Structure Determination of Cellulose Esters via Subsequent Functionalization and NMR Spectroscopy

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Summary: New paths for the fast and reliable analysis of cellulose esters (CE) via subsequent functionalization and ^{1}H NMR spectroscopy were studied. Perpropionylation of the CE is an inexpensive and efficient method. For cellulose diacetates used as representative ester well resolved ^{1}H NMR spectra were obtained, which can be used for the calculation of the over all degree of substitution (DS) and the partial DS values at position 2, 3, and 6. No transesterification occurs during the subsequent acylation and a standard deviation of $S^2 = 1.32 \times 10^{-4}$ was found for a series of experiments. In case of more complex ester structures especially with extended aliphatic moieties per-4-nitrobenzoylation need to be applied prior to NMR measurements. The spectra obtained can be completely assigned and applied for the calculation of DS values.

Keywords: analysis; degree of substitution; esterification; NMR; polysaccharide

Introduction

The efficient and reliable analysis of the degree of substitution (DS) and the pattern of functionalization of cellulose esters (CE) is still one of the major issues in the field of polysaccharide research. The reasons are the growing number of new synthesis paths for the preparation of unconventional CE[1,2], which cannot be analyzed comprehensively with the methods available. Moreover, conventional analytical tools are not sufficient for the fast determination of structural features of technical products and the establishment of structure-property relations, e.g., the solubility of cellulose acetate in water or in organic media is still not well understood.[3]

A broad variety of spectroscopic and chromatographic methods was investigated towards their use as analytical tools for the structure elucidation of CE including ^{1}H- and ^{13}C NMR spectroscopy as well as GLC, HPLC and MS.[3] For most of these methods subsequent functionalization, e.g., deuteroacetylation or methylation of the CE is essential. Complete

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subsequent derivatization is indispensable for structure determination by means of ^{1}H- and ^{13}C NMR spectroscopy in order to gain reasonable resolution of the spectra. The pioneering work of both Goodlett *et al.* in 1971[4] using ^{1}H NMR spectroscopy and Tezuka *et al.* in 1995[5] applying ^{13}C NMR measurements opened major routs for structure analysis of cellulose acetates.

Especially the efficient ^{1}H NMR spectroscopy after deuteroacetylation showed an enormous potential.[4] The partial DS values at position 2, 3, and 6 can be readily calculated from the ratio of the spectral integrals of the protons of the repeating unit and the methyl protons of the acetyl moiety. The disadvantage is the rather expensive deuteroacetylation step, which is connected with a remarkable deviation if the acetyl-*d3*-chloride is contaminated with acetyl chloride. Thus, different alternatives for a subsequent derivatization of CE for analytical purposes were studied. Among these subsequent reactions are perpropionylation, per-4-nitrobenzoylation and pertrifluoroacetylation.

Experimental

Materials

Pyridine, propionic anhydride, LiCl, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and the solvents used for product purification were obtained from Fluka. The commercial cellulose diacetate (**1**, Eastman® CA-398-3) was obtained from Eastman Chemical Company. The polymer was dried at 60°C for 24 h in vacuum. $CDCl_3$ was supplied by Aldrich and was used without further purification.

Measurements

^{1}H NMR and $^{1}H,^{1}H$ COSY NMR spectra of the esters were acquired in $CDCl_3$ at 40°C on a BRUKER AMX 400MHz spectrometer. The number of scans was 32. FTIR spectra were measured on a Bio-Rad FTS 25 PC using the KBr pellet technique. KBr tablets were dried at 100°C for 1 h to remove moisture prior to the measurement. Conventional DS determination was carried out by a back-titration method after saponification.[6]

*Perpropionylation of Cellulose Diacetate **1** at 70°C*

Perpropionylation was carried out by reacting 0.3 g (1.1 mmol) of **1** with 5 mL (39.0 mmol) propionic anhydride and 5 mL pyridine for 24 h at 70°C under stirring. The polymer was precipitated in 150 mL ethanol, washed with ethanol (200 mL) four times, and dried at 60°C under vacuum. Yield: 0.32 g (94.6 %); $DS_{Acetate}$ = 2.37 (determined by means of ^{1}H NMR spectroscopy); FTIR (KBr): 2890 ν (C-H), 1750 ν (CO_{Ester}), 1238 ν (C-O-C_{Ester}) cm^{-1}; ^{1}H NMR (of perpropionate in $CDCl_3$): δ (ppm) = 5.00 (H-3), 4.73 (H-2), 4.33 (H-1,6), 3.99 (H-6`), 3.64 (H-4), 3.48 (H-5), 2.06 (CH_3-6), 1.94 (CH_3-2), 1.88 (CH_3-3).

