irradiation with an unfiltered medium pressure mercury lamp, the films of 6F-ODA prepared directly from the polyamic acid are largely ablated in a clean process which maintains a smooth (defect free) surface while exhibiting a linear and uniform loss in IR band intensity, UV absorbance, and mass with exposure time. Additionally, while efficient chain cleavage could be induced by photolysis of 6F-ODA films with pyrex filtered (>300 nm) light from the medium pressure mercury lamp, it is necessary to use the output in the deep UV (<300nm) to observe the photooxidation process and clean, linear (with time) ablation of the polymer films. If photolysis is conducted in the absence of oxygen, even exhaustive exposure results in little chain cleavage and no photooxidative ablation. In this paper we present our initial results on the basic chemistry of the photooxidative degradation of polyimides, with emphasis on the photolabile imide moiety and the role of charge-transfer states. Use of model compounds is employed to provide a basis for interpreting the polymer results.

EXPERIMENTAL

Pyromellitic dianhydride (PMDA, Aldrich) was recrystallized from methyl ethyl ketone and vacuum sublimed prior to use. Electronic grade hexafluoroisopropylidene-2,2'-bis(phthalic anhydride) (6FDA, Hoechst Celanese) was vacuum sublimed prior to use.

Dimethylacetamide (DMAc, Aldrich) used as the solvent in the polymerization and the viscometric analyses was dried over molecular sieves and fractionally distilled under vacuum from calcium hydride. Anhydrous DMAc (Aldrich) was used in the model compound syntheses. All other solvents were used as received. The solvents used in spectroscopic characterization and photolysis experiments were spectroscopic grade.

Synthesis. The phthalimide model compounds were synthesized by dissolving the anhydride and a slight molar excess of amine in DMAc at room temperature. After stirring for thirty minutes, three moles each of pyridine (catalyst) and acetic anhydride (dehydrating agent) were introduced into the system for each mole of amic acid to be cyclized. The reaction temperature was raised to 100 $^\circ$C and maintained at that temperature for approximately four hours. Subsequently purification of the desired product involved recrystallization from either DMF or ethanol.

The preparation of the polyimide thin films has been described in the third paper (4) in this series.

Characterization. Elemental analyses were conducted by Galbraith Laboratories of Knoxville, Tennessee. Infrared absorption spectra were obtained using a Perkin-Elmer 1600 Fourier transform infrared (FT-IR) spectrophotometer with 16 spectral scans averaged at 4 cm^{-1} resolution. A Perkin-Elmer Lambda 6 UV-VIS spectrophotometer with 1 nm resolution was used to record the UV absorption. The fluorescence spectra were obtained from a SPEX Fluorolog-2 Spectrofluorometer using 1.5 mm slit widths for the excitation and emission monochromators. The fluorescence from the films were measured in the front face geometry. Fluorescence spectra were divided by the emission

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from a standardized rhodamine B solution to account for fluctuations in lamp intensity with time. All spectra were corrected. Correction files in the Spex software were used to compensate for wavelength-dependent factors (e.g. detector response, monochromator transmission, etc.).

Model compounds were analyzed on a Hewlett-Packard HP 5890A gas chromatograph (GC) equipped with a Hewlett-Packard HP-1 capillary column (crosslinked methyl silicone gum, L = 25 m, ID = 0.32 mm) and a flame ionization detector (FID).

GC/MS analyses were conducted at the Mississippi State Chemical Laboratory at Mississippi State University.

Model Compound Preparative Photolysis. The photolyses were carried out in a 500 mL photochemical reaction vessel equipped with a quartz immersion well from Ace Glass. The cold water circulating through the immersion well kept the reaction mixture at approximately room temperature. The UV source was a 450 W medium pressure immersion lamp. A Vycor 7913 filter sleeve was used to prevent excessive irradiation of the acetonitrile solvent. The concentration of the starting solutions were adjusted to possess an optical density of ~1.8 at 300 nm in acetonitrile (Fisher Optima). 500 mL of these solutions were charged to the reaction vessel. All solutions were continuously stirred during exposure to UV. The reaction vessel was vented to the atmosphere for the photolyses carried out in air to allow replenishment of any oxygen consumed. The reaction mixtures photolyzed in the absence of oxygen were bubbled with nitrogen for two hours before irradiation was started. Continuous nitrogen purge was carried out throughout the photolysis. Aliquots were taken from the reaction vessel and analyzed on

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the GC. Approximately 500 mL of certain photolyzed solutions were concentrated down to 5-15 mL. The reduced solutions were centrifuged to remove brown solids suspended in the photolyzed solutions. These particles were present in all the solutions photolyzed in air. The solutions were analyzed using GC and GC/MS.

Model Compound Quantum Yield. The output from a 450 W Canrad Hanovia (Ace Glass) medium pressure mercury lamp was passed through the desired bandpass filter (Pomfret Research Optics) to irradiate samples placed 12 cm from the source. The samples were contained within a 1 cm pathlength quartz cell equipped with a septum (Wilmad Glass).

The disappearance of the starting material and appearance of photoproducts was monitored quantitatively on a GC. The flame ionization detector response for a known amount of a particular compound was determined.

Light intensity were determined from potassium ferrioxalate actinometry. The average of the light intensity before and after photolysis was used in the quantum yield calculations. Murov's modification involving in-situ formation of the potassium ferrioxalate was used in order to avoid handling the light sensitive solid. All actinometry experiments were carried out under darkroom conditions with illumination provided by a red safelight. Blanks were run to insure the validity of the actinometer solution.

The light intensity measurements from the chemical actinometry correlated very well with readings from a International Light IL 700A Radiometer equipped with a SEE 400 detector. Adjustments for the relative responsivity of the detector at various wavelengths were made.

Polymer Solution Photolysis. The solution photolyses were carried out in a Rayonet RPR-100 photochemical reactor (Southern New England Ultraviolet) equipped with a full complement of sixteen 300 nm lamps. The solutions were placed in closed quartz test tubes and sparged with the desired gas before irradiation. A merry-go-round unit kept in the center of the test tube 4.5 cm from the front surface of the lamps and allowed uniform irradiation of the samples.

Polymer Film Photolysis. The film photolyses were conducted using the 450 W Canrad Hanovia medium pressure mercury lamp in air. The films were placed approximately 9 cm from the lamp. To analyze gaseous photoproducts, polymer films were placed in a photochemical cell (Ace Glass) equipped with a quartz window. The two-way stopcock on the cell was closed to seal in the air atmosphere and prevent the escape of volatile photoproducts. A medium pressure mercury lamp was placed in front of the quartz window to irradiate the film samples. After the film samples had disintegrated, the photolysis was ended. An IR gas cell (Wilmad Glass) with a pathlength of 10 cm and equipped with NaCl windows was used to analyze the gases in the photolysis cell. The IR gas cell was evacuated, sealed off by means of a stopcock, and connected to the photochemical cell by tubing. The stopcocks of each cell were opened to transfer gases from the photochemical cell to the IR gas cell. The gas IR cell was sealed and analysis was carried out. The background was taken as the gas IR cell contains atmospheric gases.

