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THE EFFECT OF CRYSTALLINITY AND FLEXIBILITY ON THE
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The Effect of Crystallinity and Flexibility on
the Photodegradation of Polyurethanes

by

C. E. Hoyle and K. J. Kim

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Department of Polymer Science
University of Southern Mississippi
Southern Station Box 10076
Hattiesburg, MS 39406-0076

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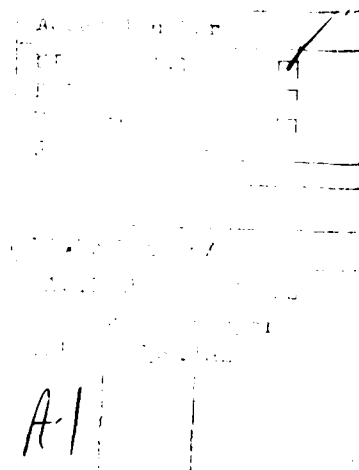
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The Effect of Crystallinity and
Flexibility on the Photodegradation of Polyurethanes

by

Charles E. Hoyle and Kyu-Jun Kim
University of Southern Mississippi
Department of Polymer Science
Southern Station Box 10076
Hattiesburg, MS 39406



Synopsis

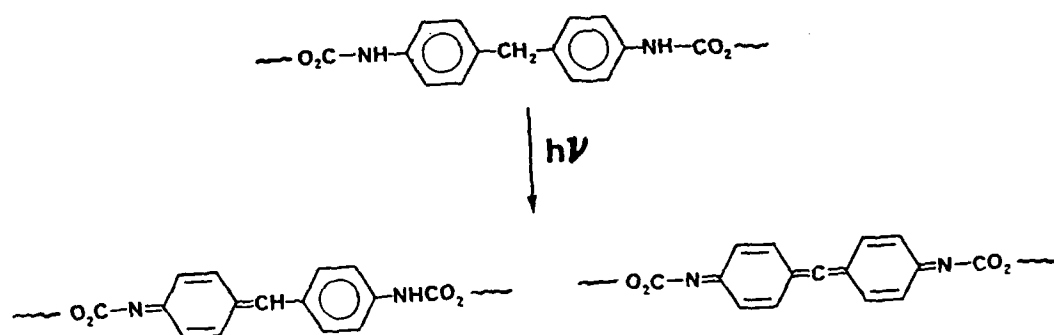
Using fluorescence spectroscopy and gel content measurements, the photolysis of simple polyurethanes based on methylene 4,4'-diphenyl-diisocyanate (MDI) is shown to depend on both the flexibility and crystallinity of the polymer. Polyurethane films based on MDI and 1,2-dodecanediol (MDI-12) can be either annealed or quenched to yield a semi-crystalline (as measured by DSC and X-ray diffraction) or amorphous film, respectively. In the case of the quenched (amorphous) film, photolysis yields an ortho photo-fries product whereas the annealed (semi-crystalline) film does not. Similarly, for a given photolysis time the annealed film generates a lower extent of cross-linked gel. In addition, photolysis of amorphous polyurethane films derived from MDI and ethylene oxide oligomers shows that for relatively inflexible polymers with only three ethylene oxide segments, little or no ortho photo-Fries rearrangement products are generated upon photolysis. In contrast, photolysis of more flexible polyurethane films with approximately thirteen ethylene linkages yields the ortho photo-Fries product. Apparently, for aromatic diisocyanate based polyurethanes, the extent and mechanism of degradation is directly dependent on the crystallinity and main-chain flexibility of the polymer.

Introduction

Since their first appearance in the 1930's, the use of aromatic diisocyanate based polyurethanes has rapidly accelerated due to their excellent physical properties. Despite their widespread use, conventional polyurethanes based on aromatic diisocyanates such as methylene 4,4'-diphenyldiisocyanate (MDI) and toluene diisocyanate (TDI--mixture of 2,4 toluene diisocyanate and 2,6-toluene diisocyanate) rapidly decompose upon exposure to ultraviolet light (1,2). This, of course, severely limits their use in situations which require even moderate exposure to sunlight. As a consequence, considerable attention has been given over the past two decades to the study of the photodegradation process of aromatic diisocyanate based polyurethanes (3-14). Despite this level of activity, the mechanism of photodegradation of aromatic polyurethanes is still not clearly understood.

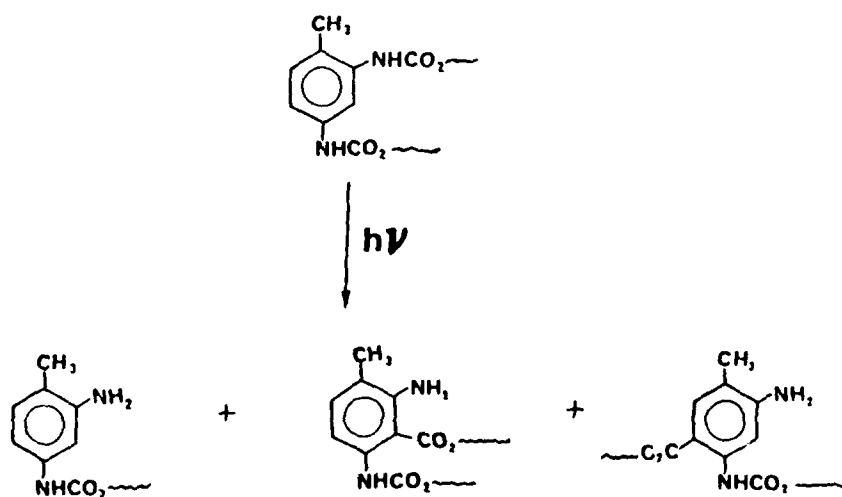
In pioneering investigations of the photodegradation of MDI and TDI based polyurethanes, Schollenberger and coworkers (4-7) and Nevskii, Tarakanov, and coworkers (8-12) both postulated the formation of mono- and diquinone imide products (Scheme I).

Scheme I



Based on model compound studies, Beachell and Chang (14) concluded that both MDI and TDI based polyurethanes photodegrade in part by a photo-Fries rearrangement process (Scheme II).

Scheme II



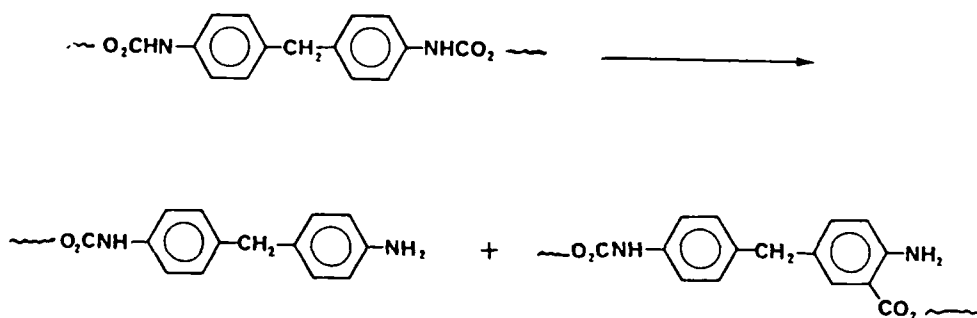
By taking into account the effect of excitation wavelength, Gardette and Lemaire (15) recently postulated that the photolysis of MDI based polyurethanes proceeds by two entirely unrelated processes (Scheme III).

