# CELLULOSE and WOOD

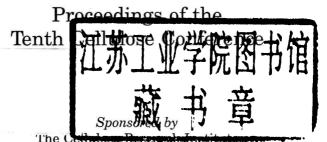
CHEMISTRY and TECHNOLOGY

Editor: Conrad Schuerch

Biogenesis and Structure of Cellulose
The Cellulose Water System
Chemistry of Cellulose and Wood
Surface Chemistry of Wood and Paper
Cellulosic Membranes

# CELLULOSE AND WOOD — CHEMISTRY AND TECHNOLOGY

Biogenesis and Structure of Cellulose The Cellulose–Water System Chemistry of Cellulose and Wood Surface Chemistry of Wood and Paper Cellulosic Membranes



State University of New York College of Environmental Science and Forestry

> Held at Syracuse, New York May 29 – June 2, 1988

#### Editor

#### Conrad Schuerch

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Proceedings of the Tenth Cellulose Conference are dedicated to Dr. Anatole Sarko, professor of chemistry, chairman of the Faculty of Chemistry, associate director of the Cellulose Research Institute, and associate member of the Polymer Research Institute at SUNY College of Environmental Science and Forestry in Syracuse, N.Y.

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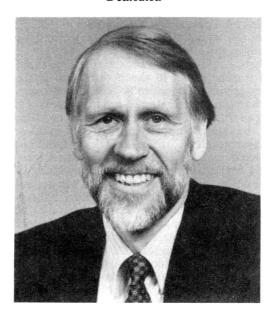
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#### **DEDICATION**

#### Anatole Sarko

To Whom the Proceedings of the Tenth Cellulose Conference Are Dedicated



The Proceedings of the Tenth Cellulose Conference are dedicated to Dr. Anatole Sarko, Professor of Chemistry, Chairman of the Faculty of Chemistry, Associate Director of the Cellulose Research Institute, and Associate Member of the Polymer Research Institute at the SUNY College of Environmental Science and Forestry in Syracuse, New York. Dr. Sarko is an internationally recognized authority on the chemistry of the polysaccharides, and especially their solid state properties. His pioneering studies on the crystallographic structure of cellulose and starch are particularly noteworthy.

Anatole Sarko was born on May 27, 1930, in Tallinn, Estonia, receiving his early education in this country and in Germany. He graduated from Uppsala College, East Orange, NJ, with a B.S. in chemistry in 1952, after which he was employed as a chemist by General Foods Corporation in 1963. In 1961 he received an M.S. in physical chemistry from the evening division of New York

University. He resumed his graduate studies in 1963 at the SUNY College of Forestry in Syracuse, where he studied under the direction of Robert H. Marchessault, using X-ray techniques to investigate the crystal structure of amylose triacetate. After having received his Ph.D. degree in physical and polymer chemistry in 1966, he continued to do research with Marchessault as a postdoctoral fellow for one year.

Dr. Sarko was appointed Assistant Professor at the SUNY College of Forestry in 1967, and has since remained at this university, now as a Professor of Chemistry. He became Acting Chairman of the Department of Chemistry in

1984, assuming his present position as Chairman in 1986.

Dr. Sarko's research until 1970 was concerned with the solid state properties of amylose. In these and later investigations, Sarko, using X-ray diffraction analysis, could establish for the first time that amylose, the linear component of starch, exists in three different crystallographic forms, depending on its origin. The native A- and B-amyloses are organized in a double helix, while the regenerated V-amylose forms a single helix. Other investigations dealt with the light-scattering characteristics of starch granules.

Since 1970, the crystallographic properties of cellulose have been one of Dr. Sarko's major research areas. Working independently, Sarko and Blackwell reported in 1974 that native cellulose I has a parallel chain arrangement and not an antiparallel, as had previously been assumed. The detailed location of the various hydrogen bonds was determined. A somewhat different pattern of hydrogen bonding could later be established for regenerated cellulose II, which had an antiparallel chain arrangement. Celluloses III and IV were later subjected to similar X-ray diffraction analyses. In recent years, Dr. Sarko has turned his attention to the mechanism of mercerization of cellulose in the solid state. It was found that there are five different polymorphs of Na-celluloses. An elegant mechanism was suggested to explain how cellulose I with parallel chains can be converted in the solid state into Na-cellulose I, which has antiparallel chains.

