

# Sonochemical Degradation of Cellulose



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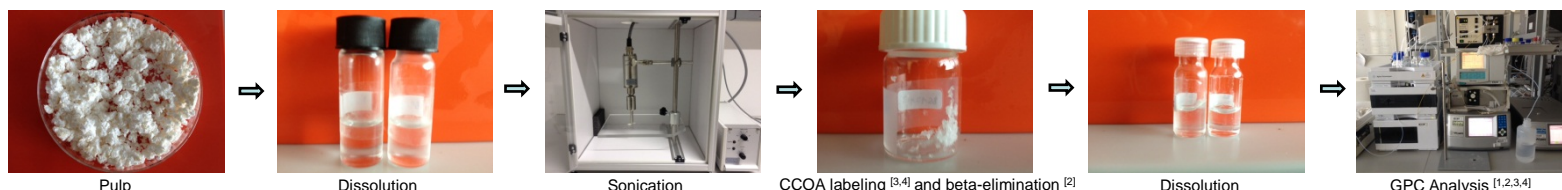


Department of Chemistry

## Introduction

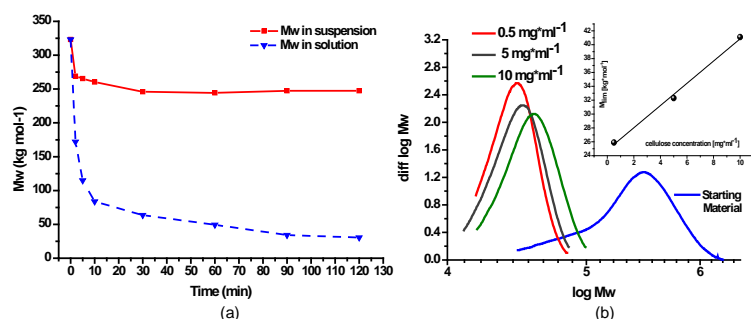
The methods available for the preparation of cellulose of lower Mw can be chemical, enzymatic, or physical. Some disadvantages for those methods might be the use of chemicals and the resulting waste discharge problems, high costs, and lower yields. Although sonochemistry - the degradation of cellulose by means of ultrasound - would appear as a quasi logical remedy here, this type of cellulose depolymerization is less used and less studied. The aim of this work was to clarify whether ultrasonic degradation of cellulose is purely hydrolytic or whether the cellulose is simultaneously oxidized.

## Experimental



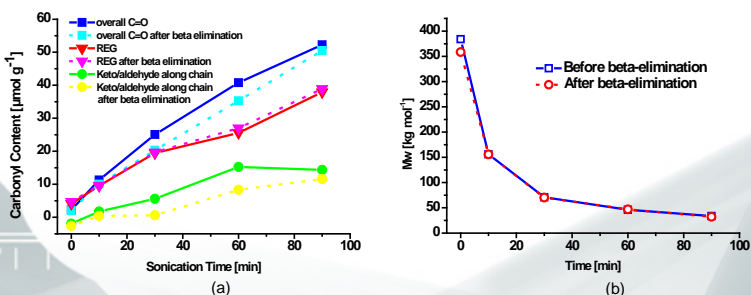
## Results and Discussion

The ultrasonic treatment of cellulose dissolved in DMAc/LiCl caused a drastic loss in Mw. After 120 min of sonication, a stable value was reached at Mw of ~ 26 kg mol<sup>-1</sup>, which is about of 8% of the starting Mw (Figure 1a). The final value of 26 kg mol<sup>-1</sup> was evidently the M<sub>lim</sub>, which is dependent on cellulose concentration (Figure 1b).



**Figure 1:** a) Course of cellulose degradation (solution in DMAc/LiCl), weighted Mw vs. sonication time. b) Linear influence of the cellulose concentration on degradation process.

