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## Second U.S.-Sweden Workshop on Photochemistry of Polymers

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Conference Reports

## Second U.S.-Sweden Workshop on Photochemistry of Polymers

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The second U.S.A.-Sweden Workshop on "Photochemistry of Polymers" was held in the board room of the California Institute of Technology ("CalTech"), Pasadena, California, from December 5 to 8, 1984. The participants were lodged in the Athenaeum, the faculty club.

The workshop was cosponsored by the U.S. National Science Foundation (NSF) and the Swedish National Board of Technical Development (STU). Professor Bengt Ranby, Stockholm, and Dr. Field H. Winslow of the AT&T Bell Laboratories cochaired the workshop. Dr. Amitave Gupta of CalTech's Jet Propulsion Laboratories was responsible for the arrangements. Twelve scientists from the United States and another dozen from Sweden comprised the formal participants, and a further number of speakers and observers were involved in special deliberations.

Dr. Terry Cole, Chief Technologist of the Jet Propulsion Laboratories, opened the meeting with greetings from his administrative officers: he summarized the objectives and importance of the workshop and emphasized its significance to the Jet Propulsion Laboratories.

The program of the workshop was divided into three parts: (1) the introductional overview of polymer photochemical research in both the United States and Sweden; (2) the actual discussions of important developments in both countries; and (3) discussion of programs presently in progress between the United States and Sweden and plans for future cooperation. The identification of specific objectives in polymer photochemistry and the determination of priorities were to be the goal of discussions in subcommittees.

The first overview on "Energy Transfer Processes" was given by Professor N.J. Turro, Columbia University, presently Visiting Professor at the California Institute of Technology. He discussed important aspects of the use of photochemistry for energy transfer processes and photoinitiation of polymerization. In particular, he pinpointed methods that have been developed to initiate free radical polymerizations by photochemical means which approach living polymerization conditions. Charge transfer and electron transfer processes involving the initiation of polymerization reactions were



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also discussed; they involve various aspects of radical polymerizations of photo-excited species which can be effected by magnetic fields.

Dr. S. S. Labana of the Ford Motor Company discussed the photochemistry of coatings, especially the present status of the current research and of research needs. He pointed out present activity in the photochemistry of coatings and mentioned that a vast amount of research is currently being done in application; the work does not now have

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a proper focus. One of the most important areas of the photochemistry of coatings is photostabilization. The prediction of the service life still needs improvement. Weather-O-meter, oxygen uptake, ATR-IR, NMR studies and nitroxide assays are still the most reliable techniques. ESR also gives reliable results if carried out properly.

The third overview was given by Dr. C. G. Willson of IBM at San Jose, who discussed the present status of research on photo-resists. In particular, he pointed out the importance of knowing who are the vendors of the resists, and where are the involvements in university laboratories and in laboratories of the semiconductor industries. The current area of activity in resist materials is directed toward shorter wavelength, higher temperature resist materials, especially x-ray resists, and photoresist involving organic/organometallic materials.

Professor B. Ranby summarized the activities on "Photochemistry of Polymers" at the Royal Institute of Technology as well as in other laboratories in Sweden and Scandinavia and pointed out especially the progress that has been made since the first U.S.-Sweden Seminar on Photochemistry of Polymers which was held in Stockholm in December 1981.

Starting with the main program, Professor N. J. Turro discussed the use of "Photochemical and Photoluminescent Probes of Water-Soluble Polymers." He pointed out the importance of photochemical reactions that can be utilized in emulsion polymerization. The effects of diffusion into and out of the micelles and the quenching of undesirable radical metal ions such as cobalt were studied. More important, however, are his new results, now firmly established, on the effect of magnetic fields during the polymerization; the importance here is that the magnetic field can interfere with the triplet state of the photoexcited radicals used for polymerization. Professor M. Almgren, Uppsala University, discussed "Photofluorescence Studies of Micelles and Polyelectrolytes." He described some of the results of his studies on the excitation energy transfer in a micelle and pointed out that a good characterization of the micelle size and the migration of ions and small molecules between micelles and vesicles in an aqueous soap is most important. "Fluorescence Probes of Polymer Structures and Polymer Chain Dynamics" was discussed by Professor C. W. Frank of Stanford University. An interesting talk was given by Dr. H. D. Becker of the Chalmers University of Technology in Gothenburg, Sweden, who discussed the intramolecular excited state interactions of bichromophoric anthracenes. He described how his group has investigated photochemical and photophysical properties of a variety of bichromophoric anthracene derivatives and how the relationship between molecule geometry and excited state properties of the molecules can be deduced from the fluorescence spectra of various bianthracene derivatives.