Dr. Sarko has also studied the crystallographic properties of several other polysaccharides, for example curdlan, dextran, galactan, lentinan, mannan, mycodextran, pachyman, and paramylon. He has established the crystal structure of maltose and gentiobiose. The results obtained with starch and cellulose have been summarized in several excellent reviews. Together with P. Zugenmaier, Sarko is currently preparing a monograph on the crystallographic properties of cellulose and cellulose derivatives. Over the years, Sarko has made important contributions toward improvements in X-ray crystallographic techniques and computer methods for conformational analysis of polysaccharides. He has also developed better methods for determining the molecular weight of polymers by light scattering and sedimentation velocity.

Anatole Sarko is not only an exceptionally innovative and productive research scientist but also a dedicated and inspiring teacher, who during the last 20 years has been responsible for six courses in polymer and physical chemistry. An excellent administrator, he has served the Faculty of Chemistry over the last four years as its chairman with great distinction, devoting much of his time and efforts to this demanding position. In 1982, Dr. Sarko organized the Ninth Cellulose Conference, and in 1988 he was responsible for a symposium on the structure of cellulose at the Tenth Cellulose Conference.

As a research scientist, Anatole Sarko has been able to inspire his graduate students, postdoctoral fellows, and other co-workers to do their best and has always given them freely of his time. As a teacher, he has upheld very high standards but also recognized the needs of students with an insufficient background. As a department chairman, he has always been willing to listen to different opinions among his faculty, while at the same time exerting a firm leadership.

Anatole Sarko's interests are not limited to research, teaching, and administration. His major hobby is skiing. He is keenly interested in current events and keeps in constant contact with colleagues in this and other countries. An internationally well known scientist in his field, he has spent much time

lecturing and doing research in France, Germany, and Japan.

Tore E. Timell

#### **Preface**

This volume constitutes the proceedings of the Tenth Cellulose Conference held at Syracuse May 29 to June 2, 1988 under the auspices of The Cellulose Research Institute of the SUNY College of Environmental Science and Forestry.

The Conference was opened with an appreciative statement of recognition and welcome by the College President, Dr. Ross Whaley, and a challenging Plenary Lecture on "Cellulosics as Advanced Materials" by Dr. Robert H. Marchessault, NSERC-Xerox Professor of McGill University. Later in the program, our horizons were broadened by Dr. Bruce Ganem of Cornell University who gave the Serendipity Lecture "Studies on the Inhibition of Carbohydrate Metabolism", of the biochemical significance potential glycosidases and the exciting The research on their inhibition. participants enjoyed two pleasant interludes, a recital by the distinguished Chinese pianist, Cui Shi-Guang, and a banquet at which Dr. Vivian Stannett of North Carolina State University gave a modest and whimsical account of his pioneering work on cellulose grafting.

The program of the Conference consisted of symposia on Cellulose Structure and Its Characterization organized by Dr. Anatole Sarko; on the Cellulose-Water System and Surface Chemistry of Cellulose, Wood and Lignin organized by Dr. Philip Luner; on Biogenesis of Cellulose organized by Dr. Tore Timell; and on Cellulosic Membranes by Dr. Israel Cabasso. In the General Papers were

xvi PREFACE

contributions on specialty products and derivatives, cellulose and wood chemistry and technology, degradation and analysis.

Local arrangements for the Conference were carefully organized by Horace Shaw and the staff of the Office of Continuing Education. Design and publicity were provided by Ronald Karns and the staff of the Publications Office. The considerable correspondence and clerical work were provided by Ragan Feidt, Liz Poda, Shirley Thomas, and Pauline Tonnesen. The Conference Committee wishes to express their appreciation to these colleagues and also to acknowledge the generous support of the Conference by the following organizations:

Proctor and Gamble Company Xerox Research Centre of Canada Dow Chemical Company Separex Corporation/Air Products and Chemicals, Inc. International Paper Company Aqualon Company

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General Chairman
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Conference Committee

