

# Progress in Cellulose Research in the Reflection of the Zellcheming Cellulose Symposium

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**Summary:** Within the general topic “Structure and Properties of Cellulose” this presentation covers some principle issues of cellulose research during the recent 50 years and their reflection in the lecture and discussion program of the “Rundgespräch” since 1959. The goal of this “Rundgespräch” was a get together of fundamental research and industrial practice for exchange of information and for cooperation, realizing an interdisciplinary approach of chemistry, physics and technology in cellulose, supplemented later by environmental problems and aspects of biology and medicine. An especially profitable area of joint activities was found in the analytics of cellulose, experiencing the entry of modern instrumental methods in cellulose research and the growing relevance of distribution spectra of various structural parameters. With respect to the “renaissance of the viscose process” during the decades after World War II, activities of the “Rundgespräch” were at first centred on the complex sequence of reactions of viscose preparation, including the evaluation of dissolving pulps, and also around the chemistry and the colloid chemistry of filament formation in the spinning process. Further central topics in the following decades were classical and new solvents for cellulose and the states of solution obtained as well as the theoretical meaning and experimental comprehension of cellulose reactivity during chemical processing. Additionally, hemicelluloses were included in the program as well as cellulosic specialties like membranes, cellulose powders, or bead cellulose. Within an integration process of cellulose research into polymer science, composites of cellulose with synthetic polymers gained more relevance in recent years. Finally, 3 highlights during the 50 years of the “Rundgespräch” are mentioned, i.e.,

- a survey of German cellulose research after the re-unification
- a presentation of the stimulating results of the large DFG-project on molecular and supramolecular structure of cellulose
- this year’s program with its really “international flair” and its wide span from the history to actual topics and further to a vision of future development.

**Keywords:** biopolymers; cellulose; functionalization of polymers; polysaccharides; structure-property relations

## Introduction

After some general remarks on the development of science and technology this presentation surveys ideas and results of

cellulose research within the past 60 years and then summarizes the reflection of this development during 50 years by the Cellulose-Chemiker-Rundgespräch (Cellulose Symposium) of Zellcheming. To the authors’ opinion, the following four topics have been essential for cellulose research and development:

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- the idea of multidisciplinary, i.e. a growing cooperation between different sciences, especially between chemistry and physics, leading also to integrating terms like polymer science
- the advance of computer techniques used now in industrial cellulose processing as well as in lab analytics and control
- a growing relevance of morphology in approaches of basic research substituting the dominating energetic approach of the 50ies
- a growing awareness of ecological problems and facts in R&D as well as in industrial production and market, simultaneously encouraging new branches of science like chemical toxicology or biotechnology.

## Review of Cellulose Research since about 1950

Research efforts and results shall be structured here according to the three areas of basic research with its concepts besides results and models of interpretation of progress in analytical techniques employed in the field considered here, and of success and disappointment of R&D in processes and products representing the economic output of six decennia.

The third point shall be treated first, without the claim of completeness, focusing on the viscose process.

### Processes and Products

#### *Supply of Pulp for Chemical Processing*

Regarding the wood species employed as raw material for dissolving pulp Eucalypt has found broad attention and acceptance due to its short cutting cycle and ways of manufacturing high alpha-pulps for high grade viscose filaments.

The use of reed like *Arundo Donax* or *Phragmites Communis* for dissolving pulp manufacturing has been rather intensely pursued between 1940 and 1960, but was

then abandoned without permanent success. According to the authors experience with reed pulp from the Donau river delta due to a too high SiO<sub>2</sub> content in the dissolving pulp can be considered as the main cause.

The sulphite process still dominating in the 50ies has been gradually substituted by the prehydrolysis sulphate pulp. Efforts of the sulphite pulping industry to compete by hot alkali refined sulphite pulp with an alpha cellulose content of 95-96% remained without permanent success due to too high production costs.

Chlorine free bleaching is now generally employed in the manufacturing of dissolving pulp to meet ecological demands either by TCF (total chlorine free) bleaching or by an ECF (elementary chlorine free) procedure, using ClO<sub>2</sub> as a bleaching agent.

