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PREFACE

100 years of cellulose fiber diffraction and the emergence of complementary techniques

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Crystallinity is a fundamental property of cellulose. Over recent years an understanding has developed of cellulose synthesized at the plasma membrane by protein complexes that add glucose sugars to linear chains and then carefully assemble those chains into crystalline fibrils with well-defined shapes, sizes and crystal phases. The nature of these crystal building blocks, their interface and association with other molecules and how they are further assembled into higher order structures, have profound effects on the emergent physical and chemical properties of cellulosic materials. The diversity of these materials found in nature suggests that cellulose producing species may have evolved different synthesis strategies in order to produce specific crystal-based architectures, and therefore properties, depending on their required biological function. That function can vary from adding mechanical strength to plant cell walls, mobility to microorganism, and colocation of bacteria in colonies near to their food source.

From a human perspective, cellulose has been an important renewable material and fuel throughout our evolution. Today, crystallinity, and how it changes during cellulosic material processing and aging, is key to the strength, reactivity and durability of materials composed of cellulose. However, crystallinity is not always a positive attribute; it prevents easy conversion

This special issue collects papers from a symposium held in April 2013 at the 245th National Meeting of the American Chemical Society in New Orleans that was organized to celebrate a milestone in cellulose research, namely "100 years of cellulose fiber diffraction and the emergence of complementary techniques". The symposium was organized by Alfred French, Paul Langan, Yoshiharu Nishiyama, and William Winter and involved thirty-seven speakers from institutes in eight different countries who presented their results in five half-day sessions that stretched over 3 days. The sessions addressed four main themes (1) molecular level structure, dynamics and hydration (2) cellulose processing (3) higher order structure (4) emerging techniques. We have arranged the papers in this issue in approximately the order they were presented at the symposium. The organizers are grateful to the American Chemical Society's Division of Cellulose and Renewable Materials and Oak Ridge National Laboratory for supporting this symposium.

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of cellulose to chemical derivatives or high-energy fermentable sugars that can then be converted to biofuels and other products. To efficiently exploit the tens of billions of tons of cellulose produced annually as a renewable carbon feedstock for emerging biomass-based biorefineries will require understanding and addressing the contribution that cellulose crystallinity makes to the recalcitrance of lignocellulosic biomass.

To the person on the street, the idea that a cotton shirt or piece of paper is composed of crystals of a sugar is almost shocking. To the cellulose scientist, however, crystallographic diffraction is one of the most common experiments done on their materials of interest. In this journal alone, the word diffraction appears in some 527 of the 1,590 articles in over 20 years of publication. Diffraction studies are carried out for two different purposes. The first is for determining the three-dimensional structure of the molecules and how they relate to each other. In the case of cellulose the chemical structure is already understood and it is the job of a diffraction study to locate the atoms so that the physical structure can be described. Understanding the detailed physical structure of cellulose reveals the principles underlying its properties. The second purpose, the one that is the basis for most of the diffraction experiments, is a routine determination of which of the numerous crystal forms are present, as well as an assessment of the degree of crystallinity. Many of the properties of cellulosic materials correlate with the variations in these two simple properties.

Historically, diffraction studies of cellulose greatly facilitated the understanding of polymers. Its diffraction pattern was first recorded in 1913, just a year after X-ray diffraction was discovered. That 100th anniversary event was celebrated by a symposium sponsored by the American Chemical Society's Division of Cellulose and Renewable Materials. The proceedings of that symposium are reported in this special issue. In the original pattern, the diffraction features were smeared into streaks because of the use of polychromatic X-rays, but patterns collected soon after that using monochromatic radiation contained distinct diffraction peaks that could be indexed using different choices of unit cell. In those early times, it was not understood how the unit cell related to the molecule inside. It took some imagination to understand that the unit cell did not contain a complete molecule, contrary to the situation for other substances. It was more than a decade later that it became understood that two extremely long molecules (relative to the unit cell dimension) ran through the unit cell, and that the ends of the molecules do not contribute significantly to the patterns.

Over the succeeding years, many other aspects of cellulose structure have been proposed with a reasonable degree of certainty from X-ray diffraction data. However, interpreting diffraction data from naturally occurring cellulosic samples is challenging because of the effect of cylindrical averaging around the fiber axis, the presence of disorder or deviations from crystal symmetry, and the complex heterogeneous nature of these samples, all of which limit the number and accuracy of the measured diffraction intensities. Major steps forward in our interpretation of X-ray diffraction data have come from not only technical and methodological advances that have improved data quantity, quality and resolution, but also the emergence of other experimental approaches that have provided additional complementary information. Notable developments include the introduction of computer-aided structure refinement methods that incorporated stereochemical constraints based on single crystal X-ray structures, the identification of two naturally occurring allomorphs of cellulose using nuclear magnetic resonance and infrared spectroscopy, the use of electron diffraction to determine the unit cells of these allomorphs and the parallel packing arrangement of chains within, and the use of neutron diffraction to determine the detailed hydrogen bonding arrangement within cellulose fibers. As the papers in this issue demonstrate, new techniques continue to emerge that can be applied to study cellulose and to continue the ongoing evolution of its understanding.

From the application of diffraction and complementary techniques, atomic resolution structures have now been proposed for most of the major crystal forms that cellulose has so far been found to adopt. The atomic coordinates from these structures are widely used to calculate the various properties of cellulose such as the elastic modulus, the vibrational and nuclear magnetic resonance spectra, and even the diffraction patterns have been calculated to not only augment experimental data but intrinsically, to also challenge the proposed crystal structures. However, our understanding is incomplete, controversies remain, and X-ray diffraction has its limitations. One of those limitations is that diffraction

reports on the presence of order within the arrangement of cellulose atoms averaged over space and time; it is difficult or impossible to provide information on some types of disorder that are functionally important. For this reason, crystallography has benefited from the development and complementary use of various spectroscopy techniques. Nuclear magnetic resonance, infrared, Raman and, more recently, neutron spectroscopy are revealing that cellulose fibers, particularly at their surfaces, are highly dynamic, with hydrogen bonds being continually formed and broken between cellulose atoms and also atoms from other interacting molecules. A complete dynamic visualization of cellulose structure is required to completely understand its physical properties and this requires the combination of several experimental methods with computer simulations.

Several papers in this issue point out that cellulose is our most abundant renewable resource and that cellulosic materials have great potential to be further developed as a feedstock to meet our future material and energy needs. As systems and synthetic biology approaches are increasingly applied to modifying cellulosic materials, the ability to genetically engineer new cellulose structures and control cellulose deposition in plants and around microbes must be developed in parallel with powerful approaches for rapidly imaging cellulose and analyzing its physical and chemical structures. The continued development of cellulose fiber diffraction and new emerging complementary techniques into the future will therefore help to advance bioengineering approaches to improving celluloses and also to provide guidelines for developing accelerated processes for the conversion of cellulose into value added products. As we look forward to high performance computers having ever-increasing power, and the development of advanced computer simulation and quantum chemical calculation methods, it seems increasingly possible that accurate computer models of cellulosic materials will be built that can be used for predictive simulations of their behavior and response to changing conditions. These models may eventually replace the need for experiments aimed at obtaining a detail understanding of the behavior of cellulose. However, an accurate and complete experimentally informed model for cellulosic materials does not yet exist, and further, any reliable computer model will require rigorous verification and refinement by direct comparison with experiments. For these reasons the continued new experiments based on the crystal structure proposals are welcome.