New Trends in the Photochemistry of Polymers

Edited by
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Preface

During the past decade, the *photochemistry of polymers* has become a field of central importance in polymer science and technology. Such applications as photopolymerisation, photocrosslinking, photostabilisation and solar energy devices have evolved from esoteric basic research specialities into industrial products. The use of photocurable coatings and printing inks is steadily gaining ground in many industries. Research on photoinitiated polymerisation has given rise to entirely new applications in microelectronics, e.g. in resists, barrier coatings, encapsulants, and printing wiring board technologies. Without the use of photoresists it would not be possible to develop modern electronic and computer industries.

In many of the above-mentioned subjects research has been carried out in the Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden, directed by Professor Bengt Rånby. On the occasion of his retirement in 1985 the International Symposium on 'New Trends in the Photochemistry of Polymers' was organised and held in Stockholm, 26–29 August 1985. We have the honour of editing the proceedings of this auspicious occasion which deals essentially with new developments in the field of polymer photochemistry. It was impossible to invite all the prominent specialists working in the photochemistry and photophysics of polymers and in the practical applications of these problems in industry. On this occasion friends and colleagues of Professor Rånby directly involved in cooperation with his department were invited to present their contribution. It is gratifying that, considering the short time schedule, most of those invited to contribute have completed their papers.

The papers presented in this book cover a very wide range of topics

important in the photochemistry and photophysics of polymers. Some lecturers review specified areas in the field while others concentrate more on the specified interest of the speakers.

Professor Webber (USA) reviews intramolecular energy transfer processes in polymers with particular emphasis on excimer kinetics, while Professor Guillet (Canada) presents a critical authoritative overview of the antenna effect in macromolecules which provides an important approach for developing polymers to harvest solar energy. Some polymers are shown here to have an energy conversion efficiency as good as chloroplasts. Professor Morawetz (USA) discusses molecular dynamics as studied by fluorescence spectroscopy for both tagged and doped polymers as well as polymer blends.

Professor Schnabel (Federal Republic of Germany) presents experimental results on the initiation of free radical polymerisation by acylphosphine oxides and derivatives, whereas Professor Wu (China) presents results on the photochemical behaviour of some monomers which contain electron donor and electron acceptor pairs.

Professor Pappas (USA) reviews the importance of radical versus cationic photopolymerisation, whereas Professor Smets (Belgium) discusses the photochemical synthesis of block copolymers with particular emphasis on efficiencies, mechanism and advantages. Professor Bamford (UK) discusses the importance of transition metal derivatives in the modification of polymers by photochemical methods and their importance in biomedical applications.

Dr Wiles (Canada) provides an overview of polyolefin photo-oxidation processes and places particular importance on the key role of hydroperoxides in photo-initiation and their removal/destruction during photostabilisation with emphasis on hindered amine light stabilisers.

Dr Winslow (USA) and Professor Weir (Canada) present results on the photochemistry of poly(ethylene-co-carbon monoxide) and polystyrene, respectively. Dr Hansen (Denmark) describes in depth unwanted photochemical reactions during the preparation and use of polymeric coatings such as delamination, chalking, erosion and colour changes.

One of the editors, Dr Allen (UK), reviews our current understanding of the mode of action of orthohydroxyaromatic and hindered piperidine light stabilisers with highlights of some of his recent work, while Professor Scott (UK) reviews the importance of antioxidant processes in polymer photostabilisation with particular emphasis on the role of the redox chain breaking donor/acceptor mechanism for most classes of light stabilisers. Professor Vogl (USA) describes his latest work on the synthesis of novel

polymerisable dibenzotriazole absorbers with particular emphasis on mechanism, efficiencies, properties and applications.

Professor Rabek (Sweden) presents a review on the applications of polymer and model systems as a means of harvesting solar energy. Professor Kagiya (Japan) presents results on the TiO_2 catalysed photolysis of water in the presence of water-soluble polymers and discusses ways of improving the efficiency of the process.

Lastly, Professor Miyama (Japan) reviews the use of photochemistry in preparing biomedical polymers with particular emphasis on photografting.

We hope that the contents of the lectures will be of value to all who attend the meeting as well as polymer scientists and technologists, chemists and biologists worldwide with an interest in this important developing field.

It is with great pleasure that we, the editors and publishers (Elsevier Applied Science Publishers Ltd), present this book on behalf of the organisers at the Royal Institute of Technology (Stockholm) to Professor Bengt Rånby in honour on his retirement and in recognition of his work. We wish him well in future years with health and happiness and hope that he will treasure this book with fond memories of us all.