#### *The Viscose Process*

With an annual production of nearly 3 million tons of filament and stable fiber the viscose process still keeps its position within the large scale processes of the chemical industry. Three principal roots were pursued since World War II in order to make filament production from pulp via the state of solution safer and more profitable, i.e. reduction of CS<sub>2</sub> and NaOH input in the viscose process without loss of filament quality, development of really new filament types of hitherto unknown quality, along the route of the viscose process, and finally efforts of R&D to replace the viscose process at least partially by an alternative route of dissolving cellulose and subsequent filament spinning from this solution.

Already at the end of World War II extensive efforts were made by the German industry to reduce the input of chemicals in viscose preparation by a more sophisticated and strictly controlled production regime (so called "Sparviskosen"). This route was continued in the following decennia by using specially trimmed surfactants in viscose preparation and spinning. In the 60ies Sihtola<sup>[1]</sup> developed a viscose process with a double alkalisation, i.e. a higher

NaOH concentration for converting the pulp to alkali cellulose, followed by a lower lye-concentration in the xanthation and dissolving steps in order to increase the CS<sub>2</sub> yield for cellulose xanthogenate formation. From a scientific point of view this procedure was really progressive but its technical realization obviously proved to be too complicated for general use. Promising today is a large scale application of the significant increase in pulp reactivity after an electron beam irradiation, which was thoroughly investigated during the recent years in the institute of wood and plant chemistry of the Technical University of Dresden,<sup>[2]</sup> resulting in technical process already successfully tested in large scale experiments. For about one century the reaction step of xanthogenation had been considered not feasible in a continuous process, but now a continuous fibre xanthation is practiced in several viscose plants.

Most remarkable results of R&D around the viscose process are the development and the production of completely new types of continuous filament and staple fiber. The so-called viscose super cord arrived on the market in the late 50ies and dominated it during the whole 60ies in the tire cord field, due to its high tenacity and elasticity. The filament is characterized by a core shell structure obtained by spinning a cellulose xanthate of higher degree of substitution from a high alpha pulp in the presence of a so-called modifier into a spinning bath of rather high Zn<sup>2+</sup> content. The surface active modifier, often an aliphatic amine or a polyethyleneoxide in combination with the Zn-ions, influences the balance between the kinetics of xanthate decomposition and structure formation of the thread. Based on similar principles is the so-called HWM (high wet modulus) process now widely employed for the production of high quality viscose staple fibre with excellent mechanical properties, especially in the wet state, a somewhat other technological route has been pursued in manufacturing the so-called polynosic type of viscose staple fibre, exhibiting a very high strength but also some tendency to fibrillate.

Many efforts have been spent in the past 60 years for finding an alternative to the viscose process avoiding the hazards of CS<sub>2</sub>. But the story of “viscose alternatives” is rather a story of failures with just one success up to now. About 1950 Rogovin<sup>[3]</sup> tried to prepare a cellulose carbonate, the optimal alternative from an ecological point of view, but unfortunately not realizable for kinetic reasons.<sup>[4]</sup> Many of the new solving systems found for cellulose during the last six decades have been tested with regard to filament spinning, sometimes up to the pilot scale as for example the N<sub>2</sub>O<sub>4</sub>/N,N-dimethylformamide (DMF) system with a cellulose nitrite as the soluble intermediate. In contrast to these routes stood the idea of permanently derivatizing cellulose with hydroxyethyl groups to the lowest degree of substitution (DS) possible for obtaining an alkali-soluble spinning dope and then to mask the hydrophilic groups after spinning. Even this procedure was developed up to the pilot scale and rendered good threads in the dry state, but not in the wet one. A real success, however, resulted from the idea to dissolve the pulp in a melt solution of NMMNO (*N*-Methyl-Morpholine-*N*-Oxide) with defined water content at a temperature of about 80 °C to 100 °C, and then to form the thread by spinning over an air-gap into an aqueous bath.<sup>[5]</sup> This process is realized now on a large scale as the so-called Lyocell Process or Tencell Process with a total annual production of 120.000 tons. Furthermore this principle provides good chances for manufacturing none-textile goods from dissolving pulp<sup>[6]</sup> and is the basis of a new procedure for preparing a cellulose blowfilm<sup>[7]</sup> with the advantages of a melt-spinning procedure. This process, developed by the Fraunhofer Institute of applied polymer research in Teltow-Seehof/Golm, was already tested in successful large scale experiments together with industry. A further alternative to the xanthogenate process now in discussion with a positive prognosis is the so-called Carbacell Process.<sup>[8]</sup> Pulp is reacted here with urea and processed to a soluble cellulose carbamate,

subsequently spun into an aqueous alkaline bath to arrive at a thread of cellulose II with good mechanical properties. As demonstrated by the Lyocell and the Carbacell Process, alternatives to the viscose process can obviously be designed and successfully realized by cellulose dissolution in a non-derivatizing solvent as well as via an intermediate covalent derivatization, but obviously these two routes lead to different filament structures and thus to different spectra of textile mechanical properties.