I. Cabasso

P. Luner

A. Sarko

C. Schuerch

T. Timell

### **CONTENTS**

| Dedication  | X1  |
|---|-----|
| Preface   | xv  |
| Plenary Lecture: Cellulosics as Advanced Materials  R.H. Marchessault   | 1   |
| Serendipity Lecture: Studies on the Inhibition of Carbohydrate  Metabolism  B. Ganem  | 21  |
| Symposium on the Cellulose<br>Structure and Its Characterization  |     |
| An X-Ray Fiber Diffraction Study of Ramie Cellulose I  R.P. Millane and T.V. Narasaiah  | 39  |
| Structural Variation of Native Cellulose Related to Its Source T. Okano, A. Koyanagi, Y. Kondo, and A. Sarko                        | 53  |
| New Structural Models for Cellulose II Derived from Packing Energy Minimization A. Sakthivel, A.F. Turbak, and R.A. Young           | 67  |
| Memory Phenomenon of the Original Crystal Structure in Allomorphs of Na-Cellulose  J. Hayashi, T. Yamada, and YI. Shimizu           | 77  |
| Computer Models of Cellulose A.D. French  | 103 |
| Electron Microscopic and X-Ray Diffraction Study of Cellulose III <sub>I</sub> and Cellulose I                                      | 119 |
| J. Sugiyama and T. Okano  | 119 |
| H. Bradford and JF. Revol   | 129 |
| Refinement of the Crystal Structure of Ramie Cellulose I with Additional Meridional X-Ray Intensities  D.P. Miller and A. Li        | 139 |
| Comparisons of Structures Proposed for Cellulose A.D. French and P.S. Howley  | 159 |
| Studies on the Structure of Cellulose Using Raman Spectroscopy and Solid State <sup>13</sup> C NMR  R.H. Atalla and D.L. VanderHart | 169 |

| A.M. Ritcey, J. Giasson, JF. Revol, and D.G. Gray   | 189                      |
|---|--------------------------|
| A Combined Electron and X-Ray Diffraction Study of Cellulose<br>Tripropionate<br>Y. Shuto, K. Okamura, JI. Azuma, F. Tanaka, and H. Chanzy  | 207                      |
| Technology of NMR Imaging in Wood P.C. Wang, S.K. Mun, J.S. Chang, and J.R. Olson   | 221                      |
| NMR Imaging of Eastern Hardwoods S.J. Chang, J.R. Olson, and P.C. Wang  | 235                      |
| Undecenyl Pyranosides as Sidechain Mesogens of Chitosan R.H. Marchessault, C.J. Monasterios, K. Holme, and L.D. Hall  | 249                      |
| The Structural Association between Cellulose and Xyloglucan in the Primary Cell Wall of Beans ( <i>Phaseolus vulgaris</i> L.)  I.E.P. Taylor and J.C. Wallace   | 273                      |
| Structural Consequences of $\beta$ (1 $\rightarrow$ 4)Glycan Modification W. T. Winter  | 283                      |
| In Vitro Exploration of Chitin Fine Structure M.L. Bade, K. Hickey, and A. Stinson  | 293                      |
| m.D. Baac, n. mency, and n. Stinson   |                          |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  | 309                      |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared<br>by Conventional and New Acetylation/Ripening Processes   | 309                      |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  |                          |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  | 309                      |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  Symposium on the Cellulose–Water System  Studies on the Water Vapor Sorption Hysteresis of Viscose Rayon and of Chemically Modified Viscose Rayon S.H. Zeronian and M.S. Kim  Moisture Sorption Properties of Acetylated Lignocellulosic Fibers R.M. Rowell and J.S. Rowell   |                          |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  Symposium on the Cellulose-Water System  Studies on the Water Vapor Sorption Hysteresis of Viscose Rayon and of Chemically Modified Viscose Rayon S.H. Zeronian and M.S. Kim  Moisture Sorption Properties of Acetylated Lignocellulosic Fibers   | 325                      |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  Symposium on the Cellulose–Water System  Studies on the Water Vapor Sorption Hysteresis of Viscose Rayon and of Chemically Modified Viscose Rayon S.H. Zeronian and M.S. Kim  Moisture Sorption Properties of Acetylated Lignocellulosic Fibers R.M. Rowell and J.S. Rowell  Nonisothermal Diffusion of Moisture in Wood  | 325                      |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  Symposium on the Cellulose–Water System  Studies on the Water Vapor Sorption Hysteresis of Viscose Rayon and of Chemically Modified Viscose Rayon S. H. Zeronian and M.S. Kim  Moisture Sorption Properties of Acetylated Lignocellulosic Fibers R.M. Rowell and J.S. Rowell  Nonisothermal Diffusion of Moisture in Wood R.M. Nelson Jr.  Volume Contraction of the Cellulose–Water System   | 325<br>343<br>357        |
| Comparative Studies of Cellulose Diacetate in Acetone as Prepared by Conventional and New Acetylation/Ripening Processes K. Ueda and S. Saka  Symposium on the Cellulose–Water System  Studies on the Water Vapor Sorption Hysteresis of Viscose Rayon and of Chemically Modified Viscose Rayon S. H. Zeronian and M.S. Kim  Moisture Sorption Properties of Acetylated Lignocellulosic Fibers R. M. Rowell and J.S. Rowell  Nonisothermal Diffusion of Moisture in Wood R. M. Nelson Jr.  Volume Contraction of the Cellulose–Water System B. Alince  The Dynamic Viscoelasticity of Celluose in Water | 325<br>343<br>357<br>379 |

