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Photodegradation of MDI Based Polyurethane/Urea Elastomers

by

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## REPORT DOCUMENTATION PAGE

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| <p>A series of polyurethane urea and polyurea elastomers based on MDI, a chain extender such as ethylene glycol or ethylene diamine, and polyethylene glycol oligomers or amine end capped modified polyethylene glycol oligomers were synthesized and characterized. Photodegradation of these polymers was monitored by UV and IR spectroscopy. A review of two systems, a polyurethane urea and a polyurea, is described in depth. Formation of photo-Fries product is observed in both the systems, although the pure polyurea exhibits a greater magnitude of change in the ultraviolet absorption spectrum.</p> |                                                      |                                                                                               |                         |
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## INTRODUCTION

There have been a number of investigations<sup>1-10</sup> of the mechanism responsible for the photodegradation of polyurethanes based on aromatic diisocyanates such as methylene 4,4'-diphenylisocyanate (MDI) and a combination of low molecular weight and oligomeric diols. Although one of the primary reactions responsible for the photodegradation of MDI based polyurethanes is the photo-Fries reactions, photoinduced processes which result in the formation of peroxides at the methylene carbon also occur. Work in our laboratory<sup>11-13</sup> has demonstrated that such factors as hydrogen bonding of the central carbonyl oxygen in the urethane linkage, the crystalline content, and the temperature of the sample in relation to the glass transition (above or below) can have a significant effect on the efficiency of the resulting photo-Fries rearrangement and related cage separation products. The cage separation products are formed by diffusion of the anilinyll and carboxyl radicals which are generated by the primary N-C bond cleavage in the carbamate moiety. In view of the numerous structural and physical parameters which we have found to effect the photodegradation of aromatic diisocyanate based polyurethanes, we suspected that the use of small aliphatic and oligomeric diamines to replace some or all of the diols might have an effect on the photodecomposition process. In this report, we present results for the photolysis of polyurethane urea and polyurea films formed by reaction of MDI with 1,2-ethylenediamine and Jeffamines® (registered trademark of Texaco Chemical Co.) which are essentially polyoxyethylene oligomers end capped with amines.

## EXPERIMENTAL

Methylene 4,4'-diphenylisocyanate (MDI, Mobay) was purified by vacuum distillation. Jeffamine® ED-2001 was obtained from Texaco Chemical Co. and dried at 45°C under vacuum for one day before use. Ethylene glycol (EG, anhydrous, 99%+) and ethylene diamine (EDA, 99%+) were obtained from Aldrich and used without further purification. Polyurethane urea/urea elastomers were synthesized by a prepolymer method<sup>14</sup>. Polymer films were cast from DMF for absorbance and infrared studies. Photolysis was carried out in a Rayonet reactor (300 nm lamps) from Southern New England Ultraviolet Company.

## RESULTS AND DISCUSSION

During the course of our investigation of the photolytic degradation of polyurethane ureas and polyureas a large number of samples were synthesized, characterized (molecular weights, thermal transitions, IR, UV, fluorescence), and subjected to various sources of UV radiation. Components used in the generation of the polyurethane ureas and polyureas included polyethylene glycol oligomers, amine capped modified polyethylene glycol oligomers (Jeffamines®), MDI and the chain extenders ethylene glycol and ethylene diamine. The selection of the particular components used in the polymer synthesis and their sequence of addition determined the exact structure of the product generated. The Jeffamine® oligomers used varied in molecular weight from 600 to 6000. All polymers investigated had a ratio of MDI to oligomer to chain extender of 2:1:1. For purposes of this preprint, a brief synopsis of only two of the systems studied are presented (see Table I for listing/description). Figures 1 and 2

show results for the changes in the absorption spectra upon photolysis of thin films of the polyurea and polyurethane urea designated in Table I as PUJ2001 and PUUJ2001, respectively. The absorption spectra of the two films in Figures 1 and 2 were adjusted by varying the film thickness to have approximately the same initial absorbance at wavelengths above approximately 275 nm. For the lamp sources utilized (Rayonet lamps with peak maxima at about 300 nm), this helps insure that the dose received by each film is approximately equal. The most interesting aspect of the results in Figures 1 and 2 is the pronounced loss of absorbance of the polyurea PUJ2001 between 250 and 300 nm during the first hour of photolysis. The polyurethane urea in contrast exhibits a slower rate of decomposition and a clear isosbestic point characteristic of formation of a single product (probably photo-Fries). The failure of the PUJ2001 to exhibit an isosbestic point may simply reflect the formation of a photo-Fries type product and subsequent rapid and efficient photolysis to non-absorbing photoproducts.