RESULTS AND DISCUSSION

A.   Photolysis of 6F-ODA Films in Air--FT-IR and GC/Mass Spectral Analysis

In order to provide a chemical description of the photoinduced decomposition of

polyimide films in air, we began by an analysis of the gaseous products evolved during

the photooxidation of the polyimide (designated 6F-ODA) made from 5,5'-[2,2,2-trifluoro-

1-1(trifluoromethyl)ethylidene] bis-1,3-isobenzofurandione (i.e. 6F) and oxydianiline (ODA).

In order to obtain FT-IR spectra of the photolyzed 6F-ODA, two thin film samples (max.

1 min. cure temp. = 300 °C) were placed behind the two quartz windows of a

photochemical cell (see Experimental). The FT-IR spectrum (Fig. 1) of the gases shows

the presence of water (1635 cm^{-1}, 3417 cm^{-1}), carbon dioxide (649 cm^{-1}, 669 cm^{-1}, 2341

cm^{-1}, 2360 cm^{-1}) and carbon monoxide (~2100 cm^{-1}) as photoproducts. An additional

peak observed at 1152 cm^{-1} may indicate trace amounts of a fluorocarbon (CF_3H)

photoproduct. A sample of the liquid on the inside of the photochemical cell after

photolysis was placed between two NaCl windows. FT-IR analysis identified the residue

as water by comparison with the FT-IR spectrum of deionized water. In order to

substantiate the results of the FT-IR analysis, a thin film of 6F-ODA (max. cure temp. =

300°C) was placed inside a quartz test tube and sealed with a rubber septum. The

septum was covered with aluminum foil to protect it from UV radiation. Irradiation with

the unfiltered output of a medium pressure Hg lamp was carried out for 30 hours. Several

peaks were detected in the GC and the mass spectral analysis of the fragmentation

pattern reveals the presence of CO (M^+ at m/e = 28), CO_2 (M^+ at m/e=44), and CF_3H(M^+

at m/e=70) in large quantities as well as a smaller but still significant amount of what appears to be benzoic acid (M⁺, m/e = 133). Similar exposure of PMDA-ODA films is expected to result in no observable gaseous products.

The FT-IR and mass spectral analysis of the photolyzed 6F-ODA films in air suggests an extensive degradation process leading to complete destruction of the film to yield small molecule photooxidation products. Our previous work (4) suggests that the process involves a sequence of events initiated by a chain-cleavage process requiring the presence of oxygen, followed by a photooxidative decomposition of the products resulting from the chain cleavage. In order to obtain complete, or at least apparently complete, ablative photooxidation of the 6F-ODA polymer, it is surely necessary to invoke the presence of a sequence of steps leading to the production of the observed CO_2, CO, and CF_3H small molecule products. Any complete reaction sequence proposed to account for the photooxidation must take into account all of these factors as well as the marked resistance to photooxidation of PMDA-ODA films.


B.   Spectral Analysis of 6F-ODA and PMDA-ODA Films

An analysis of the reaction mechanism begins with a consideration of the spectral absorption differences exhibited by thin-films (spin-cast on quartz) of 6F-ODA and PMDA-ODA shown in Figures 2 and 3. Considering first the results in Figure 2, a remarkable difference in the absorption bands between 6F-ODA and PMDA-ODA is observed. There is little doubt that this difference has its origins in the electron accepting affinity of the

PMDA moiety compared to the 6F moiety. The presence of the hexafluoroisopropylidene bridging group in the 6F dianhydride component of 6F-ODA could serve both to prevent the conjugation between the imide groups and to act as a bulky group in the polymer backbone: this is evidenced by the distinct long wavelength absorption exhibited by PMDA-ODA and not by 6F-ODA. The effect of the electron affinity of the PMDA moiety is best illustrated by the spectra in Figure 3 which vividly shows the magnitude of the red shift in the absorption spectrum of PMDA-ODA. The shift in the spectrum at long wavelengths for the PMDA-ODA film has been attributed to absorption by a conjugated (K-band) band characterized by extensive charge transfer (5-8) in the excited state from the donating aromatic diamine derived (ODA) unit of the PMDA-ODA repeat structure to the accepting PMDA derived unit. The red-shifted absorption of PMDA-ODA with a maximum, according to Ishida et al. (5), around 378 nm (3.28 eV) extends to about 500 nm. The position of the maximum of the high energy transition for PMDA-ODA (Figure 2) at 286 nm (4.33 eV) corresponds well to the 4.4 eV maximum reported by Lafemina et al. (6-8) which has been attributed to $\pi \rightarrow \pi^*$ transitions characterized by shifting of electron density from the ODA to PMDA unit. The interpretation of these bands at 4.33 eV and 3.28 eV as $\pi \rightarrow \pi^*$ transitions is consistent with results reported by Matsuo (9-10) for N-phenylmaleimide.

C.   Photolysis of PA-A Model

Since our interest is in the photochemistry of the resultant excited states of the 6F-ODA and PMDA-ODA polymers, and since we wanted a simple model which would serve in later work as a starting point for additional structural modifications to the repeat unit, i.e., different groups for x and y in structure I, we first analyzed the UV spectra (Figures 4 and 5) of the model compounds 6F-A and PA-A shown below:

6F-A

PA-A
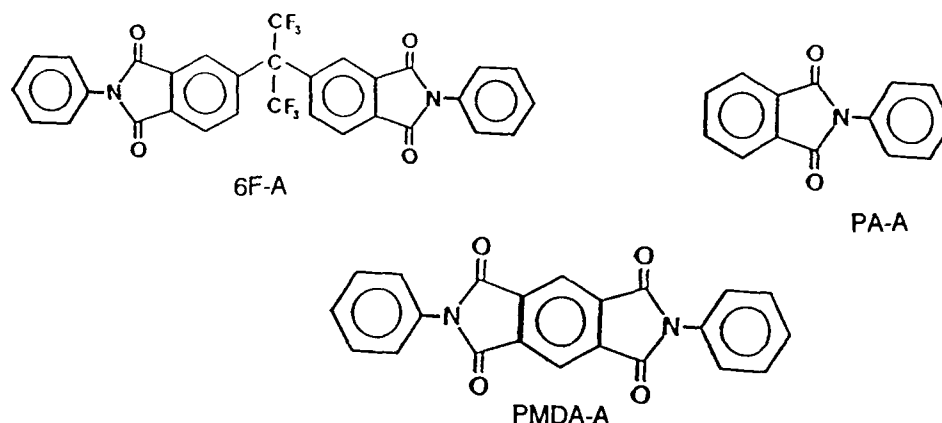
PMDA-A

6F-A and PA-A both exhibit a distinct red-shifted band. The absorption spectrum of bis-N-phenylpyromellitimide (PMDA-A) has been recently modeled by a CNDO/S3 program by LeFemina et al. (6-8) and found to exhibit a distinct transition dominated by $\pi \rightarrow \pi^*$ character and charge segregation. Though calculations were not performed for 6F-A or PA-A, the red shift in the absorption bands suggests that a contribution from a charge transfer transition is also likely for 6F-A and PA-A, although the degree of charge transfer would be less than in PMDA-A. In accordance with this speculation, we note a distinct red-shifted emission from 6F-A and PA-A, respectively, in dilute dichloromethane solutions (Figure 6 and 7). The emission maximum of PMDA-A could not be measured due to

limited solubility in solvents other than polar solvents like dimethylsulfoxide, thus precluding measurement of its fluorescence. Interestingly, analogous compounds to 6F-A and PA-A, but with N-propyl groups instead of N-phenyl groups, showed no red-shifted emission around 500 nm in dichloromethane. However, by analogy with the general position of the fluorescence emission maxima (>500 nm) obtained by Frank et al. (11-13) for PMDA-ODA, a polymer derived from the 6F dianhydride and isopropylidene dianiline (IPDA), and other similar polyimides with structural variations in either the dianhydride or diamine component used to make the polyimide, we can speculate that the emission of 6F-A and PA-A which occurs above 500 nm is from a low energy singlet state with substantial charge transfer character.

