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AN INVESTIGATION OF THE DEGRADATION AND STABILIZATION OF POLYMER SYSTEMS

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AN INVESTIGATION OF THE DEGRADATION AND STABILIZATION OF POLYMER SYSTEMS

The project on "Investigation of the Degradation and Stabilization of Polymer Systems" concentrated primarily on a detailed study of the factors which effect the photolytic decomposition of polyurethanes based on aromatic diisocyanates. An extensive investigation of the photophysics of 1,5-naphthalene diisocyanate based polyurethanes in solution was also conducted. In addition, ground work was laid to initiate studies on the photodegradation of polycarbonate, polyureas, and polyimides.

Employing both steady state and time resolved fluorescence spectroscopy to analyze the photolysis products of model compounds and polyurethane films, photo-Fries and other cleavage products were identified at the very early stages of photolytic induced decomposition. We also clearly established the critical effect of polymer main-chain flexibility, crystalline content, and hydrogen bonding on the extent of degradation of polyurethane films and coatings. Laser flash photolysis results confirmed the contribution of peroxide and aromatic ketone impurities (incorporated into all commercial polyurethanes during the synthesis and processing steps) to the photodegradation process. For methylene 4,4′-diphenyl diisocyanate (MDI) based polyurethanes, transient spectra of diphenyl methyl radicals were detected under a variety of conditions, thus providing unequivocal evidence for one of the primary modes of the initial stages of photooxidation of segmental polyurethane elastomers. A complete mechanistic description was developed to describe the degradation process.

A photophysical investigation of naphthalene diisocyanate based polyurethanes constituted one of the first detailed accounts of intra-chain excimer formation involving chromophores in the polymer backbone. The extent of the excimer formation was found to be dependent on the goodness/poorness of the solvent medium. The isolated monomer concept was employed to describe the complex fluorescence decay curves obtained for emission in the monomer and excimer emission regions.

Attached for reference are lists of technical reports, published manuscripts, and names of personnel who participated in the research.

PUBLISHED MANUSCRIPTS

1. "Photolysis of Aromatic Diisocyanate Based Polyurethanes in Solution," K. J. Kim and C. E. Hoyle, J. Polym. Sci. Chem. Ed., 24, 1879-94 (1986).
2. "The Effect of Crystallinity and Flexibility on the Photodegradation of Polyurethanes," C.E. Hoyle and K.J. Kim, J. Polym. Sci. Chem. Ed., 25, 2631-42 (1987).
3. "Photophysics of a Naphthalene Diisocyanate Based Polyurethane," C.E. Hoyle and K.J. Kim, Macromolecules, 20, 597-600 (1987).
4. "Photophysics of Polyurethanes Based on 1,5-Naphthalene Diisocyanate," C. E. Hoyle and K.J. Kim, Photophysics of Polymers: ACS Symposium Series 358, eds. C. E. Hoyle and J. M. Torkelson, ACS, Washington, DC pp. 201-18 (1987).
5. "Photolysis of Segmented Polyurethanes. The Role of Hard-Segment Content and Hydrogen Bonding," C. E. Hoyle, K. J. Kim, Y. G. No and G. L. Nelson, J. Appl. Polym. Sci., 34, 763-74 (1987).
6. "The Effect of Flexibility on the Photodegradation of Aromatic Diisocyante Based Polyurethanes," C.E. Hoyle and K.J. Kim, J. Polym. Sci. Chem. Ed., 26, 1295-1306 (1988).
7. "Excimer Formation of a Naphthalene Diisocyanate Based Polyurethane," C. E. Hoyle and K. J. Kim, Macromolecules, 21, 2100-2102 (1988).
8. "Laser Flash Photolysis of a Methylene 4,4'-Diphenyldiisocyanate (MDI) Based Polyurethane and Model Carbamates," C. E. Hoyle, Y. G. No, K. G. Malone, S. F. Thames, D. Creed, Macromolecules, 21, 2727 (1988).
9. "Flash Photolysis of Aromatic Diisocyanate Based Polyurethanes," C. E. Hoyle, Y. G. No, and K. Ezzell, "Radiation Effects on Polymer Materials," ACS Symposium Series, eds. E. Reichmanis and J. H. O'Donnell, ACS Washington, DC, pp. 43-56 (1989).
10. "Light Stabililty of Polyurethane Coatings," C. E. Hoyle, K. J. Kim, and N. Y. Gil, Proceedings of the Thirteenth Water-Borne and Higher-Solids Coatings Symposium, pp. 301-320, Feb. 5-7, 13, 301 (1986).
11. "Photophysics of Polyurethanes Based on 1,5-Naphthalene Diisocyanate," C. E. Hoyle and K.J. Kim, Polymer Photophysics Symposium, Polymer Division, ACS National Meeting, Anaheim, CA Sept. 7-10, Polymer Preprints, 27, 314 (1986).
12. "Photodegradation of Segmented Polyurethanes Based on Aromatic Diisocyanates," C. E. Hoyle, K. J. Kim, N. Y. Gil and G. L. Nelson, High Solids and Radiation Curable Coatings Symposium, Anaheim ACS Meeting, PMSE, 55, 457 (1986).
13. "Fluorescence Spectroscopy of Polyureas Based on Naphthalene Diisocyanate," C. E. Hoyle and C. H. Chang, Invited Paper, Symposium on Characterization of Polymers by Fluorescence Techniques, New Orleans ACS Meeting, August 30 - September 4, Polymer Preprints, 28, 84, (1987).
14. "Photooxidation of an MDI Based Polyurethane Elastomer," C. E. Hoyle, Y. G. No and G. L. Nelson, Polymer Division, New Orleans ACS Meeting, August 30-September 4, Polymer Preprints, 28, 415 (1987).