In order to provide additional insight into the photolysis of the PUJ2001 polyurea and PUUJ2001 polyurethane urea, samples were cast on NaCl plates and analyzed via IR as a function of photolysis time. Figures 3 and 4 show IR of PUJ2001 and PUUJ2001 films photolyzed with the 300 nm (peak maximum) Rayonet lamps for time periods of 1 and 3 hours respectively. Again, the decomposition of the polyurea is greater than for the polyurethane urea. Following, for example, the aromatic absorption at 1599 cm<sup>-1</sup> as a function of photolysis time, it can readily be seen in Figure 5 that the polyurea loses the aromatic absorption at a rate commensurate with the results for loss of UV absorbance between 250-300 nm in Figure 2.

The interesting conclusion from this limited set of results is that the polyurea PUJ2001 degrades faster upon exposure to UV radiation (centered around 300 nm), but apparent buildup of absorption in the far UV (greater than 300nm) appears to be less. This is probably an artifact of the rapid loss of the photoproduct(s) initially produced by the photolysis of the parent and urea linkage in the polyurea. It is interesting that the pure polyurea, which is capable of exhibiting hydrogen bonding between the carbonyl and two urea hydrogens, has a propensity for rapid photobleaching. Although previous work<sup>11-13</sup> in our lab suggests that a similar bleaching process occurs for thin pure polyurethane films, it doesn't appear to occur as fast as for the pure polyurea.

We know from laser flash photolysis of model systems<sup>15,16</sup> that the initial N-C bond cleavage between the aryl nitrogen and the carbonyl carbon is from a short lived singlet state. The resultant anilinyll and carboxyl radicals can recombine in the cage to either give the starting carbamate (urea) or the ortho-photo-Fries product. Alternatively, the two radicals can separate (if diffusion allows) and undergo independent reactions (for example hydrogen abstraction to yield among other products an unsubstituted (at the ortho position) aniline type products. The overall degradation process is dependent upon the distribution of the primary photo products, which can be formed by in-cage or out-of-cage processes, and their subsequent photolysis. Apparently, the combined process of generation of the primary aryl amine photoproducts and their subsequent photolysis is quite efficient for the pure polyurea.

## CONCLUSION

The results presented in this short preprint are representative of the type of data obtained for a number of polyureas and polyurethane ureas investigated in our laboratory. The actual photodegradation process of such systems is quite complicated depending on such parameters as hydrogen bonding, crystalline content, and the miscibility of hard and soft components

in the segregated polyurethane ureas. In addition, the inherent quantum yields for the cleavage in the initial photochemical process are dictated by the nature of the urethane and urea groups. A compendium of our results for all of the systems investigated in our lab, including those presented in this preprint, will be presented at the symposium.

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#### REFERENCES

1. C. S. Schollenberger, L. G. Pappas, J. C. Park, and V. V. Vickroy, *Rubber World*, 139, 81 (1960).
2. C. S. Schollenberger and K. Dinbergs, *SPE Trans.*, 1, 31 (1961).
3. C. S. Schollenberger and F. D. Stewart, *Advances in Urethane Science and Technology*, K. D. Frisch and S. L. Reegen, Eds., Technomic Publishing, Westport, CT, Vol. 2, p. 71, 1973.
4. Z. Osawa, E. L. Cheu, and Y. Ogiwara, *J. Polym. Sci. Polym. Lett. Ed.*, 13, 535 (1975).
5. Z. Osawa, E. L. Cheu, and K. Nagashima, *J. Polym. Sci. Polym. Chem. Ed.*, 15, 445 (1977).
6. Z. Osawa, *Developments in Polymer Photochemistry*, N. S. Allen, Ed., Applied Science Publishers, London, Vol. 3, p. 209, 1982.
7. L. B. Nevskii, O. G. Tarakanov, and V. K. Belyakov, *Soviet Plastics*, 10, 23 (1967).
8. L. B. Nevskii, O. G. Tarakanov, and V. K. Belyakov, *J. Polym. Sci., Part C*, 23, 193 (1968).
9. J.-L. Gardette and J. Lemaire, *Makromol. Chem.*, 183, 2415 (1982).
10. J.-L. Gardette and J. Lemaire, *Polym. Deg. and Stab.*, 6, 135 (1984).
11. C. E. Hoyle, K. J. Kim, Y. G. No, and G. L. Nelson, *J. Appl. Polym. Sci.*, 34, 763 (1987).
12. C. E. Hoyle, and K. J. Kim, *J. Polym. Sci. Polym. Chem. Ed.*, 25, 2631 (1987).
13. C. E. Hoyle, C. P. Chawla, and K. J. Kim, *J. Polym. Sci. Polym. Chem. Ed.*, 26, 1295 (1988).
14. J. H. Saunders and K. C. Frish, *Polyurethanes: Chemistry and Technology*, Interscience Publishers, New York, Vol. XVII, p. 273, 1962.
15. C. E. Hoyle, Y. G. No, K. G. Malone, S. F. Thames, and D. Creed, *Macromolecules*, 21, 2727 (1988).
16. C. E. Hoyle, K. S. Ezzell, Y. G. No, K. Malone, and S. F. Thames, *Polym. Deg. and Stab.*, 25, 325 (1989).

