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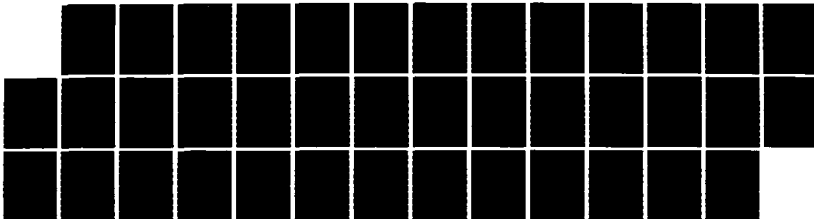
PHOTOLYSIS OF AROMATIC DIISOCYANATE BASED POLYURETHANES 1/1
IN SOLUTION(U) UNIVERSITY OF SOUTHERN MISSISSIPPI
HATTIESBURG DEPT OF POLYME. C E HOYLE ET AL. AUG 86

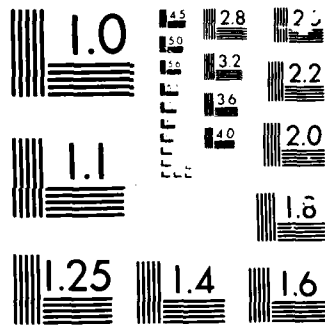
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Photolysis of Aromatic Diisocyanate Based Polyurethanes
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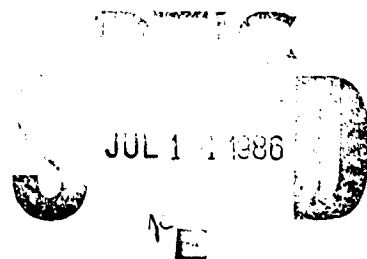
August, 1986

by

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Photolysis of Aromatic Diisocyanate Based Polyurethanes in Solution

by

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SYNOPSIS

Fluorescence analysis has been employed as an analytical technique to elucidate the photolysis mechanism of several aromatic diisocyanate based polyurethanes in solution. Based on a comparison with model arylmonocarbamates and arylbiscarbamates, the photo-Fries rearrangement and cleavage-type products found for the small model arylcarbarnates were also identified for the photolyzed polyurethanes in solution. Viscosity and absorbance change results for photolysis of both air and nitrogen saturated polyurethane solutions are consistent with a general two step mechanism for the photolysis of aromatic diisocyanate based polyurethanes.



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INTRODUCTION

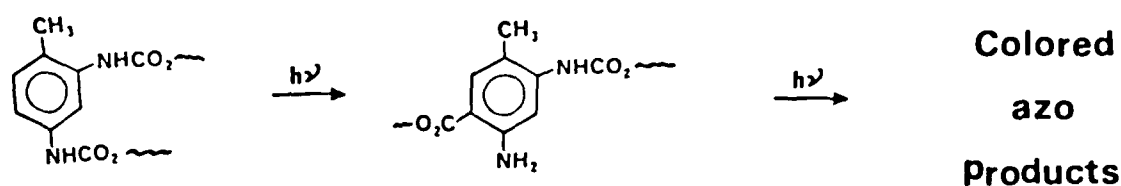
Since the commercial introduction of polyurethanes based on aromatic diisocyanates, it has been noted that they rapidly degrade and undergo severe discoloration on exposure to ultraviolet radiation^{1,2}. Thus, for applications requiring extended exposure to solar radiation, the more costly aliphatic diisocyanate based polyurethanes have been traditionally employed. Although aliphatic diisocyanate based polyurethanes also degrade upon exposure to far ultraviolet radiation, they have little or no absorbance in the range of the solar spectrum and do not produce colored products upon decomposition.

Numerous studies¹⁻¹⁴ have been conducted over the past two decades dealing with the photodecomposition of aromatic diisocyanate based polyurethanes, however, the exact mechanism of the photodecomposition process has remained somewhat obscured. Polyurethanes based on toluene diisocyanate [TDI--may be 2,4-toluene diisocyanate (2,4-TDI) or 2,6-toluene diisocyanate (2,6-TDI) or a mixture thereof] and methylene 4,4'-diphenyl diisocyanate (MDI) have received the most attention. Based on an analogy with studies of aryl monocarbamates model compounds such as ethyl N-phenylcarbamate¹⁵⁻²³, it has been implied that both MDI and TDI based polyurethanes photodecompose, at least to some extent, by a photo-Fries rearrangement process as shown in Scheme I. Beachell and Chang¹⁵ concluded that further photolysis of the subsequent primary photo-Fries products (as well as cleavage-type products) yielded colored azo compounds which were responsible for discoloration of the polyurethanes.

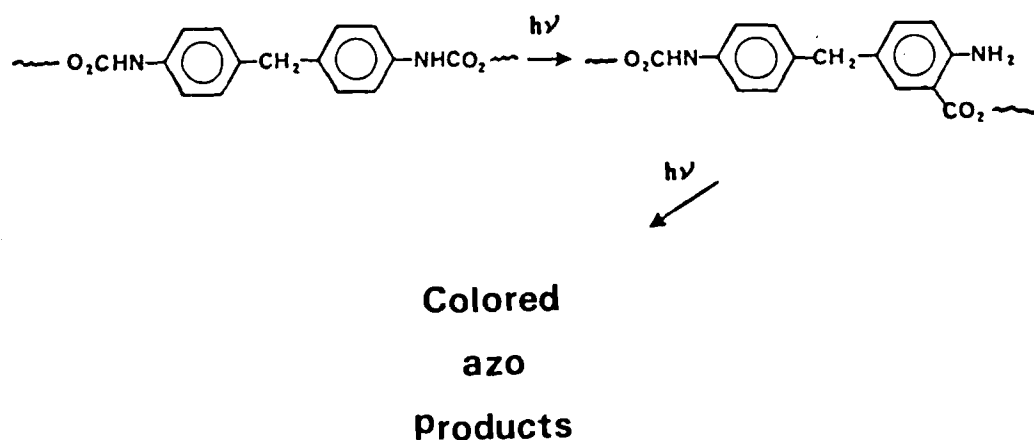
Thus, the photodegradation of MDI and TDI based polyurethanes, according to Beachell and Chang, proceeds by a two step process giving first the primary aromatic amine photoproducts followed by subsequent photolysis to give colored azo derivatives.

Scheme I

2,4-TDI based Polyurethane



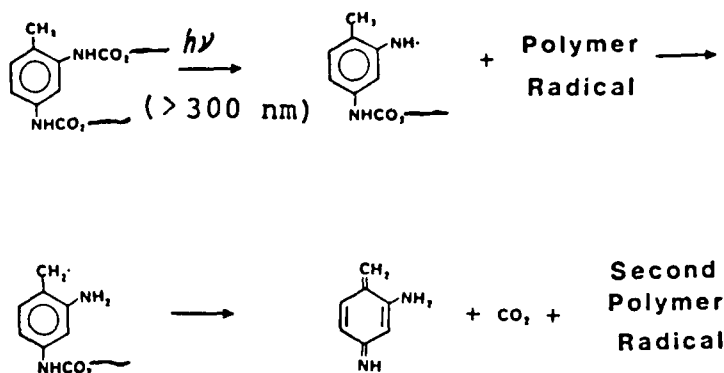
MDI based Polyurethane



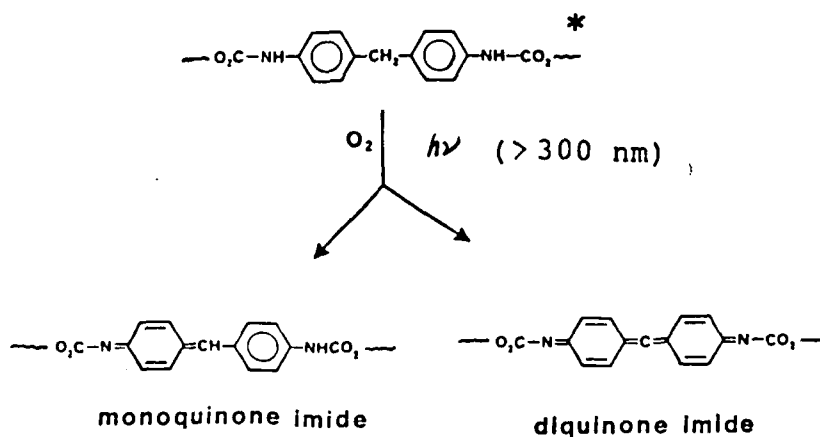
Alternately, other products, such as quinoid type compounds, have been implicated⁵⁻¹⁴ as resulting from the photolysis of MDI and TDI based polyurethanes as shown in Scheme II.

