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## Advances in Degradable Polymers

Otto Vogl

University of Massachusetts - Amherst, vogl@polysci.umass.edu

Andrea Eckert

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Conference Report

## Advances in Degradable Polymers

Andrea Eckert (a) and Otto Vogl (b)

(a) Austrian Plastics Institute, Arsenal, Objekt 221, A-1030 Wien, Austria

(b) Polytechnic University, Six MetroTech Center, Brooklyn, NY 11201, U.S.A.



Andrea Eckert



Otto Vogl

The Symposium "Advances in Degradable Polymers" was held under the auspices of the Ministry of Science and Research of Austria and under the auspices of the Austrian Plastics Institute and was organized by Dr. Brigit Blasch. It took place on October 6 and 7, 1992 at the Austrian Research Institute for Chemistry and Technology in Vienna. This Symposium, which was also the XI. International Herman F. Mark Symposium, honored Professor Bengt Ranby of the Royal Institute of Technology in Stockholm, Sweden, who received the Mark Medal of the Austrian Research Institute for Chemistry and Technology in recognition of his accomplishments in the field of polymer science, especially of photochemical reactions.

The program consisted of seventeen invited talks and one panel discussion. It was attended by about 120 participants from Austria and surrounding Central European countries. The invited speakers came from as far as Japan, Australia and the U.S.A.

The meeting was opened with a lecture by Ann-Christine Albertsson, the head of the Department of Polymer Technology, Stockholm, Sweden, entitled "Degradation of Polymers." The degradation of polymers is an important part of the knowledge of modern polymer technologies. At this time when the concern for the environment is great and basic knowledge of polymer chemistry allows the designing of new, interesting materials with unique properties, there are many applications where the degradation process of the polymer must be known.

Current trends in polymer research and the marketing of plastics

indicate an increasing demand for the development of a diversity of biodegradable polymer products with predetermined survival time. Four main fields can be distinguished: packaging materials, light weight items for one trip applications; mulch films for weed suppression and moisture retention or microclimate stabilization in agriculture; sacks and bags for the disposal of rubbish, litter and garden waste, and finally, in medical applications, in vivo in the human or animal body.

Many of the traditional bulk polymers are quite resistant toward environmental degradation, but selected modifications can render the materials susceptible to photo-oxidation and biodegradation. For biomedical use the attempts to develop degradable polymers have been focused on the synthesis of new biodegradable polymers, and also the modification of natural polymers. Aliphatic polyesters, polyanhydrides and polycarbonates were of particular interest. Most of the new materials are too expensive for non-medical use. For non-medical applications the modification of synthetic polymers have been more attractive approaches.



Bengt Ranby

Bengt Ranby of the Department of Polymer Technology, Stockholm, Sweden, and the recipient of the Mark Medal presented the plenary lecture: "Basic Reactions in Photodegradation of Some Important Polymers." Some 50 years ago it was reported that synthetic polymers such as plastics, rubbers, fibers, paints and lacquers are degraded on exposure to light. Polymers can be divided

into three groups: a) Highly photostable polymers which are commonly used without added stabilizer; b) Moderately photostable polymers which can also be used without added stabilizer; c) Poorly photostable polymers which need extensive stabilization for outdoor use.

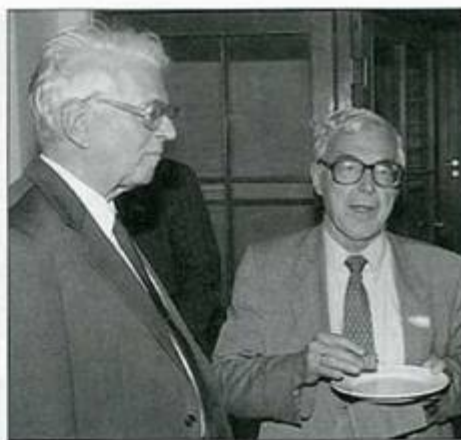
Ranby described the basic principle of photodegradation that is now well known, especially the propagation reaction of polymer peroxy radicals which involve hydrogen abstraction to give hydroperoxide groups which decompose by photolysis to radicals, carbonyl, vinyl and vinylic groups. Ketone groups on aliphatic chains absorb UV light quanta and the photoexcited state can undergo chain scission with the formation of methyl and vinyl end groups.