*Acetylation of **1** with Acetic Anhydride*

1.0 g (3.8 mmol) **1** was dissolved in 10 mL pyridine. For complete acetylation, 10 mL (101 mmol) acetic anhydride was added. The reaction mixture was heated up to 70°C for 24 h along with stirring. Isolation of the polymer **2** was carried out by precipitation into 200 mL ethanol, washing with ethanol and drying in vacuum at 60°C. Yield: 1.02 g (93.1 %); $DS_{Acetate}$ = 2.98 (determined by means of ^{1}H NMR spectroscopy after perpropionylation); FTIR (KBr): no ν (OH), 2900 ν (C-H), 1742 ν (CO_{Ester}); 1240 ν (C-O-C_{Ester}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.09 (H-3), 4.81 (H-2), 4.42 (H-1,6), 4.06 (H-6`), 3.73 (H-4), 3.56 (H-5), 2.14 (CH_3-6), 2.02(CH_3-2), 1.96 (CH_3-3).

*Investigation of the Transesterification Tendency of **2** at 120°C*

The experiment was carried out by treating 0.3 g (1.1 mmol) of **2** with 7 mL (39.0 mmol) propionic anhydride and 5 mL pyridine for 24 h at 120°C in N_2 atmosphere under stirring. The polymer was precipitated in methanol and washed with methanol (250 mL) four times and then dried at 60°C under vacuum. Yield: 0.28 g (93.3 %); $DS_{Acetate}$ = 2.98 (determined by means of ^{1}H NMR spectroscopy); FTIR (KBr): no ν (OH), 2893 ν (C-H), 1752 ν (CO_{Ester}), 1240 ν (C-O-C_{Ester}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.00 (H-3), 4.73 (H-2), 4.33 (H-1,6), 3.99 (H-6`), 3.64 (H-4), 3.48 (H-5), 2.06 (CH_3-6), 1.94 (CH_3-2), 1.88 (CH_3-3).

Acetylation of Cellulose with Acetyl Chloride/Polyvinyl Pyridine, Typical Procedure

A solution of 1.0 g (6.2 mmol) cellulose in 40 mL DMAc and 3 g LiCl was prepared according to Ref. 7. It was kept in an ice bath for 15 min. 3.88 g (37.0 mmol) polyvinyl pyridine and 2.2 mL (31.0 mmol) acetyl chloride (5 mol/mol AGU) was added carefully to the cooled solution. The system was heated to 80°C for 2 h and was kept at room temperature for 24 h. Isolation was carried out by precipitation into 200 mL ethanol, reprecipitation from DMSO, washing with ethanol and drying in vacuum at 50°C (Sample **A5**, Table 2). Yield: 1.5 g (84.9 %); $DS_{Acetate}$=2.64 (determined by means of ^{1}H NMR spectroscopy after perpropionylation); FTIR (KBr): 3502 ν (OH), 2896 ν (CH), 1744 ν (C=O_{Ester}) cm^{-1}; ^{13}C NMR (DMSO-d_6): 169.2 – 169.9 ppm (C=O), 60.3 – 102.5 ppm (cellulose backbone).

*Nitrobenzoylation of **1** with 4-Nitrobenzoyl Chloride*

0.5 g (1.9 mmol) of **1** dissolved in 8 mL *N,N*-dimethylformamide (DMF) was reacted with 1.5 g (8.1 mmol) 4-nitrobenzoyl chloride. The reaction mixture was heated to 60°C for 24 h along with stirring. Product **3** was obtained by precipitation into 200 mL ethanol, washing with 200 mL ethanol twice, and drying in vacuum at 60°C. Yield: 0.46 g (68.6 %); $DS_{Acetate}$ = 2.37 (determined by means of ^{1}H NMR); FTIR (KBr): no ν (OH), 2893 ν (C-H), 2957, 3115 ν (aromatic C-H), 1235 ν (C-O-C_{Ester}), 1532 ν (Ar-NO_2), 1752 ν (CO_{Ester}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.09 (H-3), 4.82 (H-2), 4.45 (H-1,6), 4.06 (H-6`), 3.73 (H-4), 3.56 (H-5), 2.14 (CH_3-6), 2.02 (CH_3-2), 1.88 (CH_3-3), 8.42, 8.27, 8.01, 7.92 (H-nitrobenzoate).