Scheme III

a) $h\nu > 340\text{nm}$



b) $h\nu < 340\text{nm}$



One yields the quinone-imide products proposed by Nevskii (8-12) and Schollenberger (4-7) and is activated when wavelengths of light above 340 nm are used for photolysis (Scheme III--part a). The second process leads to the formation of photo-Fries rearrangement type products and unsubstituted arylamine cleavage products in the primary photochemical process (Scheme III--part b). It occurs only when wavelengths of light below 340 nm are used for photolysis.

Upon reviewing the literature to date for photolysis of aromatic polyurethanes (those based on aromatic diisocyanates and appropriate small molecule and/or oligomeric polyols), it is obvious that little or no attention is given to the role played by the polyurethane matrix on the photodegradation process, i.e., how does polymer crystallinity and chain flexibility affect the decomposition. This point is by no means trivial since all polyurethanes do not exist in the same physical state. Thus, it may be that generalizations projected from small molecule model compound studies or studies of a single polyurethane in a particular morphological or crystalline state cannot be made with great confidence.

In the present investigation, the effect of polymer crystallinity and flexibility on the photolysis process, as revealed by both fluorescence and percent gel formation, will be measured. For the crystallinity investigation, a polyurethane based on MDI and 1,12-dodecanediol is used. It is semi-crystalline when cast and annealed; however, by quenching the film an amorphous polymer is obtained. This affords the opportunity to measure the

effect of crystallinity on the photodegradation process using a single polymer. For the flexibility investigation, two MDI based polyurethanes with different flexibility built into the aliphatic portion of the polyurethanes were chosen for photolysis. This provides a complimentary investigation to the crystallinity study.

Experimental

Methylene-4,4'-diphenyl-diisocyanate (MDI-Mobay) and 1,12-dodecanediol (Aldrich) were recrystallized from cyclohexane and 1,2-dichloroethane, respectively. Triethylene glycol (Aldrich) was distilled and dried before polymerization. Polyethylene glycol 600 (Aldrich--average molecular weight 600) was used as received.

The polyurethanes were prepared by a solution polymerization in DMSO under a nitrogen stream (18). In the case of MDI-3E (MDI + triethylene glycol) and MDI-13.2E (MDI + polyethylene glycol 600) preparations, dibutyltin dilaurate (Polysciences) (2 wt% to reagents) was used as a catalyst. The intrinsic viscosities of the resulting polymers were measured with a Ubbelohde Viscometer in DMF at 30°C (MDI-12; 0.19 dl/g; MDI-3E; 0.23 dl/g; MDI-13.2E; 0.30 dl/g).

To obtain semi-crystalline and amorphous polyurethane films (MDI-12), 0.1g of polymer was dissolved in 10 ml DMF by heating. The solution was placed in an aluminum dish (diameter 5 cm). Annealing was accomplished by evaporation of DMF while heating at 160°C for 30 minutes in a vacuum oven. Quenching of the

polyurethane film was accomplished by raising the temperature of the semi-crystalline film above the melting temperature followed by rapid cooling at room temperature.

The polyurethane films were photolyzed at 280 nm with a Xenon lamp/monochromator combination for the fluorescence analysis and at 300 nm (broad band) in a Rayonet Reactor for the gel formation study. The photolyzed polyurethane films for the gel study were dissolved in hot DMF and the insoluble gel was collected, dried in a vacuum oven, and weighed. The polyurethane solutions were irradiated in a Rayonet Reactor model RPR-100 with 300 nm (broad band) lamps.

The steady state fluorescence spectra were recorded using a Perkin Elmer fluorescence spectrophotometer model 650-10S. The wide-angle X-ray diffraction measurements were made with a Phillips PW-1720 generator (Cu target). The thermal transitions of the polymers were recorded on a Dupont 910 differential scanning calorimeter (DSC). Fluorescence decay data were obtained on a single-photon-counting apparatus from Photochemical Research Associates (PRA).

Results

In order to determine the effect of polymer crystallinity and flexibility on the photolytic degradation of MDI based polyurethanes, two sets of studies are described employing different polymers based on MDI. The results presented are representative of our investigation of aromatic diisocyanate based

polyurethanes in general, and reflect the importance of polymer structure on the photolysis process of polyurethanes.

Crystallinity Effect on Photolysis of MDI Based Polyurethane. The MDI-1,12--dodecanediol (MDI-12) polyurethane was cast as a thin film ($\sim 50 \mu$) on an aluminum dish (see experimental). The film thus formed could either be annealed (160°C , 0.5 hours) to increase its crystallinity or quenched to give a totally amorphous polymer film. The latter was accomplished by heating the film well above its crystalline melting point ($\sim 180^\circ \text{C}$) and quickly quenching at room temperature.

Before presenting the photolysis results of the quenched (amorphous) and annealed (semi-crystalline) films their physical states are considered. X-ray diffraction patterns for both the annealed and quenched films are shown in Figures 1 and 2, respectively. The annealed film (Figure 1) is characterized by a sharp-ring diffraction pattern while the quenched film (Figure 2) shows only a diffuse pattern characteristic of an amorphous polymer. DSC scans for the quenched and annealed MDI-12 films are shown in Figure 3. The quenched sample, upon heating in the DSC at a scan rate of 20°C per minute, is characterized by an exotherm ($T_{\text{ex}} = 90^\circ \text{C}$, $\Delta H_{\text{ex}} = 7.1 \text{ cal/g}$) resulting from rapid rearrangement into a physical state with short-range ordering followed by a subsequent endotherm ($T_{\text{end1}} = 148^\circ \text{C}$; $\Delta H_{\text{end1}} = 6.2 \text{ cal/g}$) corresponding to loss of short range ordering. A second smaller endotherm at 178°C ($\Delta H_{\text{end2}} = 1.0 \text{ cal/g}$) is probably due to melting of a particular microcrystalline state of MDI-12. This microcrystalline state most likely results from efficient packing

characterized by a substantially higher melting point (178°C as opposed to 148°C). The appearance of the small exotherm at 178°C probably reflects a crystallization/annealing process during the DSC run. This is supported by the fact that the heat evolved during the DSC run at 90°C ($\Delta H_{\text{ex}} = 7.1 \text{ cal/g}$) is offset by the endotherm resulting from loss of the short-range ordered state ($\Delta H_{\text{end1}} = 6.2 \text{ cal/g}$) plus the endotherm ($\Delta H_{\text{end2}} = 1.0 \text{ cal/g}$) of the microcrystalline state at 178°C. This confirms that the quenched sample, as indicated by the X-ray diffraction pattern, is primarily amorphous. It should be noted that the assignments of the exotherm peak (90°C) and the two endotherm peaks (148°C and 178°C) are tentative and based on interpretation of literature reference 11. Exact assignment of these peaks is, for our purposes, not necessary since our intention is simply to confirm the results of the X-ray diffraction measurements and not to define the complicated crystalline morphology of polyurethanes. The DSC scan of the annealed sample of MDI-12, in contrast to the quenched amorphous film, is characterized by a single large endotherm ($\Delta H = 10.3 \text{ cal/g}$) with a maximum at 178°C. This endotherm is most likely due to melting of the crystalline structure in the film generated by the annealing process. The 178°C melting point for the annealed film indicates that the crystallinity in this state is compact and probably represents a true melting point.

