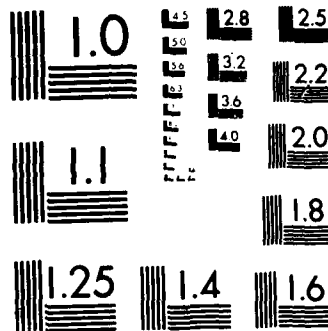


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PHOTOOXIDATION OF AN MDI BASED POLYURETHANE ELASTOMER

by

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Prepared for Publication in

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FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) PHOTOOXIDATION OF AN MDI BASED POLYURETHANE ELASTOMER. C. E. Hoyle, Y. G. No and G. L. Nelson. Department of Polymer Science, University of Southern Mississippi, S. S. Box 10076, Hattiesburg, MS 39406-0076. The photolysis of a polyurethane elastomer based on methylene 4,4'-diphenyl diisocyanate (MDI) in air and under vacuum results in the oxidation of primary photoproducts at relatively short irradiation times. The degree of crosslinked gel and the ultraviolet absorption spectra are both dependent on the presence of oxygen during the photolysis. Apparently, photolysis of the primary photoproducts (probably photo-Fries type) contributes to the degree of crosslinking generated upon photolysis. These results point out the complicated nature of one of the many reaction processes leading to the ultimate photodegradation of MDI based polyurethanes.			
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Photooxidation of an MDI Based Polyurethane Elastomer

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Introduction

Polyurethanes based on aromatic diisocyanates are characterized by yellowing, embrittlement, and physical property loss upon direct photolysis. In particular, polyurethane elastomers based on methylene 4,4'-diphenyl diisocyanate (MDI) result in dramatic increases in the UV absorption spectra with increasing photolysis times (1). This paper deals with the photolysis of a polyurethane elastomer film based on MDI at relatively short irradiation times in the absence and presence of oxygen. By using a combination of light sources, it can be inferred that the photodegradation occurs by a complicated pathway involving photooxidation of the primary products produced from the parent polyurethanes.

Experimental

The polyurethane (designated PU PEO-600) used in this study was synthesized by reacting two parts MDI with one part polyethylene oxide ((PEO) average molecular weight of 600) followed by chain extension with 1,4-butanediol according to a standard literature preparation (2). The polyurethane elastomer films were cast from dimethylformamide (DMF) on quartz plates for the absorbance studies and aluminum pans for the gel measurements. For the percent gel formation determination, the films were photolyzed in a Rayonet Reactor (Southern New England Radiation Corporation; 300 nm or 350 nm lamps) and dissolved in hot DMF. Following agitation, the insoluble gel was collected, dried in a vacuum oven and weighed. UV spectra were recorded on a Perkin-Elmer 320 dual-beam spectrometer.

Results and Discussion

Figures 1 and 2 show the UV spectra of photolyzed (300 nm lamps) PU PEO-600 films in air and vacuum, respectively. In both cases, the loss of the parent carbamate absorption (with peak maximum before photolysis at about 280 nm) is accompanied by the appearance of a new red-shifted absorbance between 300 and 400 nm. This new absorbance is probably due to an ortho photo-Fries product which has the amino group ortho to an alkyl phenolate ester giving the characteristic red-shifted absorbance of amino substituted alkyl benzoates (3). This postulation is supported by the recent report (4) that excitation at 300 nm of a photolyzed PU PEO-600 film (1 hour photolysis in either air or nitrogen) gives a fluorescence spectrum with a maximum at approximately 420 nm, which is characteristic of the red-shifted emission spectra of ortho photo-Fries products. Despite some similarities with respect to loss of the parent carbamate group and formation of the ortho photo-Fries product, there is a distinct difference in the results in air and vacuum. The vacuum photolysis shows a fairly clean conversion to product as verified by isobestic points at 240 nm and 295 nm (Figure 2). Photolysis in the presence of air (Figure 1) shows no clear isobestic points

and probably indicates that the product formed during the initial photolysis is itself being consumed in a secondary process which is dependent on the presence of oxygen. Although this supposition cannot be explicitly proven, it seems reasonable since the photo-Fries products generated in the primary photolysis step are simple substituted aryl amines which are highly susceptible to photooxidation. These results are best illustrated by magnifying the absorbance changes recorded for photolysis in vacuum (Figure 3) and air (Figure 4) and keying in on the spectrum above 300. It is clearly seen in Figure 3 that photolysis in vacuum produces products which continually increase in absorbance with photolysis time. By contrast, photolysis in air (Figures 1 and 4) produces an initial increase in the absorbance (see 1 hour photolysis curve) followed by a decrease at photolysis times of two hours. In order to provide additional information, photolysis of the PU PEO-600 film was first conducted for three hours in vacuum with absorption spectra (Figure 5) taken at hourly intervals. Following the vacuum photolysis, these films were photolyzed for two additional hours in air. Interestingly, after only one hour of photolysis in air (4 total hours: 3h vacuum + 1h air), the absorption spectrum above 300 nm decreased. If the photooxidation of the primary products were not involved, one would have expected the first hour photolysis in air to result in an increase in the absorbance.

