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

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Proceedings of the
Tenth Cellulose Conference

Sponsored by
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State University of New York
College of Environmental Science and Forestry

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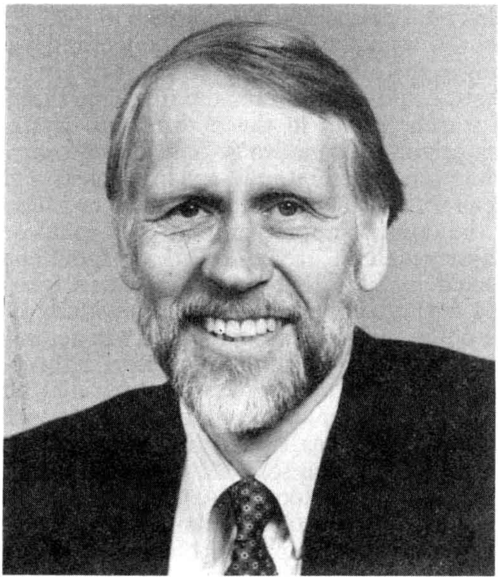
DEDICATION

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", an account of the biochemical significance of glycosidases and the exciting potential of his research on their inhibition. The 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 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
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C. Schuerch
General Chairman
Tenth Cellulose Conference

Conference Committee
I. Cabasso
P. Luner
A. Sarko
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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