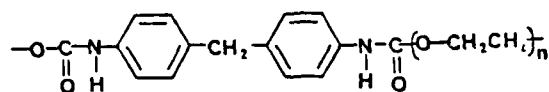
Having explored the physical state of the quenched (amorphous) and the annealed (semi-crystalline) film of MDI-12, we turn to the photolysis of each. Figure 4 shows the emission spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of the semi-crystalline (annealed) MDI-12

film before and after photolysis for 25 minutes with the 280 nm output of a Xenon lamp/monochromator system. It is evident that photolysis (Figure 4) of the annealed film yields no new emission above 400 nm. In contrast, photolysis of the amorphous (quenched) film under identical conditions is characterized by a new fluorescence peak (Figure 5) with emission maximum above 400 nm. It is well known that ortho amino substituted benzoates have a characteristic red shifted emission with maxima between 405 nm and 440 nm (17). Indeed, a detailed fluorescence decay analysis of the photolyzed film at specific wavelengths from 340 nm to 460 nm indicates the presence of two major components with lifetimes of 10.8nsec and 2.8nsec. These components can tentatively be assigned to emission from an ortho photo-Fries product (10.8nsec) and an unsubstituted arylamine cleavage product (2.8nsec) by comparison with the fluorescence lifetimes of model compounds, e.g., the fluorescence lifetime of propyl 2-amino-5-methyl benzoate is 11.1nsec and the lifetime for both p-toluidine and 4,4'-methylenedianiline is 2.6nsec in DMF. The mechanism proposed by Gardette and Lemaire (15) for photolysis of aromatic polyurethanes shown in Scheme III--part b adequately accounts for our present results. This scheme also accounts for the photo-Fries and arylamine product formation noted in an earlier report (17) for photolysis of MDI based polyurethanes in DMF. The results in Figure 5 lead to the conclusion that the crystalline content of the polyurethane matrix is an important factor in controlling the photolysis process.

In another set of experiments, the extent of the photodegradation of MDI-12, as followed by formation of

crosslinked gel, is larger in the case of the quenched (amorphous) film. This is illustrated by a plot of percent gel as a function of photolysis time (Figure 6). It is likely that the crystallinity of the polyurethane provides a medium with reduced flexibility and/or volume for the photoinitiated rearrangement processes and subsequent gel formation to take place. The results in Figure 6 are consistent with the fluorescence spectral changes and represent a concept which is crucial to the photodegradation process of MDI based polyurethanes.

Flexibility Effect on Photolysis of MDI Based Polyurethanes. In the last section, it was clearly demonstrated that the photolysis of an MDI based polyurethane (exemplified by MDI-12) is directly dependent on the crystallinity of the polymer film. In this section, the effect of polymer flexibility on the photodegradation is considered. For this study, two polymers with different degrees of main chain flexibility were prepared by reacting MDI with ethylene oxide oligomers having different numbers of oxyethylene linkages. A general structure of the repeat unit for the two polyurethanes used in this investigation is shown below.



If $n = 3$, the polyurethane is designated MDI-3E and if $n = 13.2$ (average value) the polyurethane is MDI-13.2E.

Before presenting the results for photolysis of the films of each of these two polyurethanes, the solution photolysis was conducted to provide a basis for analysis. In Figures 7 and 8, the fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of MDI-3E and MDI-13.2E before and after photolysis (Rayonet Reactor, 300 nm lamps, 2 hours) in an air saturated DMF solution (0.1g/l) are shown. Once again a detailed fluorescence decay analysis from 340 nm to 460 nm reveals two major components with lifetimes of 10.8nsec and 2.6nsec. As before, these species are tentatively assigned to the ortho photo-Fries rearrangement product (10.8nsec) and the unsubstituted arylamine cleavage product (2.6nsec) by comparison with model compounds.

In order to understand the effect of polymer backbone flexibility on the photolysis of our representative polyurethanes, each was cast as a film ($\sim 40 \mu$) from a dilute DMF solution ($1.6 \times 10^{-2} \text{ g/ml}$) onto an aluminum dish. Both of the cast films were amorphous according to DSC and X-ray diffraction. Figures 9 and 10 show fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of the two cast polyurethane films (MDI-3E and MDI-13.2E) before and after photolysis at 280 nm with a Xenon lamp/monochromator combination. For the MDI-3E films, no new fluorescence above 400 nm could be detected after photolysis for 40 minutes. However, photolysis of the MDI-13.2E film resulted in a strong new emission above 400 nm with the long-lived component of the fluorescence decay being 10.8nsec, i.e., essentially equal to the lifetime of the ortho

photo-Fries product. These results can be attributed to the high degree of flexibility afforded to the MDI-13.2E film by the large number of ethylene oxide groups in the aliphatic ether portion of the polymer. The MDI-13.2E film behaves much as it did in solution yielding a high degree of rearrangement product in rather short photolysis times. In contrast to the MDI-13.2E films, the MDI-3E films are rather stiff with only three flexible ethylene oxide groups in the aliphatic ether portion of the polymer. Thus, photolysis of these films under identical (except for a slightly longer photolysis time) conditions to the photolysis of the MDI-13.2E film yields no new emission above 400 nm due to fluorescent product formation. It is concluded that the chain flexibility can indeed be an important factor in the photolysis of aromatic polyurethanes based on MDI.

Conclusions

In summary, this paper reports the effect of crystallinity and backbone chain flexibility on the photodegradation process of aromatic polyurethanes. In general the extent of degradation upon photolysis decreases with increasing polymer stiffness and crystallinity. Since the physical state of polyurethanes is dictated by such factors as structural composition and thermal history, it cannot be assumed that just because polyurethanes contain a common photochemically reactive component, i.e. the aryl carbamate moiety, they will degrade photochemically to the same extent or by the same process. Similar results to those obtained in

this paper for polyurethanes based on diisocyanates other than MDI will be reported in a future publication.

Acknowledgement

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Figure Captions

- Figure 1. Wide angle X-ray diffraction pattern of annealed (semi-crystalline) MDI-12 polyurethane film.
- Figure 2. Wide angle X-ray diffraction pattern of quenched (amorphous) MDI-12 polyurethane film.
- Figure 3. DSC scans (20°C per minute) for quenched (curve a) and annealed (curve b) MDI-12 polyurethane films.
- Figure 4. Fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of annealed MDI-12 polyurethane film before (curve a) and after (curve b x 1; curve c x 3) photolysis with Xenon lamp/monochromator system for 25 minutes.
- Figure 5. Fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of quenched MDI-12 polyurethane film before (curve a) and after (curve b x 1; curve c x 3) photolysis with Xenon lamp/monochromator system for 20 minutes.
- Figure 6. Gel percent for quenched and annealed MDI-12 polyurethane films as a function of photolysis time with 300 nm lamps in a Rayonet Reactor.
- Figure 7. Fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of MDI-3E polyurethane in DMF before (curve a) and after (curve b) photolysis with 300 nm lamps in a Rayonet Reactor for 120 minutes.
- Figure 8. Fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of MDI-13.2E polyurethane in DMF before (curve a) and after (curve b) photolysis with 300 nm lamps in a Rayonet Reactor for 120 minutes.
- Figure 9. Fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of MDI-3E polyurethane film before (curve a) and after (curve b) photolysis with Xenon lamp/monochromator system for 40 minutes.
- Figure 10. Fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of MDI-13.2E polyurethane film before (curve a) and after (curve b) photolysis with Xenon lamp/monochromator system for 25 minutes.