Scheme II

2,4-TDI based Polyurethane



MDI based Polyurethane



Although this (Scheme II) is one possible mechanism for polyurethane photodegradation which may well be, in some cases, one of the major pathways for photolytic decomposition, our present study deals only

with the photo-Fries type mechanism.

In previous investigations we concentrated on the photolytic decomposition of aryl monocarbamates¹⁹⁻²⁰ which serve as model compounds for MDI and TDI based polyurethanes. In this paper we follow the solution photolysis of both arylmonocarbamates and arylbiscarbamates using fluorescence spectroscopy. The results from these model compounds are used to interpret the photolysis of four aromatic diisocyanate based polyurethanes in solution. From analysis of changes in the fluorescence spectra of the polyurethane solutions, unequivocal evidence for formation of photo-Fries products is obtained.

EXPERIMENTAL

Materials

Methylene-bis-(4-cyclohexylisocyanate) (S-MDI) (Mobay), 2,4-toluene diisocyanate (99.5 % Mobay), and 2,6-toluene diisocyanate (Aldrich) were purified by distillation before use.

Methylene-bis-(4-phenylisocyanate) (Mobay) was recrystallized from cyclohexane. p-Phenylene diisocyanate (PPDI) (Armak) was purified by sublimation. Dimethyl sulfoxide (Baker) and hexamethyl phosphoramide (Aldrich) were distilled and dried before use. Diols used in the preparation of the polyurethanes (Aldrich) were distilled or recrystallized from 1,2-dichloroethane. The preparation of various model mono- and biscarbamates and photo-Fries products has been reported in an earlier paper²⁰. Polyurethanes were prepared by a solution polymerization²⁴. A typical example is given. To a solution

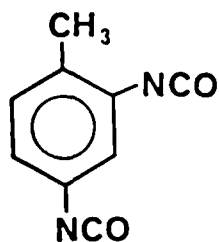
of 3.0 g (1.2×10^{-2} mol) of MDI in 10 ml of DMSO, was added with stirring, 2.1 g (1.2×10^{-2} mol) of 1,10-decanediol in 10ml of DMSO dropwise through an addition funnel under a nitrogen stream. The reaction mixture was heated up to 115°C. After stirring at 115°C for 2 hours, the resulting viscous mixture was diluted with 40 ml of dimethylformamide (DMF) and poured dropwise into 1 l of deionized water to precipitate the polymer. The isolated polymer was washed with fresh water and dried in a vacuum oven. Except for the polymerization of the p-phenylene diisocyanate based polyurethane, where hexamethyl phosphoramide was used as a solvent, all other polyurethanes were made by a similiar procedure.

Instrumentation/Procedure

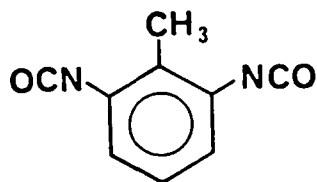
Fluorescence spectra were recorded using a Perkin-Elmer fluorescence spectrophotometer model 650-10S. Absorption spectra were recorded using a Perkin-Elmer UV/Visible spectrophotometer, model 320. All solutions were exposed in a Rayonet Reactor model RPR-100 with appropriate lamps. Dilute solution viscosities (0.5g/dl) were measured in DMF at 25°C with a size 50 Cannon-Fenske viscometer.

RESULTS and DISCUSSION

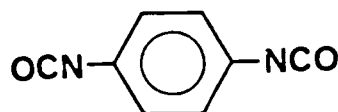
In this investigation, the focus of attention is aimed at establishing the viability of a photo-Fries rearrangement mechanism in the solution photolysis of polyurethanes based on the four diisocyanates shown below:



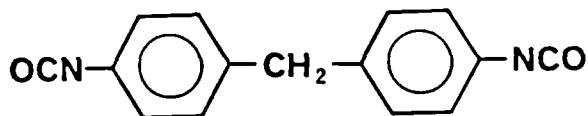
2,4-TDI



2,6-TDI



PPDI



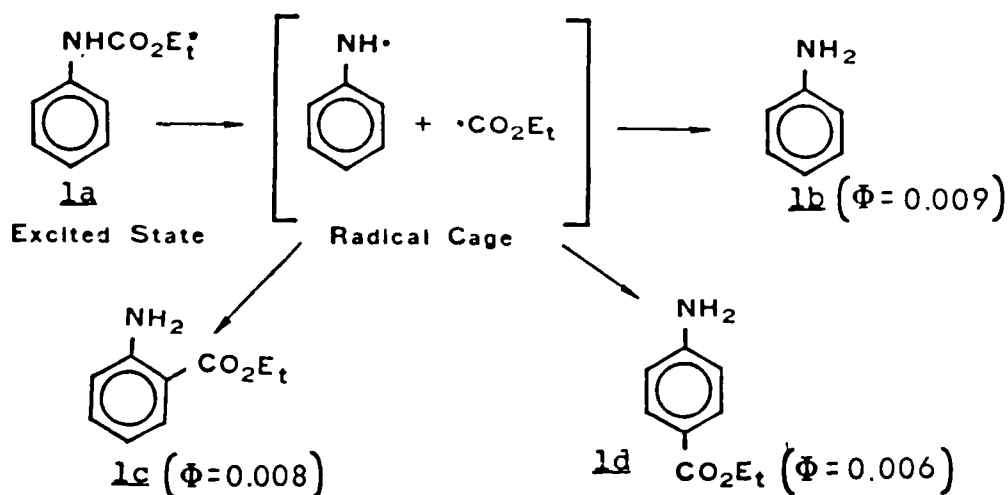
MDI

Before directly analyzing actual polyurethanes, it is necessary to first give careful consideration to the fluorescence analysis of photolyzed solutions of arylmonocarbamates and the propyl arylbiscarbamates of the diisocyanates used to make each of the polyurethanes under consideration. Having established the credibility of the fluorescence technique for analysis of the photolysis of model arylcarbamate compounds, it is a simple step to extend this analysis to investigate the photolysis of aromatic diisocyanate based polyurethanes in solution. It should be pointed out that other methods such as GC, HPLC, IR, etc. which are often readily adapted to identification of the photolysis products of small molecules, cannot so easily be applied to study in detail the photolysis of polymer systems since the products formed are still (usually) attached directly to the polymer chain. In contrast, once the utility of the fluorescence technique is established for analysis of the photolysis of the model arylmonocarbamates and arylbiscarbamates, it can readily be adapted, unlike GC or HPLC analysis, to studies of the arylcarbamate functional group in polyurethane polymers.

Photolysis of Model Arylmonocarbamates and Arylbiscarbamates
in DMF Solution

As previously reported by several groups¹⁵⁻²³, the photolysis of the model compound ethyl N-phenylcarbamate(1a) results in the formation of aniline(1b), o-amino ethylbenzoate(1c) and p-amino benzoate(1d) as shown in Scheme III below.

