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Determination of γ-Value and Xanthate Group Distribution on Viscose by Liquid-State ^{1}H NMR Spectroscopy

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Introduction and Objectives

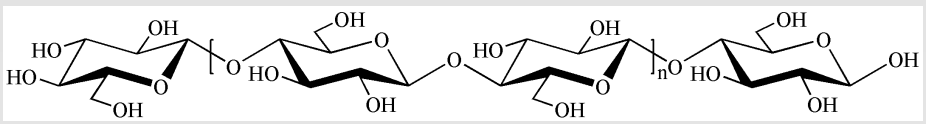

Figure 1: Cellulose Structure.
Viscose fibres are made from cellulose, a polysaccharide consisting of anhydroglucose units linked by (1→4)-β-D-glucosidic bonds.
During the viscose process cellulose is treated with sodium hydroxide to yield alkali cellulose. This alkali cellulose is then treated with carbon disulfide to form a solution of sodium cellulose xanthate, which is called viscose. This solution is pumped through a spinneret into a dilute sulphuric acid bath where the cellulose is regenerated as fine filaments as the xanthate decomposes.
The number of xanthate groups (γ-value) and their distribution influence the chemical characteristics of the cellulose xanthate. The γ-value can be determined by iodometric titration. This, however, tells nothing about the location of the xanthate groups in the cellulose molecules. Therefore, a NMR-method hat to be developed to yield this information.

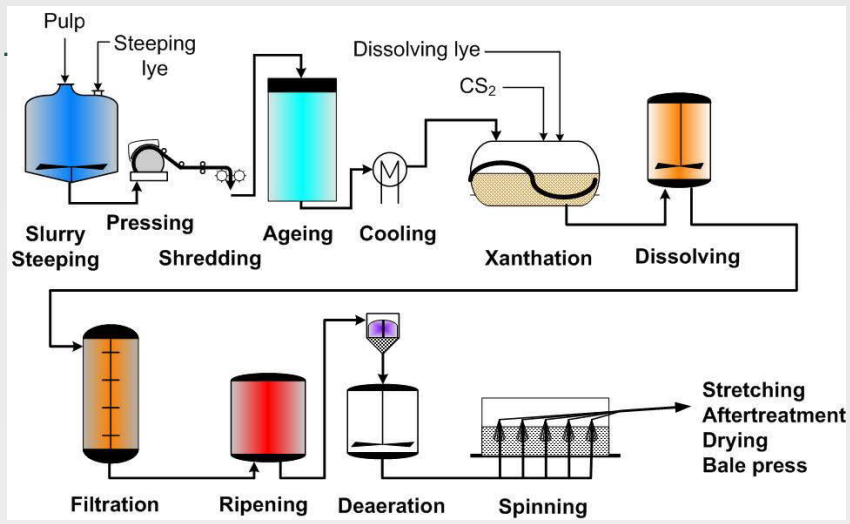

Figure 2: Viscose process.

Experimental

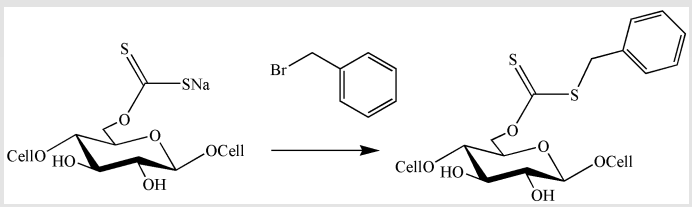

Figure 3: Cellulose xanthate stabilization with benzyl bromide.
Cellulose xanthate is an unstable system regarding temperature changes and variation of the pH-value. Therefore all xanthate groups were stabilized by derivatization with benzyl bromide [1].
Cellulose xanthate was dissolved in deionized water, the pH-value was set to 7-7.5 with acetic acid and benzyl bromide was added to the solution to start the stabilization reaction. After washing and drying the stabilized viscose was investigated by liquid-state ^{1}H NMR Spectroscopy in D_2O.

Determination of γ-Value and of the Xanthate Distribution

$$\gamma[\%] = 100 \frac{\frac{A(H8)}{5}}{\frac{A(H1,2,3,4,5,6,6',7) - \frac{2A(H8)}{5}}{7}}$$

$$DS(OHx)[\%] = 100 \frac{A(OHx)}{A(OH2,3,6)}$$

$$F(OHx)[\%] = DS(OHx) \frac{300 - \gamma}{300}$$

$$Fxanthation, x[\%] = 33{,}3 - F(OHx)$$

$$DSxanthation, x[\%] = 100 \frac{Fxanthation, x}{Fxanthation, 2,3,6}$$

$$\gamma x = DSxanthation, x \cdot \gamma$$

DS…degree of substitution

F…Fraction of substituted carbons on position x of AGU

Results

The stabilisation of the xanthate groups on viscose followed by measurement of proton NMR-spectra proved to be a suitable method to analyse the substitution pattern of viscose.
When comparing the iodometric method for the determination of the γ-value with the NMR method a systematic deviation for the samples of about 5 %. can be observed (Table 1).

Table 1: Results of γ-value determination of selected viscose samples by NMR and iodometric analysis.

γ-value by NMR [%]	γ-value iodometric [%]
38.6	43.9
43.9	49.0

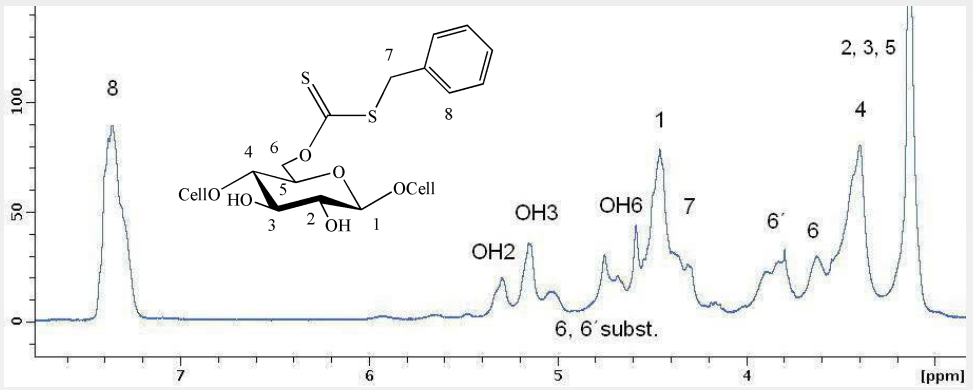

Figure 4: ^{1}H NMR spectrum of stabilized viscose at 300 MHz at 60°C.

References
1. Dominiak, K., 13C-NMR-spektroskopische Untersuchungen zur Substituentenverteilung Cellulosexanthogenaten, in Fakultät III - Prozesswissenschaften2008, Technische Universität Berlin: Berlin. p. 124.

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