A Novel Method for Analysis of Xanthate Group Distribution in Viscoses

Axel Rußler,[1] *Thomas Lange,*[1] *Antje Potthast,*[1] *Thomas Rosenau,*[1] *Elena Berger-Nicoletti,*[1] *Herbert Sixta,*[2] *Paul Kosma**[1]

[1] University of Natural Resources and Applied Life Sciences, Christian-Doppler-Laboratory and Department of Chemistry, Muthgasse 18, A – 1190 Vienna, Austria
Fax: (+43) 1 36006 6059; E-mail: paul.kosma@boku.ac.at
[2] Lenzing R & D, A – 4860 Lenzing, Austria

Summary: Analytical monitoring of xanthation in the viscose process along with xanthate group analysis in the viscose material is a long-debated problem in cellulose chemistry. The task is rendered extremely intricate by the lability of the starting material and the harshness of the reaction medium, which adds to a lack of suitable analytical approaches. In a four-years' endeavor in our lab, a method is being developed which allows to analyze the distribution of xanthate groups in viscoses relative to the anhydroglucose units and along the cellulose chain.
In a first step the xanthate groups are stabilized by alkylation, which was optimized towards quantitative conversion. In a second step, the remaining free hydroxyl groups are protected by carbanilation, followed by selective removal of the stabilized xanthate groups. Steps two and three thus generate an inverse image of the initial xanthate pattern. In the forth and fifth step, the liberated hydroxyl groups are methylated, and the carbanilates are removed, so that in the overall process the xanthates were replaced by methyl groups. All reaction steps have been comprehensively tested with regard to completeness of conversion and orthogonality of the protecting groups.

Keywords: methylation analysis; substitution pattern; viscose; xanthates

Introduction

Although the beginning of the viscose process dates back over hundred years, analytical monitoring of xanthation in the viscose process along with xanthate group analysis in the viscose material is a long-debated problem in cellulose chemistry. The task is rendered extremely intricate by the lability of the starting material, the harshness of the xanthation

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medium, the high migration tendency of xanthate groups, and finally a lack of suitable analytical approaches.

However, the degree and the homogeneity of substitution have a crucial influence on the characteristics of the viscose solution, the spinning performance, and the properties of the regenerated fibers. Previous analytical investigations on cellulose xanthate provided only overall substitution parameters, and analytical knowledge is largely restricted to some old general rules, such as that there is a decrease in γ-value (degree of substitution, average number of xanthate groups per 100 anhydroglucose [AGU] units) during the ripening of the viscose, or migration of xanthate groups.[1] Various attempts to overcome these problems have been presented in the past, but with limited success. Fink *et al.*[2] described a method for the stabilization of xanthate groups by alkylation using *N,N*-dimethyl-chloroacetamide, while Schurz and Zimmerl[3] used *N,N*-diethylchloroacetamide. Purves *et al.*[3] used *S*-methylation of cellulose xanthate followed by acetylation of remaining free hydroxyl groups, but failed to remove the xanthate esters selectively. For a review see Götze[4]. Willard and Pacsu[4] transformed *S*-benzoylated cellulose xanthate into the more readily hydrolyzable monothiocarbonate. This functionality was selectively removed and the hydroxyl groups thereby liberated were methylated. Unfortunately, this approach was not optimized and worked only for viscose samples having undergone an ageing step, so-called "ripening". Another approach was selected by Fischer and coworkers[5] who studied viscose solutions by gel permeation chromatography (GPC). This way, information about the xanthate group distribution in relation to the molecular weight of the polymer backbone was obtained, but the degree of substitution (DS) at positions 2, 3 and 6 of the anhydroglucose units remained inaccessible. NMR experiments by König *et al.*[6] addressed the latter question employing viscose samples prepared with ^{13}C-enriched CS_2, but this method was not applicable to industrial viscose samples. Thus, there was still no general method available for substituent distribution analysis in viscose samples.