Fig. 1

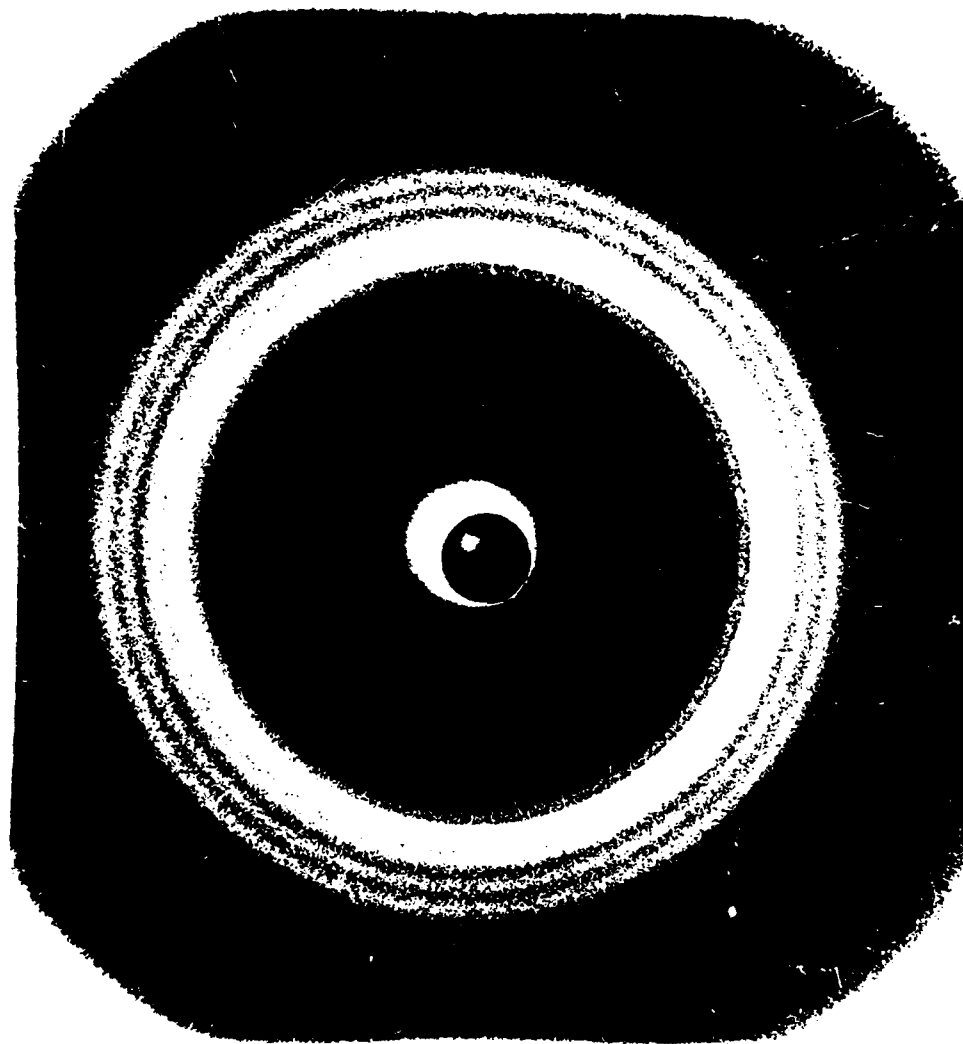


Fig. 2

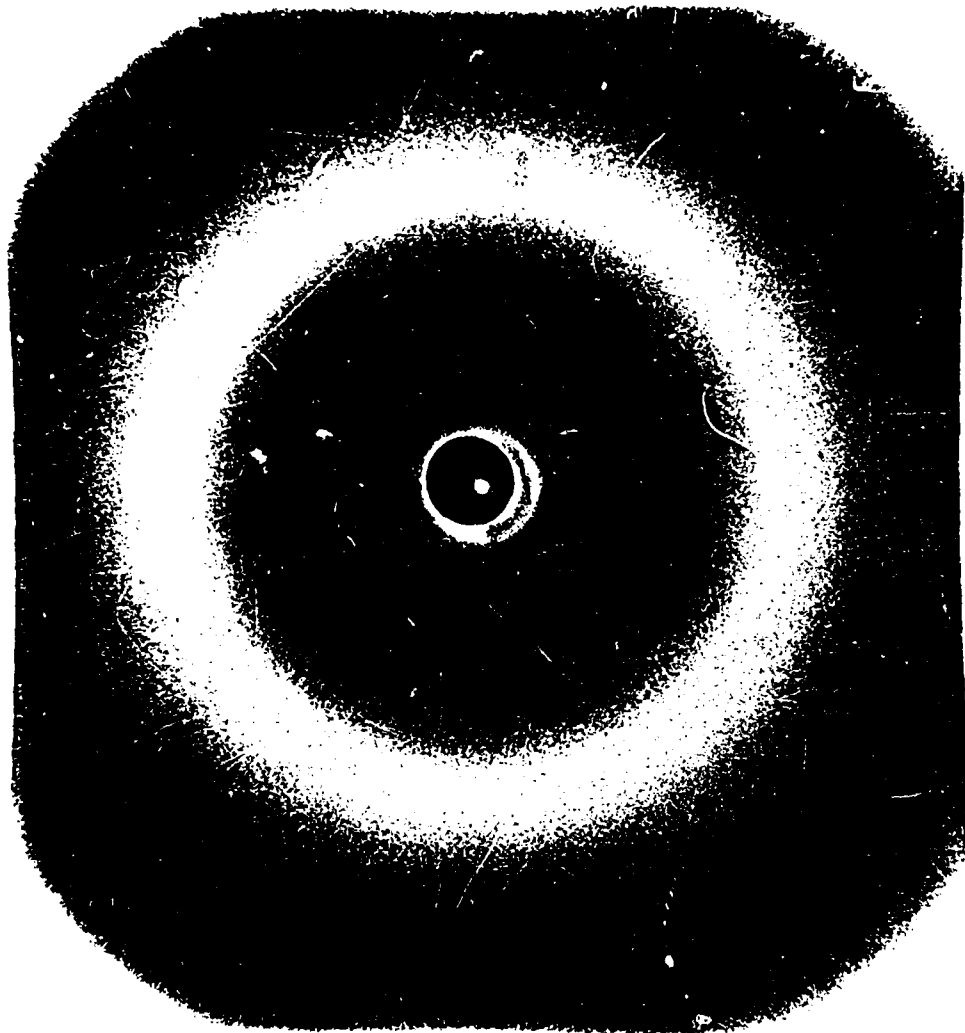


Fig. 3