*Nitrobenzoylation of **1** with 4-Nitrobenzoic Acid/N,N-Carbonyldiimidazole (CDI)*

3.09 g (18.5 mmol) 4-nitrobenzoic acid was dissolved in 20 mL DMSO followed by 3.0 g (18.5 mmol) CDI to prepare the 4-nitrobenzoyl imidazolide and the mixture was stirred over night. 1.0 g (3.8 mmol) of reprecipitated **1** (from THF into ethanol) was dissolved in 20 mL DMSO. The solutions were mixed and heated to 60°C for 16 h under stirring. Isolation of the polymer was carried out by precipitation into 200 mL ethanol. Polymer **4** was washed with 200 mL ethanol three times and dried in vacuum at 60°C. Yield: 1.05 g (78.4 %); DS = 2.60 (determined by means of ^{1}H NMR); FTIR (KBr): no ν (OH), 2893 ν (C-H), 2959, 3100 ν (aromatic C-H), 1235 ν (C-O-C_{Ester}), 1531 ν (Ar-NO_2), 1752 ν (CO_{Ester}) cm^{-1}; ^{1}H NMR

($CDCl_3$): δ (ppm) = 5.00 (H-3), 4.73 (H-2), 4.33 (H-1,6), 3.98 (H-6`), 3.67 (H-4), 3.48 (H-5), 2.05 (CH_3-6), 1.94(CH_3-2), 1.87 (CH_3-3), 8.43, 8.27, 8.01, 7.94 (H-nitrobenzoate).

*Trifluoroacetylation of **1** with Trifluoroacetic Acid/CDI*

3.0 g (18.5 mmol) CDI was added to 1.43 mL (18.5 mmol) trifluoroacetic acid in 20 mL DMSO. The mixture was stirred overnight at room temperature then added to the solution of 1.0 g (3.8 mmol) **1** (reprecipitated and dried) in 10 mL DMSO. The reaction mixture was stirred for 24 h at 60°C under N_2. The homogeneous reaction mixture was precipitated in 200 mL methanol and the polymer was collected by filtration. After washing with 250 mL methanol three times, the polymer **5** was dried at 60°C under vacuum. Yield: 0.73 g (59.6 %); FTIR (KBr): 3450-3480 ν (OH), 2890 ν (CH), 1790-1750 ν ($C{=}O_{Ester}$) cm^{-1}.

^1H NMR ($CDCl_3$): δ (ppm) = 3.42-5.09 (H-1-6), 2.06 (CH_3-6), 1.99 (CH_3-2), 1.93 (CH_3-3).

Results and Discussion

Perpropionylation of cellulose esters (CE) in combination with ^1H NMR experiments was studied as inexpensive and efficient alternative to the deuteroacetylation, which was applied first for the structure analysis of cellulose acetate by Goodlett.[4] A commercial cellulose diacetate (**1**) was treated with excess of propionic anhydride in pyridine. Complete derivatization of all free OH groups was confirmed by the disappearance of a band in the FTIR spectra (3460 cm^{-1}). The mixed ester obtained was well soluble in $CDCl_3$ and could be investigated by standard ^1H NMR as shown in Figure 1. Peaks for propionate functions were determined at 1.03-1.07 ppm (CH_3 propionate in position 2 and 3), 1.21 ppm (CH_3-propionate in position 6), and at 2.21-2.37 ppm for the CH_2 moiety of the propionate moieties. Three separate peaks can be observed for CH_3 groups of acetyl moieties at 1.92 ppm (position 3), at 1.97 ppm (position 2), and 2.08 ppm (position 6). The signals for protons of the anhydroglucose unit (AGU) were found in the range from 3.51 to 5.05 ppm.