| Structural Change of Water Restrained in Cellulosic Hollow Fibers  T. Hatakeyama, S. Yamamoto, S. Hirose, and H. Hatakeyama | 431  |
|---|------|
| Study of Percolation Transition in Cellulose Pulps and Latexes in the Microwave Domain                                      | 4.47 |
| F. Henry and P. Noe   | 447  |
| Symposium on the  |      |
| Biogenesis of Cellulose   |      |
| Purification of Cellulose Synthase from Acetobacter xylinum  FC. Lin and R.M. Brown Jr.                                     | 473  |
| Electron Diffraction Analysis of Altered Cellulose: Implications for Cellulose Biogenesis  C.H. Haigler and H. Chanzy       | 493  |
| The Nascent Structure of Bacterial Cellulose A. Kai, J. Kogusuri, T. Koseki, and H. Kitamura                                | 507  |
| The Role of Cyclic Diguanylic Acid in the Regulation of Bacterial Cellulose Synthesis                                       |      |
| M. Benziman, P. Ross, D. Amikam, R. Mayer, H. Weinhouse, P. Weinberger-Ohana, and D. Michaeli                               | 519  |
| Cellulose Biosynthesis in Acetobacter xylinum: A Genetic Approach I.M. Saxena and R.M. Brown Jr.                            | 537  |
| Acetobacter xylinum as a Model System for Cloning of Genes Involved in the Synthesis of Cellulose S. Valla                  | 559  |
| Prospects for the Commercialization of the Biosynthesis of Microbial Cellulose  | 000  |
| D.G. White and R.M. Brown Jr.   | 573  |
| Evolution of the Cellulosic Cell Wall in the Charophyceae  A. T. Hotchkiss Jr. and R.M. Brown Jr.                           | 591  |
| The Evolution of the Cell Wall in Green Algae: Scales, Glycoproteins, and Cellulose D.S. Domozych                           | 611  |
| Cellulosic Cell Walls of Red Algae  | 011  |
| M.R. Gretz and C.M. Vollmer   | 623  |
| Cellulose Biogenesis and a Decade of Progress: A Personal Perspective R.M. Brown Jr.  | 639  |
| A New Cellulose Synthesizing Complex in Vaucheria hamata and Its Relation to Microfibril Assembly                           | 050  |
| S. Mizuta, E.M. Roberts, and R.M. Brown Jr  | 659  |
| Cellulose: New Insights Based on Recent Electron Microscopic<br>Findings  |      |
| S. Kuga and R.M. Brown Jr.  | 677  |