"Electric Singlet Energy Transfer and Quenching in Aromatic Polymers" was presented by Dr. A. Gupta. He has very carefully studied copolymers of 2(2-hydroxy-5-vinyl-phenyl)2H-benzotriazole and styrene, determined the excitation spectra and the quenching effects that are obtained by the benzotriazole moiety of the macromolecules. A most interesting talk was given by Professor B. Ranby on the "Photoinitiated Graft and Copolymerization onto Polymer Surfaces." Ultraviolet grafting of volatile monomers from acetone solution, with benzophenone as the sensitizer, gave effective surface grafting. A very low level of grafting (mono-

molecular layer) and rather thick (up to 1000 Å) layers of photografting of monomers onto a variety of polymers could be achieved. These graft polymers were characterized and the surface properties of the polymer films studied.

"Recent Developments in Resist Chemistry" were discussed by Dr. C. G. Willson; this talk concentrated on both positive and negative resists. It was concluded that the future in the resist polymer area appears to be in positive resists. Some new polymers, particularly silicon-containing polymers, have been the focus of recent research in this area. Some organometallic polymers are also of interest for this application. Dr. P. Klemchuk of the Ciba-Geigy Corporation presented some "Recent Research in Polymerization and Polymerstabilization Systems." He mentioned briefly novel antioxidants and also new HALS stabilizers and the mechanism of their action. New 2(2-hydroxyphenyl)2H-benzotriazoles of low molecular weight and HALS stabilizers of oligomeric and polymeric structure were also mentioned. "Photodegradation of Aromatic Polyesters" was briefly discussed by Professor J. Kops of the Department of Polymer Technology, Technical University, located in Lyngby, Denmark. He is interested primarily in liquid crystalline aromatic polyesters and their degradation under various thermal and photochemical conditions. An interesting talk was given by Professor C. E. Hoyle on the "Photodegradation and Photostabilization of Polyurethanes." He has studied the photofries rearrangements of polyurethanes leading to polymeric amines and other degradation products. The photostabilization of polyurethanes is still one of the most difficult tasks in polymer degradation, even though autooxidation of polyurethanes is also a problem.

"Application of Polymers in Solar Energy Technologies" was the subject of Dr. J. F. Rabek's lecture; he emphasized the need to know long-term properties of polymeric materials which have potential applications in solar energy technology and solar energy conversion such as passive solar heating systems, solar collectors, solar luminescence, solar concentrators, encapsulation of photovoltaic cells with polymeric materials, and solar energy storage. The polymers involved in solar energy application must maintain optical, chemical, and mechanical properties during long exposure to solar (ultraviolet, visible, and infrared) radiation.

In addition to these more formal talks, a number of short presentations were given by U.S. and Swedish scientists. They included "Photoinitiated, Cationic Polymerizations," where polymerizations were carried out on polymeric surfaces, as described by Dr. A. Hult of the Royal Institute of Technology. The proper modification of polymer surfaces by photochemical techniques is novel and potentially very important. Polymers can be deposited on or close to a polymer surface by allowing the monomers to penetrate the surface together with an initiator; in the slightly swollen surface, polymerization was photoinitiated using sulfonium ion initiators. Irradiating the polymer samples caused cationic photopolymerization of the monomers and surface grafting.

Dr. J. Lucki of the Royal Institute of Technology discussed "Interaction Between HALS Compounds and Antioxidants" for the photostabilization of polybutadiene. Dr. R. Jaffe of the Ames NASA Laboratory described his work on "Elucidation of Polymer Properties" by quantum mechanical calculations. Dr. R. Liang of the Jet Propulsion Laboratories presented his work on "Time Resolved ESR Studies" during



the photodegradation of polymeric materials. Dr. J. Hilborn of the Royal Institute of Technology discussed "Crosslinking of Elastomers," and Dr. K. Abbas of Bofors Plast AB, the "Aging of Kevlar/Epoxy Composites." Professor A. C. Albertsson from the Royal Institute of Technology presented her work on "Polymerizable and Polymeric Ultraviolet Stabilizers." Finally, Professor J. Guillet from the University of Toronto gave a futuristic talk with novel speculations on the prospects of chemical synthesis using photochemistry, and the direct preparation for organic compounds using natural sunlight.

In addition to these presentations which varied in length, three subcommittees convened to evaluate the consequences of the recommendations of the first U.S.-Sweden Workshop and the results to date of the cooperative programs that were initiated at that time. The subcommittees also tried to define important areas of research in photochemistry of polymers and possible areas of continuing cooperation between American and Swedish scientists and their research groups. The three subcommittees were headed by Professor Otto Vogl, Polytechnic Institute of New York, on "Photodegradation and Photostabilization," Professor M. Almgren, University of Uppsala, on "Photoinitiation and Photochemistry of Polymers," and Dr. C. G. Willson, IBM, San Jose, on "Photoresist Materials."