The signals can be completely assigned showing only one peak per proton (assignment see Experimental), i.e., the existence of acetyl and propionyl moieties in the molecule does not induce a signal splitting of the AGU protons. A $^1H,^1H$ COSY NMR spectrum of this region is displayed in Figure 1 confirming the assignment. Consequently, the spectral integrals of the

protons of the AGU and the methyl protons of the propionyl moiety can be applied to calculate the partial DS and the over all DS values of the acetate applying Equation 1 and 2.

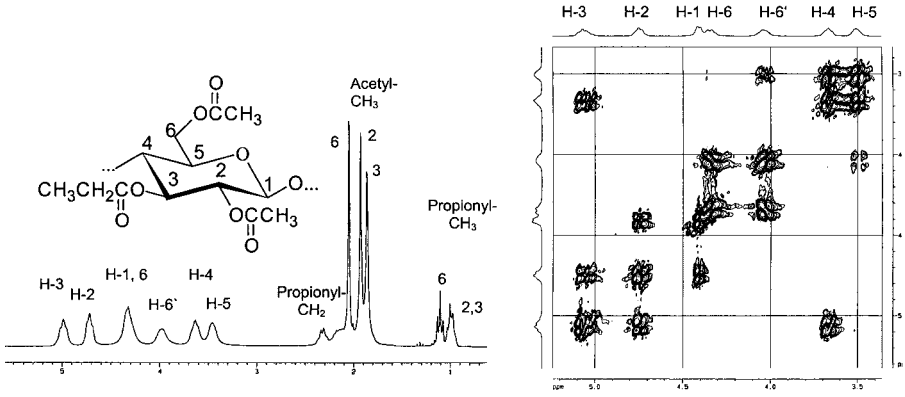

Figure 1. ^{1}H NMR spectrum (left) and $^{1}H,^{1}H$ COSY NMR spectrum (right, the area of the protons of the anhydroglucose unit is displayed) of cellulose acetate propionate prepared by complete propionylation of a commercial cellulose diacetate ($CDCl_3$, NS 32).

$$DS_{Acyl} = 3 - \frac{7 \times I_{H,\,Propionyl}}{3 \times I_{H,\,AGU}} \qquad I = \text{Integral}$$

(Equation 1)

$$DS_{Acyl}(n) = 1 - \frac{7 \times I_{H,\,Propionyl}(n)}{3 \times I_{H,\,AGU}} \qquad \begin{array}{l} I = \text{Integral} \\ n = \text{Position 2, 3 or 6} \end{array}$$

(Equation 2)

The limits and the reliability of the method were studied. To investigate the tendency of cellulose acetate towards transesterification during the subsequent propionylation, completely acetylated cellulose was applied. The cellulose triacetate (**2**) was treated at temperatures of 60, 80, and 120°C, respectively, with the propionylation mixture consisting of pyridine and propionic anhydride. After isolation, in any case only signals for the cellulose triacetate at

1.92 – 2.09 ppm (CH_3-acetyl) and between 3.52 – 5.05 ppm (AGU) were found. No additional peaks appeared meaning no transesterification occurred. Moreover, propionylation experiments were carried out at temperatures between 60 and 120°C with **1** showing no significant changes in the DS and the distribution of the substituents. In addition, perpropionylated cellulose diacetate were prepared under the same conditions and each sample was analyzed four times by means of ^{1}H NMR spectroscopy. The results summarized in Table 1 confirm the accuracy of the method and yield a standard deviation of $S^2 = 1{,}32 \times 10^{-4}$. It has to be mentioned that a prerequisite to this reliability of the method is complete removal of all impurities from the samples, i.e., drying at 60°C in vacuum. If water or free acetic acid is present a much higher deviation is observed.

Table 1. Degree of substitution (DS) values calculated from ^{1}H NMR spectra of perpropionylated cellulose diacetate. The cellulose diacetate was propionylated twice (series 1 and series 2) and measured four times by ^{1}H NMR spectroscopy.