| E.M. Roberts, I.M. Saxena, and R.M. Brown Jr.   | 689 |
|---|-----|
| In Vitro Regulation of Plant β-Glucan Synthase: A Native Activator and Its Synthetic Analogues  M. Benziman, T. Callaghan, P. Ross, P. Weinberger-Ohana, and G. Wohlman | 705 |
| The Biosynthesis of $(1\rightarrow 4)$ - $\beta$ -D-Glucan by Lupinus albus D.O. Brummond   | 721 |
| Molecular Size of 1,4-β-Linked Products Formed by Membranes from UDP-Glucose  R. Gordon and G. Maclachlan   | 739 |
| The Relationship between the Synthesis of Cellulose and Callose in Higher Plants  D.P. Delmer   | 749 |
| Helicoidal Arrays of Cellulose in Quince Seed Epidermis: Evidence for Cell Wall Self-Assembly in the Plant Cell Periplasm J.H.M. Willison and R.M. Abeysekera           | 765 |
| Helicoidal Order in the Periplasmic Cellulose Arrays of Quince<br>Seed Epidermis: A Hypothesis for Its Origin<br>R.M. Abeysekera  | 783 |
| Inhibitor Effects on Putative Cellulose Synthetase Complexes of Vascular Plants  W. Herth   | 795 |
| The Role of the Cytoskeleton during Oriented Microfibril Deposition. II. Microfibril Disposition in Cells with Disrupted Cytoskeletons R.W. Seagull                     | 811 |
| Potential Use of Affinity Labels in Subunit Identification Studies of (1,3)-β-Glucan Synthase  B.P. Wasserman, S.M. Read, D.J. Frost, T.L. Mason,                       |     |
| R.R. Drake, and B.E. Haley  | 827 |
| General Papers  |     |
| Mechanisms of Formation of the Major Volatile Products from the<br>Pyrolysis of Cellulose   |     |
| M. Essig, G.N. Richards, and E. Schenck   | 841 |
| Accelerated Thermal Degradation of Pulp Sheets: Effect of Beating and Importance of Humidity S.B. Lee, J. Bogaard, and R.L. Feller                                      | 863 |
| The Effects of Mode of Calcium Carbonate Deposition on<br>Thermal Decomposition of Cellulose and Flame Retardant<br>Treated Cellulose                                   |     |
| I.R. Hardin, L.J. Martin, and Y. Qiu  | 885 |

| Viscose Rayon Coating of Fibers and Yarns  B. Collier, J. Collier, and H. Modh  | 907   |
|---|-------|
| Cellulose in Depth Filtration Media   | 929   |
| C. T. Badenhop  | 948   |
| Copolymer Structures  R. Narayan  | 945   |
| Analysis of Polysaccharide Degradation Products  G.K. Bonn and H.F. Hormeyer  | 963   |
| FTIR Internal Reflectance Spectra and Bonding of Wood Surfaces Activated with Non-Conventional Agents A.J. Michell and J.P. Yuritta                         | 975   |
| Second Derivative FTIR Spectra of Woods  A.J. Michell   | 995   |
| A New <sup>13</sup> C-NMR Approach for Determination of Substituent Distribution in Cellulose Ethers Y. Tezuka, K. Imai, M. Oshima, and T. Chiba            | 1011  |
| Multivariate Characterization of Pulp Using Solid State C-13 NMR  | 1023  |
| Effect of Sulfur Dioxide on Wood Surface Quality D.NS. Hon and W.Y. Chao  | 1037  |
| Oxidative Modification of Cellulose by Ozone  M.P. Godsay and M. Lewin  | 1059  |
| Anthraquinone Pulping and Its Effect on the Supermolecular Structure and Accessibility of Cotton Cellulose M.A. Abou-State, S.A. Helmy, and N.A.A. El-Ghany | 1085  |
| Some Physical Properties of Cellulose Derivatives Prepared by Homogeneous Periodate Oxidation T. Morooka, M. Norimoto, and T. Yamada                        | 1103  |
| Preparation and Redox Behavior of Cellulose Derivatives Having Viologen Moiety T. Sato, Y. Nambu, and T. Endo   |       |
| Molecular Design of Linear Aromatic Polymers Derived from<br>Phenols Related to Lignin<br>S. Hirose, H. Hatakeyama, K. Nakamura, and                        | 11.00 |
| T. Hatakeyama  Environmental Stress Responses in Molecular Parameters of Cotton Cellulose   | 1133  |
| J.D. Timpa and D.F. Wanjura   | 1145  |
| Z. Koran  | 1157  |
| Variables Affecting the Longitudinal Flow of Gas in Hardwoods E. T. Choong, S. Achmadi, and F.O. Tesoro   | 1175  |