Since the changes in absorbance recorded in Figures 1-5 result from chemical reactions which are difficult, if not impossible, to accurately analyze in polymer films, one can only speculate on the results. However, one fact seems quite clear, photolytic oxidation of the primary products produced during the initial photolysis phase of polyurethanes plays an important role in the overall composite photochemistry of aromatic polyurethane films. At this point, one is tempted to speculate that the concentration of the primary product (i.e., the photo-Fries product) would eventually reach a steady state with concomitant loss to produce a set of secondary products responsible for discoloration of the film. If, as suggested by Beachell and Chang (5), the secondary photolysis is a photooxidation of the photo-Fries product to yield highly colored aromatic compounds or crosslinks, then one would also expect to see a marked effect of oxygen on the amount of crosslinked gel formed upon photolysis. This is indeed the case. Photolysis of a PU PEO-600 film in a Rayonet Reactor (300 nm lamps) for 8 hours yields 26 percent crosslinked insoluble gel if carried out in air and 10 percent gel if conducted in vacuum. Furthermore, photolysis of the PU PEO-600 film first in vacuum (3 hour, 300 nm lamps), followed by an additional 3 hours of photolysis in air (350 nm lamps) yields an insoluble gel content of 22 percent. Photolysis first in vacuum (3 hours) with the 300 nm lamps followed by photolysis for 3 hours in vacuum with the 350 nm lamps yields only 9 percent gel. These data are collected in Table I. From these results it is quite obvious that not only the loss of the primary photolysis products (as recorded by the absorption spectrum) but also the percent gel, which reflects the degree of crosslinking, depends on the presence of oxygen in the system. In addition, since the gel formation studies were conducted, at least in part, with the 350 nm lamps which provide direct excitation of the primary photo-Fries product, it can be speculated that the crosslinking results from photooxidation of the primary products, perhaps by formation of the azo linkage as

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suggested earlier. Unfortunately, a combination of the low degree of crosslinking required for insolubilization of the polyurethane coupled with the relative inactivity of azo compounds in the infrared make it impossible to identify such products, although we see, as do others, a number of new IR peaks generated upon photolysis. It is sufficient to say that the crosslinking is a photooxidative process involving the primary photolysis product.

Conclusion

Our results to date reflect the difficult problems associated with analysis of polyurethane photochemistry. However, we do note a correlation between oxygen and the absorbance changes and crosslinking of aromatic polyurethane films upon photolysis. Our analysis has not taken into account the formation and/or oxidative destruction of quinoid type compounds which are often suggested as photolysis products of aromatic polyurethanes. Frankly, we have been able to obtain only indirect and quite conflicting evidence for proof of the existence of the quinoid type products, either in the literature or from our own analysis. Despite the fact that some evidence does exist for quinoid formation (6-8), and that we have in the past published (9) quantum mechanical calculations predicting quinoid type product formation, we feel that more concrete proof of their existence is still required. Finally, we are currently engaged in a detailed FT-IR analysis of photolyzed polyurethane films.

Acknowledgement

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Table I

Photolysis of PEO-600 Films

Sample	Photolysis (300 nm Lamps)*	Photolysis (350 nm Lamps)*	Percent GeI
1	8 hr (air)	---	26
2	8 hr (vacuum)	---	10
3	3 hr (vacuum)	3 hr (air)	22
4	4 hr (vacuum)	3 hr (vacuum)	9

*Photolysis conducted in Rayonet Reactor with lamps as designated.

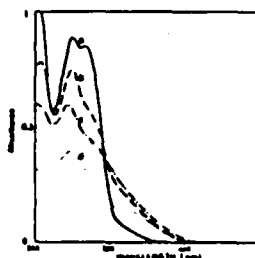


Fig. 1. UV spectral changes on photolysis (300 nm lamps) of PU-PEO 600 film in air. (a) 0 hr, (b) 0.5 hr, (c) 1 hr, (d) 2 hr.

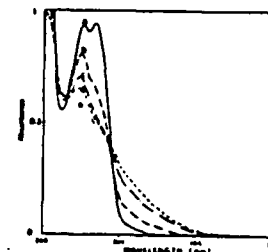


Fig. 2. UV spectral changes on photolysis (300 nm lamps) of PU-PEO 600 film in vacuum. (a) 0 hr, (b) 1 hr, (c) 2 hr, (d) 3 hr, (e) 4 hr.

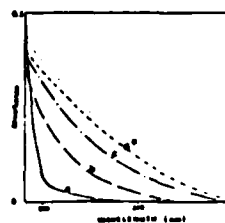


Fig. 3. UV spectral changes on photolysis (300 nm lamps) of PU-PEO 600 film in vacuum. (a) 0 hr, (b) 1 hr, (c) 2 hr, (d) 3 hr, (e) 4 hr.

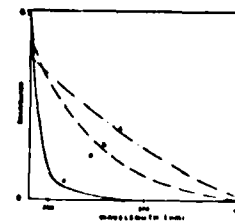


Fig. 4. UV spectral changes on photolysis (300 nm lamps) of PU-PEO 600 film in air. (a) 0 hr, (b) 0.5 hr, (c) 1 hr, (d) 2 hr.

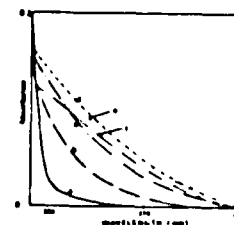


Fig. 5. UV spectral changes on photolysis (300 nm lamps) of PU-PEO 600 film in vacuum (hours 1, 2 and 3) and air (hours 4 and 5). (a) 0 hr, (b) 1 hr, (c) 2 hr, (d) 3 hr, (e) 4 hr, (f) 5 hr.

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