Chain terminations are due to radical combination to inactive products. Photodegradation of a polymer is usually related to sensitizers present in the form of impurities or modified groups which absorb light quanta and transfer the energy to cause polymer reactions. Commercial polymeric materials may contain such external and internal impurities from manufacture, processing and fabrication. Cellulose has a broad absorption spectrum; by photolysis in the near UV light the glycosidic bonds are broken and the radicals on the 4th carbon add molecular oxygen to form a peroxy radical which is rapidly rearranged. Formyl radicals are also formed in photolysis of cellulose by splitting off the hydroxymethylene group of the 6th carbon atom of the glucose ring.

Polyolefins and diene copolymers may be photo-stabilized by very complex reactions which are being extensively investigated. Polypropylene is more sensitive to photo-oxidation than polyethylene due to the tertiary bonded hydrogen along the chains which are easier to abstract than primary and secondary hydrogen. Polystyrene often has peroxy groups incorporated in the main chain of the polymer. During the free radical polymerization of styrene, trace amounts of oxygen are incorporated in the polymer chain by copolymerization of styrene with oxygen. Photolysis of these peroxy groups gives alkoxy radicals and tertiary carbon radicals by hydrogen abstraction. The sometimes significant yellowing of polystyrene is due to conjugated unsaturation and quinone formation. Polyacrylates and methacrylates are photodegraded in the same way. However the main reactions are main-chain scission and monomer formation (unzipping) from the new chain ends. Polymethacrylates are considered the most photochemically stable polymers of the commonly used materials. They show very little discoloration and are used extensively for transparent sheets and domes.

"Structural Studies on Polymers as Prerequisite for Degradation" was discussed by Josef Schurz of the University of Graz, Graz, Austria. He pointed out that the structure of polymers determines the accessibility for degrading agents of both chemical and microbial origin. Structure determinations are therefore an important prerequisite for degradation processes. For thermoplastic products, it was shown that both crystallinity and orientation vary significantly over both the cross section and the distance from the gate of the molded structure. Such changes are reported for polypropylene. For regenerated cellulose fibers, structural differences exist between fibers spun according to the specific spinning process. The kinetics of enzymatic degradation is significantly different from that of native or regenerated cellulose.

Klaus Hummel of the Technical University, Graz, Austria discussed the "Degradation of Unsaturated Polymers by Olefin Metathesis." Polymers with carbon-carbon double bonds in their



**Burkart Philipp and Josef Schurz**

main chain and crosslinked polymers in particular can be selectively cleaved by olefin metathesis in the presence of low molecular olefins and metathesis catalysts. In this way, single polymer units can be codegraded with low molecular olefins or with cyclic olefins. Metathesis degradation could be a destructive method for crosslinked polymer matrices and allows one to examine the filler that is present in the polymeric material. It could in principle be an ideal way of recycling plastic wastes with high double bond content.



**Gerhard Reinisch**

"Photoreactions of Polymers — Mechanisms and Applications" was presented by Gerhard Reinisch of the Ecology-Technology and Research Organization, Berlin-Adlershof, Germany. Photoreactions of polymers are technically used for cross-linking and for the production of graft polymers. Information storage processes are



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based on laser induced rearrangements of liquid crystalline polymers. For a long period, the objective of polymer research was to suppress aging processes in polymeric materials caused by sunlight. A well-aimed and fast photodegradation of polymers within strict limits is one of the currently actively studied applications of polymer photoreactions. These processes are investigated for microelectronic technology. Synthesis and degradation reactions of polymers for applications were discussed and the optical and topochemical conditions for microstructuring were evaluated. On the other hand, in order to degrade polymer sheets which cannot practically be recycled, photochemical decomposition reactions had been considered for some time. Newer approaches for practical applications of photodegradation of waste sheet material are based on the addition of activating complex compounds.