The subcommittee on "Photodegradation and Photostabilization" reported that two cooperative programs based on the recommendations of the first workshop are continuing between the Royal Institute of Technology and the Polytechnic Institute of New York. One area of research focuses on "Polymerizable and Polymeric Stabilizers" and the other on "Detection of Permanently-Linked Stabilizers [polymer-bound stabilizers] by ESCA and ATR-IR." Both projects have been working very effectively and have already led to several publications and lecture presentations. It was predicted that additional work will be developed between the two research groups on "Photochemical Grafting of Polymerizable Stabilizers on Polymeric Surfaces."

Exchanges of scientists are being planned in the form of visiting professorships and industrial sabbaticals of 6 to 12 months' duration. Professor Turro is scheduled to give a short course at the Royal Institute of Technology, as Professor Vogl had done over ten years ago.

The subcommittee on "Photodegradation and Photostabilization" has concluded (as a similar committee did at the end of the first U.S.-Sweden Workshop) that research on "New and More Efficient Techniques to Predict Service Life of Polymers" is of continuing interest and most important. Other areas of research, which were considered important, but less urgent, include "Polymerizable and Permanent Ultraviolet Stabilizers," "Photophysics [quenching] of Novel Stabilizers and Stabilizing Systems," "Photo-Induced Environmental Aging," "Combined [synergistic and/or antagonistic] Effects of Additives for Photostabilization," and "Stabilization and Modification of Polymer Surfaces."

The subcommittee on "Photochemistry and Photoinitiation of Polymer Reactions" concluded that various types of cooperation between individual scientists and between research groups should be pursued, and the first contacts were initiated for cooperative programs. It was established that visiting professors and scientists from both countries could be accommodated in various laboratories during the coming year or two.

In the "Photoresist Area," a definite cooperative effort between laboratories of the two countries has been established; especially effective is the involvement of the IBM laboratory in San Jose, where young Swedish scientists have been spending a few months to a year.

This second U.S.-Sweden Workshop was considered very successful in several ways. A number of new and younger participants were welcomed, while continuity between the first and second workshops was carefully maintained by retaining some of the most important senior scientists in key positions to guarantee continued cooperation between the scientific communities of the two countries in the area of photochemistry of polymers.

It was recognized that this second U.S.-Sweden Workshop on Photochemistry of Polymers has been an important scientific event, especially on the Swedish side. Dr. K. Lindmen, representing the STU, was an important participant during the entire meeting and played an important and active role in all deliberations. Helen Albom from the Swedish consulate in Los Angeles and Van der Stamm, the science attache of the Swedish consulate, were present at a reception given by the Chemistry Department of CalTech on one of the evenings of the workshop meeting.

The consensus was that the interaction between scientists of the United States and Sweden who are interested in photochemistry of polymers has been effective; new friendships have been established and old ones have been intensified. It was particularly gratifying to see how much activity has evolved from the recommendations of the first workshop, and it is expected that interaction between American and Swedish scientists in this field will continue and will gather momentum. The participants have already expressed their desire to meet again in about three years in Sweden, when all the new cooperative programs will have been put into effect and some of the results can be discussed, together with new ideas, new prospects and opportunities in the area of photochemistry of polymers.

#### Workshop Participants

U.S.A.: C. C. Bard (Eastman Kodak Company); C. W. Frank (Stanford University); C. E. Hoyle (University of Southern Mississippi); J. E. Guillet (University of Toronto, Canada); A. Gupta (Jet Propulsion Laboratories); P. P. Klemchuk (Ciba-Geigy Corporation); S. S. Labana (Ford Motor Company); N. J. Turro (Columbia University); O. Vogl (Polytechnic Institute of New York); C. G. Willson (IBM Research Laboratories); F. H. Winslow (AT&T, Bell Laboratories); A. H. Zewail (California Institute of Technology).

Sweden: K. Abbas (Bofors Plast AB); A. C. Albertsson (Royal Institute of Technology); M. Almgren (Uppsala University); H. D. Becker (Göteborg University); W. Garrett (University of Queensland, Australia); S. Gothe (A. B. Wilk, Becker); J. Hilborn (Royal Institute of Technology); A. Hults (Royal Institute of Technology); J. Kops (The Technical University, Lyngby, Denmark); J. Lucki (Royal Institute of Technology); J. F. Rabek (Royal Institute of Technology); B. Ranby (Royal Institute of Technology).

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