The total number of C=O is the sum of reducing end groups (REGs) and aldehyde (C-6) / keto (C-2, C-3) groups along the chain. When cellulose is hydrolyzed the chain is cleaved, and the REG content increases. The difference between total carbonyl content and (theoretical) amount of reducing ends is the amount of keto (aldehyde) groups along the chain (Figure 2a). Beta-elimination reactions are induced by alkali and cause cleavage of the glycosidic bond next to a carbonyl at either C-2, C-3, or C-6. In all cases, the alkoxy substituent in beta-position relative to the carbonyl group is cleaved off. The outcome of beta-elimination reaction in dependence on the carbonyl position is shown in Scheme 1.

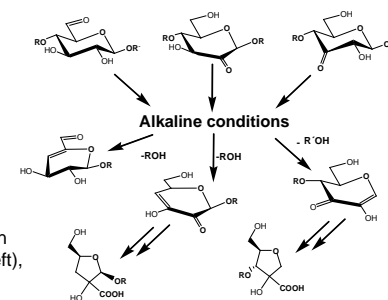


**Figure 2:** a) Changes in the oxidation state (carbonyl content) of cellulose over sonication time. b) Weighted-average Mw of cellulose before and after beta-elimination by alkaline treatment.

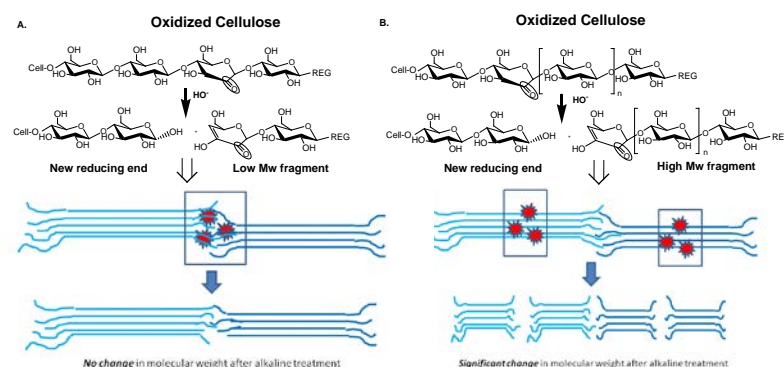
## References

- [1] Potthast, A., *et al.* (2006), *Holzforschung*, 61, 662-667.
- [2] Potthast, A., *et al.* (2009), *Holzforschung*, 63, 12-17.
- [3] Röhring, J., *et al.* (2002a), *Biomacromolecules*, 3, 959-968.
- [4] Röhring, J., *et al.* (2002b), *Biomacromolecules*, 3, 969-975.
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The cleavage of the glycosidic bond next to the carbonyl function causes chain fragmentation in any case, and the length of the two resulting chain fragments depends on the position of the carbonyl group along the cellulose chain (Scheme 2).



**Scheme 1.** Alkali-induced beta-elimination reaction starting from carbonyls at C-6 (left), C-2 (middle), and C-3 (right).



**Scheme 2.** Length of the two cellulose fragments upon a beta-elimination process in dependence of the position of the carbonyls along the cellulose chain.

Along-chain carbonyl groups were introduced at or very close to the reducing end or to the opposite terminal chain end, so that the cleaved-off low-Mw fragments are very small and the decrease in the Mw of the long chain is so minor that it cannot be detected by GPC (Figure 2b).

## Conclusions

Ultrasonic treatment of cellulose in solution changed the Mw drastically. The sonochemical degradation is faster at higher temperatures and at lower cellulose concentrations. In addition to the hydrolytic cleavage, oxidation also occurred as seen by introduction of carbonyl groups along the chain. These functionalities are introduced at or very close to the terminal glucopyranose units. Sonochemical cellulose cleavage thus occurs according to a binary mechanism that is both hydrolytic and oxidative. The cellulose chain is cleaved and at the same time oxidized at or close to the spot cleavage.

## Acknowledgement

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