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XPS-Characterisation of (Surface-)Modified Cellulose

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Introduction

Cellulose is the most abundant natural organic polymer on earth. Although both cellulose and its derivatives have been used in various fields of application for years, it is highly desirable to identify novel cellulose derivatives to further increase the use of this polymer to substitute or complement polymeric materials based on crude oil.

Experimental

X-ray Photoelectron Spectroscopy (XPS):

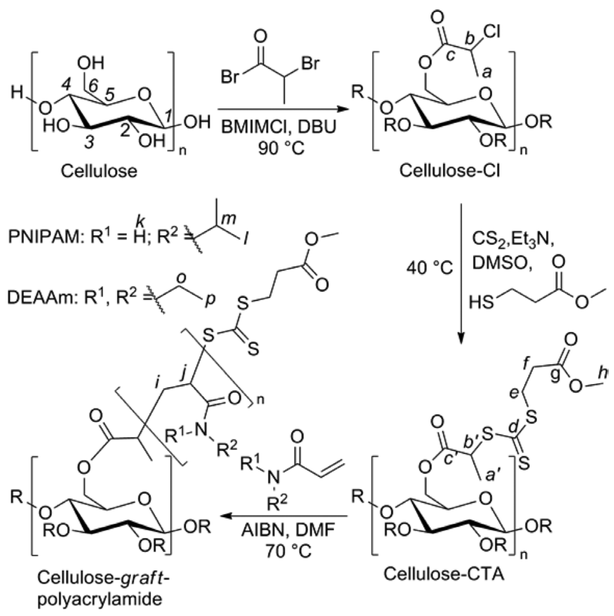
ThermoFisher Scientific **K-Alpha** Spectrometer

- Micro-focused mono-AlKα X-ray source,
- Charge compensation with low energy electrons and Ar^+-Ions,
- Avantage software for data acquisition and processing.

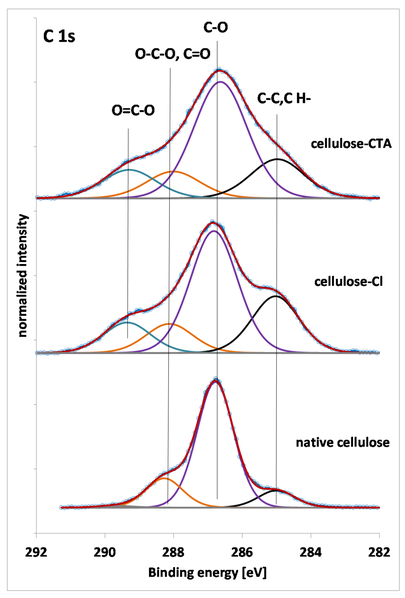
ToF-SIMS **ToF.SIMS 5**, ION-TOF GmbH, Münster, Deutschland

Temperature Responsive Cellulose-*graft*-Copolymers via Cellulose Functionalization in an Ionic Liquid [1]

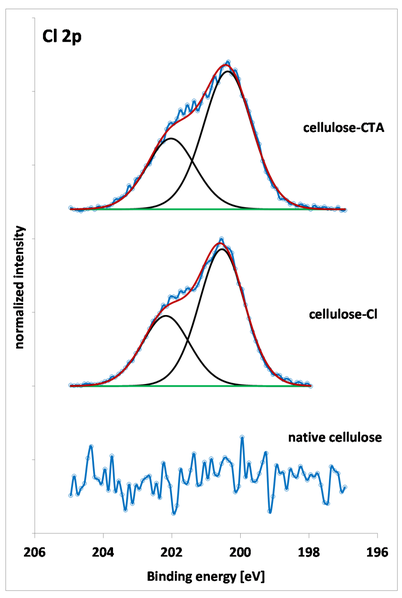
A promising approach toward new cellulose-based materials is homogeneous functionalization of cellulose in solution. Since the discovery of ionic liquids (IL) as solvents for native cellulose, an increasing interest in these solvents (or IL/cosolvent mixtures) for cellulose functionalization can be noticed. Ideally, the homogeneous functionalization yields soluble products, while minimizing degradation of the cellulose backbone during functionalization.



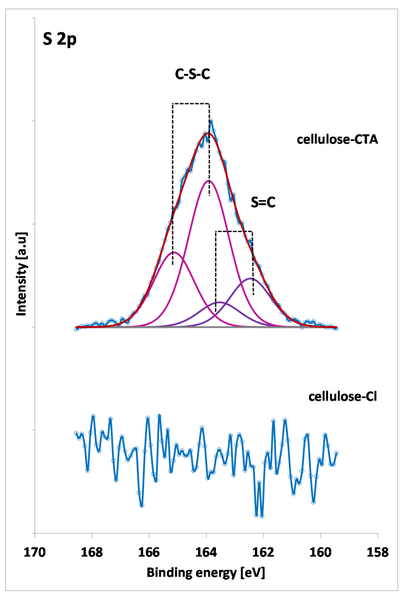
Synthetic pathway to cellulose-*graft*-polyacrylamide copolymers via RAFT (Reversible Addition-Fragmentation Chain Transfer) - Polymerization.