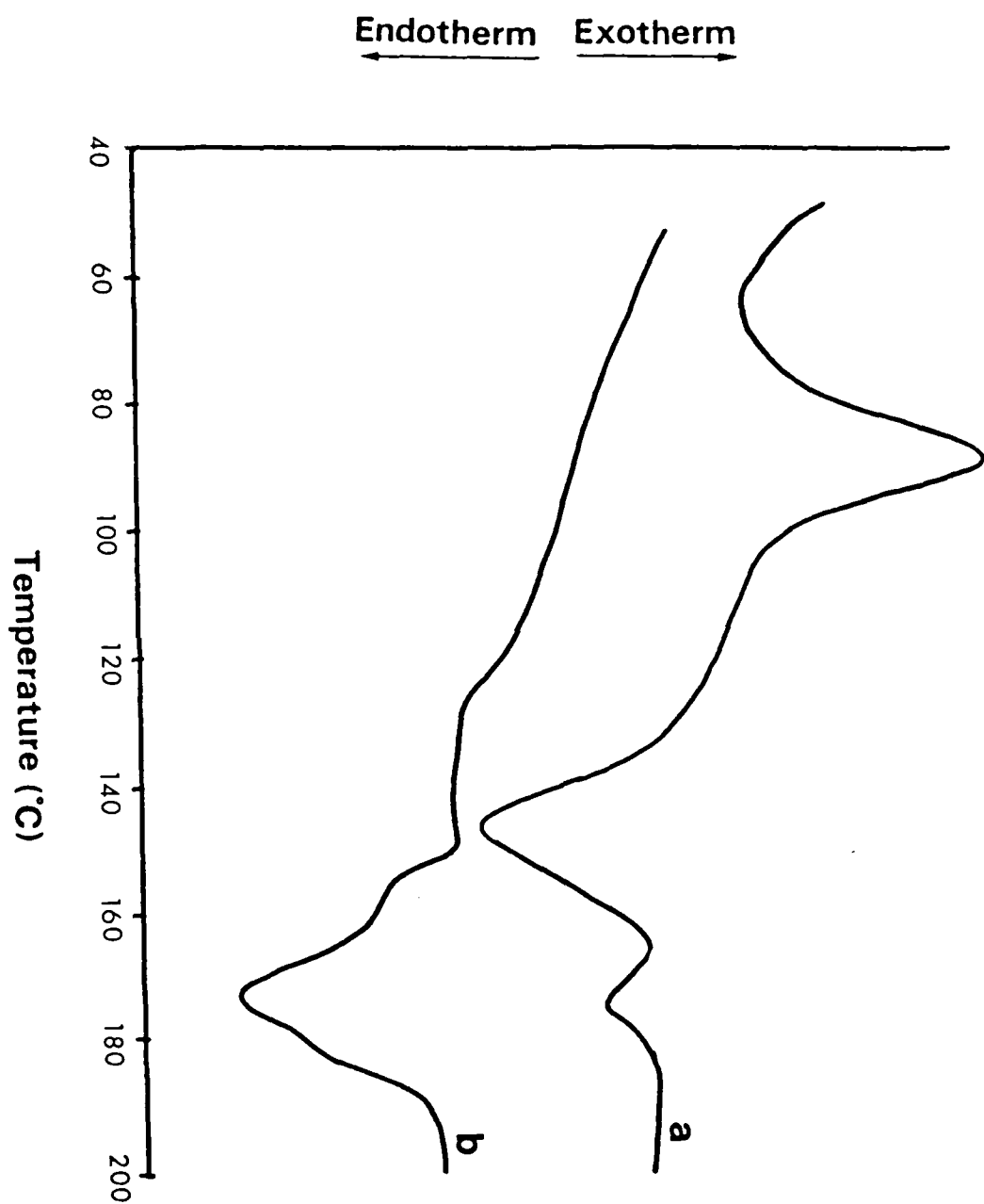


Fig. 4

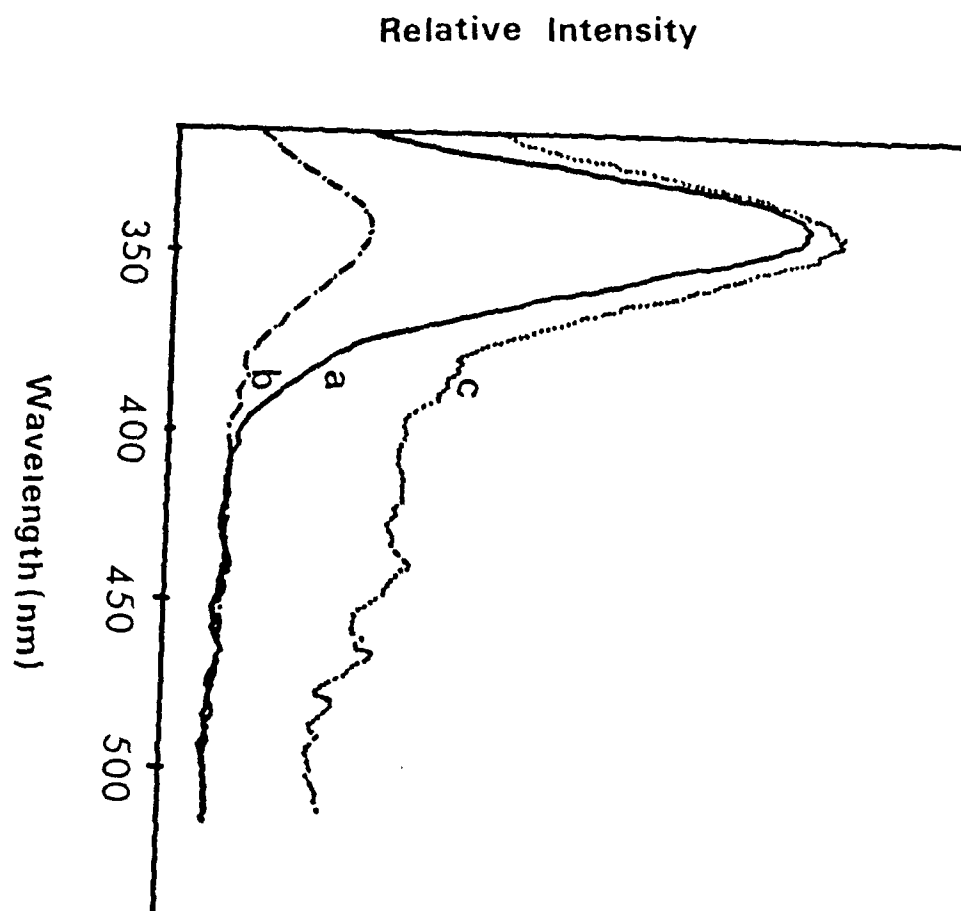


Fig. 5