To study the substituent homogeneity and its effects on the physical properties of the viscose solution and those of the spun fiber, analysis of the distribution of the xanthate

groups within the anhydroglucose unit (AGU) is the first step, meaning determination of number (0 – 3) and position (2-O, 3-O, 6-O) of xanthate substituents per AGU, which is followed by substituent analysis along the polymer chain. In the present work, we wish to communicate our studies on a chemo-analytical approach to analyze the xanthate substitution pattern per anhydroglucose unit in laboratory and industrial viscose samples.

Results and Discussion

One way to tackle the problem of substituent analysis in viscoses was to transform the xanthation pattern in an identical methylation pattern in order to make the material accessible to a standard methylation analysis. This required, however, a number of reactions, which had to be optimized separately in terms of selectivity, near-quantitative yields, and orthogonality of protecting groups. The individual reaction steps were tested and optimized at first by means of carbohydrate model compounds, such as cyclohexanol (**1**), *trans*-cyclohexane-1,2-diol (**2**) and methyl 4-*O*-methyl-*β*-D-glucopyranoside (**3**),[7] before using genuine viscose samples.

The stabilization of the xanthate groups by alkylation was optimized as a first step. Among numerous reagents tested, only *N*-phenyl-2-iodoacetamide (**4**), *N*-methyl-*N*-phenyl-2-iodoacetamide (**5**) and allyl bromide (**6**) proved to be effective, providing "stabilized viscose samples", in which the traditionally determined γ-value[8] agreed with that calculated from elemental analysis of the alkylated material. The rather labile xanthate groups were thus transformed into quite stable xanthate esters, which are suitable for further chemical modifications due to their surprisingly high temperature and pH-resistance with good solubility in polar organic solvents. For compound **14** we for example found a decomposition temperature of 100 °C in DMSO and a stable pH-range from pH 2 to pH 9.

The stabilization reagents are either commercially available (**6**) or accessible by simple reactions in gram scale as outlined in Figure 1 (compounds **4** and **5**). The ready reaction of

iodoacetamides with the xanthates was expected as these compounds were widely used in protein chemistry for the alkylation of cysteine residues.[9]

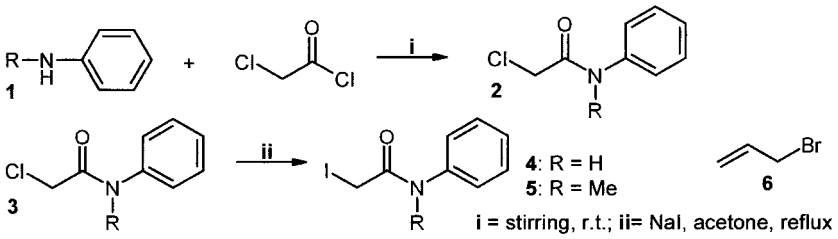

Figure 1. Alkylating agents **4** – **6** as used for the stabilization of viscose samples.

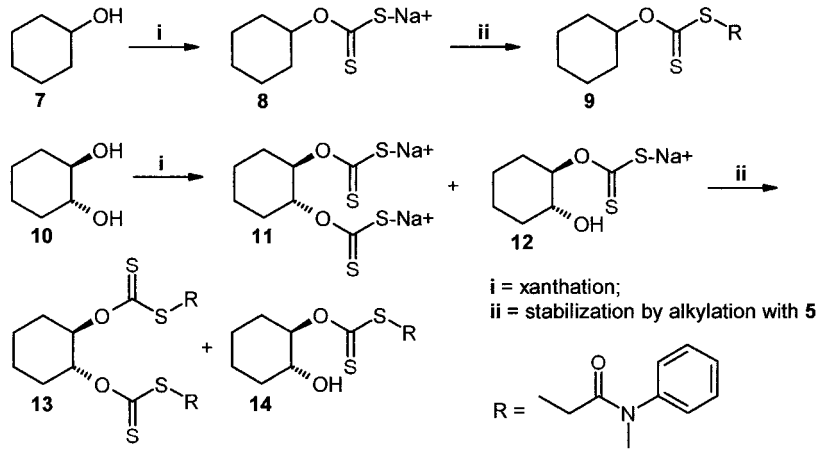

Figure 2. Synthesis of stabilized xanthates from model compounds **1** and **2**.