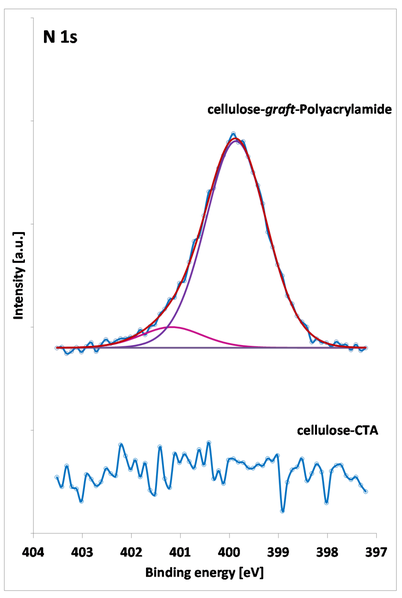
C 1s XP spectra.
As expected for cellulose-Cl an increase in O=C-O and C-H, C-C content as compared to native cellulose can be observed.
For cellulose-CTA, the expected increase in O-C=O is and C-O is confirmed.



Cl 2p XP spectra.
Whereas no chlorine is detected for filter paper, the chlorine content increases for cellulose-Cl (5,6 at%) and is subsequently decreased in cellulose-CTA (4,2 at%). This observation is expected for a successful partial replacement of chlorine with trithiocarbonates.



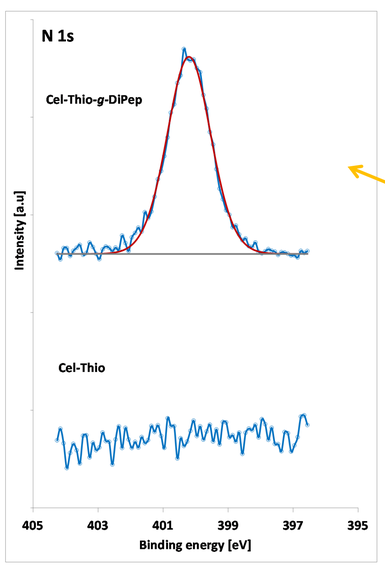
S 2p XP spectra.
No sulfur can be detected in cellulose-Cl (and native cellulose, not shown here), but for cellulose-CTA the introduction of trithiocarbonate moieties is confirmed by detection of sulfur. The S 2p signal can be decomposed in two components C-S-C and C=S as expected for trithiocarbonates.

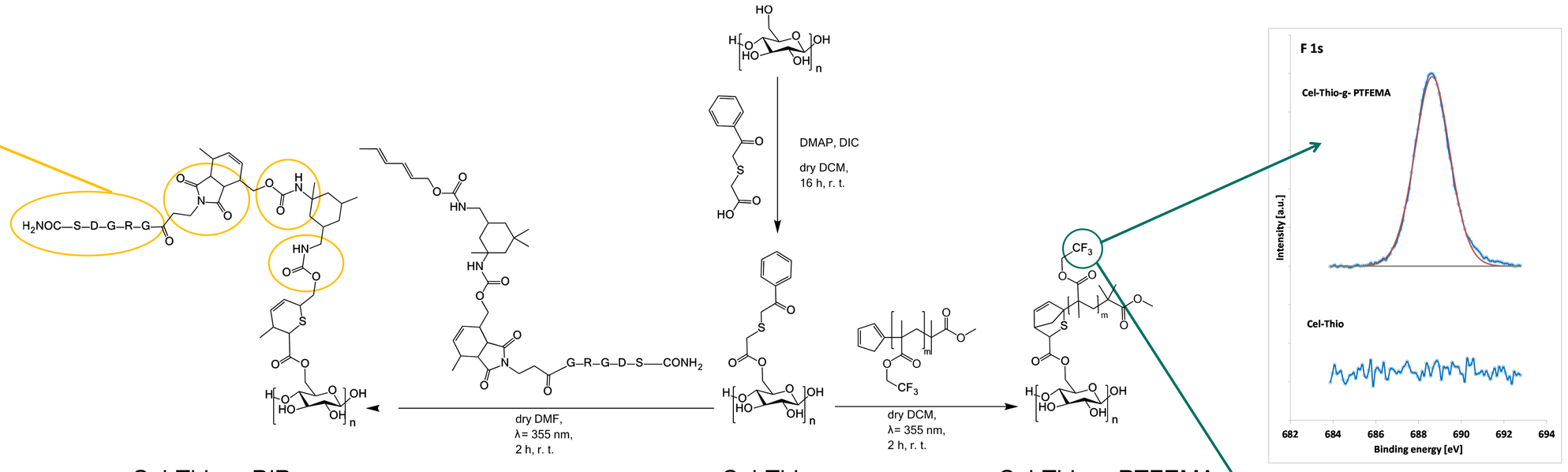


N 1s XP spectra.
For cellulose-CTA as well as for the corresponding cellulose-Cl and native cellulose (not shown here) no nitrogen can be detected. For the grafted sample after 2h of polymerization the nitrogen content is significant and evidences the presence of amide and amine groups. The additional peak at 401.0 eV is probably due to positively charged nitrogen.