In selecting a compound for modeling the photolysis of 6F-ODA, PA-A would seem to be quite reasonable for two reasons. First, it exhibits emission from a charge transfer state, and although it is not an exact analog of the repeat unit in 6F-ODA, products of PA-A should be readily isolated since there is only one reactive imide group instead of two as for 6F-A. This limits the number of primary photoproducts and thus simplifies the product identification and quantum yield measurements without loss of accuracy or relevance to the main problem of determining the primary process leading to the rapid photooxidative degradation of 6F-ODA. Analysis of the photochemistry of PA-A in air saturated solutions should provide a sound fundamental basis for extension in subsequent future work to compounds with substituents on the N-phenyl ring. For example, $-OC_6H_5$, $-CH_2C_6H_5$, $-C(CF_3)_2C_6H_5$, and other appropriate groups can be substituted in the para-position of the N-phenyl group and the effect on the

photochemistry can be evaluated. The interested reader is referred to the reviews by Coyle (14) and Mazzochi (15) and references therein for an overview of alkylphthalimide and N-araalkylphthalimide photochemistry in primarily deaerated environments.

Photolysis of PA-A in acetonitrile (air saturated) was conducted in a 500 mL reaction vessel equipped with a quartz immersion well. A flow of cold water was circulated through the immersion well to keep the reaction mixture at approximately room temperature, thus reducing evaporation of the solvent during photolysis. The UV source, a 450 W medium pressure mercury lamp, was filtered by a Vycor sleeve to limit direct excitation of the acetonitrile solvent. The reaction progress was followed by taking aliquots periodically and analyzing by gas chromatography. After four hours the photolyzed solution (approximately 500 mL) was concentrated to between 5 and 15 mL and analyzed by gas chromatography. The primary products found by the preparative photolysis are phthalic anhydride and phthalimide (about 1/10 the concentration of phthalic anhydride) with smaller amounts of nitrobenzene. These three products, detected by the comparison of retention times of the photolyzed solution with those of authentic samples, have also been characterized by mass spectroscopy. The other product present in detectable quantity is benzoic acid. It should be noted that up to 50 additional photoproducts in very small yields were detected by gas chromatography. Plots of concentration of N-phenylphthalimide and the photoproducts phthalic anhydride and phthalimide as a function of photolysis time in the 500 mL reaction vessel are given in Figure 8. It is obvious that the two major photoproducts are themselves quite photolabile and rapidly decompose upon exposure to the Vycor filtered mercury light.

Since phthalic anhydride is the component produced in the highest yield in an oxygen atmosphere, it was photolyzed under similar conditions. Figure 9 indicates a rapid depletion of phthalic anhydride with photolysis time (photolysis of solutions of phthalimide and nitrobenzene show similar results). Thus, it is not surprising that we observed (Figure 8) the photolysis of phthalic anhydride during the photolysis of N-phenylphthalimide. Furthermore, the secondary photolysis of phthalic anhydride, phthalimide, and nitrobenzene in an air saturated system provides a reasonable explanation for the ultimate complete photooxidative ablation of 6F-ODA films in air. It is also noteworthy that one of the principal components in the photooxidation of phthalic anhydride is benzoic acid, which, as indicated previously is also found as a minor product in the photolysis of PA-A. Other unidentified products are also formed. It seems appropriate to suggest that the benzoic acid produced in the photolysis of PA-A in air comes, at least in part, from the photooxidation of phthalic anhydride, which itself is generated as a primary photooxidation product of PA-A. Interestingly, we found that benzoic acid is also rapidly decomposed upon photolysis in aerobic conditions in acetonitrile solution. Although products have not been identified, it would seem that decarboxylation (see reference 16) is at least one viable mechanism for photolytic breakdown of benzoic acid.

A plot (Figure 10) of the concentration of phthalic anhydride, phthalimide, and nitrobenzene formed in the photolysis of an N-phenylphthalimide solution with a mercury lamp filtered with Pyrex (>300 nm light primarily) shows a continuous buildup of phthalic anhydride and phthalimide and nitrobenzene, with no indication of extensive secondary

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photolysis of these primary products. These results are probably due to the differences in absorption between N-phenylphthalimide, phthalimide, phthalic anhydride and nitrobenzene as shown in Figures 11 and 12 in contrast to the red-shifted absorption of PA-A.

When large scale photolysis of PA-A with the unfiltered mercury lamp was attempted in a nitrogen purged acetonitrile solution, following identical procedures to that used for the preparative photolysis in air, an extremely small amount of phthalimide, phthalic anhydride, and nitrobenzene was formed in the first few hours (<10 hours) of photolysis with less than 10 percent of the starting PA-A being consumed. Continual photolysis for up to 120 hours gave no additional product buildup. Apparently the small amounts of photoproducts formed initially were due to some residual oxygen not removed by the continuous nitrogen flow through the 500 mL solution. (Also, there may well be some water present in the acetonitrile which is responsible, in part, for the initial photoproducts formed.) These photolysis results in a nitrogen purged solution are in excellent agreement with our findings for photolysis of the 6F-ODA polyimide films with an unfiltered mercury lamp in a nitrogen atmosphere where no decrease in either molecular weight (chain cleavage), IR spectral intensity, or weight loss was found after 96 hours photolysis time. This of course contrasts with the rapid photooxidative decomposition of 6F-ODA films in air, or PA-A in air saturated acetonitrile.

At this juncture, it is worth considering the origin of nitrobenzene as one of the products from photolysis of N-phenylphthalimide. Just as benzoic acid is probably produced by photolysis of the primary photoproduct phthalic anhydride, it may be that

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nitrobenzene is produced by photolysis of a primary photoproduct which decomposes very rapidly in an air saturated solution. One such primary photoproduct which is quite feasible is nitrosobenzene. Unfortunately, due to complications in detecting nitrosobenzene, we cannot conclusively prove its existence as a primary photoproduct. However, nitrosobenzene does have a distinct red-shifted absorption band (Figure 12b) with maximum above 300 nm, and its quantum yield for loss is 0.6 thus ensuring rapid decomposition and difficulty in detecting if formed. A similar conclusion was reached by Carlsson et al. in analysis of the photochemistry of a fully aromatic amide (17).