NORMAN S. ALLEN
JAN F. RABEK

Contents*

* The names of invited speakers are printed in capitals. Only these speakers are included in the List of Contributors on pp. xiii–xv.

Professor Bengt Rånby: Contributions to Science and Technology of Polymers

HERMAN MARK
Polytechnic Institute of New York, New York, USA

In early Spring 1920—far north in Sweden near the Arctic Circle—a baby boy Bengt was born to the family on the Västaback farm; two years later the father took over the management of a cooperative dairy farm near by. The mother was a schoolteacher in the village.

1922—Sweden, the land of forests and lakes, of great natural resources of scientists and pioneers; 1922—Meeting of the German Scientists and Physicians in Leipzig; General Chairman Svante Arrhenius, major topics of discussion: Organic Chemistry, Willstaetter and von Euler; Colloid Chemistry, Svedberg; X-ray Physics, Manne Siegbahn.

Wood—the wealth of the land—was the prime target for intense activities, particularly how to isolate and purify its value-dominating component: *cellulose*. Klason, Hägglund, Erdtman and Adler and later Stockman and Gierer provided important fundamentals; tentative but very attractive results of M. Polanyi in Berlin and K. Freudenberg in Heidelberg permitted the suggestion of a long chain structure of cellulose. H. Staudinger, coming from rubber and polystyrene—not from cellulose—dispelled, not too easily, all doubts with the concept of *macromolecules*.

When this all started, Bengt was only two years old but the waves of this *revolutionary* aspect and its enormous *practical* consequences are even now producing innovations far beyond their original limits—and Bengt is still happily and successfully floating on them.

After a remarkably accelerated public and intermediate education Bengt entered Uppsala University—Sweden's scientific Mecca—and began, surprisingly but very interestingly, with the most basic disciplines: Astronomy; Mathematics and Theoretical Physics. B.Sc. in 1940 at the age 20. Then came Military Service and—in 1943—the first 'job', Assistant in Svedberg's Institute of the Uppsala University—hired by Sven Brohult,

Svedberg's right hand at the time. Nils Gralén, a rising star of these days and later for many years the leader of Sweden's modern Textile Research Institute in Göteborg, was in charge as Bengt's first supervisor. And the main topic was *cellulose*. All aspects on a broad front: on molecular and supermolecular level; configuration, conformation, hydrogen bonding, steric hindrance, thermodynamics and others. In 1952, PhD and successor to Gralén.

It was at that time that the Polytechnic Institute of Brooklyn had received from American Companies a number of fellowships to study new aspects of Polymer Science on a broad basis. Bengt Rånby got one of them—from Du Pont and in 1952 came to Brooklyn. Later, he and also others very kindly evaluated their stay at Poly as 'formative and of immense value'. Let me try today—with the hindsight of more than 30 years—to explain the impact of our 'way of work' on so different visitors from abroad: it was an unusual and delicate blend of discipline and freedom: hard and good work had to be done at any time. There were specialists available to insure that: Charlie Overberger, Bruno Zimm, Paul Doty, Turner Alfrey, Isidor Fankuchen and others, but beyond that: the sky was the limit. And what a sky! Debye and Flory at Cornell, Onsager and Fuoss at Yale and Tobolsky at Princeton. Short junkets in crowded cars to Wilmington, Bell Telephone, Allied Chemical, Cyanamide and even to Dow in Michigan. And on top of it, all summer long, the fabulous Gordon Research Conferences. There: exchange of experience, approaches and results in polymer research went on freely for a whole week in the invigorating air of New Hampshire: confidence was established and friendships were formed.

Rånby returned to Sweden in 1953 as a 'Docent of Physical Chemistry' at the University of Uppsala. But not for too long—somewhere on the lawns of Colby College in New Hampshire a bait had been prepared and in 1956 he was back in the USA. This time it was *cellulose* again. R and D Project Manager at the American Viscose Corporation in Markus Hook, PA, invited by Dr H. Cudd, Vice President, who created this new R and D Division. Rayon was in danger—nylon, the acrylics and polyesters were building up. A new basic understanding of the structure and texture of cellulosics was needed and its conversion into useful properties: action of modifiers, rayon tyre cord with improved 'fatigue', high wet modulus and 'polynosic' types. For Rånby these were just the two sides of one coin: fundamental knowledge made it *exist*—practical results let it *persist*.

But to make sure, during his years at American Viscose, Bengt studied also the new competing materials: *polyolefins* for fiber and film.

