Carbamoylation Applied for Structure Determination of Cellulose Derivatives

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Summary: Carbamoylation of cellulose esters (CE) and investigation of the mixed derivatives obtained with NMR spectroscopy represents a useful analytical tool for the determination of the degree of substitution (DS) and analysis of the distribution of substituents on the level of the anhydroglucose unit (AGU). Especially the carbethoxymethylcarbamoylation and the ethylcarbamoylation of CE combined with ^{1}H NMR spectroscopy are efficient and inexpensive ways to gain information on the over-all DS and partial DS values in position 2, 3, and 6 of the AGU. Complete subsequent phenylcarbamoylation can be achieved even for CE with bulky substituents, e.g., adamantanecarboxylic acid esters. In addition to NMR experiments the carbamoylated CE were studied by HPLC after complete chain degradation. Carbethoxymethylcarbamoylation has turned out to be the most useful tool for this path. Chromatograms comparable to carboxymethylated cellulose (CMC) were obtained, which can be exploited to calculate the mole fractions of the basic building units (un-, mono-, di- and tri-substituted glucoses) of the polymer. Comparison with statistic calculations gave a first hint on the distribution of substituents along the polymer chain. For a commercial cellulose diacetate a statistic pattern of substitution was determined.

Keywords: carbamates; esters; high performance liquid chromatography (HPLC); NMR; polysaccharide

Introduction

A number of analytical paths were developed for structure determination of organic and inorganic cellulose esters (CE) applying NMR spectroscopy and chromatography, which are reasonable if a complete subsequent derivatization of the remaining OH groups can be guaranteed.[1] On one hand, completely functionalized derivatives are an indispensable prerequisite to gain a sufficient resolution of the ^{1}H and ^{13}C NMR spectra, which can be applied for the determination of the pattern of functionalization.[2-4] Especially the peracylation (preferably peracetylation and perpropionylation) are used today. On the other hand, applying chromatography as analytical tool, complete chain degradation has to be carried out resulting in

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a cleavage of ester bonds as well. State of the art is transformation of the pattern of functionalization by permethylation of the free OH groups into the inverse pattern. The primary functional group may be cleaved simultaneously during chain degradation or may be entirely removed by special treatments.[5-7] In any case the subsequent functionalization must not lead to cleavage or migration of the primary substituents and it has to be complete to give correct analytical data.

Surprisingly, up to now the conversion of CE with isocyanates as subsequent functionalization in the context of analysis was not investigated. Besides the high reactivity of isocyanates, which should guarantee a complete conversion of the free OH groups of CE under mild conditions, the carbamates formed show a remarkable stability against acid-catalysed hydrolysis.[8]

The synthesis of aliphatic and aromatic carbamates of cellulose is well known.[9] The derivatives are extensively used as chromatographic material, for studying the molecular weight of the polymer by GPC and to investigate structure forming processes in solution state.[10-14] The majority of the studies were carried out with differently substituted phenyl isocyanates where complete carbamoylation of the polymer backbone was easily achieved. This paper deals with the subsequent ethyl-, phenyl-, and carbethoxymethyl carbamoylation of cellulose esters and NMR spectroscopic and HPL chromatographic analysis of the derivatives obtained.

Experimental

Materials

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. Cellulose acetate with DS 0.8 was prepared by acidic deacylation.[4] 1-Adamantanecarboxylic acid esters of cellulose (**2**, cellulose adamantate) were prepared according to Ref. 15. $CDCl_3$ and CD_2Cl_2 were supplied by Aldrich. All solvents and isocyanates were supplied by Fluka and were used as received.

For HPLC the samples were hydrolyzed with 70 % (v/v) $HClO_4$ within 10 min at 25 °C and after dilution with nine-fold amount of water 16 h at 100 °C. After careful neutralization with 2M aqueous KOH solution and keeping at 4 °C for 1 h (to guarantee a complete precipitation of $KClO_4$, which was separated by filtration), the solution was reduced to approximately 5 mL. The samples (20 μL) were analyzed by means of HPLC equipment (JASCO): two Bio-Rad

Aminex HPX-87 H columns, an intelligent pump (PU-980), a RI detector (RI 930), a chiral detector (OR-990), a multiwavelength detector (MD 1510) and HPLC software (BOR-WIN).