Scheme III



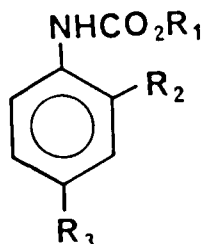
The quantum yields for product formation were determined, as described in an earlier paper²⁰, by GC analysis. The change in the absorption spectrum of 1a on exposure to UV radiation (254 nm, Rayonet Reactor) is shown in Figure 1 for a solution of 1a in cyclohexane. New peaks which appear in the absorption spectrum after photolysis are attributed to 1b and 1d ($\lambda_{\text{max}} = 290$ to 300 nm) and 1c ($\lambda_{\text{max}} = 335$ nm) by comparison with authentic samples of each dissolved in cyclohexane. Although similar shifts in the absorption spectrum can be obtained for photolysis of aromatic diisocyanate based polyurethane

solutions, interpretation is not as straightforward as in the case of the simple monocarbamate 1a.

In order to provide a sound base for the identification of photolysis products of aromatic diisocyanate based polyurethanes we first analyze the fluorescence spectra of several model arylmonocarbamates and their respective photo-Fries and aniline products. Considering first the case of 1a, a significant difference in the fluorescence peak maximum is noted for the parent carbamate (Figure 2) compared with the photo-Fries products 1c and 1d (Figure 3 and Figure 4, respectively) and aniline 1b (Figure 5). Thus, while the carbamate 1a has a maximum at approximately 301 ± 2 nm, the para photo-Fries product 1c and cleavage product aniline 1b have red-shifted maxima at 335 ± 2 nm and 337 ± 2 nm respectively. The ortho photo-Fries product 1d, however, has a maximum above 400 nm (405 ± 5 nm). Presumably, the carboxylate group substituted ortho to the amino group results in a stabilized excited state. Additionally, since the absorption spectrum of 1d is also red shifted, i.e, there is a peak in the absorption spectrum at 335 nm, excitation of 1d at either 280 nm or 335 nm results in emission with maximum at 405 ± 3 nm. Having examined the fluorescence spectra of the simple carbamate 1a and each of the resulting products 1b, 1c and 1d, the change in fluorescence spectrum resulting from photolysis of a solution of 1a (Figure 6-DMF solvent) is interpreted in view of the individual spectra in Figures 2-5. As can be seen, there is a decrease in the peak fluorescence maximum at 301 nm upon photolysis (Rayonet Reactor, 300 nm lamps) accompanied by the appearance of two new peaks with maxima at 335 ± 2 nm and 405 ± 3 nm corresponding to emission from a combination of 1b and 1d (Figures 5 and 4) and 1c (Figure 3),

respectively.

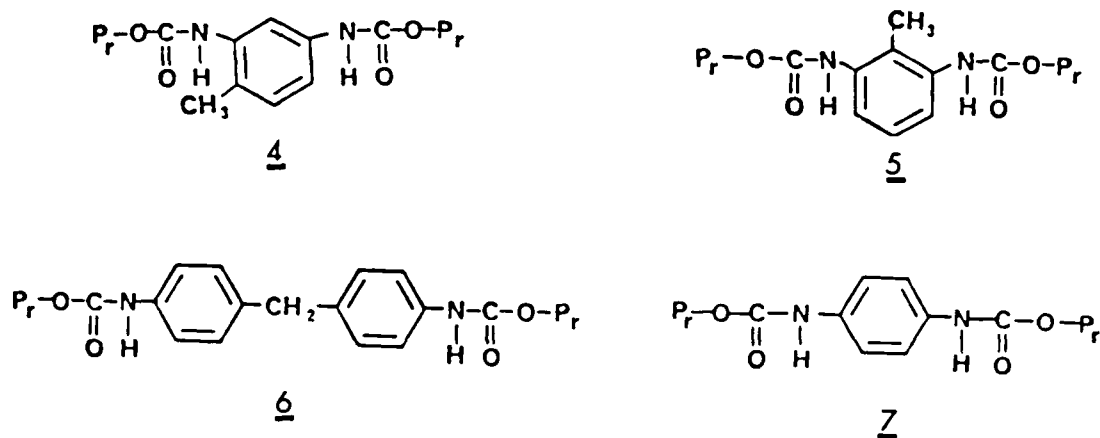
In earlier papers, attention was given to the effect of methyl group ring placement on the photolysis of arylcarbamates with respect to the reaction products formed. Subsequent analogies to the photodegradation of polymeric systems based on aromatic diisocyanates were made. In accordance with this reasoning we recorded the fluorescence spectra of the methyl group ring substituted arylcarbamates 2 and 3 as well as carbamate 1 and the resultant ortho photo-Fries, para photo-Fries, and methyl substituted aniline cleavage products expected from photolysis of each parent arylcarbamate. These results are presented in Tables I-IV with a summary given in Table V showing the typical fluorescence maxima corresponding to each general type of functionality.



- | | |
|----------|---|
| <u>1</u> | $\text{R}_1 = \text{Et}; \text{R}_2, \text{R}_3 = \text{H}$ |
| <u>2</u> | $\text{R}_1 = \text{Pr}; \text{R}_2 = \text{CH}_3; \text{R}_3 = \text{H}$ |
| <u>3</u> | $\text{R}_1 = \text{Pr}; \text{R}_2 = \text{H}; \text{R}_3 = \text{CH}_3$ |

The composite results in Table V can then be used to interpret the results (Table VI) obtained for photolysis of model compounds 1 through 3 in solution. Most noticeable in the case of carbamates 1 through 3 is the formation of the para photo-Fries and methyl substituted aniline cleavage products (emission at 335 ± 5 nm) and the formation of the ortho photo-Fries products (emission at 410 ± 5 nm). This is completely consistent with the GC results obtained previously.

In order to extend the investigation of polyurethane model systems to more realistic models, the following biscarbamates of several aromatic diisocyanates were synthesized.



The fluorescence maxima of biscarbamates 4-7 are given in Table VII along with the new emission peaks resulting from their photolysis (Rayonet reactor, 300 nm lamps). In each case the fluorescence due to the aryl carbamate chromophore is diminished upon photolysis with the appearance of two new broad structureless peaks, one at approximately 340 ± 7 nm and one above 400 nm. This phenomena is graphically illustrated in Figure 7 which shows the fluorescence spectra of the propyl biscarbamate of 2,4-TDI at various photolysis times. It is apparent, as is the case for the simple arylmonocarbamates 1-3, that photolysis of the propyl arylbiscarbamates 4-7 leads to the corresponding para photo-Fries and aniline type cleavage products with emission maxima around 340 nm and the ortho photo-Fries products with emission maxima around 410-440 nm.

Photolysis of Aromatic Diisocyanate Based Polyurethanes

Figures 8 through 11 show results of the fluorescence spectral changes resulting from the photolysis of polyurethanes based on 2,4-TDI, 2,6-TDI, MDI and PPDI. In each case, the fluorescence emission of the parent carbamate group with maximum at 310 ± 5 nm decreases with increasing photolysis time (Rayonet Reactor, 300 nm lamps) and is replaced by two broad structureless peaks with maxima at 340 nm and 410 nm. These peaks can be readily assigned by analogy with the arylmonocarbamate and arylbiscarbamate photolysis studies to para photo-Fries and/or aniline type cleavage products (340 nm maximum emission) and ortho photo-Fries products (410 nm maximum emission). The results for photolysis of the four aromatic diisocyanate based polyurethanes are summarized in Table VIII. Results (Table VIII) for photolysis of the aliphatic diisocyanate polyurethane based on methylene-bis-(4-cyclohexylisocyanate) and decanediol show no emission either before or after photolysis. This provides a strong argument that indeed the fluorescence in the aromatic diisocyanate based polyurethane solutions, both before and after photolysis, can be attributed to fluorescence from aromatic chromophores and not an impurity and/or product resulting from photolysis of the aliphatic portion of the polyurethanes. In summary, for photolysis of aromatic diisocyanate based polyurethanes in DMF solution, comparison of the fluorescence spectra both before and after photolysis with fluorescence of model arylmono- and arylbiscarbamates before and after leads to the conclusion that photo-Fries rearrangement (ortho and where possible para) and cleavage products are formed.