Within two years his personality, his working style and efficiency became

known. There is always a need for good people in a large country like the USA, and in 1959 a prestigious dual position was offered to him by the farsighted Professor Edwin Jahn, Dean of Science: Research Professor of Pulp and Paper Technology at the State University of New York and Director of the Empire State Paper Research Institute at the College of Forestry in Syracuse, N.Y.

Apparently the background was still *wood* and *cellulose*; why not? After all he was a Swede and a leader in the field. But Rånby had been looking around carefully during these years: a wave of new *concepts*—chain folding—new *tools*—Ziegler–Natta catalysts—and new *procedures*—Michael Szwarc's 'living polymers' (right on his doorstep) had introduced new and fascinating approaches: it was not only cellulose any more, it was polymers; *all* polymers. At the same time Bengt went through the traditional transition of all of us: we develop from the *things* to the *people*; manipulate first with chemicals, cooperate then with chemists and, finally, have to deal with *executives*. He met no difficulties on any level.

One of his earlier supervisors, a keen observer of the American scene with inherent linguistic sense told me one day in 1960: Bengt is 'smart'.

Interesting and stimulating publications, well organized and conducted symposia, remarkable successes in the organization of teaching and research did not remain unnoticed in Sweden. The pressing need for a modern center to cultivate this new discipline condensed in a call of significance: to organize and to run the first and only *Department of Polymer Technology* in Stockholm and, in fact, in Scandinavia.

1961—home is the sailor, home from the sea and his ship is full of valuable cargo: patience, experience and optimism. The new responsibility is heavy but the ingredients for success are there: leadership, people, space and money.

Of prime importance was the decision which main path the new Department should take? Evidently there existed several options: concentrate on certain materials, or on certain methods of preparation, characterization and processing. After careful deliberation Rånby decided to study, on a broad front, the interaction of light with polymers. There was a truly wide range: new polymers can be prepared by photosynthesis and photopolymerization; existing systems may be modified by controlled degradation or crosslinking, they may be stabilized by reactive additives, by the removal of sensitive groups, ring closure or other similar reactions. Quantitative studies on free radical formation with UV and ESR spectroscopy had started already in 1963 with several associates such as Hiroshi Yoshida, Göran Mählhammar and Peter Carstensen and led to a

series of publications; they were followed (since 1970) by the investigation of free radical polymerization with Koichi Takakura and Zenzi Izumi; of photosensitized reactions of various dienes, polystyrene, PVC and polyester together with Jan Rabek, Zenon Joffe, Julia Lucki and others. The amount of new information grew and its incorporation into the existing art had to be done on a larger scale. That means nothing else but writing or—at least editing—monographs and comprehensive volumes. Hence:

1972: Kinell, Rånby and Reio; *ESR Applications to Polymer Research.*
1975: Rånby and Rabek; *Photodegradation, Photooxidation and Photostabilization of Polymers.*
1976: Same authors; *Singlet Oxygen Reactions with Organic Compounds and Polymers* and
1977: Same authors; *ESR Spectroscopy in Polymer Research.*
1979: Same authors; *Long Term Properties of Polymers and Polymeric Materials*

The work in the laboratory continued along different lines—A-C Albertsson, G. Canbäck, S. Paul, T. Skrowronski, G. Arct, S. Göthe, A. Hult and others; the number of publications swelled to more than 300.

Still Rånby did not forget his first love, cellulose, and developed with R. Mehrotra, L. Gädda, C. Rodehed, J. Persson, D. Zuchowska and others new methods to modify starch and cellulose by graft copolymerization.

The time had come to delegate responsibility, to form working groups and teams in order to gain time for the only activity, which Rånby alone could perform: high level international representation in Western Europe, Japan, The Americas, China and all over the world. We all know and dislike the hectic days of such visits but for the Department of Polymer Technology at the Royal Institute in Stockholm they became important and, very fortunately, Bengt is an agile and indefatigable traveller: airport, plane, taxi, lecture hall, taxi, hotel, airport and so on. Within a few years the Department was a shining star in the Galaxy of Polymer Science Centers.

Very difficult to achieve and equally difficult to maintain!

Here we are: I told you what he did and how it was done. But, now that others will soon—January 1986—take over responsibility and representation; what is Rånby going to do?

In Brooklyn we have a saying: the first 30 years of your life you are doing what you are told to do, the next 30 years you are doing what you are paid for and—if there is anything left after that—then you can do what you

really want. Bengt, the young man, has many such years left. What will he do? Keep himself busy—to be sure! Maintain contact with all friends all over the world, think about new polymers and new applications, new ideas and new dreams. And then the sky only is the limit beyond that. And—Bengt—what a sky!