**Bengt Ranby    Andrea Eckert    Hartwig Hoecker**

Hartwig Hoecker of the Wool Research Institute, Aachen, Germany discussed the "Thermodynamic Recycling on the Ring Opening Polymerization and Ring Closing Depolymerization." Ring opening polymerization of various cyclic monomers such as the cationic polymerization of tetrahydrofuran, anionic polymerization of caprolactone, the metathetic polymerization of cyclooctene and the anionic or cationic polymerization of cyclohexamethyltrisiloxane has been extensively investigated. In connection with such ring opening polymerizations, the monomer-polymer equilibrium (ceiling temperature) and/or the formation of the ring-chain equilibrium have also been studied. In the last few years ring opening polymerization and copolymerization of cyclic carbonates, provided monomers mostly by depolymerization of the polymers. New polymer recycling concepts are taking into account the depolymerization and repolymerization equilibria. It relies on the ceiling temperature principle. Cases that are being considered based on this concept are aliphatic polycarbonates and block copolymers with carbonate ester and ether blocks.

James H. O'Donnell presented his work on "Radiation Degradation of Elastomers" which was carried out in cooperation with David J.T. Hill, Senake M.C. Perera, Peter J. Pomery and Andrew K. Whittaker at the University of Queensland, Brisbane,



**James H. O'Donnell & Bengt Ranby**

Australia. High energy irradiation produces changes in the polymer properties of polymeric materials, which may be beneficial or deleterious. The changes may range from an unavoidable exposure to a radiation environment to the use of radiation as a processing aid. Molecular changes in such reactions can be classified as crosslinking, polymer chain scission or structural modification of the macromolecules or the formation of small molecules. The effect of radiation can be deduced from the knowledge of the changes in molecular structure and of the reactive intermediate species. Elastomers are an important class of polymeric materials. Their elastomeric properties are highly sensitive to irradiation. Depending on the molecular structure, either crosslinking or scission may be predominant. Polyolefins undergo both crosslinking and scission of the polymer molecule. Polydienes upon irradiation cause carbon-carbon bonds to form crosslinks with high yields and with high conversion. Polyisobutylene causes the formation of small molecules exclusively, without crosslinking. Substitution by chlorine or bromine in the structure of polyisobutylene increases the ability for degradation. Consequently, the knowledge of the structure of the polymer is essential for the process of degradation by irradiation.

Michele Edge of Manchester Polytechnic, Manchester, England, described the "Environmental Degradation of Poly(ethylene terephthalate) by Hydrolysis." Crystalline and amorphous poly(ethylene terephthalate) (PET) sheets have been exposed to both thermal and UV aging. Environmental breakdown has been investigated by aging in dry or wet soils at low or high humidity, and, in the absence or presence of UV exposure to cause UV degradation. For highly oriented PET both chain-scission and cross-linking reactions are evident. In the case of amorphous PET crystallization exhibits an initial increase of stability due to plasticization and annealing.

"Stability and Degradation of Polymethacrylates with Controlled Structure" was discussed by Koichi Hatada of Osaka University, Toyonaka, Japan. Polymethacrylates upon heating or irradiation, degrade relatively easily to lower molecular weight compounds or to monomers. This is often noticed in sheet extrusion of poly(methyl methacrylate) (PMMA). The degradation of PMMA and



Koichi Hatada

subsequently the stability of methacrylate polymers, strongly relates to the type of ester groups of the methacrylates, to the end groups of the polymers, to their molecular weight, to their molecular weight distribution, and to their stereoregularity and, in the case of copolymers, to the copolymer composition. Isotactic and syndiotactic PMMAs have been prepared by living polymerization systems. Homo- and copolymers of various methacrylates with carefully controlled structures have also been synthesized.

The degradation temperature and the mechanism of the degradation of PMMA depends greatly on the type of end groups since the initiation usually starts from the chain ends of the polymers. PMMA prepared by radical polymerization has some unsaturated end groups; the decomposition temperature of the polymers decreased with increasing amounts of these double bonds. Special techniques such as polymerization in the presence of a transfer agent could be utilized to prepare polymethacrylates of increased thermal stability.

Tacticity of polymethacrylates was found to strongly affect the degradation of polymethacrylates; isotactic polymers degrade faster than syndiotactic polymers. An excellent example for the lower stability of isotactic polymethacrylates is their higher sensitivity as electron-beam or X-ray resist; isotactic PMMA is also more rapidly hydrolyzed to isotactic polymethacrylic acid than the corresponding syndiotactic PMMA. In methacrylate copolymers, the decomposition was found to depend on the copolymer compositions. The thermal properties of the copolymers could be controlled by changing the copolymer composition. In some cases block copolymers have decomposition temperatures different from those of the corresponding homopolymers. With the advanced knowledge of the stereochemistry and the techniques of macromolecular engineering, of stereospecific control and of the control of copolymer composition for the synthesis of methacrylate polymers, we can now satisfactorily control the stability/property relationship of



At the meeting

polymethacrylates by tailor-making the specific structures and the endgroups of the polymers.