Having established that the photo-Fries rearrangement process is a viable mechanism for the photolysis of aromatic diisocyanate based

polyurethanes in solution, it should be interesting to measure other properties which are effected by the photo-Fries/cleavage type process. Figure 12 shows the change in viscosity of a 2,4-TDI/octanediol based polyurethane upon photolysis both in the absence and presence of oxygen. There is initially, both in oxygen and nitrogen saturated solutions, a rapid drop in the reduced viscosity upon photolysis followed by a leveling off with increased photolysis time. These results are fully consistent with the cleavage products noted for photolysis of the 2,4-TDI based polyurethane using fluorescence analysis (Figure 8). The insensitivity of the cleavage process to oxygen inhibition can readily be explained by the short singlet lifetimes (@ 5 nsec) of arylcarbamate chromophores previously reported for both model arylcarbamates and aromatic diisocyanate based polyurethanes^{2,17}. Thus, it appears as though the cleavage process in the TDI based polyurethane in DMF solution results in chain scission of the polymer backbone and, due to the short lifetime of the arylcarbamate singlet state, this chain scission process is insensitive to oxygen inhibition.

Unlike the changes in viscosity found for photolysis of the 2,4-TDI/octanediol based polyurethane in solution, changes in absorbance at wavalengths above 400 nm are found to be highly dependent on the presence of oxygen as shown in Figure 13. This is consistent with secondary photolysis of the primary photo-Fries and cleavage-type aromatic amine products to give colored secondary aromatic azo compounds since oxygen is necessary for photooxidation of aromatic amines to azo derivatives. Thus, our results confirm a two-step process (generation of aromatic amines followed by their photooxidation) for photolysis of aromatic diisocyanate based

polyurethanes as proposed by Beachell and Chang¹⁵.

CONCLUSION

Techniques have been developed to follow the photolysis of aromatic diisocyanate based polyurethanes in solution. Based on the fluorescence analysis of photolyzed solution of small molecule model arylmonocarbamates and arylbiscarbamates, photo-Fries/cleavage type products for the photolysis of aromatic diisocyanate based polyurethanes were identified. Additionally, results for viscosity and absorbance changes for photolysis of a typical 2,4-TDI based polyurethane are consistent with a two step mechanism for the photolysis of aromatic diisocyanate based polyurethanes proposed by Beachell and Chang¹⁵. Although confirming evidence for the photo-Fries rearrangement process has been presented, this does not exclude the formation of quinoid-type products proposed by previous workers. It is certainly conceivable, as postulated by Gardette and Lemaire¹⁴, that both types of products are formed upon photolysis. Work in progress, which builds upon the precepts presented in this paper, utilizes the fluorescence technique to probe the photolysis of polyurethanes in the solid state and to elucidate the effect of polymer morphology and flexibility on the photo-Fries rearrangements of amorphous and semi-crystalline polyurethanes.

ACKNOWLEDGMENT

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FIGURES

Figure 1. UV absorbance change on photolysis of 2.5×10^{-4} M ethyl N-phenylcarbamate in cyclohexane with Rayonet Reactor (254 nm lamps) for 30 minutes. (a) Before photolysis — (b) After Photolysis —.——

Figure 2. Fluorescence spectrum ($\lambda_{ex} = 280$ nm) of 5×10^{-3} M ethyl N-phenylcarbamate in DMF.

Figure 3. Fluorescence spectrum ($\lambda_{ex} = 280$ nm) of 5×10^{-3} M 2-amino ethylbenzoate in DMF.

Figure 4. Fluorescence spectrum ($\lambda_{ex} = 280$ nm) of 5×10^{-3} M 4-amino ethylbenzoate in DMF.

Figure 5. Fluorescence spectrum ($\lambda_{ex} = 280$ nm) of 5×10^{-3} M aniline in DMF.

Figure 6. Fluorescence spectral change ($\lambda_{ex} = 280$ nm) on photolysis of 5×10^{-3} M ethyl N-phenylcarbamate with Rayonet Reactor (300 nm lamps) for 5 hours. (a) Before photolysis — (b) After photolysis —.——

Figure 7. Fluorescence spectral change ($\lambda_{ex} = 280$ nm) on photolysis of 5×10^{-3} M 2,4-TDI bispropylcarbamate in DMF with Rayonet Reactor (300 nm lamps). (a) 0 hr; — (b) 1 hr; — (c) 2 hr; (d) 3 hr; ○○○○○○

Figure 13. UV absorbance change (1 cm pathlength cell) on photolysis of 0.5 g/dl 2,4-TDI based polyurethane in DMF with Rayonet Reactor (300 nm lamps).

- (a) oxygen atmosphere; ●
- (b) nitrogen atmosphere; ○

Table I

Fluorescence spectral data of model monocarbamates^a

<u>Model Carbamate</u>	<u>Emission Maximum (nm)</u>
ethyl N-phenylcarbamate (<u>1</u>)	301
propyl N-o-tolylcarbamate (<u>2</u>)	302
propyl N-p-tolylcarbamate (<u>3</u>)	311

^a280 nm excitation; 5×10^{-3} M in DMF

Table II

Fluorescence spectral data of model ortho photo-Fries products^a

<u>ortho Photo-Fries Product</u>	<u>Emission Maximum (nm)</u>
o-amino ethylbenzoate	405
2-amino-3-methyl propylbenzoate	409
2-amino-5-methyl propylbenzoate	416

^a280 nm or 335 nm excitation; 1×10^{-4} M in DMF

Table III

Fluorescence spectral data of model para photo-Fries products^a

<u>para Photo-Fries Product</u>	<u>Emission Maximum (nm)</u>
p-amino ethylbenzoate	335
3-methyl-4-amino propylbenzoate	340

^a280 nm or 300 nm excitation; 5×10^{-5} M in DMF

Table IV

Fluorescence spectral data of model cleavage-type products^a

<u>Free Amine</u>	<u>Emission Maximum (nm)</u>
aniline	337
o-toluidine	348
p-toluidine	337

^a280 nm or 300 nm excitation; 2.5×10^{-4} M in DMF

Table V
Fluorescence spectral data of model compounds summary^a

Compound	Emission Maximum (nm)
Carbamate	305±5
Aniline	342±5
ortho Photo-Fries Product	410±5
para Photo-Fries Product	338±5

^a280 nm excitation in DMF

Table IV
Fluorescence spectra^a for photolyzed solutions^b of model
arylcarbamates

Model Carbamate	Emission Maximum (nm)
ethyl N-phenylcarbamate (1)	335,405
propyl N-o-tolylcarbamate (2)	340,409
propyl N-p-tolylcarbamate (3)	337,416

^a280 nm excitation; 5×10^{-3} M in DMF

^bnitrogen atmosphere, 300 nm Rayonet Reactor, 30 minutes

Table VII
Fluorescence spectral changes for photolysis of model
arylbiscarbamates

Model Biscarbamate	Emission Maxima ^a (before photolysis) (nm)	Emission Maxima ^a (after photolysis) ^b (nm)
<u>4</u>	313	345,425
<u>5</u>	313	340,408
<u>6</u>	311	333,414
<u>7</u>	330	345,440