Methods

Ethylcarbamoylation of Cellulose Diacetate (1)

1.0 g (3.8 mmol) cellulose diacetate (**1**) was dissolved in 12 mL pyridine. 5 mL (63.2 mmol) ethyl isocyanate was added over a period of 1 h. The mixture was agitated for 40 h at 60 °C. Isolation was carried out by pouring the reaction mixture into 150 mL methanol. The product **4** was filtered off and reprecipitated from chloroform into 50 mL ethanol, filtered off, washed and dried in vacuum. Yield: 1.1 g (94.9 %); $DS_{Acetate}$ = 2.43, DS_{EC} = 0.56 (determined by means of ^{1}H NMR spectroscopy and elemental analysis); FTIR (KBr): no ν(OH), 3356 ν(NH), 2909, 2853 ν(CH), 1742 ν(CO_{ester}) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.05 (H-3), 4.75 (H-2), 4.42, 4.33 (H-1,6), 4.04 (H-6`), 3.69 (H-4), 3.52 (H-5), 3.19 (CH_2-carbamate), 2.09 (CH_3-6), 1.97 (CH_3-2), 1.92 (CH_3-2), 1.11 (CH_3-carbamate).

Conversion of 1 with Ethylisocyanato Acetate

1.0 g (3.8 mmol) **1** was allowed to react with 4 mL (35.6 mmol) ethylisocyanato acetate in 30 mL pyridine at 100 °C for 16 h under stirring. An additional portion of 4 mL (35.7 mmol) ethylisocyanato acetate was added and then stirred for another 16 h at 100 °C. Polymer **5** was isolated by precipitation in 200 mL ethanol and washing with 100 mL ethanol two times. The sample was dried in vacuum at 60 °C. Yield: 1.1 g (94.8 %); $DS_{Acetatate}$ = 2.46, DS_{EEC} = 0.54 (determined by means of ^{1}H NMR spectroscopy); ^{13}C NMR ($CDCl_3$): δ (ppm) = 169.4 - 171.3 (CO-acetate); 154.9 (CO-carbamate), 100.2 – 61.7 (C atoms of the modified anhydroglucose unit), 43.1 (CH_2-carbamate) 20.9 (CH_3-acetate), 14.5 (CH_3-carbamate); ^{1}H NMR ($CDCl_3$): δ (ppm) = 5.07 (H-3), 4.79 (H-2), 4.41 (H-1,6), 3.98 (H-6`), 3.72 (H-4), 3.55 (H-5), 4.18, 3.88 (CH_2-carbamate), 2.08 (CH_3-6), 1.97 (CH_3-2), 1.93 (CH_3-2), 1.28 (CH_3-carbamate).

Phenylcarbamoylation of 1

1.0 g (3.8 mmol) cellulose diacetate (**1**) was dissolved in 12 mL pyridine. 5 mL (46.0 mmol) phenyl isocyanate was added over a period of 1 h. After stirring the mixture for 40 h at room

temperature it was poured into 150 mL methanol. The product **6** was filtered off and reprecipitated from chloroform into 50 mL ethanol, filtered off, washed and dried in vacuum. Yield: 1.1 g (86.6 %); $DS_{Acetate}$ = 2,36, DS_{PhCarb} = 0.65 (determined by means of ^{1}H NMR spectroscopy and elemental analysis); FTIR (KBr): no ν(OH), 3356 ν(NH), 2909, 2853 ν(CH), 1742 $\nu(CO_{ester})$ cm^{-1}; ^{13}C NMR ($CDCl_3$) δ (ppm): = 169.1 - 171.3 ($CO_{acetate}$); 156.2, 154.7 ($CO_{carbamate}$), 100.2 – 63.1 (C atoms of the modified anhydroglucose unit), 21.4 (C atoms of the acetyl moiety); ^{1}H NMR ($CDCl_3$): δ = 9.28 (NH), 7.26, 7.16, 6.89 ($H_{aromatic}$ -carbamate), 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 - 1.88 (CH_3-acetate).

Phenylcarbamoylation of Adamantoyl Cellulose (2)

To a mixture of 1.0 g (3.4 mmol modified AGU) adamantoyl cellulose (**2**, DS 0.90) in 20 mL pyridine 2.0 mL (18.3 mmol) phenylisocyanate was added over a period of 1 h under stirring. After stirring the homogeneous mixture for 24 h at room temperature, it was poured into 100 mL ethanol. The product **7** was filtered off and reprecipitated from DMSO into 150 mL ethanol, filtered off, washed and dried in vacuum. Yield: 1.5 g (83.4 %); DS_{Ad} = 0.90, $DS_{PheCarb}$ = 2.18 (determined by means of ^{1}H NMR spectroscopy and elemental analysis); FTIR (KBr): no ν(OH), 3344 ν(NH), 3059 $\nu(C\text{-}H_{aromatic})$, 2909, 2853 ν(CH), 1742 $\nu(CO_{ester})$, 1602 $\nu(C{=}C_{aromatic})$ cm^{-1}; ^{13}C NMR ($CDCl_3$): δ (ppm) = 169.1 – 169.9 (CO_{Ad}), 156.2, 154.7 (CO_{carbam}), 141.2, 131.2, 125.2, 121.4 ($C_{aromatic}$), 100.2 – 63.1 (C atoms of the modified anhydroglucose unit), 39.9 – 27.7 (C atoms of the adamantane moiety) ppm; ^{1}H NMR (DMSO-d_6): δ = 9.28 (NH), 7.26, 7.16, 6.89 ($H_{aromatic}$), 5.06 – 3.50 (H-1 – H-6), 2.00 – 1.50 (H-adamantane).