| Fiber Dimension Analysis of Five Selected Juvenile Hardwoods P. Chow, G.L. Rolfe, and D. Wei  | 1197 |
|---|------|
| A Chemical Kinetics Approach to Wood Swelling  H. West and W.B. Banks   |      |
| Kinetics of Sulphonation of Cellulose Fibres  | 1210 |
| B. Lönnberg and J. Jäkärä   | 1235 |
| Ultrafiltration of Kraft Black Liquor — Distribution of Solutes and Influence on Viscosity and Heat Value K. Forss, E.M. Pulkkinen, and PE. Sågfors | 1253 |
| Light Bleaching of Paper in the Presence of Sulfur-Containing Compounds S.B. Lee  | 1273 |
|   |      |
| Symposium on  |      |
| Cellulosic Membranes  | :    |
| The Structure of Dense Glassy Polymeric Films   |      |
| R.E. Kesting  | 1291 |
| Cellulose Acetate Mixed Esters as Polymers for Reverse Osmosis Membranes R.E. Kesting   | 1301 |
| Evaluation in CA Gas Separation Membrane for Upgrading  |      |
| Hog Waste Biogas in R.O.C. T.W. Tseng, Y.H. Chang, J.S. Lee, S.Y. Wang, and S.N. Tong   | 1317 |
| The Use of Cellulosic Membranes in Medicine   | 1011 |
| P. Konstantin   | 1333 |
| Transport Phenomena in Reverse Osmosis Cellulose Acetate<br>Membranes   |      |
| M.D. Afonso and M.N. de Pinho   | 1347 |
| Cellulose Blends with Synthetic Polymers — High Performance<br>Membranes  |      |
| I. Cabasso  | 1361 |
|   |      |
| Symposium on the  |      |
| Surface Chemistry of  |      |
| Cellulose, Wood, and Lignin   |      |
| Physical and Chemical Modifications of the Surface Properties of Cellulosic Fibers  |      |
| J.C. Arthur Jr.   | 1383 |
| Surface Chemistry of Oxidized Wood  D. NS. Hon  | 1401 |

| of Rosin and Synthetic Sized Bond-Type Papers  J. Borch and A.G. Miller   |
|---|
| Ink Absorption by Cellulosic Paper in Calligraphy R. Oye and T. Okayama   |
| Conductometric Titration of Cellulosic Fibres  A.M. Scallan, S. Katz, and D.S. Argyropoulos   |
| Sorption of Alkyd Resins on Cellulose  K. Johansson, G. Ström, and P. Stenius   |
| Kinetics of Liquid Spreading along a Paper Surface G. Ström   |
| The Wetting Properties of Hydrophobically Modified Cellulose Surfaces A.F. Toussaint and P. Luner   |
| Mechanistic Aspects of Alkenyl Succinic Anhydride Sizing of Paper  J.C. Roberts and W.R. Wan Daud   |
| Applications of Flow Visualization Techniques in Flocculation Analysis  F. Onabe and C. Sohn  |
| Surface Charge of Calcium Carbonate in Water and Its Interaction with Cellulose Fibers B. Siffert and P. Fimbel   |
| Determination of Surface Charge of Cellulose Fibre by Potentiometric Titration and Polyelectrolyte Titration R.I.S. Gill, T.M. Herrington, and J.C. Petzold |
| Considerations in the Continuous Monitoring of Charge in Cellulosic Fiber Systems  A.M. Springer and M. Kumar   |
| Author Index  |

## CELLULOSICS AS ADVANCED MATERIALS

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#### **SYNOPSIS**

Because of its unconventional polymeric properties, cellulose is a unique material for functions ranging from information storage to energy conservation. Biomimetic aspects of cellulose utilization: extended chain materials, chemical recognition-based processes, materials based on the higher order structure of cellulosics are discussed in the context of state of the art polymer science. Amphiphilic, hydrogel, and chirality properties of cellulose are used as examples of advanced materials attributes.

#### INTRODUCTION

Value-added materials with advanced performance in electronic, mechanical and optical applications are being actively researched. Cellulosics are generally not considered for these applications because molecular design demands degrees of freedom which cellulosics don't provide. This bias against the polymer which was the prototype for the development of polymer science seems more the result of ignorance than fact. In the following pages I will try to provide examples where cellulosics are in the running for high-tech applications, provided targeted advanced development is undertaken with perseverance.

At the recent IUPAC CHEMRAWN VI conference [1] in Tokyo the theme "Advanced Materials for Innovations in Energy, Transportation and Communications" focussed on the relation of materials to technical progress (Fig. 1). In particular, the biomimetic aspects with examples relating to intelligent devices, photosynthesis, energy conversion etc. were emphasized. The unique success of cellulosics in membrane devices is an advanced materials success. Cellulose is a polymer with unconventional properties and has potential for functions ranging from information storage to energy conservation. But like all