^a280 nm excitation; 5×10^{-4} M in DMF

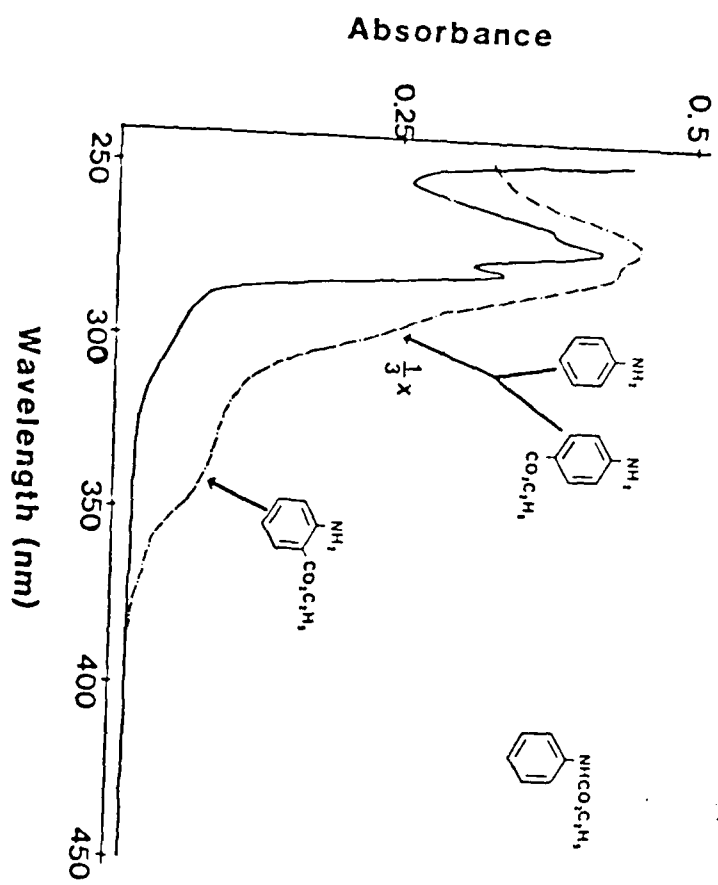
^bnitrogen atmosphere, 300 nm Rayonet Reactor, 2 hours

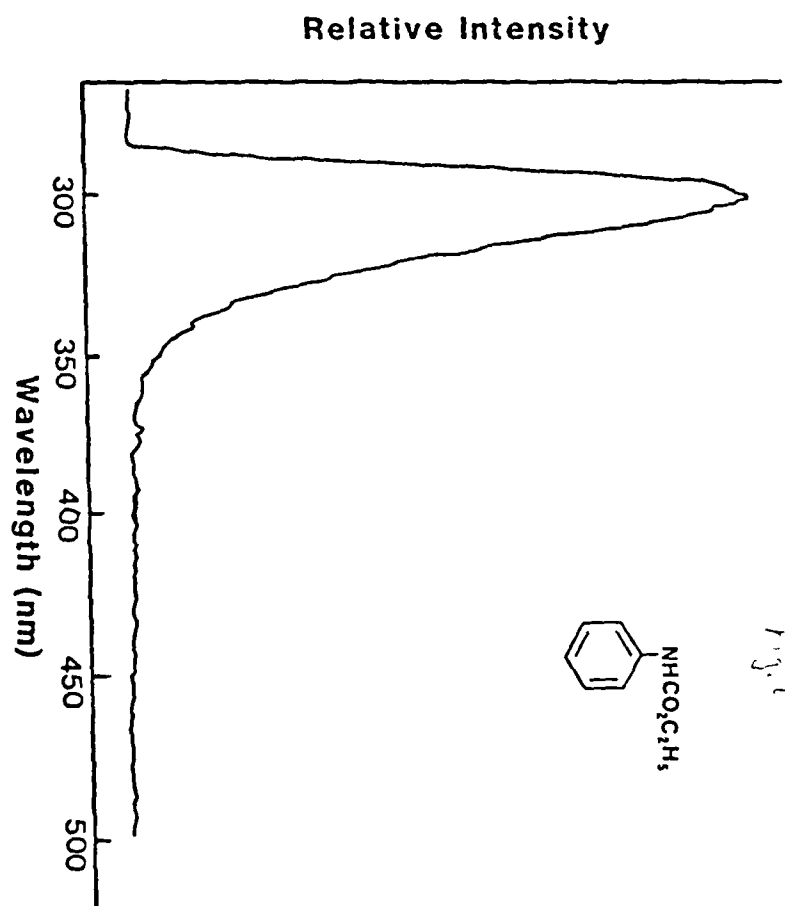
Table VIII
Fluorescence spectra^a for photolyzed solutions^b of polyurethanes

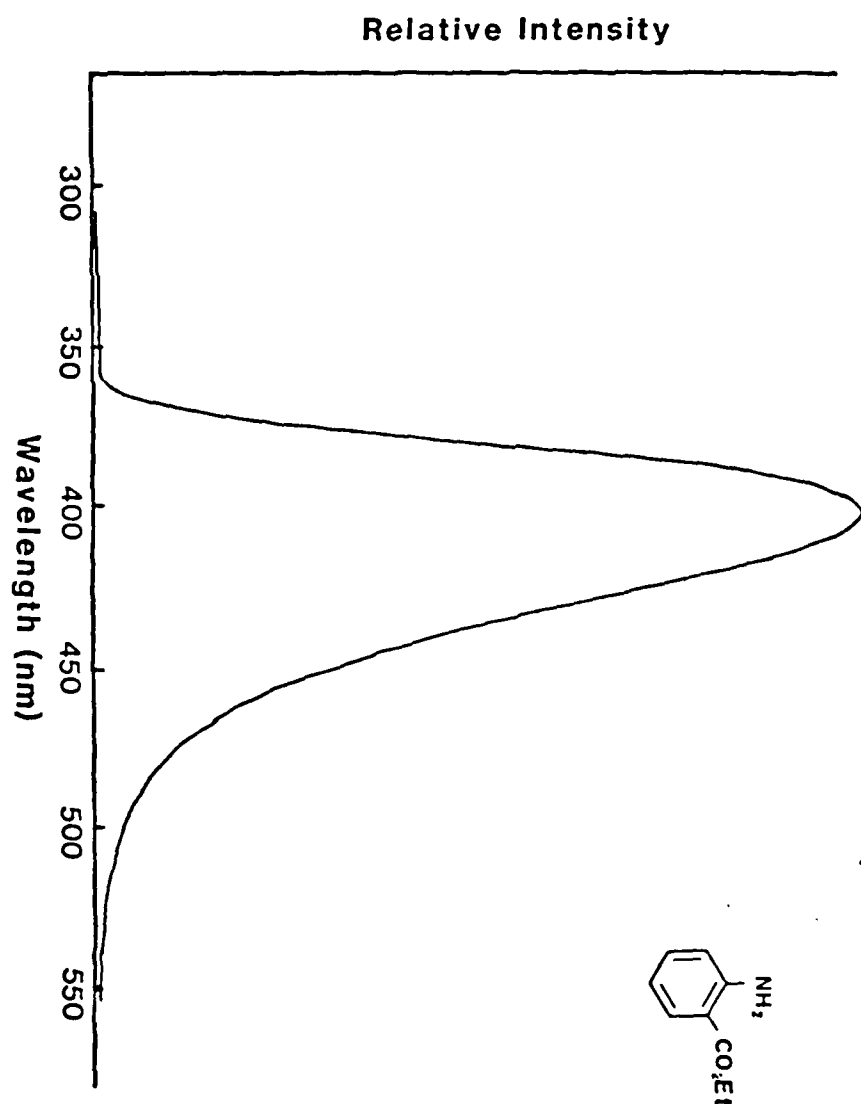
Polyurethane (Structural Unit)	Emission Maxima (nm)
2,4-TDI (1,10-decanediol)	330,425
2,6-TDI (1,10-decanediol)	340,410
MDI (1,10-decanediol)	340,420
PPDI (2,2'-oxydiethanol)	336,445
S-MDI (1,10-decanediol)	—, —