D.   Quantum Yields

In order to provide a quantitative description of the photodecomposition of PA-A, quantum yields were determined for disappearance and subsequent product formation in acetonitrile. The disappearance quantum yield for PA-A in acetonitrile is 6.3×10^{-4} indicating a low, but nonetheless significant, process for decomposition in the presence of air. The quantum yield for phthalic anhydride and phthalimide formation are 2.8×10^{-4} and 2.3×10^{-5}, respectively (estimated approximate upper limit value; due to low yield, the true quantum yield may be slightly lower). (Note that due to the error in calculating quantum yields for low efficiency processes, the quantum yields for product formation may not add up to the disappearance quantum yield). Finally, we should mention that the efficiency for loss of PMDA-A is extremely difficult to determine due to sparing solubility in organic solvents suitable for photolysis studies. However, a crude estimate based on

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UV analysis indicates that the quantum yield for loss is probably, at least an order of magnitude less than for PA-A. This is in agreement with and certainly suggested by the difference in stability between PMDA-ODA and 6F-ODA films. Additional work is currently being conducted on compounds similar in functionality to PMDA-A, but with solubilizing groups, to obtain exact disappearance and product formation quantum yields.

CONCLUSIONS

From the results of both model compounds and polyimide films it is apparent that photolysis of aryl phthalimides in air leads to the formation of phthalic anhydride as the major product, as well as other products. While PA-A is not an exact replica of the repeat unit in the 6F-ODA polymer, it still serves as a reasonable guide for photolysis studies, at least to a first approximation. The phthalic anhydride may be formed from a cleavage of the nitrogen-carbonyl bond to give a diradical (Scheme I) which, although its predominant reaction is efficient unimolecular coupling to yield the starting imide, may be intercepted by oxygen in a rather low probability, but nonetheless significant, competing bimolecular process. A similar reaction with oxygen has been proposed for the fate of the radical species generated upon photolysis of bis-arylamides (17). The low quantum yield (2.8×10^{-4}) results from the efficiency of the rapid ring closure. Nitrosobenzene, which has an absorption above 300 nm and efficiently converts to nitrobenzene upon photolysis, and phthalic anhydride might be expected to be formed from the intermediate generated by reaction of the diradical and oxygen. Other mechanisms involving, for example, singlet

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oxygen or direct oxygen addition to an excited state cannot be excluded. The phthalimide probably forms by direct nitrogen-phenyl bond cleavage. As indicated previously, phthalic anhydride, phthalimide, and nitrobenzene all readily decompose photochemically when exposed to light with wavelength less than 300 nm.

Finally, we note that a change of substituents on the N-phenyl ring, as well as an alteration of the diphthalimide portion of the imide repeat unit in the polymer chain, can no doubt affect the efficiency of product formation. This could result both from changes in the degree of charge-transfer in the excited state as well as the effect of substituents on the efficiency of coupling of the proposed diradical intermediate versus its reaction with oxygen. Thus, the effect of using a pyromellitimide unit instead of the 6F bisphthalimide unit in the dianhydride based portion of the repeat unit should indeed have a marked effect on the photostability, as experimental evidence in this paper demonstrates. The effect of substituents on the N-phenyl ring as well as the spin multiplicity of excited states leading to product formation will be the subjects of future work in our laboratory.

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SCHEME 1

R

N

O

O

R

N

O

C

C

O

O_2

O

O

O

+ Other Product(s)
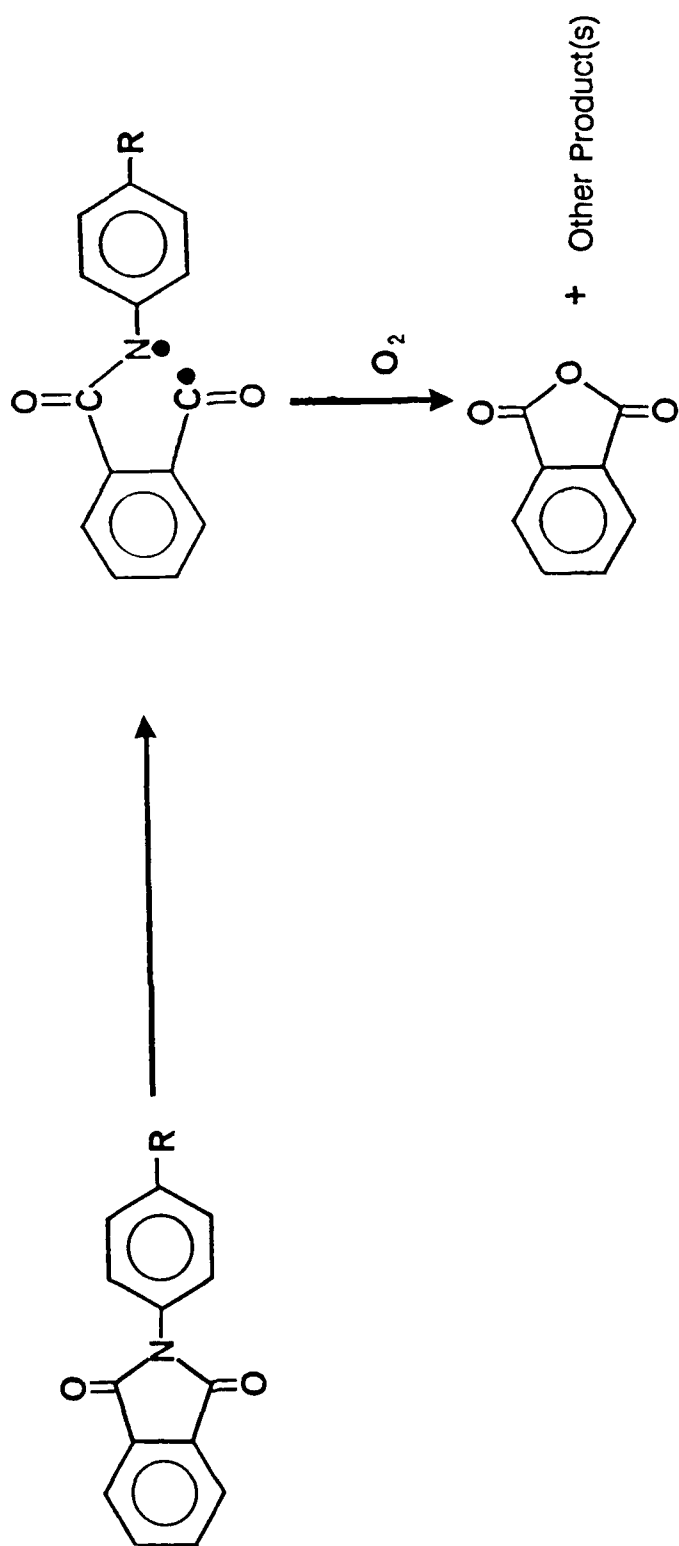
FIGURE CAPTIONS

Figure 1.　　IR spectrum of gaseous photoproducts produced by photolysis of 6F-ODA with an unfiltered medium pressure mercury lamp in air for 30 hours.

Figure 2.　　Absorption spectra of thin 6F-ODA and PMDA-ODA films.

Figure 3.　　Absorption spectra of thick 6F-ODA and PMDA-ODA films.

Figure 4.　　Absorption spectrum of 5.0×10^{-5}M 6F-A in dichloromethane.

Figure 5.　　Absorption spectrum of 6.9×10^{-5}M PA-A in dichloromethane.

Figure 6.　　Fluorescence spectrum of 4.0×10^{-4}M 6F-A in dichloromethane; $\lambda_{ex} = 325$ nm.