#### *Survey of Results of R&D in other Areas of Cellulose Products*

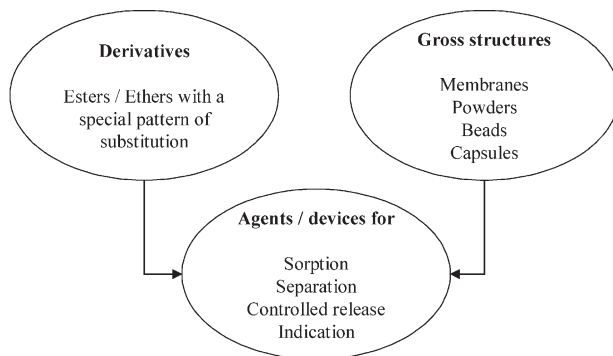
Leaving aside cellulose products at the borderline of cellulose chemistry like non-wovens, sanitary sorbents or composites with cellulose, the progress within the last 60 years can be visualized according to Figure 1. In the area of cellulose ethers and esters development and realization of a host of end-used tailored special products is characteristic, often provided with more than one substituent as for example with alkyl-hydroxyethyl ethers. On the other hand we observe an industrial realization of new cellulose gross structures like membranes, powders, beads or capsules.

Although cellulose film is known for many decades as a packaging material, the development and production of cellulose haemodialysis membranes can be seen as a remarkable achievement of R&D in the previous half century and as a contribution

of cellulose research to the preservation of human life.<sup>[9]</sup> Cellulose powders, mostly obtained by a combination of partial hydrolysis, and mechanical disintegration find now widespread use in pharmacy and in chromatography.<sup>[10]</sup> Cellulose beads<sup>[11]</sup> obtained by decomposition of cellulose xanthate or acetate or cellulose based capsules offer good opportunities as carriers or as media for sorption or separation in medicine, biochemistry or biotechnology. As prosperous for the future the combination of gross structure variation and variation of type and pattern of substitution can be visioned.

#### **Progress in Cellulose Analytics**

A real stormy evolution occurred in a whole area of cellulose analytics during the last 60 years. In the 40ies when I started my professional activities in an analytical laboratory of the viscose industry, the whole field was still dominated by wet chemistry in aqueous systems mostly with a volumetric end point determination. The pentosan content of a dissolving pulp for example was assessed after transformation to furfural and its determination by a rather ritualized special iodometric titration. Today we find nearly no instrumental technique that is not also employed in our area of science. The analytics of cellulose and its derivatives is widely integrated into polymer analysis and gained



**Figure 1.**  
Scheme of progress in cellulose-based specialties.

profit also from the progress on synthetic polymers. We have now complete series of automated and computerized instruments at our disposition. Chromatographic separation techniques and a wide variety of spectrometric methods especially NMR<sup>[12]</sup>, mass spectrometry and recently Raman spectroscopy must be specially mentioned as they paved the way for determining substitution pattern within the anhydroglucose unit and along the chain. Also the rapid development of electron microscopy with today's techniques of quantitative image evaluation must be mentioned. Table 1 presents some key words summarizing today's state of cellulose analytics.

To the authors opinion, three areas of progress must be emphasized here, i.e. the relevance of imaging techniques, the concepts and techniques for determining spectra of distribution instead of average values and the necessity of standardization of established procedures for a national and international comparison of analytical criteria. Regarding the activities of Zellcheming the merits of Otmar Töppel shall be mentioned here explicitly.