From the model compounds **1** and **2** stabilized xanthates were prepared in good yields as shown in Figure 2. Methyl 4-*O*-methyl-*β*-D-glucopyranoside (**3**) was an especially valuable model compound as it represented a model of one AGU unit of cellulose, from which several stabilized xanthates with different substitution patterns were prepared (Figure 3) and comprehensively analytically characterized.[10]

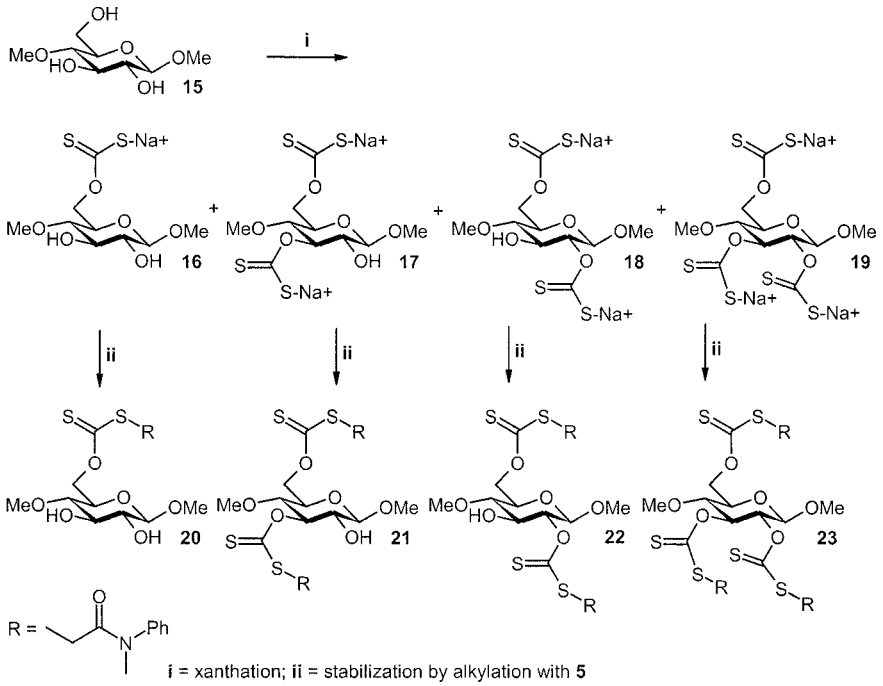

Figure 3. Synthesis of model xanthates from model compound **3**.

Alkylatively stabilized xanthated models (**9, 13, 14, 20-23**) and viscose samples are white solids, which can be stored over prolonged times. The stabilization of viscose samples by alkylation with either of the reagents **4**–**6** is thus an appropriate means to convert the labile and difficult-to-handle xanthates into a stable and tractable material, which can now be subject to analytical methods or be used in further chemical manipulations. Unfortunately, the alkylatively stabilized viscose samples were not stable enough to tolerate total hydrolysis of the cellulosic polymer, which would have been the easiest approach to a direct determination of the xanthation pattern.

In theory, methylation of the free OH groups in the stabilized viscose samples followed by removal of the alkylated xanthate esters would produce a methylation pattern inverse to the xanthate substitution, which would thus constitute a simpler way to determine the original xanthation pattern. Unfortunately, direct methylation of the stabilized cellulose xanthate was not possible due to extensive side reactions caused by the strongly nucleophilic character of the sulfur in the alkyl xanthate groups.

Thus a detour proved to be necessary, the introduction of a temporary protecting group at the remaining free hydroxyls of the stabilized viscose samples. As the second step in the analysis sequence, these positions were readily protected by carbanilation using phenyl isocyanate in pyridine at slightly elevated temperature, based on a method by Hall and Horne.[11] Carbanilates were used because of their small migration tendency and their higher stability – e.g. in comparison to acetates – and their beneficial effect on the solubility. After carbanilation, no free OH groups remained in the model compounds (see Figure 4) or the respective viscose, as they either carried stabilized xanthate moiety or a phenylcarbamoyl group.