Twenty Years of Polymer Photochemistry in the Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden

JAN F. RABEK

Research on polymer photochemistry in the Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden, was started by B. Rånby at the beginning of 1963. The first publication by H. Yoshida and B. Rånby appeared on the study of ESR spectra of free radicals formed and trapped in polypropylene[1,2] and polyethylene[2] after ultra-violet radiation. Further work with P. Carstensen was extended to the ESR study of free radicals formed during the photodegradation of polyisobutylene[3,4] and other elastomers (cis-1,4-polybutadiene, cis-1,4-polyisoprene and cis-1,4-polypiperylene).[5-10] The photodegradation of polyethylene was then studied by G. Mälhammar in a dissertation for Tekn.lic. degree. To make polymeric materials more acceptable environmentally, paraffins and carbonyl compounds were added to polyolefins and PVC, which made them more susceptible to photo-oxidation.

The photochemical programme was then extended to sensitised polymer reactions in cooperation with J. F. Rabek who joined the department in 1971. The mechanisms of polymer photodegradation, photo-oxidation and photostabilisation were studied in a programme, directed by B. Rånby and J. F. Rabek, and carried out by J. Lucki, Z. Joffe, G. Canbäck, D. Lala and visiting scientists from Poland (J. Arct, T. A. Skowronski) and from China (S. K. Wu, Y. Y. Yang, S. Z. Jian, C. S. Dai, R. Liu and others).

Studies on the degradation of commercially available polymers have concentrated on polyolefins,[11,12] polystyrene,[16,17,31,38,41-43,49,53] poly(vinyl chloride),[18,25,26,30,36,48,50,52,54,59,74,80,81,99,100] polybutadiene,[8,10,27,39,40,44-47,55,56,58-61,76] polynorbornene,[65,66] unsaturated polyesters,[62,68,77,89] copolymers of butadiene/acrylonitrile[73] and ethylene/vinyl acetate[75] and polymer blends.[59,75]

Photosensitised degradation and/or crosslinking studies on polymers

have also formed part of these researches.[14,15,18,24,28,37,51,72] The reactions of several sensitisers such as benzophenone,[13] 4-chlorobenzophenone,[81] hexachlorobenzene,[81] quinones,[17,20,81] tetrahydrofuran,[25,54] anthracene,[31,38] N-methyl-2-benzoyl-beta-naphthiazoline,[35,40] 1,3-diphenylisobenzofuran,[56] various dyes[27,39,45] and metal salts[11,50,52] have also been examined and their modes of action established.

Special attention has been given to the effect of commercial additives such as thermostabilisers,[30,74] pigments[80] and lubricants[99] on the photooxidative degradation of poly(vinyl chloride).

A great part of the research programme has been devoted to singlet oxygen oxidation of unsaturated polymers such as polybutadiene,[19,21-23,27,29,32-34,45-47,58] polynorbornene[66] and polyene structures in partially dehydrochlorinated poly(vinyl chloride).[48]

Stemming from this research, studies of the stabilisation against photochemical[60,63,64,69,71,76-78,82,83,89-91,98] and singlet oxygen[44,45,60,70,71,76,84] oxidative degradation have been further developed. Some work focused on the antagonistic/synergistic effects between photostabilisers, antioxidants and other additives.[82-84,91,98]

In addition to the references quoted, parts of the results from these researches were presented at three international meetings organised by the department:

1. 22nd Nobel Symposium on *ESR Applications to Polymer Research*, Stockholm, 1972.[10-12]
2. IUPAC Symposium on *Long Term Properties of Polymers and Polymeric Materials*, Stockholm, 1976.[49-52]
3. EUCHEM Conference on *Singlet Oxygen Reactions with Organic Compounds and Polymers*, Stockholm, 1976.[32,33]

Starting in 1977, B. Rånby has initiated and developed a new research programme on the photopolymerisation, photocuring and photocrosslinking of polymers[85-88,92-97] in cooperation with S. Göthe, A. Hult, G. Broodh, J. Hilborn, K. Allmér and visiting scientists from China, Y. L. Chen, P. Y. Zhang, Z. M. Gao and B. J. Qu.

In order to present the most recent achievements in coatings technology an *International EUCHEM Conference on Photopolymerization and Photocrosslinking of Organic Coatings* was organised in Stockholm in 1980.

Studies of the photoinitiated crosslinking and surface modifications of polyesters, polyolefins and rubber polymers, are currently in progress.

From the beginning of this programme the department has had broad