Two examples from recent publications may illustrate these rather abstract statements and demonstrate the efficiency of combining a scientific concept with modern instrumental techniques. Mischnik et al.<sup>[13]</sup> promoted the application of mass-spectrometry in cellulose analytics and employed this technique together with statistical models to elucidate the course of degradation processes of cellulose. Potthast et al.<sup>[14]</sup> arrived at a quantitative description of carbonyl and carboxyl group distribution in cellulose samples in dependence of molar mass distribution by combining fluorescence spectrometry with the concept of

**Table 1.**  
Progress in cellulose analytics.

Instrumental techniques instead of "wet chemistry"
Integration of cellulose analytics into the entity of polymer analytics
Assessment of spectra of distribution instead of average values
Standardization of established analytical procedures

distribution spectra, pointing also to the practical consequences of their findings for preserving and restoring historic documents and books as a contribution of cellulose research to our national culture.

### Role of Basic Research in Cellulosics during the Recent Six Decades

#### "State of the Art" 1950

In the midst of the last century, Staudingers concept of the polymer chain with covalent links between the monomer units had been generally accepted, last not least due to convincing experiments on polymeranalogous reactions with cellulose performed in the Freiburg group. Knowledge on solid state structure of cellulose was mainly based on wide angle X-ray scattering (WAXS)-diagrams yielding the lattice-dimension of the crystalline part of the structure. Investigations of the fibrillar structure of cellulose were mainly performed by light microscopy; the techniques of electron microscopy were still in the beginning. Knowledge on kinetics and mechanism of the complex reaction sequence in the viscose process was still rather incomplete and the same statement held true for other reactions of cellulose derivatization and degradation despite the progress in experimental organic chemistry of cellulose in the 40ies substantially owed to the work of Rogovin.<sup>[15]</sup>

#### Review of Progress since about 1950

Turning now to the second half of the previous century, Table 2 summarizes some important areas of research without the claim of completeness. The topics listed here shall be commented briefly, referring mainly on the results of German research groups as the principle contributors to our symposium, and combining scientific concepts, experimental results and models of interpretation.

#### Solid state structure

Two routes were pursued: further efforts to analyze the fine structure of the polymer

**Table 2.**

Areas of basic cellulose research.

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Solid state structure of cellulose
Reactivity of dissolving pulp
Degradation of cellulose
Activation of cellulose
Kinetics and mechanism of the viscose process
Search for new solvents for cellulose
State of dissolution in cellulose-containing systems
New derivatization reactions and derivatives
Regioselective derivatization of cellulose
Role of the pattern of substitution in determining product properties
Interdisciplinary cooperation of cellulose research with the life- and the material sciences

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preferentially by X-ray techniques and investigations of the fibrillar structure of cellulose by means of electron microscopy, regarding the first route some of the models for interpretation shall be mentioned here briefly, beginning with the old crystalline amorphous two-face concept followed later by Kargin's conception of chain puzzles and then by the idea of a continuous order spectrum and finally the conception of chain-folding presented by Manley<sup>[16]</sup> and that of agglomeration of ordered regions as discussed by Lenz, Schurz and Wrentschur<sup>[17]</sup> for regenerated cellulose fibres obtained via a derivatizing solvent. Regarding the fibrillar structure of cellulose the central problem for many years was that of the existence of a so called "elementary fibril", with important contributions given by Fengel.<sup>[18]</sup> From this principal problem of cellulose solid state structure the question of pulp reactivity in derivatization or dissolution evolved as a side-branch together with that of structural criteria responsible here, forming a further link between chemistry and physics of cellulose and keeping cellulose scientists active up to now in factories and institutes. Connected with cellulose solid state structure is also the century-old research topic of cellulose degradation. Pioneering results were presented here during the past 50 years especially with regard to enzymatic cellulose degradation so for example by Puls and his group<sup>[19]</sup> in Hamburg. Polymer physics generally enlarged its view during the past 50 years from a purely analytical branch of

science describing given structures to a more active role of participation in processes of structure formation. A convincing example from our field of work is the development of a cellulose blow film spun from a melt-solution of the polymer in amine oxide.<sup>[7]</sup>

#### *Research on the Viscose Process*

Until the end of the 70s the kinetics and mechanism of the viscose process have been a central problem in cellulose research and development stimulating further research in cellulose solid state structure as well as in cellulose solutions and structure formation from solution and in the chemistry of cellulose derivatization. A century-old problem, still keeping chemists and physicists busy, is the first step of the process, i.e. the formation of alkali-cellulose. Table 3 lists some landmarks during the past 80 years and demonstrates how step by step new faces of the chemical, physical and colloidal structural changes during this reaction could be unveiled. Regarding the further steps of the viscose process the results obtained by Treiber<sup>[28]</sup> and by Krässig<sup>[29]</sup> on cellulose xanthation and those of Klare and Gröbe<sup>[30]</sup> on the role of the zinc ions in filament formation during the viscose spinning process shall be mentioned here especially, also in connection with Zellcheming activities.