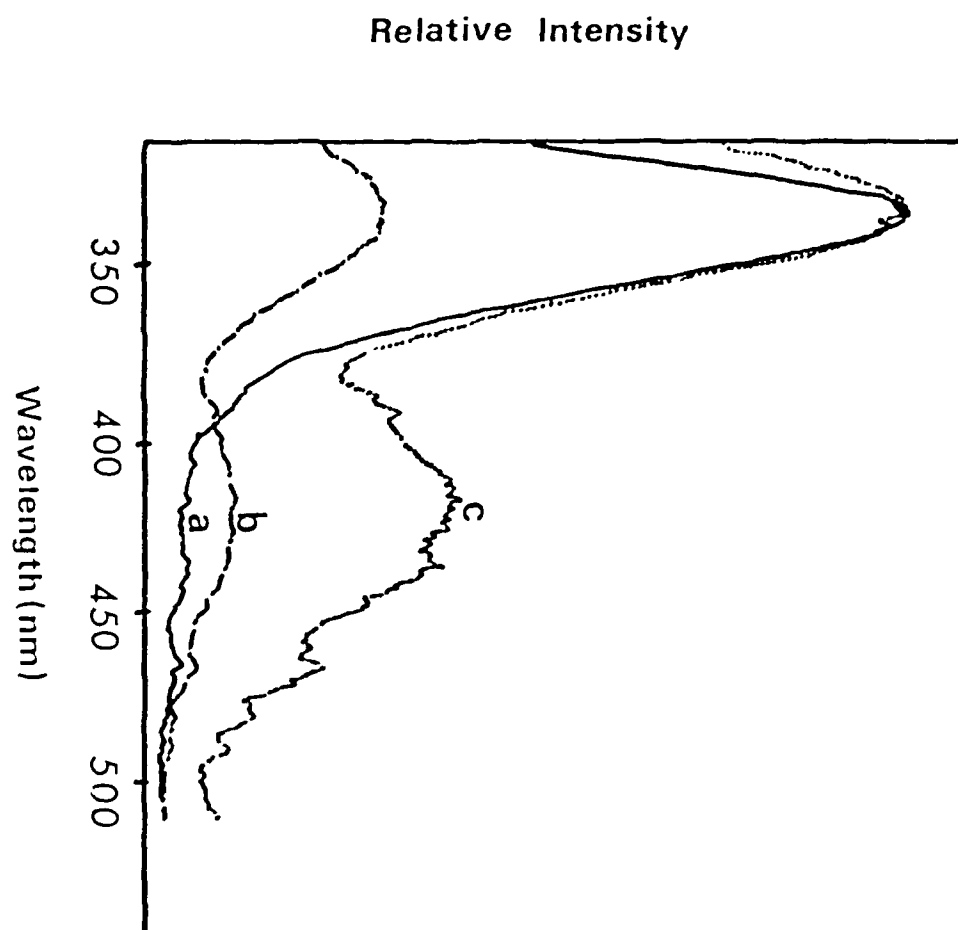


Fig. 6

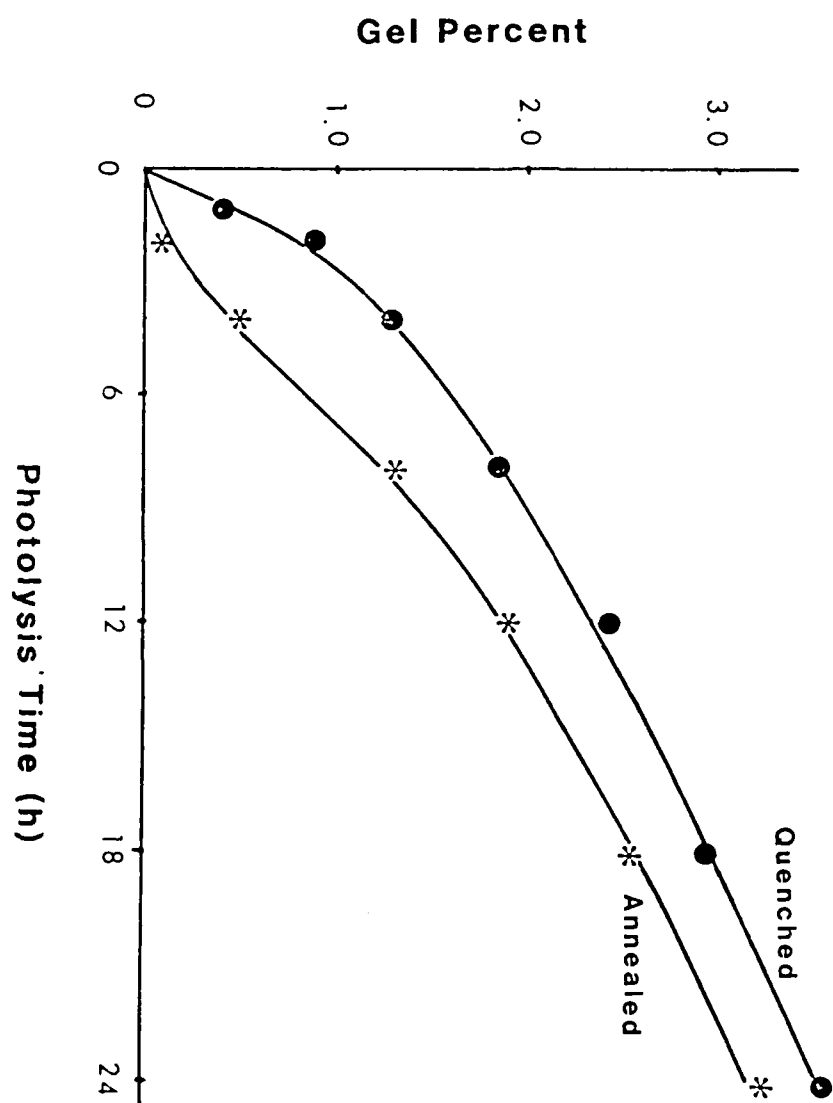


Fig. 7

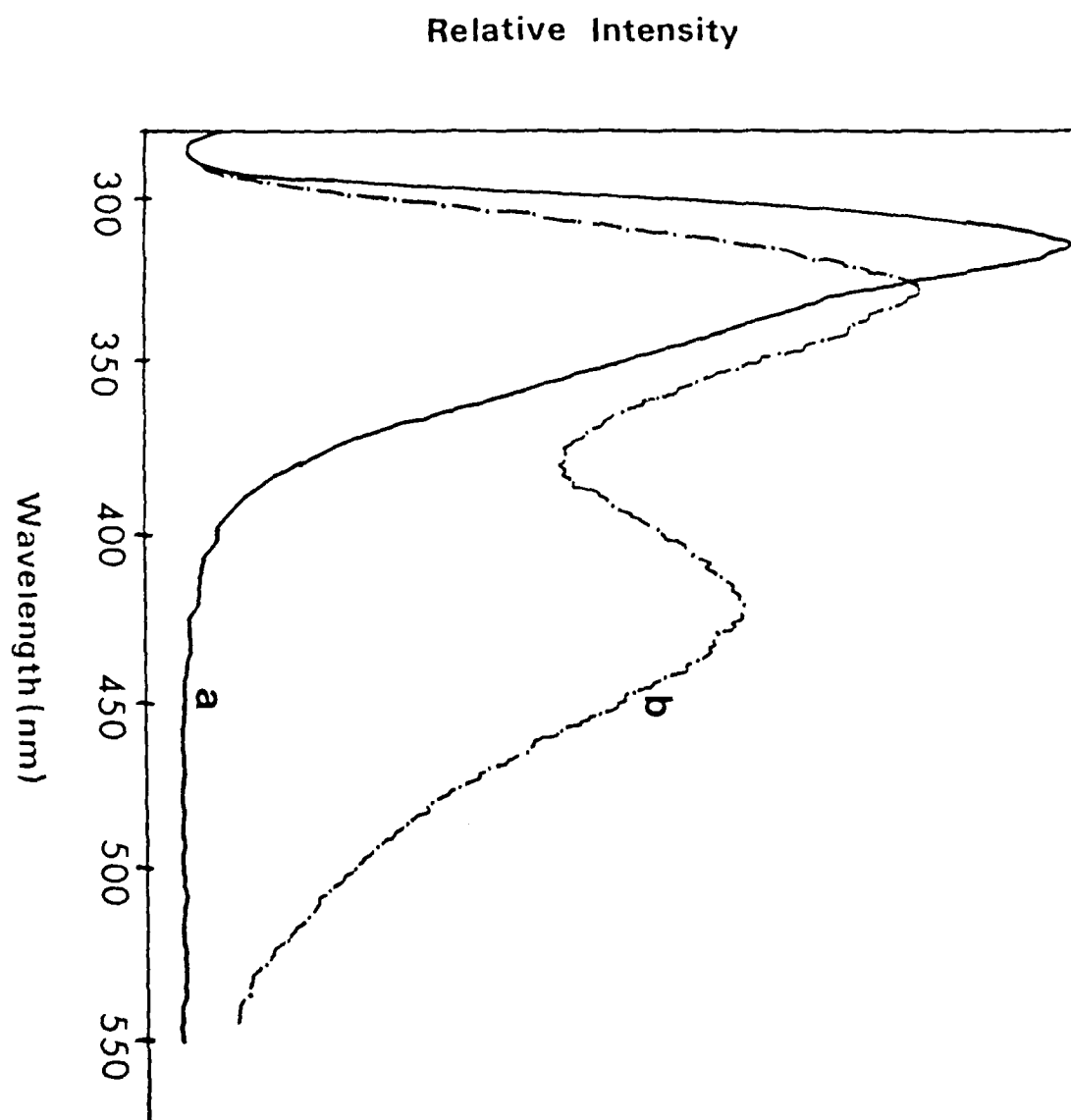