DS series 1	DS series 2
2.35	2.37
2.35	2.37
2.32	2.38
2.32	2.38

A series of cellulose acetates with DS values in the range from 0.4 to 2.6 was prepared and studied by means of propionylation and ^{1}H NMR spectroscopy. The cellulose acetates were accessible by conversion of cellulose dissolved in *N,N*-dimethylacetamide (DMAc)/LiCl with acetyl chloride using polyvinyl pyridine as base. The DS was adjusted by the molar ratio AGU/acetyl chloride. All samples were perpropionylated via the standard procedure, i.e., conversion with pyridine and propionic anhydride for 24 h at 70°C. Again FTIR spectroscopy showed no bands for free OH groups after perpropionylation, i.e., no signals between 3300 and 3500 cm^{-1} occurs. The DS values for the acetate content ($DS_{Acetate}$), the propionate content ($DS_{Propionate}$), and the over all DS (DS_Σ), which were obtained from ^{1}H NMR spectra, are displayed in Table 2. DS_Σ values in the range 2.97 to 3.01 were found, which is in the frame of the standard deviation of the method for all samples analyzed. Therefore, the procedure can be applied for all types of cellulose acetates. Besides the $DS_{Acetate}$ the method yields partial DS values by evaluation of the three separate signals for CH_3 groups of the

acetyl moieties at 1.92 ppm (position 3), at 1.97 ppm (position 2) and 2.08 ppm (position 6). The partial DS values determined confirm the pronounced acetylation of the primary OH groups during homogeneous acetylation with acetyl chloride (Table 2).

Table 2. Conditions of the acetylation of cellulose dissolved in *N,N*-dimethylacetamide/LiCl with acetyl chloride in the presence of cross-linked polyvinyl pyridine and degree of substitution (DS) determined via ^{1}H NMR spectroscopy after perpropionylation.

No.	Molar ratio		DS_{Acetyl}			$DS_{Propionyl}$	$DS_{\Sigma Ac+Prop}$
	Acetyl chloride/ AGU	Base/ AGU	Position 6	Position 2,3	Σ		
A1	1.0	1.2	0.35	0.13	0.48	2.49	2.97
A2	2.0	2.4	0.82	0.51	1.33	1.66	2.99
A3	3.0	3.6	0.91	0.65	1.56	1.41	2.97
A4	4.5	4.5	1.0	1.24	2.24	0.77	3.01
A5	5.0	6.0	1.0	1.62	2.62	0.37	2.99

Numerous new cellulose esters with a wide variety of functional groups were synthesized within the last years applying new synthesis paths.[1,2] Especially the *in situ* activation of the carboxylic acid with *p*-toluenesulfonyl chloride (tosyl chloride)[8-10], *N,N'*-carbonyldiimidazole (CDI)[11], and iminium chloride[12], as well as homogeneous conversion of cellulose dissolved in DMAc/LiCl[8-12] or in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride[13,14] yielded new structures. Attempts were made to analyze such cellulose esters with the method described.

The propionylation can be applied for aromatic and unsaturated cellulose derivatives with ^{1}H NMR signals of the substituents in the region higher than 5.1 ppm. Thus, cellulose furoates with additional peaks at 7.56, 7.20, and 6.50 ppm and the 3-(2-furyl)-acrylic acid esters of cellulose with additional peaks at 7.82, 7.50, 6.87, 6.57, and 6.23 ppm were analyzed via this path.[13] Moreover, alicyclic esters of cellulose, e.g., the ester of the adamantane carboxylic acid can be studied. A representative ^{1}H,^{1}H COSY NMR spectrum of a perpropionylated cellulose adamantane carboxylic acid ester is shown in Figure 2. The signals for the protons of the two substituents are well resolved and can be used for the calculation of the DS according to Equation 1.

In case of CE with extended aliphatic moieties, e.g., fatty acid esters, the ^{1}H NMR spectra of the perpropionylated derivatives could not be assigned because of signal overlapping of the

protons corresponding to the different ester moieties. Therefore, per-4-nitrobenzoylation and pertrifluoroacetylation reactions were investigated. The advantage is that a nitrobenzoylation introduces only signals at about 7.5 – 9.0 ppm in the ^{1}H NMR spectra. No additional peaks would appear in case of the trifluoroacetylation. These new subsequent steps for the analysis of CE by means of ^{1}H NMR spectroscopy were again carried out using a cellulose diacetate as model compound because of the simple structure of the substituent and the expected simplicity of the resulting spectra.