#### *Cellulose Solvents and Solutions*

Another complex topic of cellulose research in the past 50 years was the search for new cellulose solvents and the elucidation of their way of action. In the 50ies and 60ies Jayme<sup>[31]</sup> and his group in Darmstadt found several new metal complex solvents especially the aqueous alkaline tartaric ferric acid complex (FeTNa). In the seventies the solvent action of this system and the solvent action of some binary inorganic-organic solvent systems like N<sub>2</sub>O<sub>4</sub>/DMF or LiCl/*N,N*-dimethyl acetamide were described. Significant contributions to the molecular mechanism of dissolution in metal complexes and some salt-containing systems have been given by

**Table 3.**

Some landmarks of research on alkali cellulose formation.

Relation between swelling and alkali uptake	Heuser und Bartunek um 1925 <sup>[20]</sup>
WAXS-Diagram of Na-cellulose	Katz and Mark 1925 <sup>[21]</sup>
Concept of “apparent” and “real” alkali uptake	Schwarzkopf <sup>[22]</sup>
Concept of the roll of hydrate shells in the reaction of cellulose with aqueous NaOH	Bartunek <sup>[23]</sup>
Concept of partial reversibility of alkali cellulose formation	Hayashi <sup>[24]</sup>
Results and model of partial reversibility	Fink et al. <sup>[25]</sup>
Concept of the “Reactive Structural Fractions” in alkali cellulose formation	Fink et al. <sup>[26]</sup>
Kinetics of alkali cellulose formation and model of interpretation; Model of a parallel-antiparallel rearrangement of chains by alkalization	Fink et al. 1999; Okano and Sarko <sup>[27]</sup>

Burchard<sup>[32]</sup> and by Klüfers<sup>[33]</sup>, employing modern instrumental techniques, especially NMR. The non-derivatizing solvent NMMNO<sup>[34]</sup> rather soon became the basis of the only realized alternative to the viscose process. Investigations by Rosenau<sup>[35]</sup> on the complex roots of thermal decomposition of this amineoxide can be seen as a valuable contribution to the safety of this new process. Since the end of this century ionic liquids like alkyl-substituted imidazolium chloride give rise to lively discussions as new cellulose solvents.<sup>[36]</sup>

The successful search for new cellulose solvent systems in the second half of the past century promoted two other areas of cellulose research, i.e. investigations of the state of solutions and efforts to enhance the accessibility of the solid state structure to the action of the solvent by a so called activation.<sup>[37]</sup> For this purpose many chemical and physical procedures are available now as for example special modes of mechanical disintegration, the action of cellulolytic enzymes or a treatment with aliphatic amines. The “state of solution”, i.e. the extent of lateral order between the macromolecules, finally down to a so called molecular solution was found to depend on solvent - solid state order of the specimen and on its molar mass and molar mass distribution. Experimental techniques preferentially employed were light scattering, sedimentation in the ultracentrifuge and rheology. Regarding the latter one the extensive studies of Schurz<sup>[38]</sup> with a proposal for a classification of the states

of solution shall be cited here. Practical relevance for the viscose industry gained the optical or conductometrical assessment of inhomogeneities (gel particles) in the spinning dope<sup>[39]</sup> during the seventies. As a special state of solution, liquid crystalline systems with cellulose were described especially by Zugenmaier<sup>[40]</sup> and his group.

#### Cellulose Derivatization

The large number of new cellulose solvents including many with non-aqueous media the elaboration of procedures for cellulose activation and the rather convenient access to substitution patterns via NMR stimulated a new boom in the organic chemistry of cellulose since the late seventies leading to the preparation and exploration of new cellulose derivatives like silyl cellulose or cellulose nitrite or sulphate. Furthermore, the experimental techniques available now paved the way to regioselective substitution within the anhydroglucose unit and also along the cellulose chain, and to a better understanding of the role of substitution pattern on sample properties. The results obtained in this field at the University of Jena of Klemm<sup>[41]</sup> and Heinze<sup>[42]</sup> and at the Fraunhofer-Institute of applied polymer research in Teltow-Seehof/Golm especially by Philipp et al.<sup>[43]</sup> shall be mentioned here as examples.

