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Item Type	article;article
Authors	Vogl, Otto;Ranby, Bengt
Download date	2026-06-15 02:01:30
Link to Item	<a href="https://hdl.handle.net/20.500.14394/23045">https://hdl.handle.net/20.500.14394/23045</a>



## U.S.-Sweden Workshop on Photodegradation and Photostabilization of Polymers

Bengt Ranby and Otto Vogl  
Department of Polymer Technology, Royal Institute of Technology, S-100 44, Stockholm, Sweden; and Polymer Science & Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003 U.S.A.



Bengt Ranby

In Stockholm, Sweden, a U.S.-Sweden Workshop on "Photodegradation and Photostabilization of Polymers" was held from December 7-10, 1981, at the Park Hotel, Karlavagen. This Workshop was sponsored by the Swedish National Board for Technical Development (STU) and the National Science Foundation (NSF). Dr. F. H. Winslow (Bell Laboratories) and Professor B. Ranby (Royal Institute of Technology) acted as Co-chairmen. There were 10 participants from the United States—Amitava Gupta, P. P. Klemchuk, S. S. Labana, F. R. Mayo, D. C. Neckers, S. P. Pappas, A. M. Trozzolo, O. Vogl, S. E. Webber, and F. H. Winslow; and a similar number from Sweden—A. Holmstrom, K. Abbas, B. Ranby, J. E. Rabek, J. Lucki, A. Hult, S. Gothe, T. Skowronski and G. Ramme. In addition, Professor J. E. Guillet from Canada and Professor J. Kops from Denmark, also participated in the conference.

The program consisted of overview reports on photochemical research on polymers in Sweden (by B. Ranby) and the U.S.A. (F. H. Winslow), a number of official and informal presentations, a session in which the priorities in research and cooperations between Sweden and the U.S. on photodegradation and photostabilization of polymers were discussed and a concluding session. Time was also set aside to visit important academic laboratories in both Stockholm and Uppsala.

While the sponsorship of this meeting was jointly handled by the NSF and STU, the actual proceedings of the meeting were in the hands of the International Department of STU. Mr. Paul Forsgren, Head of the Department of Industrial Processes, STU, gave the introduction. Also present from the STU organization were Dr. Ingela Agrell from the International Department and Mr. Kjell Lindman, Head of the Polymers and Composites Program. STU was host for local arrangements and hospitality.

Dr. Winslow summarized the activities in the United States of polymer research, the present state of polymer research and polymer education in the United States primarily based on the recently published National Academy of Science report "Polymer Science and Engineering: Needs, Opportunities, Challenges." He also discussed the activities in polymer photochemistry and photophysics that are being carried out in laboratories other than those represented by the participants of the symposium, the importance of photochemistry and photophysics in solar energy projects and industrial research and presented specific activities in industrial laboratories. He also mentioned some U.S. research programs on photoresists, and on photodegradation of various polymeric materials including acrylates and PVC. B. Ranby discussed the photophysical and photochemical work on polymers in Sweden with particular emphasis on flash photolysis and high-speed spectroscopy which started in Uppsala in the 1950's, and the sensitized photodegradation and photooxidation studies including ESR spectroscopy of radicals and singlet oxygen reactions, which started in Stockholm in the 1960's, and the more recent studies of photolysis of aromatic and unsaturated polyesters.

Five main lectures on "Photodegradation and Photostabilization of Polymers" were then presented. S. P. Pappas paid particular attention to the sensitization and excitation in polymeric systems including the degradation of aliphatic polymers, photo-catalytic activity of TiO<sub>2</sub> and the photostabilization of aromatic polymer films. S. E. Webber discussed "Energy Transfer in Polymer Systems" which was divided into the behavior of the singlet state, where the excitonic transport between neighboring groups, the Forster transfer to "trap," and the segmental collisions were considered and compared it to the triplet state where only excitonic transfers are likely. Discussed were also the photochemical implications of energy transfer, the energy transfer to reactive stabilizer sites which can enhance or retard photodegradation or the fact that polymer coils could act as "antenna" for photochemical reactions.