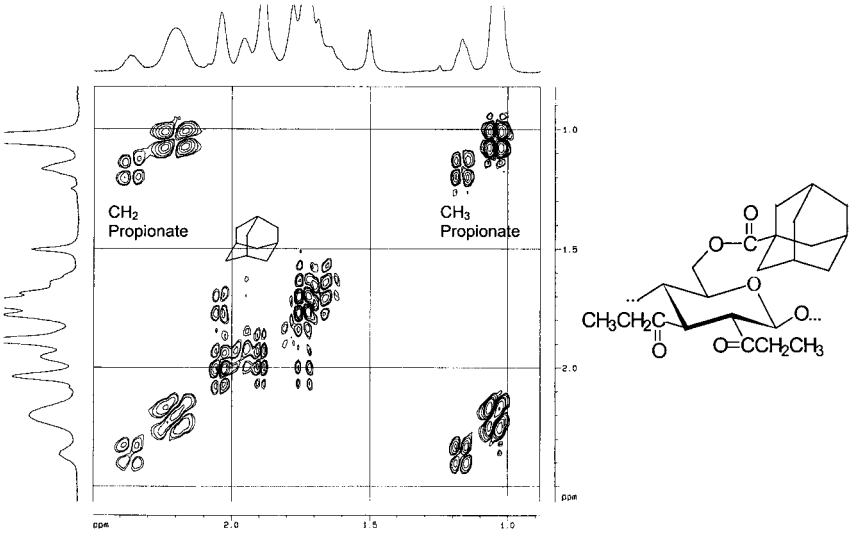

Figure 2. ^{1}H,^{1}H COSY NMR spectrum of a perpropionylated cellulose adamantane carboxylic acid ester. The area of the protons of the substituents is displayed ($CDCl_3$, NS 32).

Subsequent 4-nitrobenzoylation is possible via two paths, i.e., conversion of the 4-nitrobenzoic acid with CDI and "one-pot reaction" with the CE in DMSO or reaction of the CE in pyridine with 4-nitrobenzoyl chloride (Figure 3).

FTIR studies confirmed that the treatment of cellulose diacetate with 4-nitrobenzoyl chloride (molar ratio of AGU/reagent 1/3) in DMF for 24 h at 60°C is sufficient for a complete functionalization of the free OH groups. The product is well soluble in $CDCl_3$. A standard ^{1}H NMR spectrum is shown in Figure 4.

Peaks for the 4-nitrobenzoyl functions were found in the region 7.92-8.42 ppm. Three separate peaks can be observed for the CH_3 group of the acetyl function at 1.88 ppm (position 3), at 2.02 ppm (position 2), and 2.14 ppm (position 6). The signals for protons of the AGU between 3.46 and 5.09 are equally well resolved compared to perpropionylated samples. The signals can be completely assigned (see Experimental). No signal splitting of the AGU protons is induced by the existence of acetyl and 4-nitrobenzoyl moieties in the polymer. Thus, the $DS_{Acetate}$ can be determined from the ratio of the spectral integrals of the AGU protons and the methyl protons of the acetyl moiety (Equation 1). In addition the DS of nitrobenzoylation ($DS_{Nitrobenz}$) is available from the spectral integrals of the protons of the AGU and the aromatic protons of 4-nitrobenzoyl moieties. Thus, the content of acetylation can be calculated according to $DS_{Acetate} = 3 - DS_{Nitrobenz}$. The average values $DS_{Acetate}$ obtained by these two methods was 2.37 for the commercial cellulose diacetate **1**, which is in good agreement with the values determined via perpropionylation and ^1H NMR spectroscopy.