#### Final Remarks

At the end of this review on 60 years of cellulose research two points may be stressed again, i.e. the benefits of an

interdisciplinary cooperation and the benefits of a research philosophy considering scientific concepts systemic experimental work and theoretical models of interpretation as a unity. Besides the cooperation between chemistry and physics, widely realized today, the connection of cellulose research to the life sciences and to material sciences can be seen as an asset for future success.

#### The Reflection of Progress in Cellulose Research in the Programs and Discussions of the Cellulose Symposium (Cellulose-Chemiker-Rundgespräch) of Zellcheming

Without doubt it was a good decision by the initiators of the symposium Richard Bartunek and Joseph Schurz to start it on a small scale as an exchange of ideas and experience between the German cellulose experts in industry and universities to bridge the gap between applied and basic research. Another good idea was the well-poised change in program shaping between a central topic and a rather free registration of papers over all the areas of cellulose research and development.

Table 4 informs on the frequency of special topics in our programs. Already the general topic in 1959 "Fine Structure of Cellulose"<sup>[44]</sup> determined the general course of this symposium, treating the fine structure of cellulose itself as well as the chemistry of cellulose reactions, especially alkali cellulose formation.

During the 60ies (Table 5) the entity of the viscose process remained in the centre of the program to which already then Scandinavian groups especially from Sweden gave important contributions. The merits of Erich Treiber on the scientific level of the symposium are to be mentioned

**Table 4.**

Frequency of some central topics in the Cellulose Symposium of Zellcheming from 1959 to 2008.

Topic	Frequency
Structure and properties	11
Analytics	10
Solvents and state of solution	6
Products and derivatives of cellulose	6

**Table 5.**

Selected topics of the Cellulose Symposium of Zellcheming in the Sixties.

Solid State Structure of Cellulose
Viscose Process
Pulp evaluation
Alkali cellulose formation
Xanthation
Thread formation from viscose
States of solution of dissolved cellulose
Biogenesis of cellulose

here. The authors remember well the vivid and sometimes controversial discussions on the state of cellulose solutions in dilute and technical systems, when the opinions of morphologically oriented groups like that of Dolmetsch met those of physico-chemical oriented ones like that of Marx-Figini.

In the 70ies (Table 6) the scope of the program was definitely enlarged including now procedures of delignification and new products like cellulose powders or membranes. A special ZETA-potential symposium in 1975 formed a bridge to paper technology and contributions on membranes for haemodialysis already started the connection to medicine.

In the 80ies (Table 7) the program was centred around a better utilization of the biomass of wood inclusive hemicelluloses as a raw material for a variety of polymer products, while the route to low molecular products was seen rather sceptical. Regarding cellulose derivatization, procedures of activation and degradation with their influence of accessibility and reactivity

**Table 6.**

Selected topics of the Cellulose Symposium of Zellcheming in the 70ies.

Broadening of the scope of the program by presentations on
Delignification
Non-wovens
Cellulose powders
Cellulose membranes
Analytics of celluloses
Assessment of gel particles
Patterns of cellulose swelling
Application of spectroscopic techniques
Special symposium on Zeta-Potential of pulp and paper in 1975



**Table 7.**

Selected topics of the Cellulose Symposium of Zellcheming in the 80ies.

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General topic: "Utilization of the Biomass of Wood"  
 New products from cellulose and hemicellulose  
 Derivatization and derivatives of cellulose  
*Cellulose reactions in homogeneous systems*  
*Silyl cellulose*  
*Cellulose sulphate and phosphate*  
 Formation of liquid crystalline systems with  
 cellulotics  
 Application of modern instrumental techniques in  
 cellulose analytics

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were discussed, and also cellulose reactions performed in homogenous systems were presented.

The contribution on cellulose analytics accentuated the relevance of modern instrumental techniques, and this trend was also continued in the 90s.

A real highlight was the symposium of 1991 after the German reunification: for the first time all the groups active in cellulose research in the eastern part of Germany had an opportunity to present their results.