B. Ranby discussed the many problems involved in singlet oxygen generation and reactions of singlet oxygen with polymers and brought up some unsolved problems. J. F. Rabek, in his discussion on "Photodegradat-



tion and Photooxidation Reactions," brought the participants up to date with the newest development in this field; he discussed degradation mechanisms, initiation of photooxidation and various new methods to study photodegradation. P. P. Klemchuk discussed the "Ultra-violet Degradation and Stabilization of Polymers." He presented the various aspects by which polymers can undergo degradation and the use of stabilizing additives, for example, ultraviolet absorbers, hindered amine light stabilizers, nickel compounds as quenchers, benzoate esters, trivalent phosphorous compounds, hindered amines and thiosynergist combined. In addition, specific subjects were discussed by J. Kops on the "Photodegradation of Polystyrene-Poly(2,6-dimethyl-1,4-phenylene oxide) Blends." J. E. Guillet discussed "New Aspects and New Approaches for Prediction of Photooxidation of Synthetic Polymers." This work involves the computer modeling of 31 reactions involved in the photooxidation and the initial successes in predicting the reaction products on the basis of the knowledge of individual reaction constants. A. Gupta discussed the "Excitation of Photostabilizers and the Mechanism of Photodegradation of Copolymers of Methyl Methacrylate and Vinyl Derivatives of Ultraviolet Absorbers." An additional talk was given by O. Vogl on "Polymerizable and Polymerbound Ultraviolet Absorbers," who discussed the rapidly growing interest in the nonleachable and nonmobile ultraviolet screening agents.

After the discussion of all the individual subjects, the participants were divided into three groups. One group consisted of those interested in singlet oxygen and other excited states with A. M. Trozzolo and B. Ranby as the coordinators. It was concluded that not only singlet oxygen but all activated forms of oxygen should be taken into consideration when discussing interaction of photoexcited oxygen with polymeric materials. Studies of specific importance would be the interaction of polydienes with polynuclear aromatics as sensitizers, particularly how sensitization occurs to each singlet oxygen; it was also suggested in discussions that the triplet states, especially those of high energy, should not be limited to the carbonyl group. Additional studies of model compounds for polystyrene with singlet oxygen but also the reaction of singlet oxygen with 1,2-polybutadiene, and with polymers with furan-containing units and the general desensitization and utilization of singlet oxygen should be carried out.

The group on energy transfer was coordinated by S. E. Webber who discussed the various ways that

energy transfer could be and should be studied. It concluded that in this field the most important problem is the interaction of polymer chemists, people that synthesize well-defined and pure polymer systems, the photophysicists to test new ideas and to study systems. The problem of "antenna" was found to be of particular interest and well-defined copolymers that trap in the polymer chain or as end groups would be desirable for further studies.

By far the largest group was organized by F. J. Rabek (11 participants) on photooxidation and photostabilization. It was found that the investigation of the methods of accelerated aging and understanding of performance lifetime of polymers is of greatest importance; the comparison of individual test methods and their practical and theoretical value has been an area of interest and some of the predictions of accelerated tests should probably be coordinated with the development of computerized techniques for the investigation of the appearance of individual chemical groups in the polymer. Also of great importance were found to be the problems and developments of attached and built-in ultraviolet stabilizers and this is presently the field of greatest interest for photostabilization. Other problems of substantial interest but also important in this field is the effect of morphology on photodegradation, the effects of pigments on photostability and photodegradation and the mechanism and "turn over" on radical scavenging. Of lesser but still of some interest was the implication of the stability of natural polymers for prediction of lifetime of synthetic polymers, but also the general effect of hydrolysis, the light-induced hydrolytic degradation and a review of the relative importance of photooxidation on hydrolysis.

Time was also set aside for a visit to the Department of Polymer Technology, the Royal Institute of Technology in Stockholm, where the ongoing work on photochemistry was presented and the equipment for photochemical research program was demonstrated. The remainder of the day was set aside for a visit to the Department of Physical Chemistry, the University of Uppsala (Professor S. Claesson) where the flash experiment, the ultra-fast spectroscopy particularly the emission spectroscopy, was demonstrated by Dr. G. Ramberg. A visit was also made to the Department of Physics, University of Uppsala (Professor Siegbahn's laboratory) where the 1981 Nobel Laureate in Physics (Dr. G. Siegbahn) who is the 1981 Nobel Laureate in Physics) where an ESCA spectrometer was shown by Dr. U. Gelius.

The final conclusions of the meeting on "Photodegradation and Photostabilization of Polymers" were that the possibility of further research cooperation between the United States and Sweden on photodegradation of polymers should be explored and current research projects expanded. It was found that enhanced exchange of information, the possibility of fellowships for graduate students and visiting scientists should be pursued. It was concluded that this meeting had been very time stimulating and most successful.

The week of the U.S.-Sweden Workshop included also the day when the Nobel Prizes were awarded. Arrangements had been made by Professor Ranby for the foreign participants of the Workshop to be invited to the Nobel ceremony at the Concert Hall where the awards were presented by the King of Sweden and to the City Hall of Stockholm for the Nobel banquet and the subsequent Nobel Ball. The event made this meeting an unusually rare and memorable occasion.