Jan Sebenda of the Institute of Macromolecular Chemistry, Prague, Czechoslovakia, presented his work on "The Effect of Polymerization Conditions on the Degradability of Polyamide 6." Degradation of polymers initiated by heat or irradiation is strongly effected by trace-impurities. With polyamides, end groups have to be regarded as active foreign structures. In caprolactam the rate of thermooxidation can be changed by an order of magnitude by the proportion of the amine and carboxylic end group concentrations. Particular polymerization methods (anionic, cationic, hydrolytic) and polymerization temperature was found to influence the rate of thermooxidation of Nylon 6 and that of other lactam polymers. Based on these correlations, polyamides of higher stability could be produced even without stabilizing additives, just by choosing such polymerization catalysts and polymerization conditions which produce polyamides with stable end groups and with the absence of foreign structures.

The "Synthesis of Degradation of Polymers Containing Polyacetal Segments" was the subject of the discussion of Eric J. Goethals of the University of Ghent, Ghent, Belgium. Polyacetals were obtained by cationic ring-opening polymerization of cyclic acetals. Depending on the monomer structure, polymers with a wide variety of physical properties could be synthesized. Many polyacetals were degradable when treated with cationic initiators, due to their low ceiling temperature. Acetal functions were also cleaved by acid-catalyzed hydrolysis or alcoholysis. Consequently, linear or cross-linked polyacetals can be degraded to monomers (by depolymerization) or to mixtures of aldehydes and diols (by hydrolysis). In segmental copolymers (including segmented polymer networks) the polyacetal segments could be degraded selectively that means without effecting the second polymer chain. This selective degradation provided information on the mechanism of network formation.

Zbigniew Jedlinski of the Institute of Polymer Chemistry, Zabrze, Poland discussed "Recent Progress in the Synthesis of Polylactones and Their Applications as Degradable Engineering Materials." A strong demand has arisen for biodegradable polymers as packaging materials and in particular as biocompatible materials for various applications in biology and medicine. Various polyesters obtained by polymerization of lactones, lactide and cyclic carbonates are well known to be degradable polymers. A new procedure has been developed to synthesize biodegradable "tailor-made" polyesters





Zbigniew Jedlinski

with well defined mechanical, physical and chemical properties including biodegradability. For this purpose new anionic initiators have been employed, capable of producing living homopolymers, block polymers or "star" shaped polymers via the "living" polymerization process. New initiators and novel combinations of them with cation complexing agents such as crown ethers and cryptands were used. Alkali metal supermolecular complexes of potassium or sodium naphthalenides with crown ethers or cryptands and some new carbanions appear to be new and effective initiators for ring-opening polymerization reactions. Structure/property relationships of some new materials based on polymers from lactones, lactides, and vinyl monomers have been studied. The synthesis of block and functional polymers exhibited the characteristics of degradable materials.

Burkart Philipp of the Max Planck Institute of Colloid and Surface Chemistry, Teltow, Germany described his work on "Organic Solvent Systems for Cellulose as Biodegradable Polymer and Their Potential Areas of Application in Cellulose Spinning and Derivatization." A most important area of the application of novel organic solvent systems for the transformation of cellulose pulp to fibers and films have shown great progress in the context of searching for alternatives for the viscose process. The choice of such solvents was found to be limited because of economic, ecological and technological reasons. The research problem today consists in the identification of the different physical structures which exist in fibers spun from derivatizing or non-derivatizing spinning systems. Advantages and limitations of the regioselective homogeneous systems were discussed with regard to product properties.