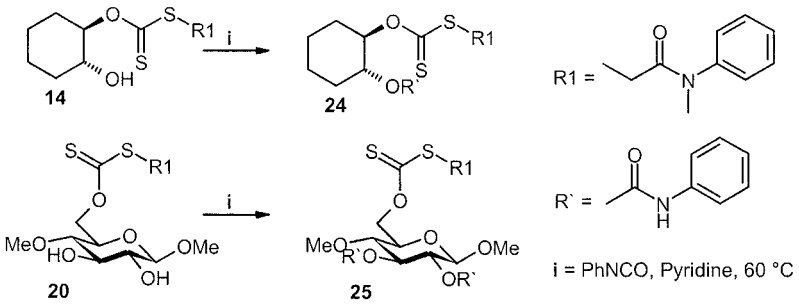

Figure 4. Carbanilation reaction of model compounds **14** and **20**.

While the preceding steps are relatively easy to achieve in a complete and selective way, the following step – selective cleavage of the stabilized xanthate groups – was rather

intricate. The stabilized xanthate groups in the carbanilates proved to be surprisingly stable towards all types of hydrolysis conditions, so that either the xanthates remained unaffected under milder conditions or the carbanilates were partially removed along with the xanthates by more drastic treatments. All attempts to remove the alkylated xanthates completely and selectively – leaving the carbanilates intact – failed at our hands. Consequently, the xanthate esters were transformed into monothiocarbonate esters by treatment with mercury(II) acetate, according to Pacsu,[4] as step three of the analytical sequence. This method proved to be superior to similar approaches using nitrosyl compounds,[12] benzeneselenic acid anhydride,[13] or potassium permanganate,[14] as it was distinguished by a quick, mild and complete conversion, simply by stirring in wet THF, DMF, or dioxane for several minutes. Caution must be exercised to avoid yield losses due to adsorption on Celite®, which was required to separate the product from the finely precipitated mercury salts. The search for a less toxic reagent to conduct this specific conversion was not successful.

As step four of the reaction sequence, the monothiocarbonate esters were simply cleaved with sodium methoxide in a solvent mixture of DMF/THF (v:v=1/5) or trimethyl phosphate/THF (v:v=1/5). In neat THF the reaction rate was too low, causing side reactions as the reaction time had to be overly prolonged. Using only a dipolar aprotic solvent on the other hand, rendered selective cleavage impossible. In the above solvent mixture, the reaction was fully compatible with the carbanilate protecting groups and showed no undesirable side reactions even after days, as confirmed by NMR. Removal of the alkylated xanthate groups produced a material with an inverse substitution pattern relative to the xanthogenated starting material: the xanthate groups in the starting material were transformed into free hydroxyls, while the free OH groups in the former were converted into carbanilates.

After removal of the THF by evaporation, only the DMF or trimethyl phosphate remains together with the partly carbanilated cellulose. In this solvent, the liberated hydroxyl groups were now methylated by methyl triflate, according to the method of Prehm.[15-16] The

compatibility of the reaction conditions with the carbanilates was once again tested with model compounds. Under the methylation conditions, also *N*-methylation of the phenylcarbamoyl moieties occurred.

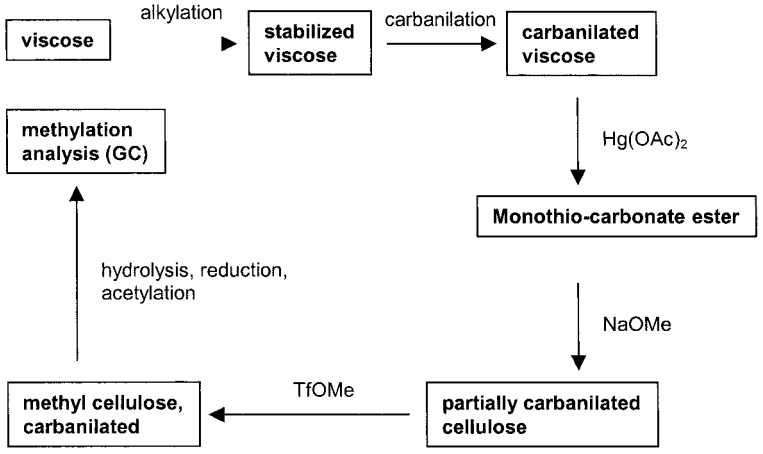

Figure 5. General scheme of the reaction sequence.