Fig. 8

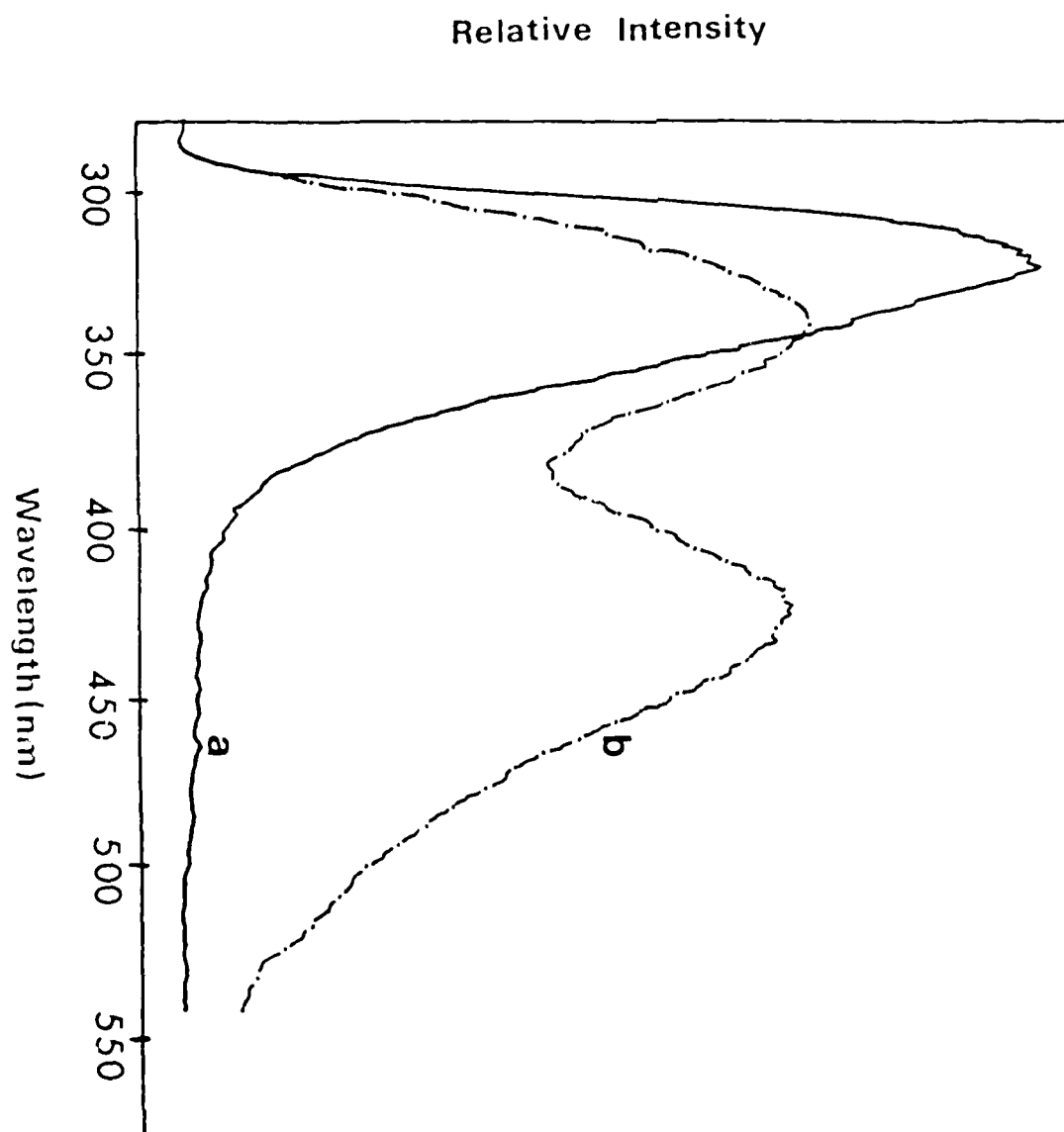


Fig. 9

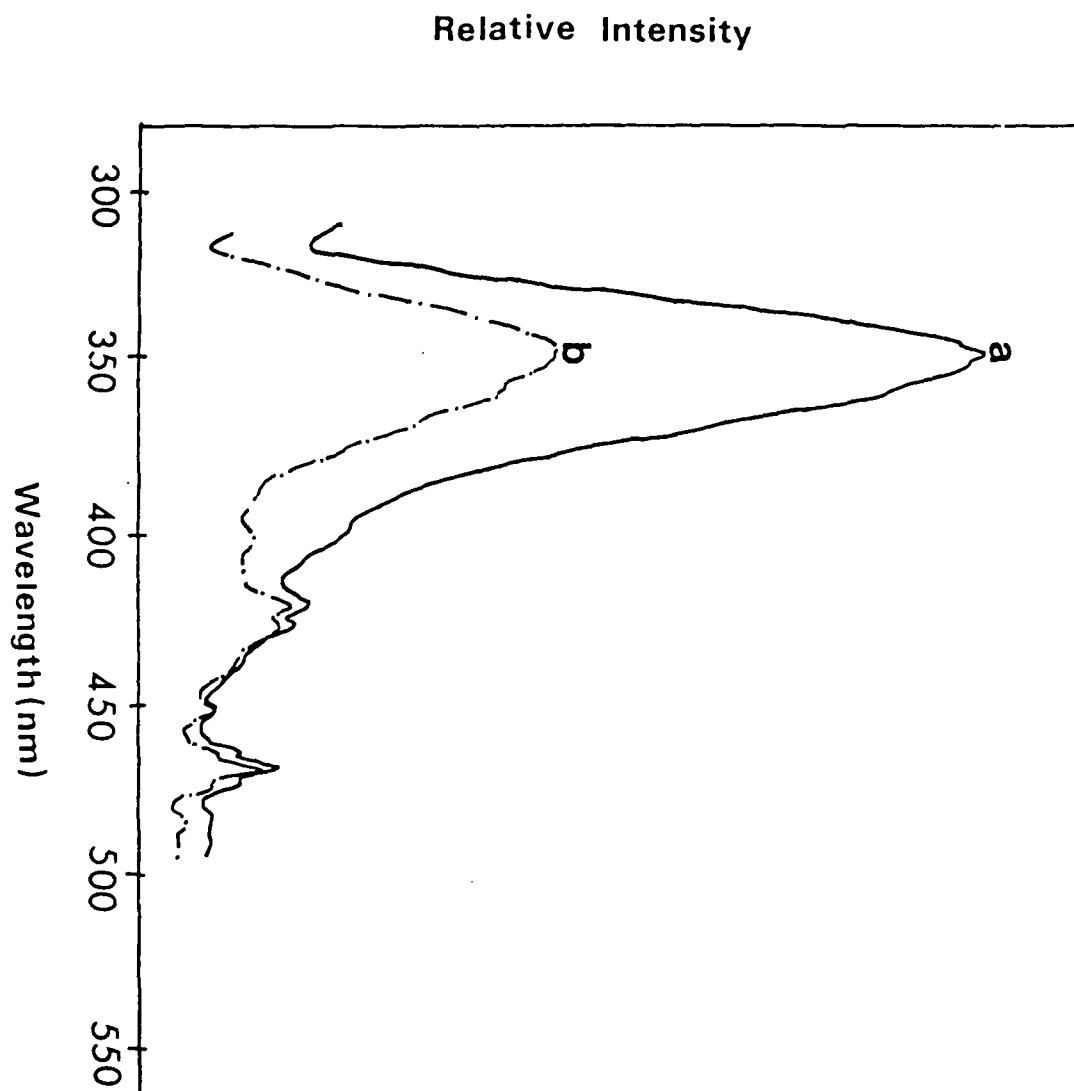