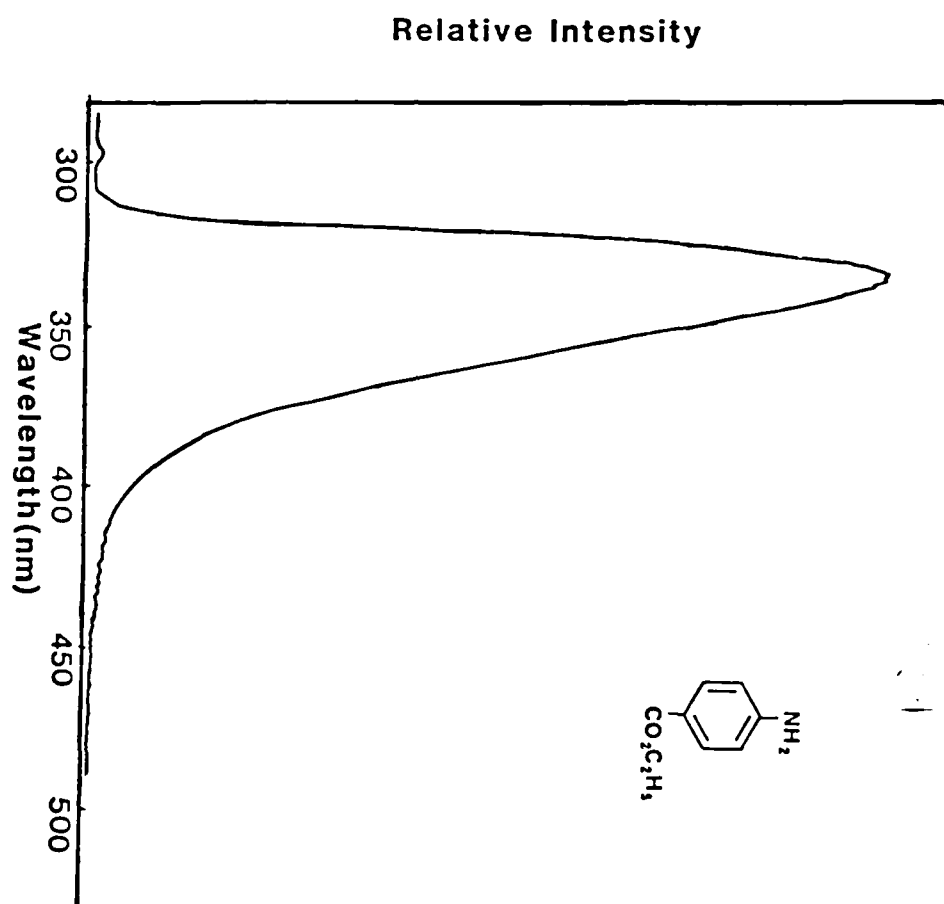
^a280 nm excitation; 5×10^{-4} g/ml in DMF

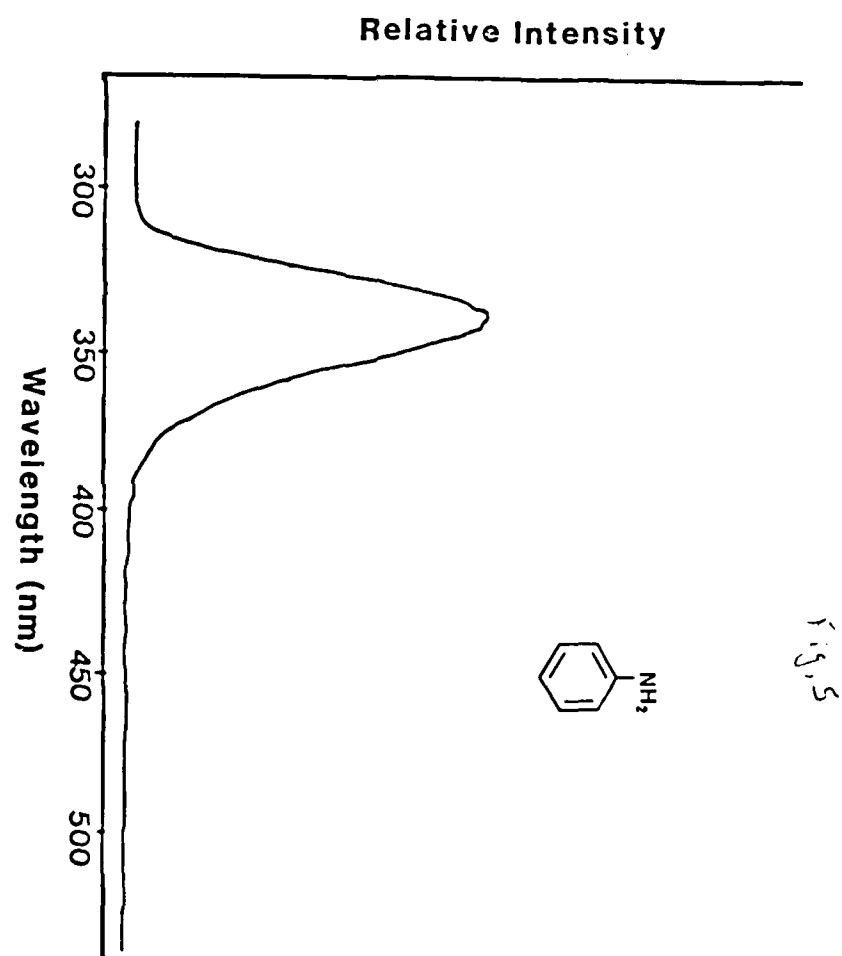
^bnitrogen atmosphere, 300 nm Rayonet Reactor, 2 hours