Results and Discussion

Ethylcarbamates of Cellulose Acetate

Ethylcarbamoylation of a commercial cellulose diacetate (**1**) was carried out by conversion of the polymer in pyridine with ethyl isocyanate. FTIR spectra revealed the absence of bands for free hydroxyl functions in the region of 3400 - 3700 cm^{-1}. A degree of substitution of ethylcarbamoylation (DS_{EC}) of 0.56 was determined using elemental analysis. The polymer is readily soluble in chloroform. ^1H NMR spectroscopy yielded a well resolved spectrum comparable to perpropionylated cellulose acetates. Thus, three separate peaks can be observed for CH_3 groups of acetyl functions at 1.90 ppm (position 3), at 1.98 ppm (position 2) and 2.08 ppm (position 6). The ethylcarbamate (EC) causes proton signals at 1.09 ppm for the CH_3 group and at 3.19 for the CH_2 moieties. In the region from 3.52 to 5.04 ppm the signals for protons of the anhydroglucose unit (AGU) were found. Via $^1H,^1H$ COSY NMR spectroscopy (Figure 1) complete signal assignment was possible (see experimental section).

DS calculation was carried out using the ratio of spectral integrals for signals of the AGU protons and the acetyl protons or the protons of the ethylcarbamate moiety. A $DS_{Acetate}$ value of 2.43 and DS_{EC} 0.56 were determined, which is in good agreement with the results obtained via perpropionylation ($DS_{Acetate}$ 2.37) and elemental analysis. The partial DS values at the three reactive sides can be calculated from the three CH_3-acetyl signals (see above) applying a Lorentzian type line shape analysis. Partial degrees of acetylation of 0.88 for C-6, 0.71 for C-3 and 0.84 for C-2 were found. These results show that ethylcarbamoylation of CE and ^1H NMR spectroscopy of the mixed derivative is comparable to the analysis via perpropionylation or deuteroacetylation in terms of reliability and efficiency.

Carbethoxymethylcarbamates of Cellulose Acetate

Ethylisocyanato acetate was first applied for the conversion with cellulose and amylose by Huseman et al.[16] Tris-carbethoxymethylcarbamates of the polysaccharides were obtained by a two step conversion. A comparable procedure was applied for the subsequent derivatization of cellulose diacetate **1**. Complete functionalization of the mixed derivative **5** was concluded from FTIR spectra (no OH vibration at 3400 - 3700 cm^{-1}) and ^{13}C NMR spectra. In the ^{13}C NMR spectra (Figure 2a) no signals for unsubstituted primary CH_2-OH functions and for

unsubstituted C-2 atoms were determined, which would show peaks at about 60 ppm (CH_2-OH) and at about 103 ppm for C-1 influenced by C-2. Two sets of signals in the carbonyl region were determined corresponding to the ester functions (169.4 - 171.3 ppm) and the carbamoyl function (154.9 ppm). Peaks at 14.5, 20.9, and 43.1 ppm are caused by the aliphatic carbon atoms of the substituents.