The central topic of the symposium in the 90s (compare Table 8) was the problem of chemistry and environment in our area of science, including a better utilization of cellulose and hemicelluloses, ecologically safer routes of pulping by using principles of biotechnology. These ecologically oriented presentations were supplemented by contributions on the role of molar mass in derivatization and on the role of substitution patterns in determining the material properties of cellulose derivatives. New instrumental routes for the assessment

**Table 8.**

Selected topics of the Cellulose Symposium of Zellcheming in the 90ies.

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General topic: "Oecological aspects of cellulose processing"  
 Cellulose and hemicellulose as resources for the chemical industry  
 Ecological safe delignification and bleaching  
 Biotechnology in pulp production  
 Routes to higher pulp reactivity  
 Patterns of substitution in cellulose derivatives  
 Analytics of functional groups in pulp  
 Presentation of the results of the DFG-Project

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of functional groups in cellulose stood in the centre of contributions to cellulose analytics and raised a new attention to this old problem. Joined efforts of the cellulose industry and of institutes succeeded in 1996 in establishing a large DFG-project "Cellulose and cellulose derivatives – molecular and supramolecular structure design"<sup>[45]</sup>, to promote basic research in the whole area of production and processing of cellulose. The results were presented in the annual symposia at the end of the past and the beginning of this century. All these contributions demonstrated the ample, but not yet exhausted possibilities to modify chemical and supramolecular structures of the polymer and proposed possible applications. Remarkable was the extent to which multi-step reactions at the cellulose macromolecule can be controlled today.

The program since 2000 (compare Table 9) is characterized by a growing international participation and show again the broad variety of chemical and physical modification of cellulose and hemicelluloses. New aspects of by-product utilization were presented as for example a modification of lignin by *N*-containing groups to a humus substitute for desert soil. All the bacterial cellulose and its processing to filaments for

**Table 9.**

Selected topics of the Cellulose Symposium of Zellcheming since the year 2000.

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Presentation of the results of the DFG-Project  
 Utilization of by-products of pulping  
 Variations of the cellulose skeleton:  
*cellulose*<sub>1α</sub>, *cellulose*<sub>β</sub>, *dendrimers of cellulose*  
 Interaction of cellulose with systems containing amino groups  
*Activation of pulp with urea and with amines*  
*Homogeneous reaction of cellulose solutions in NMMNO*  
*Cellulose derivatization in ionic liquids*  
*News from the Lyocell<sup>®</sup> and the Carbacell<sup>®</sup> process*  
 Cellulose analytics  
*Assessment of pattern of substitution along the chain*  
*Determination of residual chromophores*  
*Application of FT-Raman-Spectroscopy*  
 Combination of NMR with a quantitative chemical reaction  
 Transformation in the analysis of cellulose derivatives  
 Cellulose processing  
*Cellulose blow film from a melt solution in NMMNO*  
*Structure and properties of cellulose composites with synthetic polymers*

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surgery found attention and continued the sequence of information on the biogenesis of cellulose in our symposium. News on polymer skeleton modification were descriptions of the recently found modifications cellulose I $_{\alpha}$  and cellulose I $_{\beta}$  with their small, but significant differences in material properties and of the first dendrimers of cellulose with bulky ester groups. In cellulose chemistry interactions of the polymer with *N*-containing systems dominated. Ionic liquids found attention not only as solvents but also as reaction media for homogeneous derivatization. Reports on a new process for manufacturing cellulose blow film via an amineoxide melt solution of the polymer and of structure in properties of composites of cellulose with synthetic polymers especially thermoplastics indicated new prospects in cellulose processing. Generally the Cellulose Symposium (Cellulose-Chemiker-Rundgespräch) reflected and supplemented in a rather perfect way the philosophy of cellulose research in Germany in the past 60 years. Already for this reason the Cellulose Symposium within the annual meeting of Zellcheming should be continued. Besides the big polymer conferences, which in the future, should give some more attention to cellulose for a better integration into the entity of polymer science, our cellulose symposium is a necessity to provide a place of exchange of ideas and results between basic and applied research in order to promote new contacts and cooperation between industry and institutes.

Furthermore, this symposium offers a unique opportunity to derive and discuss new ideas and models from experimental results within a meeting of active experts and to discuss them critically within a relaxed atmosphere, last not least with the goal of new concepts for our field of science.

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