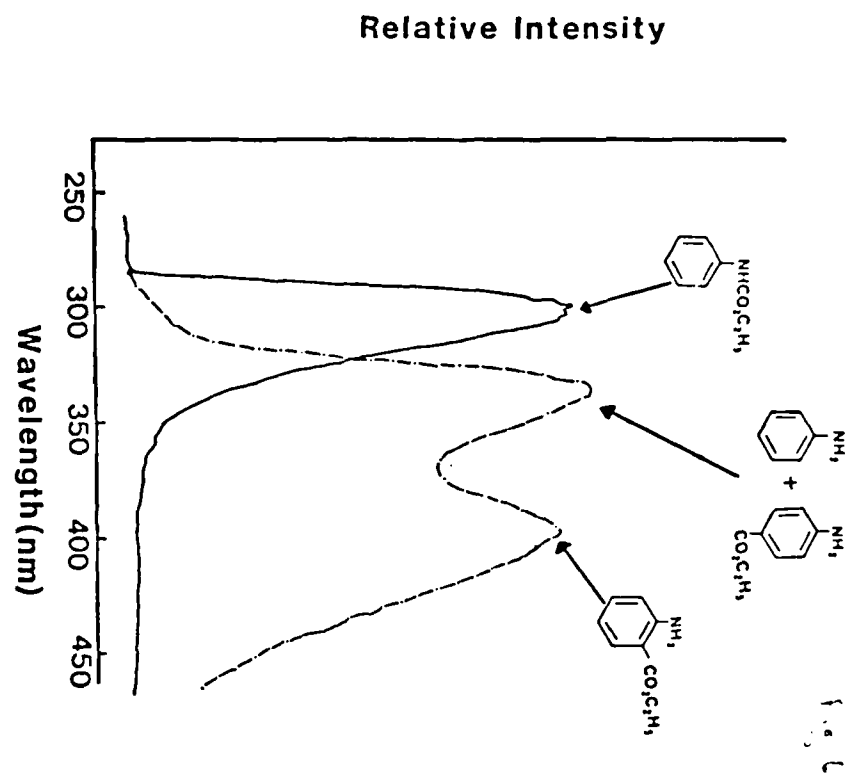


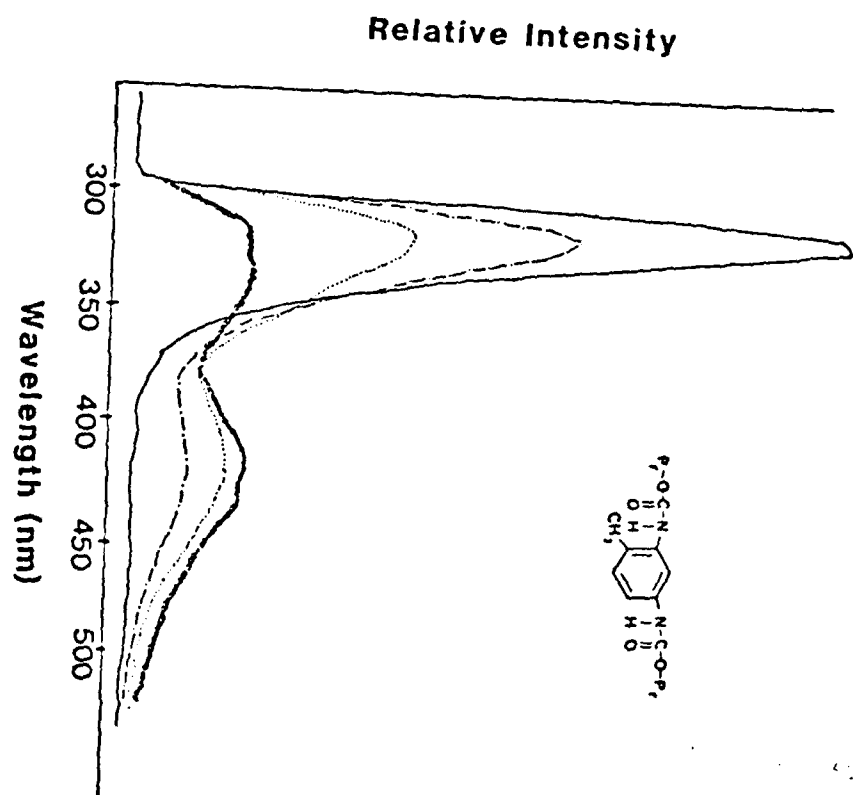


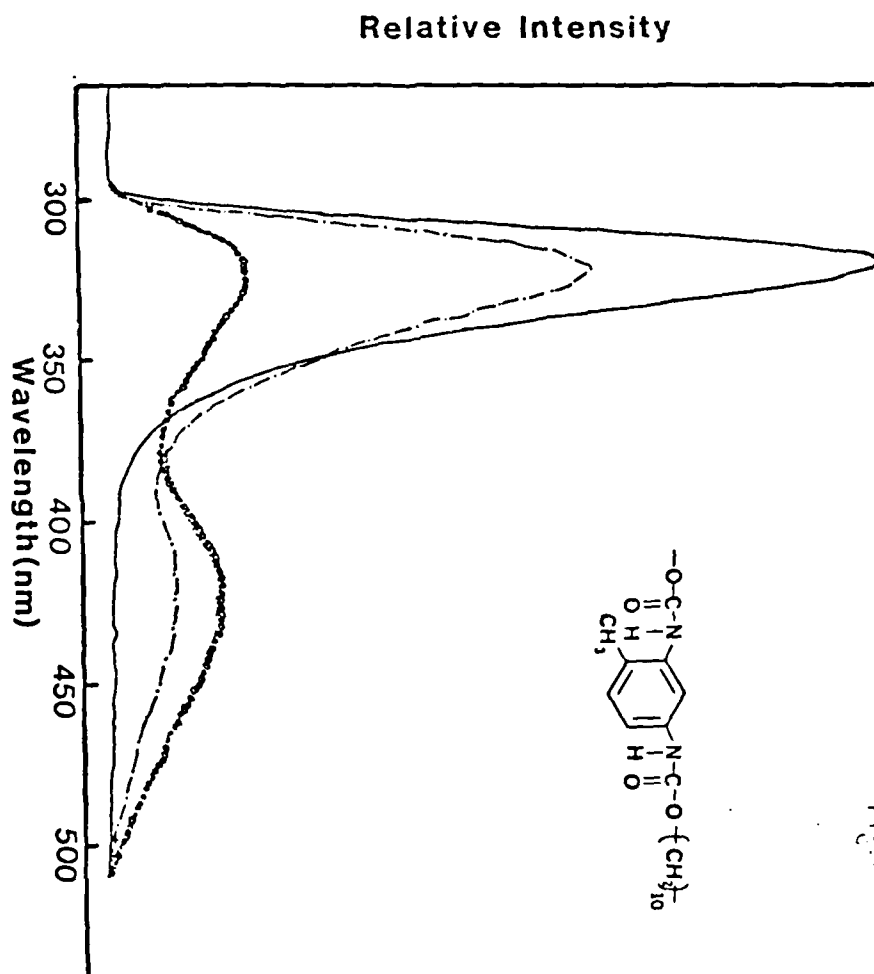


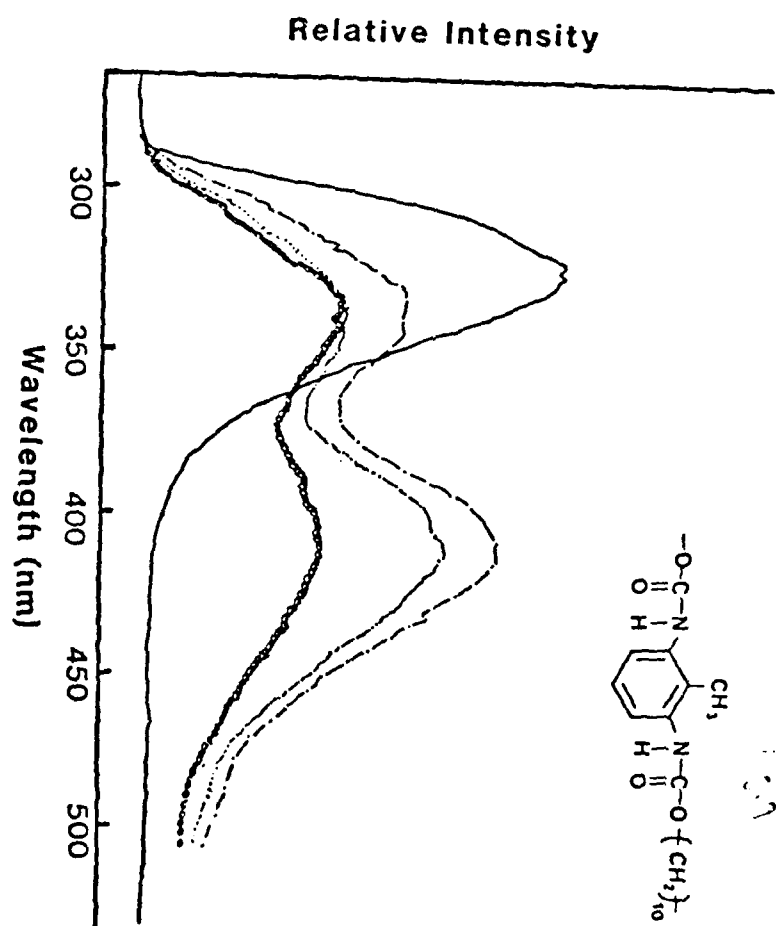


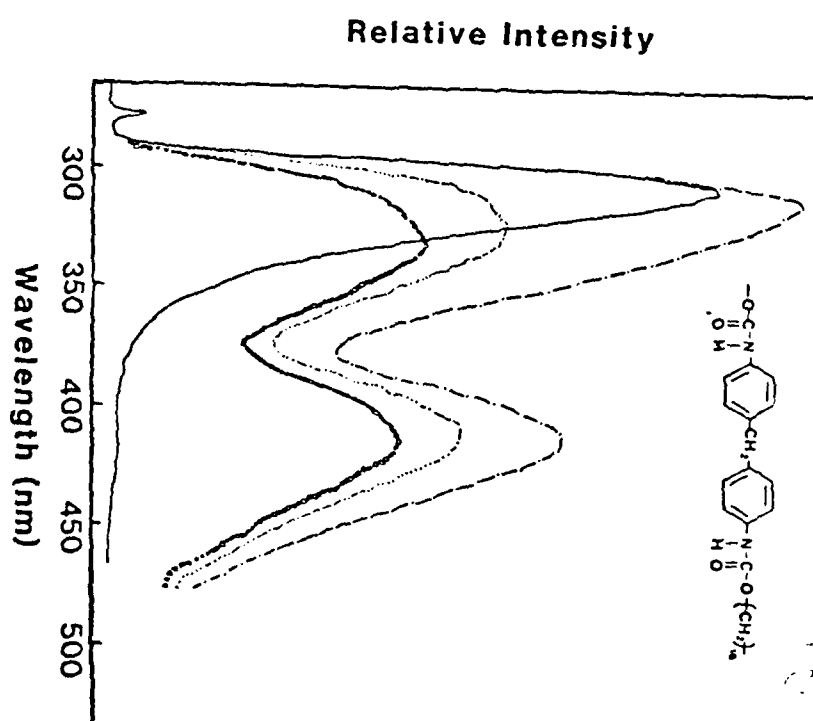