With methylation of the liberated hydroxyl groups – as the last reaction in the analytical sequence – the originally present xanthate substitution pattern was now accurately changed into a methyl substitution pattern, with the free hydroxyl groups of the starting material still being carbanilated.

The partially methylated cellulose thus obtained offers now the opportunity to carry out standard methylation analysis, which is routinely used in polysaccharide analysis,[17-19] on xanthated model compounds and genuine viscose samples. For that purpose, the polymeric methylated material is first hydrolyzed. However, due to the complete substitution with sterically demanding groups and hydrophobization of the polymer a direct hydrolysis into monomer units proved to be impossible under sufficiently mild acidic conditions. However, cleavage of the carbanilate groups beforehand by addition of excess sodium

methanolate provided partly methylated cellulose, which was then readily accessible to standard hydrolysis procedures. The resulting monomer units are now reduced and acetylated. The methylated alditol acetates are then quantified by gas chromatography in a classical methylation analysis,[18-19] affording directly the substitution pattern per anhydroglucose unit.

The general analysis strategy is exemplarily shown in Figure 4 by means of an AGU carrying one xanthate substituent in 6-position, explaining the five reaction steps needed to convert the xanthate pattern into a methylation pattern, and the subsequent methylation analysis. Application of the novel analytical approach to different viscose samples, and influence of xanthation parameters on the substituent distribution will be reported in due course.

Conclusion

The presented analytical procedure allows for the first time determining the substituent distribution with respect to the anhydroglucose units in viscose samples (normal and modal viscose samples) by chemically converting the xanthate substitution into a methyl substitution, followed by standard methylation analysis. Modifications of the method can provide information about the substitution pattern along the polymeric backbone as well, or allow analysis of soluble intermediates by NMR, which are topics of current research in our lab.

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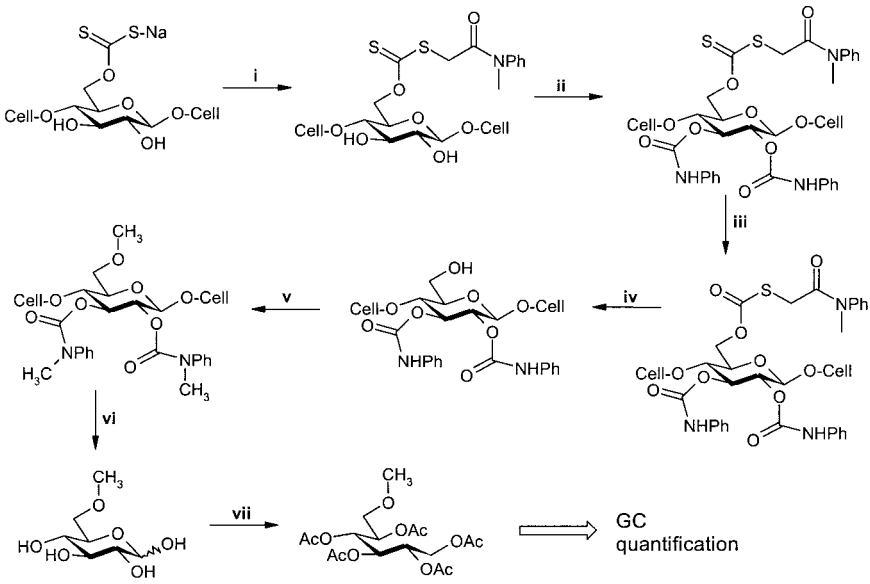

i = **5**, r.t., 1 h; **ii** = PhNCO, pyridine, 60° C; **iii** = wet dioxane, $Hg(OAc)_2$, **iv** = NaOMe, Me_3PO_4/THF (1:5), **v** = TfOMe, Me_3PO_4, 2,6-di-*t*-butyl-4-methylpyridine, 70°C, **vi** = acidic hydrolysis, **vii** = reduction, acetylation

Figure 6. Determination of substituent distribution per AGU in viscose samples: analysis principle, reaction sequence, and reagents used.

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