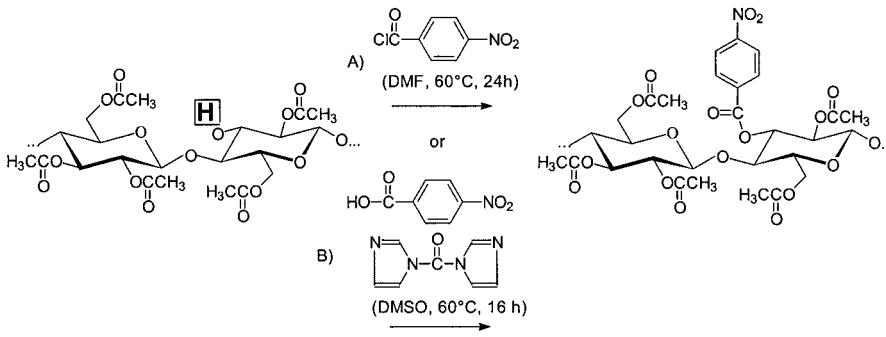

Figure 3. Schematic plot of the two paths of per-4-nitrobenzoylation.

The second path for subsequent nitrobenzoylation of CE was carried out homogeneously in DMSO exploiting the imidazolide of 4-nitrobenzoic acid, which can be prepared easily by reacting 4-nitrobenzoic acid with CDI in DMSO at room temperature. The product obtained from the reaction of the imidazolide with **1** was completely functionalized. ^1H NMR spectra of the cellulose acetate 4-nitrobenzoate prepared by this procedure revealed exactly the same

signal pattern but the $DS_{Acetate}$ calculated is much higher in the range of 2.7. This observation might be attributed to the existence of free acetic acid in the commercial CDA sample. CDI could form the acetyl imidazolide, which in turn may react with the remaining OH groups of the polymer. Reprecipitation of the **1** from THF and drying at 60°C in vacuum was applied to remove the free acid. The $DS_{Acetate}$ obtained was still in the range of 2.60.

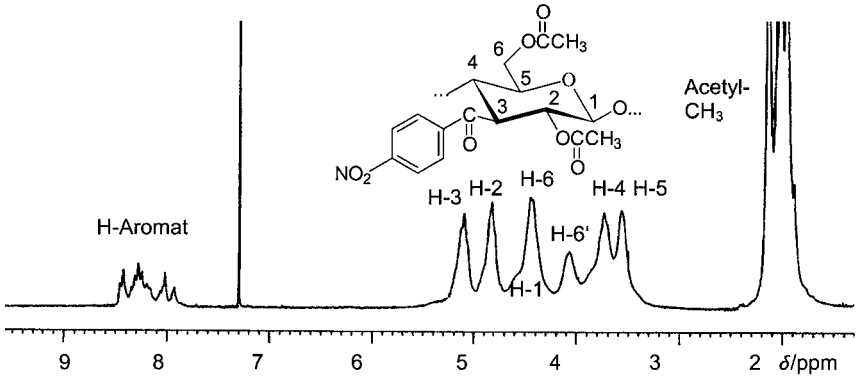

Figure 4. ^{1}H NMR spectrum of a per-4-nitrobenzoylated cellulose acetate ($CDCl_3$, NS 32).

A comparable behavior was observed for the subsequent trifluoroacetylation. Both the conversion of untreated **1** with trifluoroacetyl imidazolide as well as the reaction with trifluoroacetic anhydride (TFAA) yielded $DS_{Acetate}$ values higher than 2.6. In case of the subsequent functionalization with TFAA this could be explained with the well-known impeller mechanism.[15] Moreover, the high tendency of the trifluoroacetyl function towards hydrolysis and electronic effects, which also prevent the preparation of fully functionalized cellulose trifluoroacetate may cause problems. In addition, the spectra obtained for cellulose acetate trifluoroacetate samples show a complex pattern of signals (Figure 5) in the area of the AGU protons (3.5 to 5.1 ppm), which might be due to the chemical diversity of the two substituents. Consequently, pertrifluoroacetylation seems no proper tool for the analysis of CE by means of ^{1}H NMR spectroscopy.