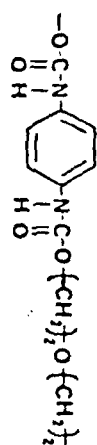
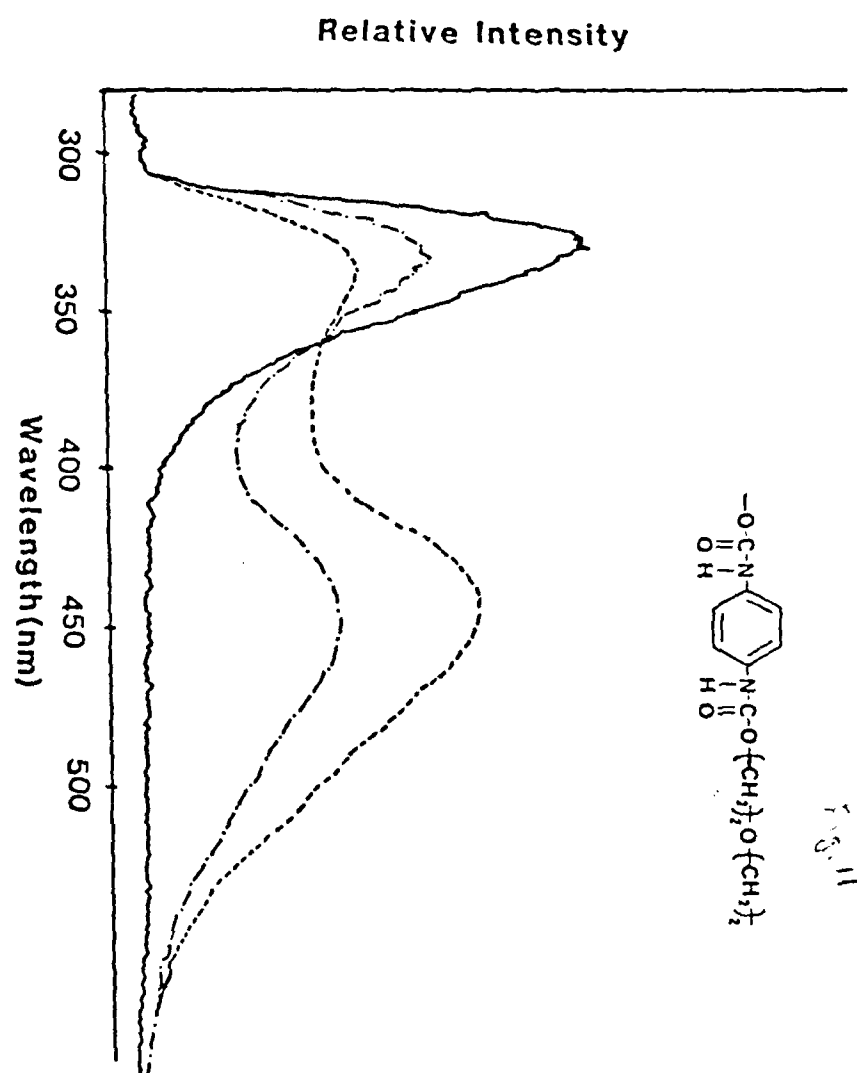
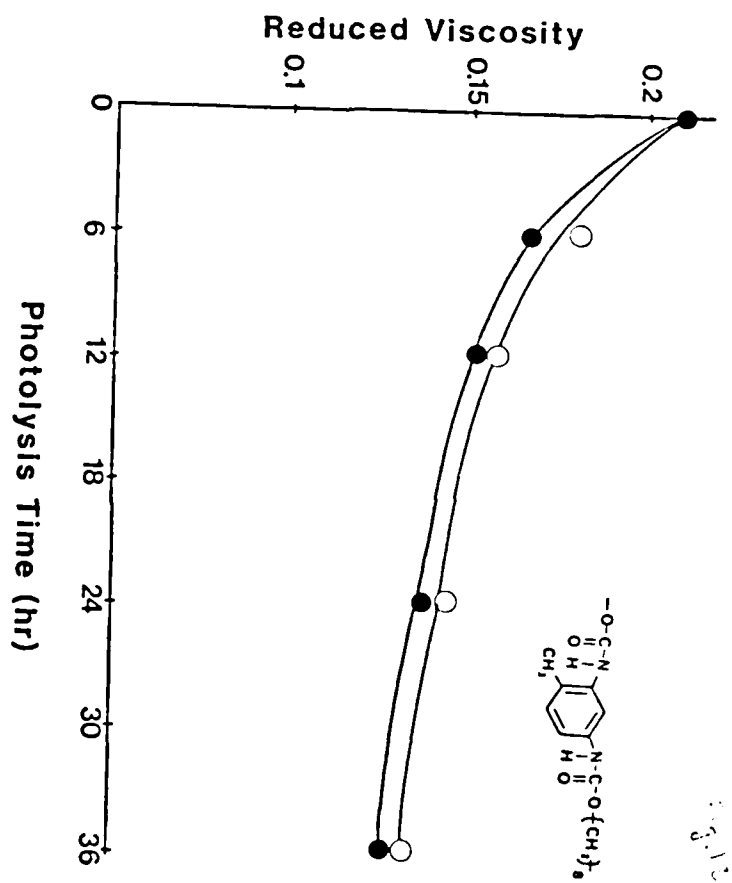
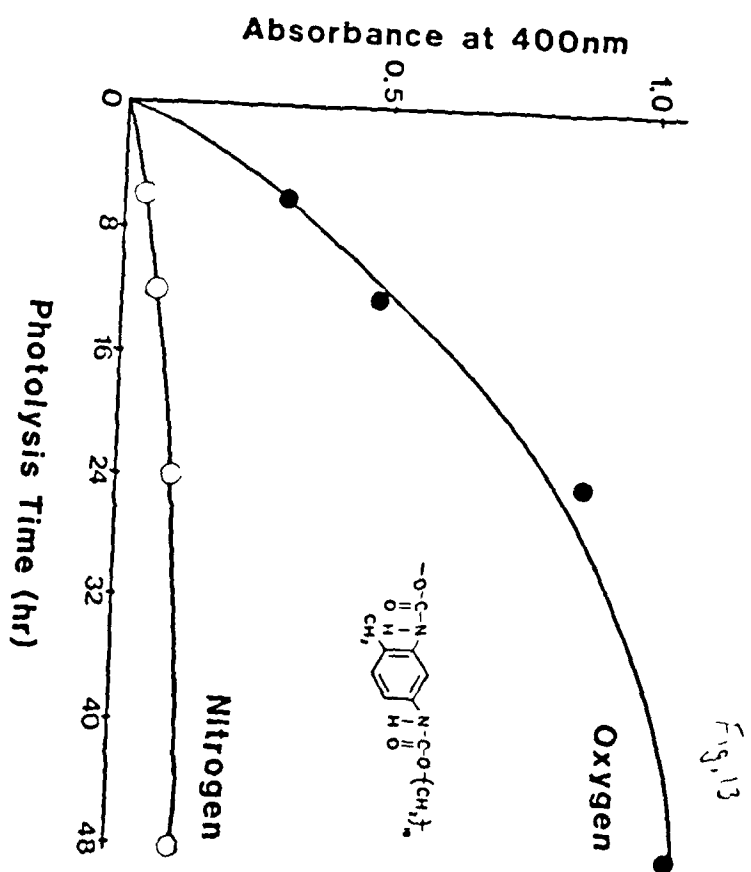


Fig. 11





END

DT/C

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