Figure 7.　　Fluorescence spectrum of 4.0×10^{-4}M PA-A in dichloromethane; $\lambda_{ex} = 325$ nm.

Figure 8.　　Concentration of N-phenylphthalimide (★), phthalic anhydride (o), and phthalimide (◊) upon photolysis of a 1.0×10^{-3}M solution of N-phenylphthalimide in acetonitrile in immersion well apparatus with Vycor filtered 450 W medium pressure mercury lamp.

Figure 9.　　Concentration of phthalic anhydride in acetonitrile as a function of photolysis time in immersion well apparatus with Vycor filtered 450 W medium pressure mercury lamp.

Figure 10.　　Concentration of N-phenylphthalimide (★), phthalic anhydride (o), phthalimide (◊), and nitrobenzene (□) upon photolysis of N-phenylphthalimide in acetonitrile in air saturated immersion well apparatus with Pyrex filtered medium pressure mercury lamp.

Figure 11.   Absorption spectra of PA-A and several photoproducts in CH_2Cl_2 (a) 3.87

x 10^{-4} M; PA-A (b) 5.0 x 10^{-4} M, phthalic anhydride; (c) 5.0 x 10^{-4}M,

phthalimide.

Figure 12.   Absorption spectra of nitrobenzene and nitrosobenzene in CH_2Cl_2 (a) 1.12
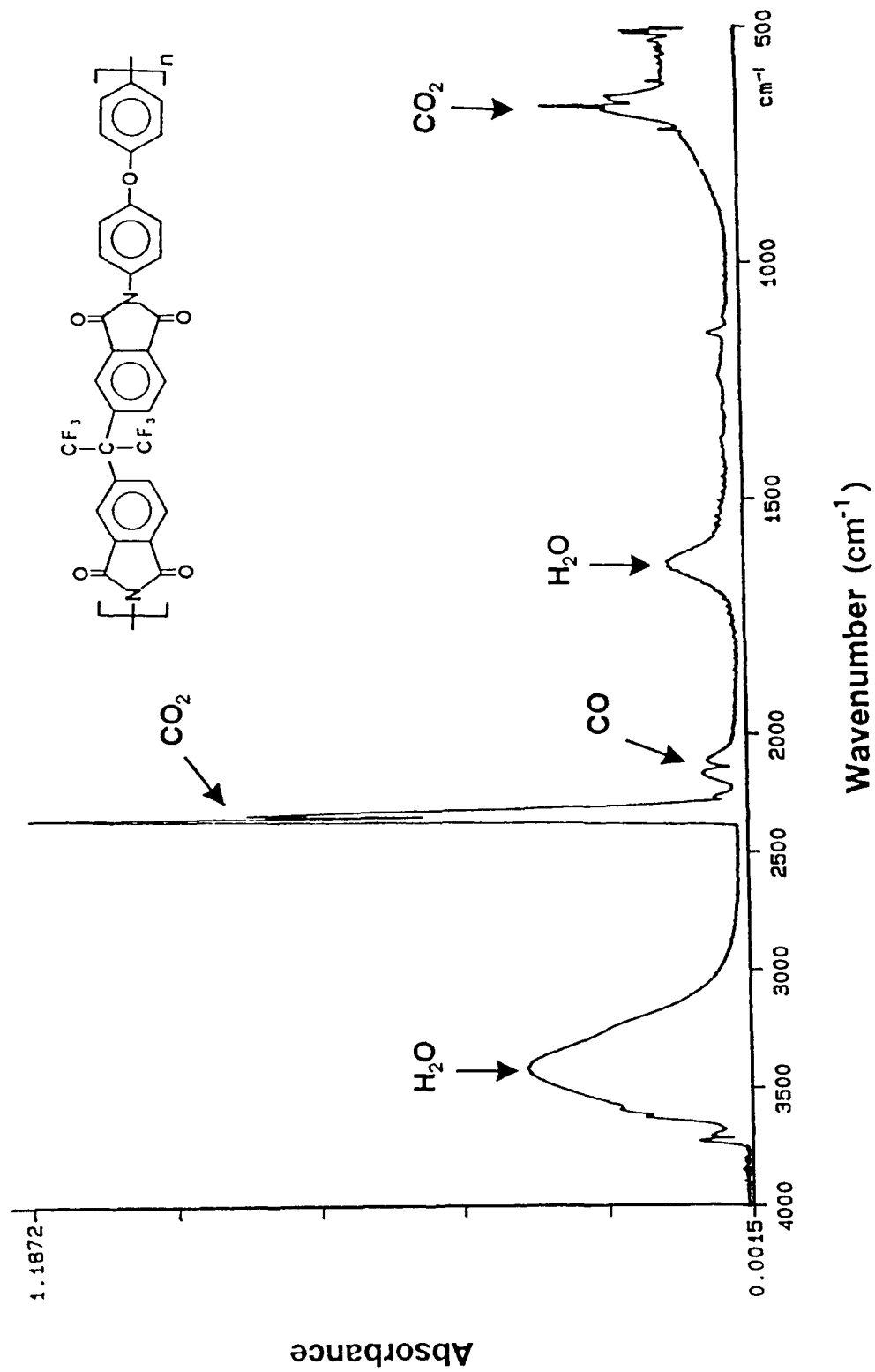
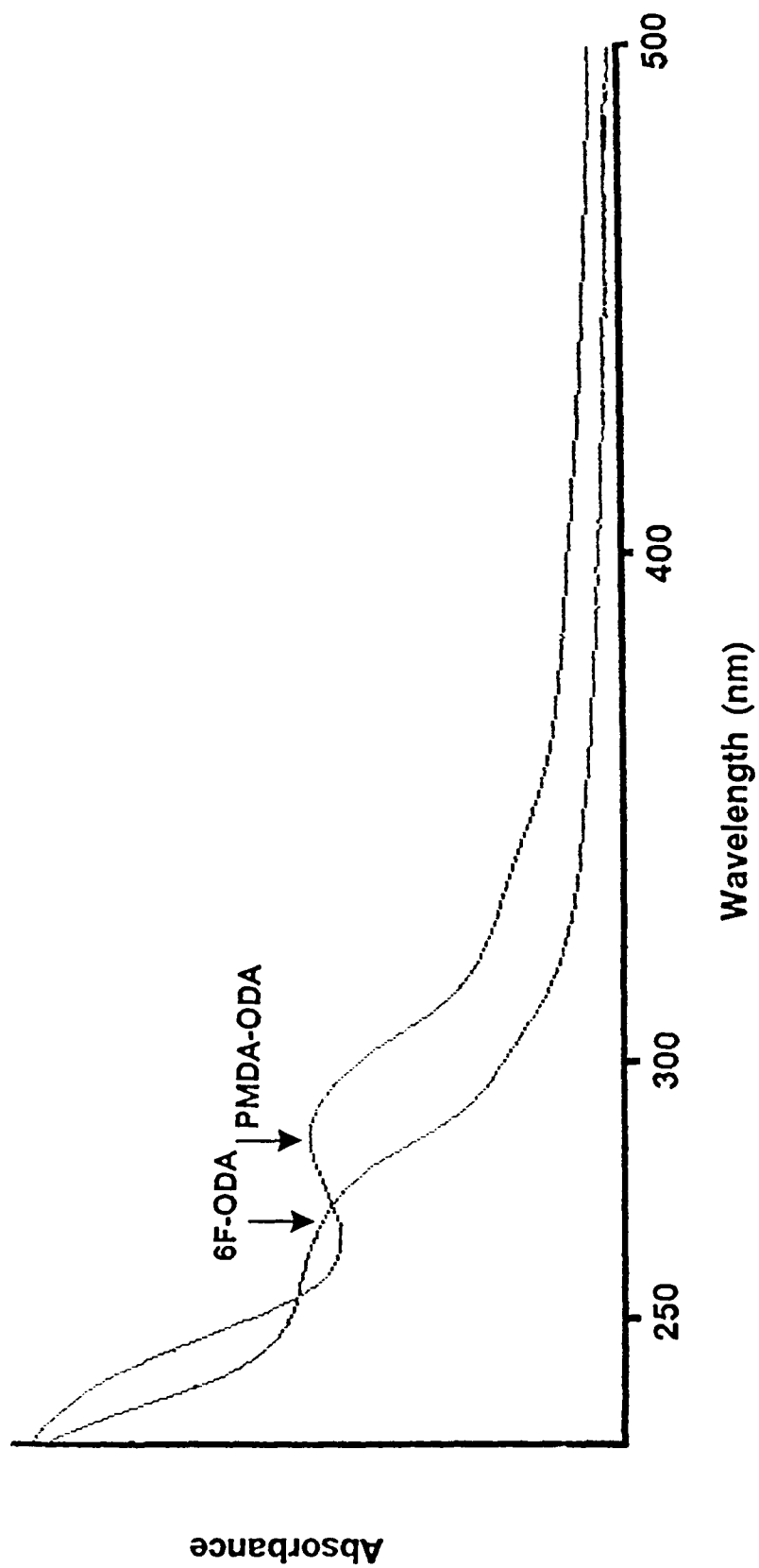x 10^{-4} M, nitrobenzene; (b) 1.03 x 10^{-4} M, nitrosobenzene.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5
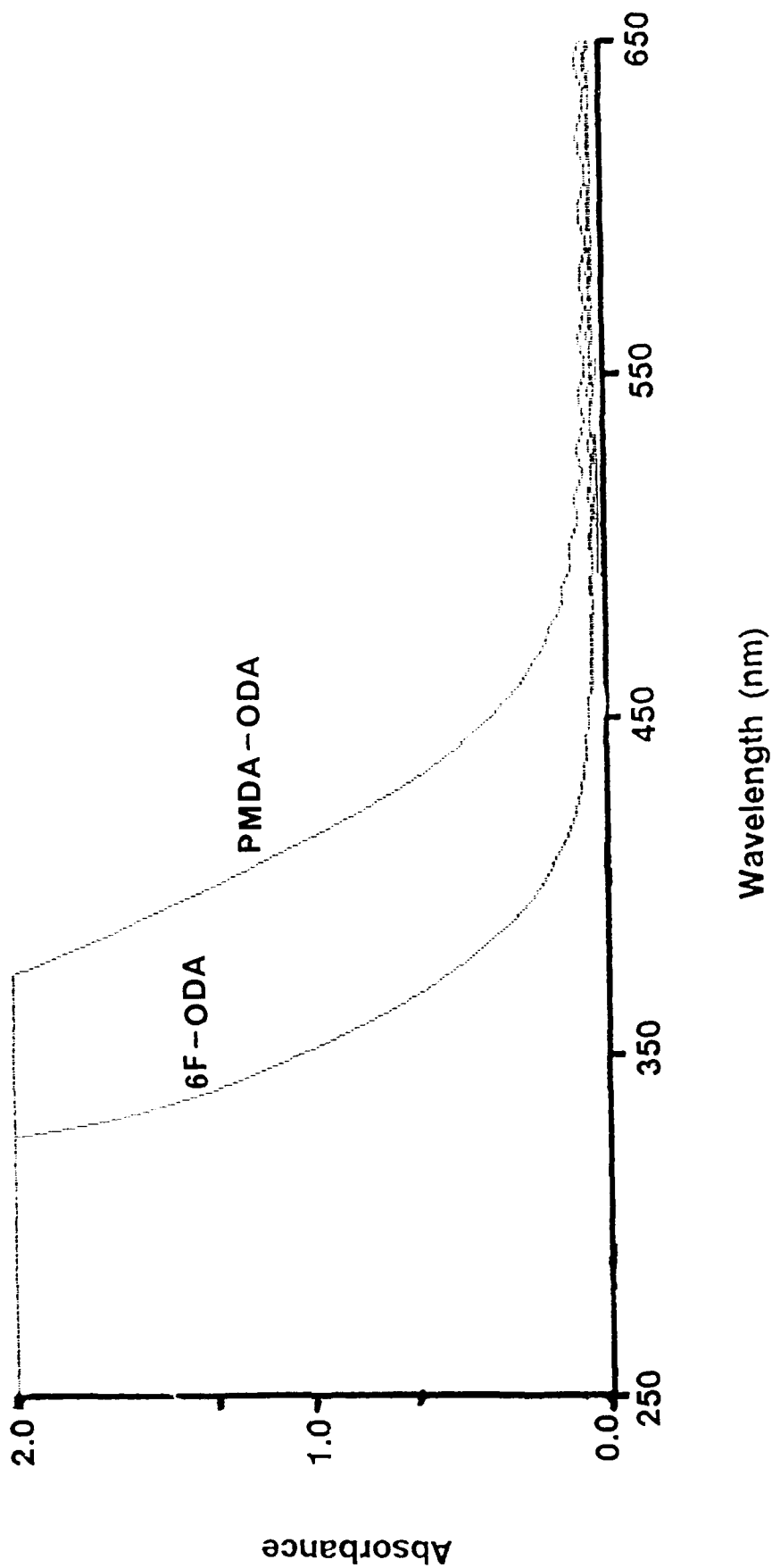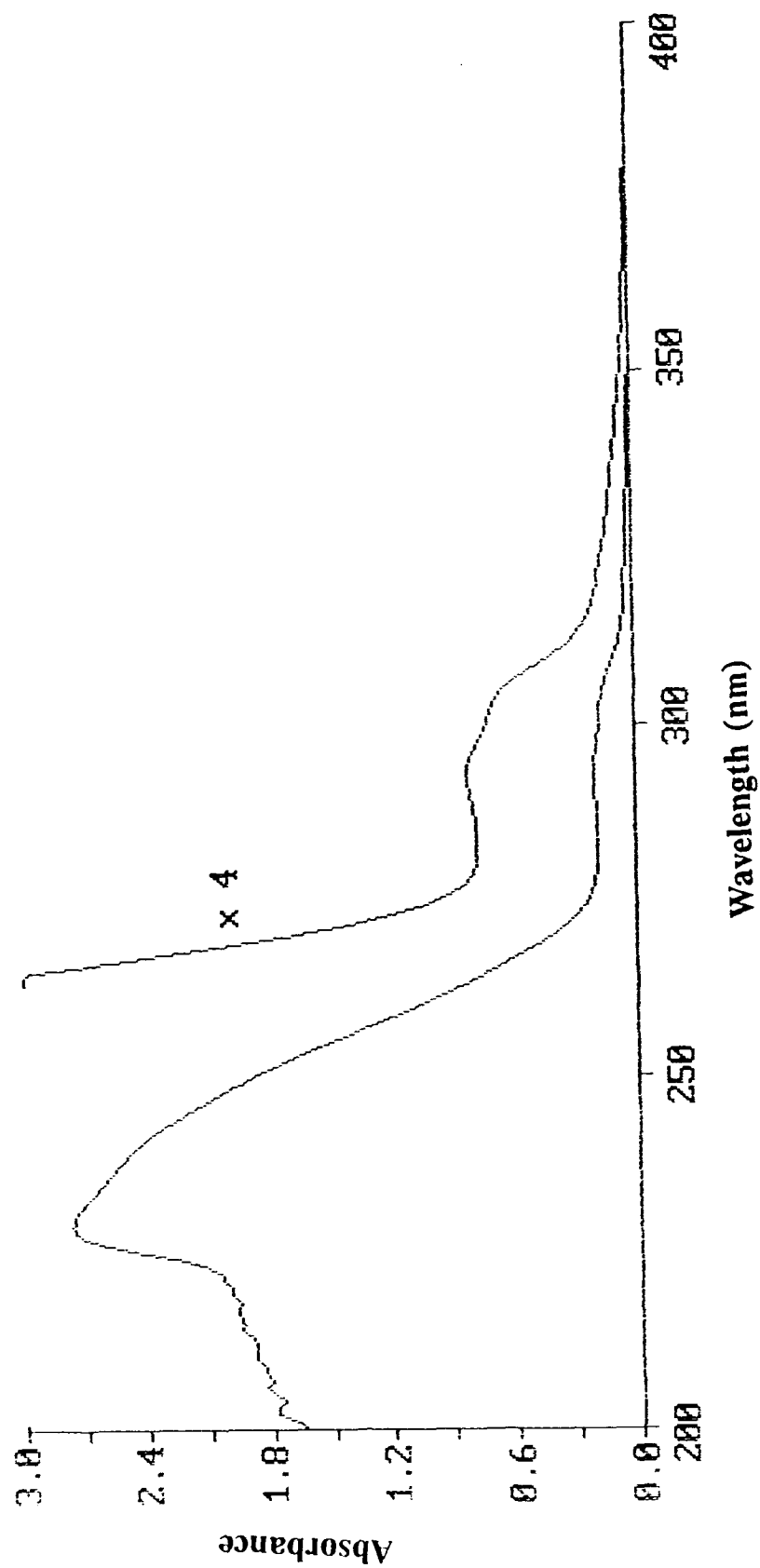
Wavelength (nm)

