

SPEAKER



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BIOGRAPHY

Thomas Rosenau has studied Chemistry at Dresden University of Technology and received his doctorate there and did his PhD at the same institution and at NC State University in Raleigh, USA, where he also spent some time as a postdoc. He habilitated in organic chemistry at BOKU University Vienna, where he is currently full professor at the Department of Chemistry. He heads the Institute for Chemistry of Renewable Resources, and the Austrian Biorefinery Center Tulln (ABCT), and is also Adjunct Professor of Fiber Chemistry at Shinshu University, Japan and Adjunct Professor at the Johan Gadolin Process Chemistry Center, Abo Academy, Turku, Finland. Thomas conducts research in Organic Chemistry, Green Chemistry and Analytical Chemistry, mainly focusing on the two biopolymers cellulose (structure, modification, aging and yellowing, paper, fibers) and lignin (structure, utilization, analytical method development), as well as on plant extractives and antioxidants. He has received several major international scientific awards, e.g. the Anselme Payen Award of the American Chemical Society 2014, and the Hayashi Jisuke International Cellulose Award in 2007, and with his institute won the 1st prize in the 2018 Green Chemistry Challenge of the Royal Society of Chemistry. He is Elected Fellow of the International Academy of Wood Science (IAWS), Fellow of the Japanese Academy of Sciences and Fellow of the Royal Society of Chemistry, UK and member of several journal editorial boards and committees of international conferences. He has published 450 SCI papers, 24 book chapters and 2 books.

LECTURE

T. Rosenau, A. Potthast, M. Bacher, H. Hettegger, S. Böhmendorfer, T. Hosoya, Y. Yoneda, T. Dietz and A.D. French

Cellulosic chromophores – Minute concentrations and huge effects

The CRI (“chromophore release and identification”) procedure has been developed more than a decade ago as the first generally applicable method for isolation and identification of residual chromophores in/on cellulosic materials, which are responsible for brightness losses (“yellowing”), being the most evident aging effect of cellulosic materials. The extremely low concentration of these colored compounds, in the ppm to ppb range, has been the main difficulty in their isolation and exact structural characterization. The CRI-technique has been successfully applied to native celluloses (cellulose I allomorph: pulps, cotton, bacterial cellulose), regenerated cellulose products (cellulose II allomorph: fibers such as Lyocell or rayon, mercerized cellulose), and even cellulose derivatives (carboxymethyl cellulose, cellulose triacetate, cellulose 2.5 acetate), providing well-defined chromophoric structures in all cases.

Chromophores in bleached pulps are either primary or secondary chromophores. Secondary chromophores involve process chemicals in their formation and obviously differ strongly between different cellulosic matrices. The structures of the primary chromophores, by contrast, are largely independent of the respective cellulosic product since they are made up of carbohydrates and their degradation/oxidation products under different degradation / recondensation conditions. The three key chromophore classes – and thus the main sources of color, both the remaining color after bleaching and the newly generated color upon brightness reversion – are 2,5-dihydroxy-[1,4]benzoquinones, 5,8-dihydroxy-[1,4]naphthoquinones, and 2-hydroxyacetophenones. The key chromophores are significantly more resistant towards conventional bleaching than other (mostly quinoid) chromophores due to their exceptionally strong resonance stabilization: they are consistently found as the residual chromophores which “survive” bleaching much longer than other chromophores. They also represent (global) minima on the C-H-O thermodynamic stability maps, which accounts for their ready reformation upon brightness reversion from low-molecular weight degradation products, such as C₂-C₄ hydroxyaldehydes, hydroxyketones and hydroxyacids. Based on the knowledge of the exact chromophore structure of the residual / remaining chromophores it was possible in several cases to optimize bleaching sequences and to target even higher brightness and brightness stability.

In the first part of the talk, the chromophore isolation approach (CRI method), the structures of the chromophores isolated from different cellulosic materials and the structures of the key chromophores will be briefly recalled. In the second part, in-depth mechanistic studies on chromophore formation and formation pathways are presented, e.g. with regard to the roles of polysaccharidic carbonyls and carboxyls in chromophore formation. While carbonyls are strongly chromogenic, carboxyls are not chromogenic themselves, but promote the formation of chromophores from carbonyl-containing precursors. Already a single “oxidized spot” – one carbonyl in an anhydroglucose unit (AGU) – is sufficient to generate exactly the key chromophores found in the pulps. A third part addresses chromophore formation from hexeneuronic acids (HexA). The same techniques, CRI method and NMR spectroscopy in combination with isotopic labeling, allowed structural elucidation also in this case of the HexA-derived chromophores. Their structure is, in addition, highly relevant with regard to humins, i.e. deeply colored byproducts of many biorefinery approaches involving polysaccharide degradation.