"The Degradation of the Polymer Structure of Wood by Wetting and Drying" was discussed by J. Johan Lindberg of the Department of Polymer Technology of the University of Helsinki, Helsinki, Finland. This work was done in cooperation with Matti Laantera and Asko Sneek. Wood is a versatile construction material which competes favorably in many cases with synthetic polymers. Many outdoor applications limit the use of wood because of its biodegradability and on its changes in the structure on repeated drying and wetting. As water and chemicals penetrate, the cell structure of wood changes. This process is a temperature dependent



J. Johan Lindberg

diffusion controlled, partly non-linear process which strongly influences the mechanical and viscoelastic properties of wood. Pine and spruce wood have been studied and the mechanism and morphological aspects of the mechanical destruction process in wood has been studied.

Specifically, the viscoelasticity is markedly influenced by the number of hydrogen bonds between the cellulose fibers and the amorphous wood components. On mechanical extension and/or bending the disruption of the cell structures was found to be generally initiated along the middle lamella where the lignin content was highest and the fiber content lowest; the point of equilibrium moisture content seemed to be an important point of inflexion of various physical properties such as cell dimension anisotropy and viscoelasticity. The cell structure and its topology could be defined quite properly by only one number, the fractal dimension parameter obtained by computer aided picture imaging. It was concluded that the influence of extractables on the mechanical



Klaus Lederer

A. Narbeshuber

stability of wood was considerable. The removal of these materials reduced the water sensitivity and increased the volume stability of the structure.

Karl Tiefenbacher of the Franz Haas Waffelmaschinen Co., Leobendorf, Austria described "Starch Based Foamed Materials - Use and Degradation Properties." He pointed out that starch is an important renewable raw material and starch-based, foamed materials have found various applications, such as trays and containers for fast food. He also emphasized the significance of degradation waste management and its influence on the development of durable packing units. The author discussed critically the advantages of the use of renewable raw materials but he also stressed the misuse of the term "biodegradable."



**Speakers of the meeting**

"Biodegradable Plastics Based on Cellulose Acetate" was the subject of the lecture of Alexander Ach of the Bartelle Institute, Frankfurt, Germany. Cellulose acetate is in principle biodegradable, although degradation proceeds extremely slowly. Cellulose acetate will decompose in the soil but it will take many years, even decades, until the degradation is complete. Cellulose based materials can however, be recycled and can be incinerated very efficiently and without residues.

Fionnuala Wynne of ICI, Frankfurt, Germany described "PHB/V - a Natural Biodegradable Thermoplastic Polymer." The polymer consists of hydroxybutyrate units with between 0 and 30% of hydroxyvalerate units incorporated randomly throughout the polymer chain. The hydroxyvalerate units have been introduced by the addition of propionic acid to the normal fermentation process. Polyhydroxybutyrate (PHB) is now produced from pure glucose at the amount of 2 pounds of glucose to produce one pound of polyhydroxybutyrate. It is hoped that the process could be also carried out with impure sugars such as molasses or sugar solutions from beet sugar. However, there is no indication that this prospect could actually be achieved and polyhydroxybutyrate could be prepared on a technical scale based on these starting materials. It was also pointed out that PHB could be safely incinerated.

At the end of the Symposium, as it is traditionally the case for Mark Symposia, a panel discussion was held under the leadership of Professor Otto Vogl of the Polytechnic University, Brooklyn, New York. The panel members were: Bengt Ranby, Royal Institute of Technology, Stockholm, Sweden; Manfred Raetzsch, PCD Polymere, Linz, Austria; Klaus Hummel, Technical University, Graz, Austria; and Ferenc Tudos of the Central Research Institute



**The panel discussion**

of Chemistry, Budapest, Hungary. The panel discussion focussed on the options for the disposal of polymeric materials. Some of the disposal problems that were discussed were the degradation of rubbers, especially the "tire problem." The possibility of utilizing the metathesis reaction for the degradation of vulcanized rubber was discussed and the disposal of poly(vinyl chloride) (PVC). For PVC, it was concluded that PVC will be used in the long term because of its overall favorable properties at an acceptable price, especially for pipes under ground. There will be short term problems because of some immediate problems for the disposal of PVC.

One other aspect of the discussion on polymer degradation became very clear during the panel discussion, following earlier arguments during the symposium. The panel concluded unanimously that while, recycling, composting and land fill applications for plastic materials must be considered and discussed for a long time, the only viable long-range solution for plastics disposal is combustion with the recovery of the energy. It was estimated that not more than 10 to a maximum of 15% of the plastic materials can ultimately be recycled; polyesters, especially PET and polyamides are prime candidates. It was concluded that only specialty and high value polymers could be and would be worthwhile to be recycled. The general warning by the experts was that materials based on commodity plastics such as polyolefins, by the time they are ready to be recycled usually has undergone such severe degradation and changes of properties that the material is substantially useless for reapplication.