Absorbance

× 4

Fig. 6

Relative Intensity

Wavelength (nm)

400   450   500   550   600

Fig.7

Relative Intensity

Wavelength (nm)

400 450 500 550 600
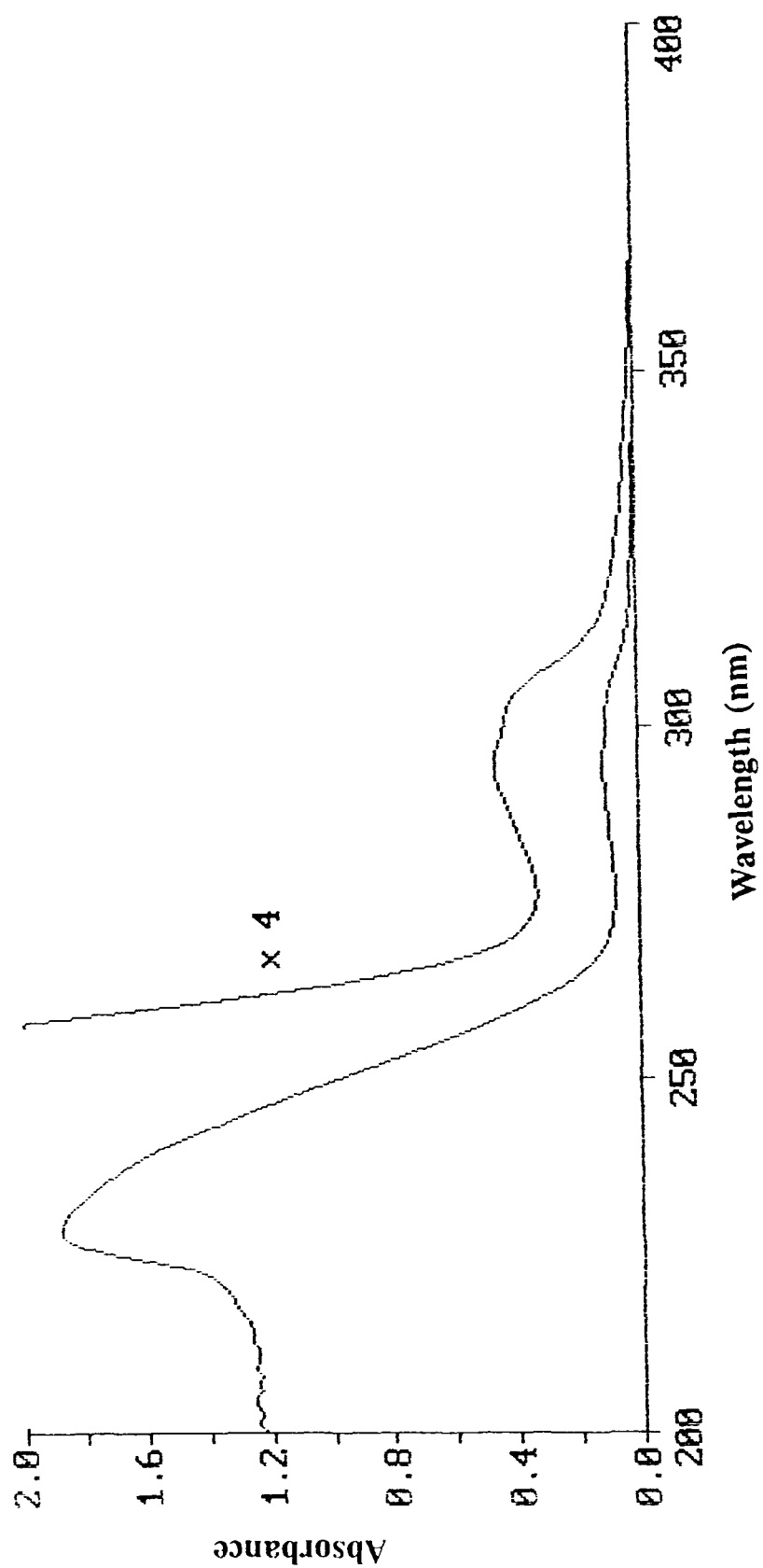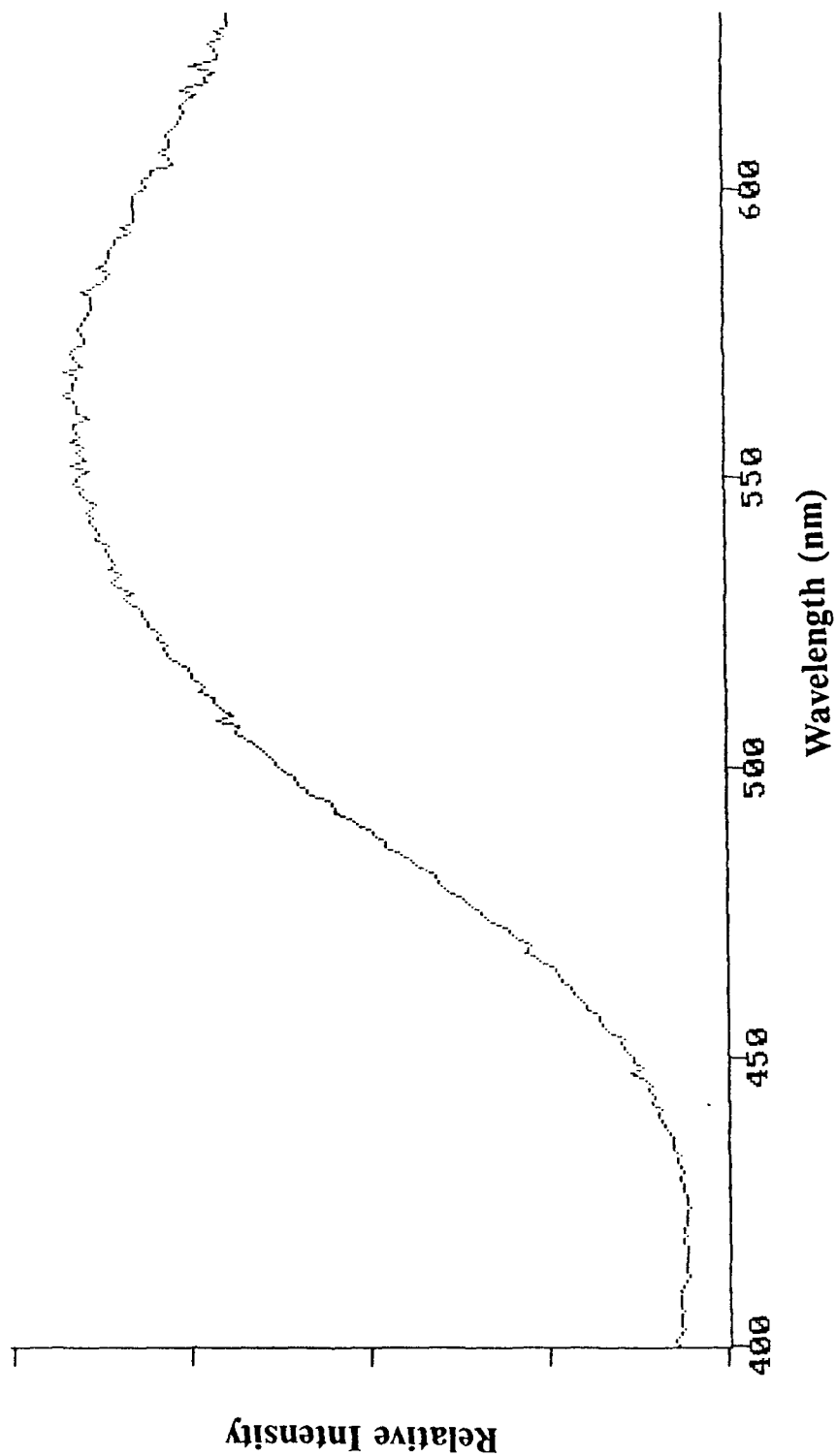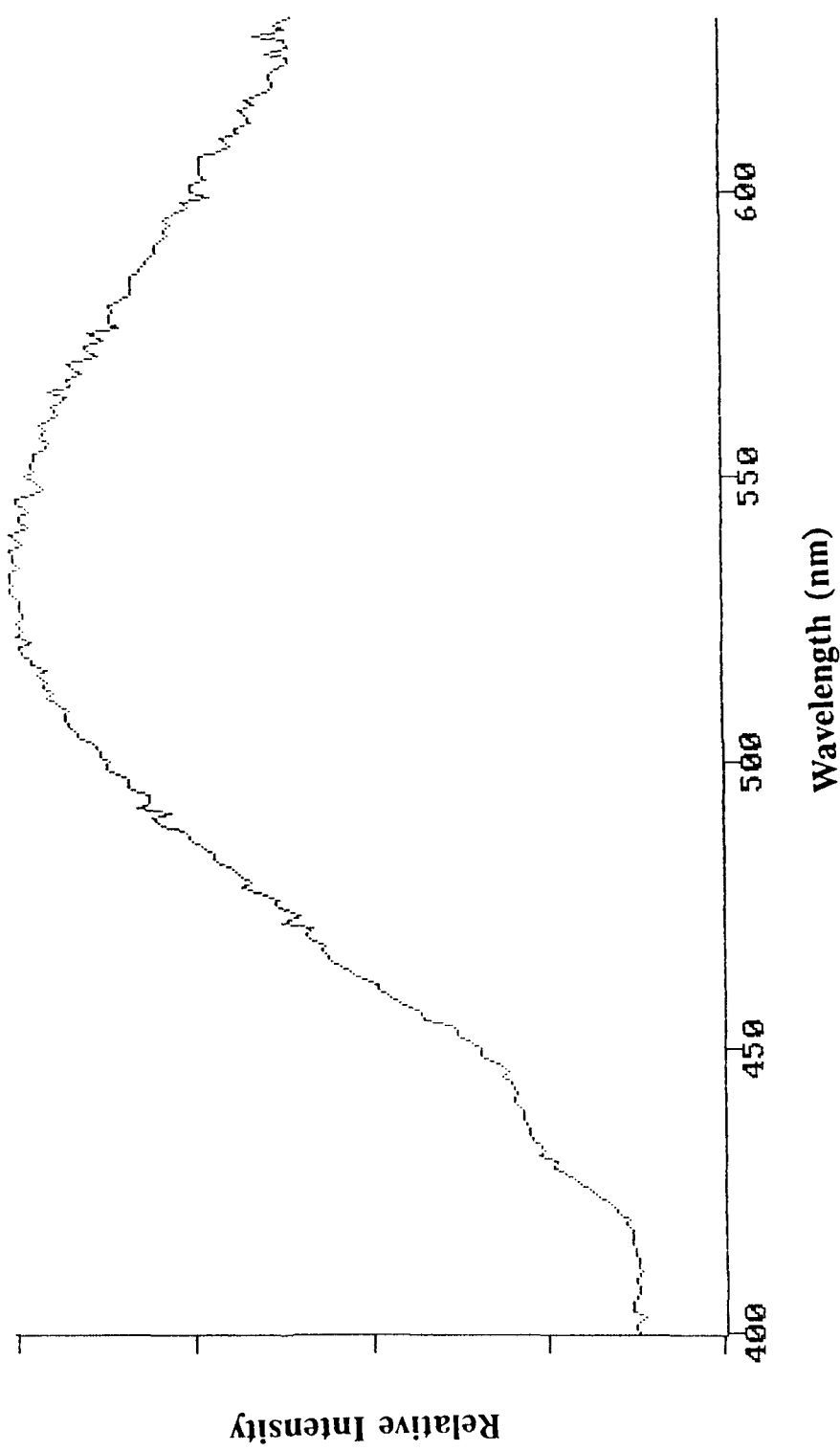
Fig 8

Fig 9

Fig. 10

Fig.11

Fig.12