TECHNICAL REPORTS

1. C. E. Hoyle, K. J. Kim, Y. G. No, "Light Stability of Polyurethane Coatings," Technical Report Number 1, June 16 (1986).
2. C. E. Hoyle and K. J. Kim, "Photolysis of Aromatic Diisocyanate Based Polyurethanes in Solution," Technical Report Number 2, June 16 (1986).
3. C. E. Hoyle, Y. G. No, K. J. Kim and G. L. Nelson, "Photodegradation of Segmented Polyurethanes Based on Aromatic Diisocyanates," Technical Report Number 3, June 16 (1986).
4. C. E. Hoyle and K. J. Kim, "Photophysics of Polyurethanes Based on 1,5-Naphthalene Diisocyanate," Technical Report Number 4, June 16 (1986).
5. C. E. Hoyle and K. J. Kim, "The Effect of Crystallinity and Flexibility on the Photodegradation of Polyurethanes," Technical Report Number 5, September 24 (1986).
6. C. E. Hoyle and K. J. Kim, "Photophysics of a Naphthalene Diisocyanate Based Polyurethane," Technical Report Number 6, September 24 (1986).
7. C. E. Hoyle, K. J. Kim, Y. G. No, and G. L. Nelson, "Photolysis of Segmented Polyurethanes. The Role of Hard-Segment Content and Hydrogen Bonding." Technical Report Number 7, September 24 (1986).
8. C. E. Hoyle and K. J. Kim, "Photophysics of Polyurethanes Based on 1,5-Naphthalene Diisocyanate in Solution and Film," Technical Report Number 8, September 24 (1986).
9. C. E. Hoyle, Y. G. No and G. L. Nelson, "Photooxidation of an MDI Based Polyurethane Elastomer," Technical Report Number 9, July 29 (1987).
10. C. E. Hoyle and C. H. Chang, "Fluorescence of Polyureas Based on 1,5-Naphthalene Diisocyanate," Technical Report Number 10, July 29 (1987).
11. C. E. Hoyle and Kyu-Jun Kim, "Excimer Formation of a Naphthalene Diisocyanate Based Polyurethane in Solution," Technical Report Number 11, July 29 (1987).
12. C. E. Hoyle and K. J. Kim, "The Effect of Flexibility on the Photodegradation of Aromatic Diisocyanate-Based Polyurethanes," Technical Report Number 12, July 29 (1987).
13. C. E. Hoyle, Y. G. No, K. G. Malone, S. F. Thames and D. Creed, "Laser Flash Photolysis of a Methylene 4,4′-Diphenyldiisocyanate (MDI) Based Polyurethane and Model Carbamates," Technical Report Number 13, March 11 (1988).
14. C. E. Hoyle and Y. G. No, "Flash Photolysis of Aromatic Diisocyanate Based Polyurethanes," Technical Report Number 14, March 11 (1988).

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