The panel showed much more enthusiasm for the idea of thermal degradation of plastics material. Both the combustion in the presence of oxygen to CO<sub>2</sub>, as well as the thermal degradation in the presence of hydrogen to form directly low molecular weight, hydrocarbon type materials was considered of great importance for their potentials for practical solutions.

It was concluded that each case of plastics recovery, of plastics recycling and plastics disposal will have to be studied very carefully based on the type of material and the cost tolerance for the disposal of plastics materials, but no sweeping conclusions could be drawn. Ultimately the question was asked whether the research moneys that are now being invested for the development of recycling and composting systems could not more effectively be invested in the development of high quality and selective incinerating systems as a means for efficient and final plastics disposal.

The Mark Medal was presented to Professor Bengt Ranby and to Dr. Ernst Poecksteiner, President of the Dietzel Company on



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Wednesday evening in the Palais Starhemberg which is the location of the Ministry of Science and Technology. The medal was presented by the Vice President of the Republic of Austria and Minister of Science and Research, Dr. Erhart Busek.



**Bengt  
Ranby**

**Ann Christine  
Albertsson**

**Ambassador  
of Sweden  
to Austria**

The selection of the recipient of the Mark Medal is made annually and an International Symposium is arranged for this occasion. The subject of the symposium is usually tailored according to the scientific interest of the recipient. Since 1989 radical changes have been made in the organization of the symposium and in the contents of the symposium. The Mark Symposia are now truly International Symposia. This year, speakers came from as far as Japan, Australia, Sweden, Finland, Poland, Czechoslovakia and the U.S.A. The manuscripts based on the presentations of the symposiums are now being published as a special issue with silver cover in the Journal of Macromolecular Chemistry. For many years the Symposium language was German; the presentations are now almost exclusively in the more suitable international language – English. It can only be hoped that English very soon will finally be adopted as the conference language.

### Conclusion of the Mark Symposium (Jane C. Vogl)

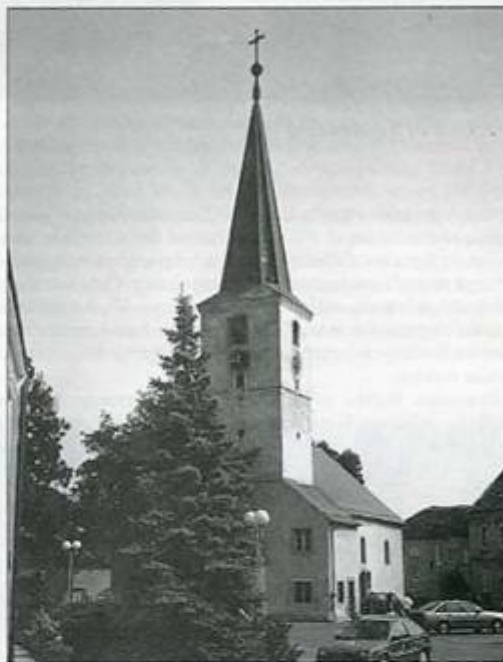
For the last four years, it had been a tradition to conclude the Mark Symposium in an informal gathering at a traditional Austrian winehouse in or near Vienna. Since this year's Symposium coincided roughly with Otto Vogl's 65th birthday it was decided to combine the farewell banquet/reception with this occasion. The Weinhaus Schafner in Otto Vogl's birthplace in Traiskirchen, 20 miles south of Vienna, was selected for this occasion. The organizers, speakers and selected participants of the Symposium as well as some of his former colleagues and friends joined us for this celebration.

The guests were first received by the mayor of the City, Fritz Knotzer and the Municipal Council in the city hall of Traiskirchen.



**Mayor Fritz Knotzer**

**Otto Vogl**



**Main Square, Traiskirchen**

It was an excellent opportunity for participants of the Symposium to meet informally in a congenial atmosphere which gave a particular flavor to the conclusion of the Symposium.