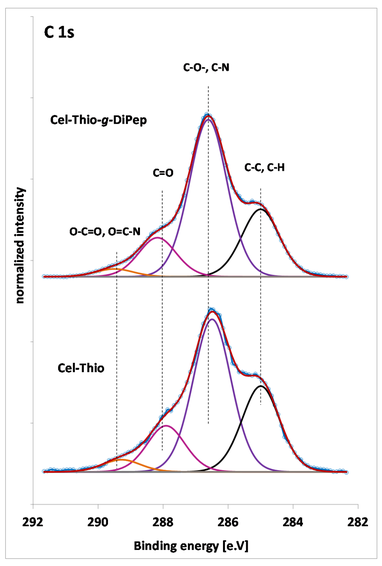
Ambient Temperature Ligation of Diene Functional Polymer and Peptide Strands onto Cellulose [2]

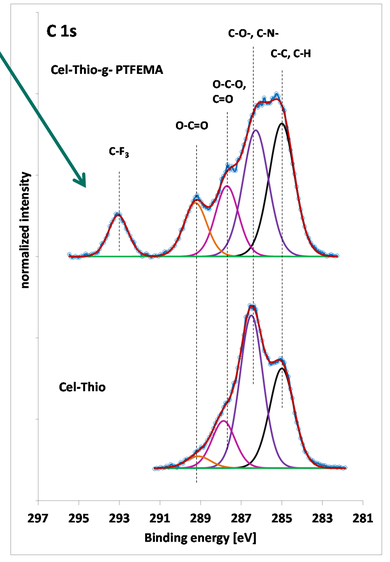
A novel ambient temperature avenue is introduced to functionalize solid cellulose substrates in a modular fashion with synthetic polymer strands (poly(trifluoroethylmethacrylate), PTFEMA, and an Arg-Gly-Asp (RGD) containing peptide sequence. The protocol relies on a hetero Diels–Alder reaction between an activated thiocarbonyl functionality and a diene species.





Cel-Thio-*g*-DiPep Cel-Thio Cel-Thio-*g*-PTFEMA



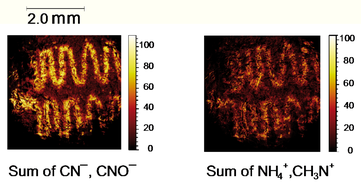


General strategy followed in the photochemical part of the study:
Based on phenacyl sulfide-modified cellulose (Cel-Thio), two species are attached with spatial resolution.

Route left:
Photochemically driven ligation of a RGD-containing peptide sequence.

C 1s and N 1s XP spectra of Cel-Thio and the diene-peptide-functionalized cellulose Cel-Thio-*g*-DiPep. The successful reaction can be monitored via the appearance of a nitrogen species.

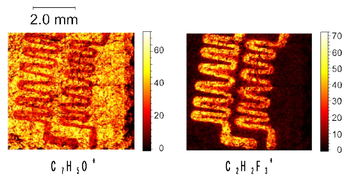
ToF-SIMS imaging on phenacyl sulfide cellulose functionalized with a RGD-containing peptide (Cel-Thio-*g*-DiPep). The line pattern can be associated with the CN^- and CNO^- fragments (left) and NH_4^+ and CH_3N^+ (right) present in the immobilized peptide.



Route right:
Photochemically driven ligation of poly(trifluoroethylmethacrylate).

C 1s and F 1s XP spectra. The successful reaction is verified based on the appearance of F 1s peaks of the fluorinated species and a new C 1s signal attributed to the CF_3 group.

ToF-SIMS imaging of the spatially resolved patterning of Cel-Thio-*g*-PTFEMA. The line pattern represents the fragments $C_7H_5O^+$ (left) and $C_2H_2F_3^+$ (right).



KIT – University of the State of Baden-Wuerttemberg and
National Research Center of the Helmholtz Association

[1] Hufendiek A., Trouillet V., Meier M.A.R., Barner-Kowollik C., *Biomacromolecules*. 2014, 15, 2563-2572

[2] Tischer T., Claus T. K., Oehlenschlaeger K. K., Trouillet V., Bruns M., Welle A., Linkert K., Goldmann A. S., Börner H. G., Barner-Kowollik C., *Macromol. Rapid Commun*. 2014, 35, 1121-1127