Conclusions

It can be shown that perpropionylation and ^{1}H NMR spectroscopy is a powerful alternative to the analytical tools used for structure analysis of cellulose esters today. The subsequent step is a safe modification of the polymer and ^{1}H NMR spectroscopy is a rather fast and inexpensive method compared to the analysis usually applied, e.g., ^{13}C NMR spectroscopy or chromatography. In contrast to the deuteroacetylation applied first for the analysis of cellulose esters mainly for the cellulose acetate, propionylation is much cheaper and more reliable because impurities of the reagent do not result in a pronounced deviation as in case of the deuteroacetylation. In addition, the propionylation yields a separate pattern of peaks in the ^{1}H NMR spectra, which can be applied for "controlling" the subsequent modification in terms of completeness and structural uniformity. Per-4-nitrobenzoylation was found to be a very nice tool for the analysis of cellulose esters with a more complex structure. The application of alternative esterification steps is still under investigation

In addition to the subsequent esterification steps described, the reaction with isocyanates can be exploited. Besides ^{1}H NMR spectroscopy these derivatives may be investigated by chromatographic methods after selective degradation because of the higher stability of the carbamate moieties bound towards hydrolysis. This path is subject of ongoing research. First results are presented in a separate paper in this volume.

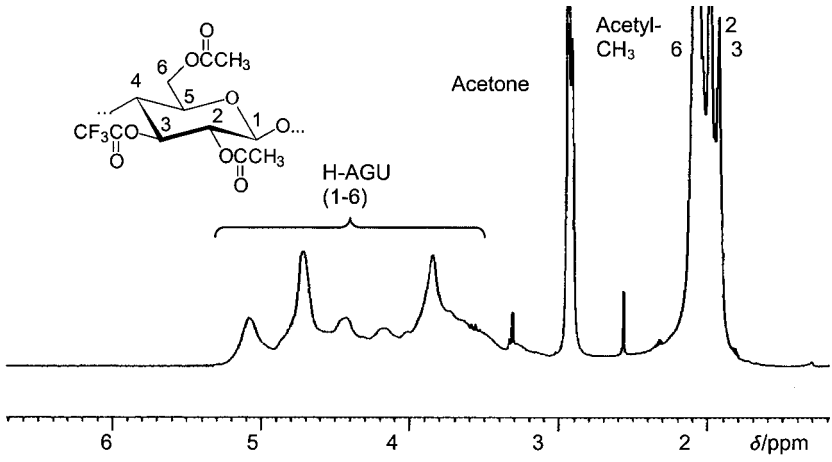

Figure 5. ^{1}H NMR spectrum of a pertrifluoroacetylated cellulose acetate ($CDCl_3$, NS 32).

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[1] K. Edgar, C.M. Buchanan, J.S. Debenham, P.A. Rundquist, B.D. Seiler, M.C. Shelton, D. Tindall, *Prog. Polym. Sci.* **2001**, *26*, 1605.
[2] Th. Heinze, T. Liebert, *Prog. Polym. Sci.* **2001**, *26*, 1689.
[3] Th. Heinze, T. Liebert, *Macromol. Symp.* **2004**, *208*, 167.
[4] V.W. Goodlett, J.F. Dougherty, H.W. Patton, *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 155.
[5] Y. Tezuka, Y. Tsuchiya, *Carbohydr. Res.* **1995**, *273*, 83.
[6] Y. Shimuzu, J. Hayashi, *Sen-I Gakkaishi* **1988,** *44,* 451.
[7] Th. Heinze, T. Liebert, K. Pfeiffer, M.A. Hussain, *Cellulose* **2003,** *10,* 283.
[8] W.G. Glasser, U. Becker, J.G. Todd, *Carbohydr. Polym.* **2000**, *42*, 393.
[9] J.E. Sealey, C.E. Frazier, G. Samaranayake, W.G. Glasser, *J. Polym. Sci., Part B: Polym. Phys.* **2000,** *38,* 486.
[10] Th. Heinze, J. Schaller, *Macromol. Chem. Phys.* **2000,** *201*, 1214.
[11] D. Gräbner, T. Liebert, Th. Heinze, *Cellulose* **2002,** *9*, 193.
[12] M.A. Hussain, T. Liebert, Th. Heinze, *Polymer News* **2004,** *29,* 14.
[13] M.A. Hussain, T. Liebert, Th. Heinze, *Macromol. Rapid Commun.* **2004,** *25,* 916.
[14] Th. Heinze, R. Dicke, A. Koschella, A.H. Kull, E.-A. Klohr, W. Koch, W. *Macromol. Chem. Phys.* **2000**, *201*, 627.
[15] F. Müller, *Papier (Darmstadt)* **1985**, *39*, 591.