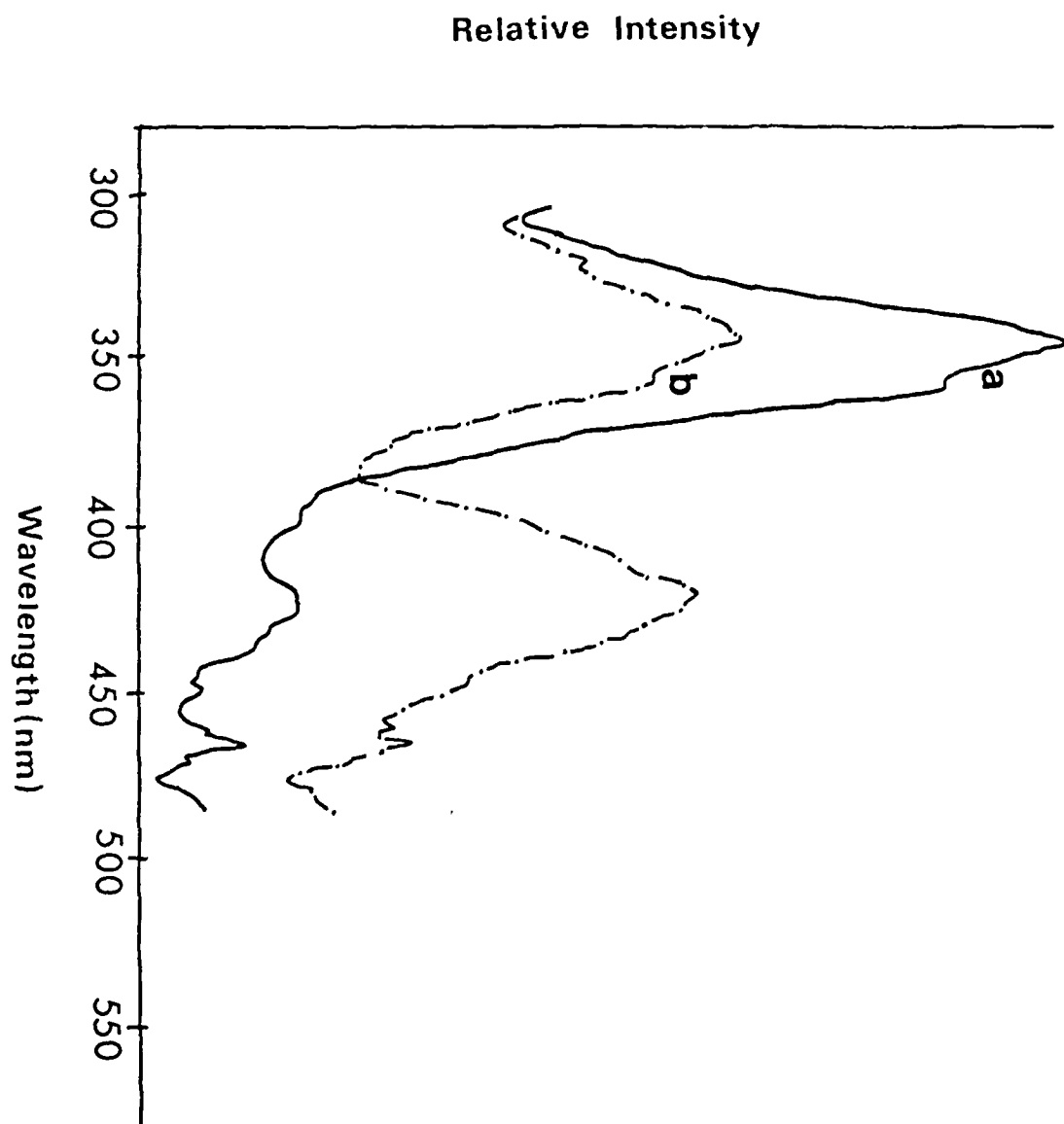


Fig. 10



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