Table I

| Polymer  | Composition                     |
|----------|---------------------------------|
| PUJ2001  | MDI:Jeffamine 2001:EDA is 2:1:1 |
| PUUJ2001 | MDI:Jeffamine 2001:EG is 2:1:1  |

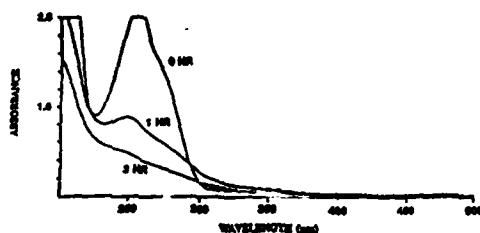


Fig. 1 UV spectral changes on photolysis of PUJ2001 film.

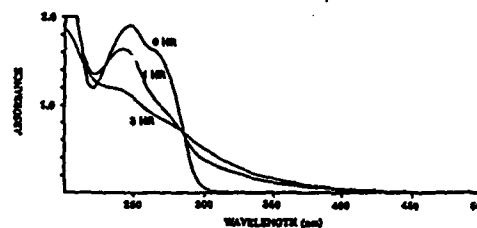


Fig. 2 UV spectral changes on photolysis of PUUJ2001 film.

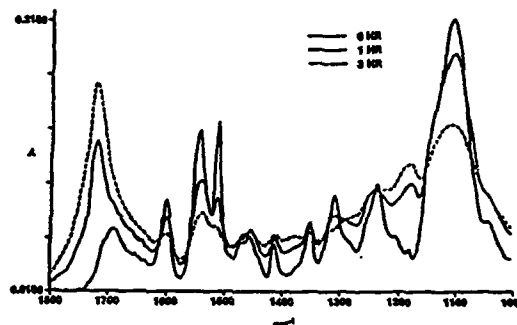


Fig. 3 IR spectral changes on photolysis of PUJ2001 film.

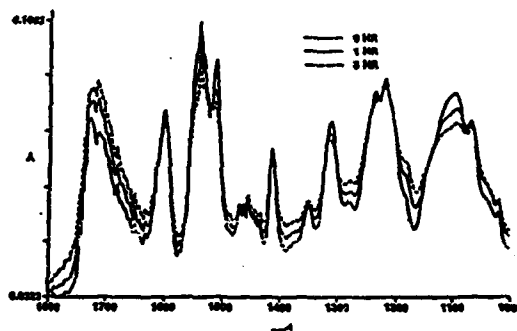


Fig. 4 IR spectral changes on photolysis of PUUJ2001 film.

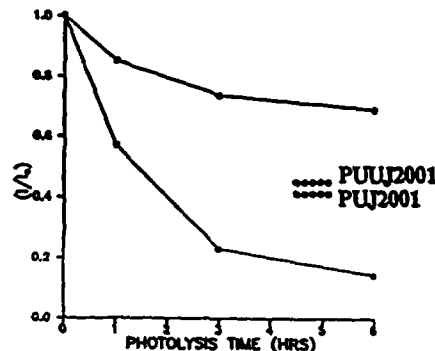


Fig. 5 Plot of aromatic absorption at 1599  $\text{cm}^{-1}$  as a function of photolysis time.

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