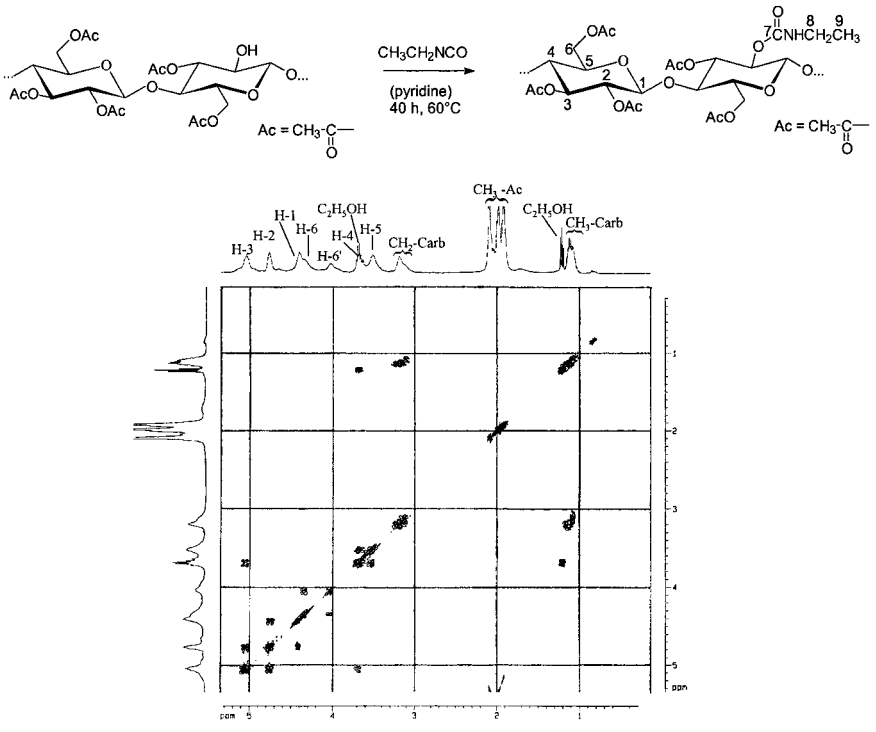

Figure 1. Reaction scheme for a subsequent ethylcarbamoylation and $^1H,^1H$ COSY NMR spectrum of ethylcarbamoylated cellulose diacetate ($CDCl_3$, NS 32).

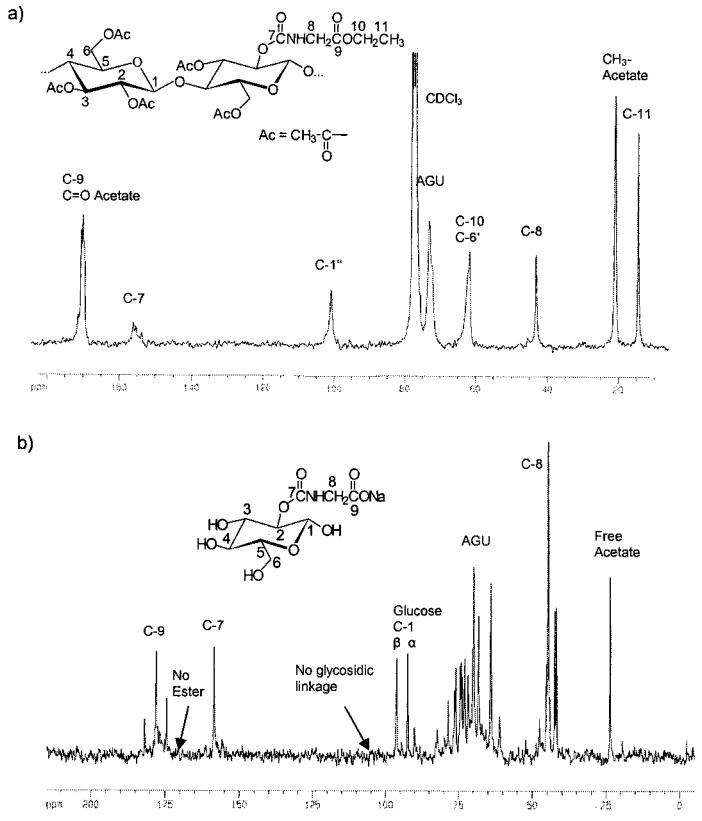

Figure 2. ^{13}C NMR spectrum of a carbethoxymethylcarbamate of cellulose diacetate before (a; $CDCl_3$, NS 20000) and after (b; D_2O, 12200) hydrolysis with perchloric acid.

The ^1H NMR spectrum of the sample **5** is equally well resolved as in case of the ethyl carbamates. A $^1H,^1H$ COSY NMR spectrum was acquired for the signal assignment (Figure 3). Peaks for the CH_2-moieties of the ethylcarbamate are located in the region of the AGU at 4.18 and 3.88 ppm. Therefore, Lorentzian type line shape analysis need to be applied before DS calculation. The $DS_{Acetate}$ value of 2.46 was determined from the ratio of the spectral integrals for the AGU protons and the methyl function of the acetate and the methyl function of the carbamate. This value was confirmed if it is determined form the spectral integrals of the

methyl function of the acetate and the methyl function of the carbamate assuming that the sum of these integral areas represent a $DS_{\Sigma Acetate+Carbamate}$ of 3. The partial DS at the three reactive sites can be obtained from the three CH_3 acetyl signals at 1.91 (on C-3), 1.96 (on C-2) and 2.08 ppm (on C-6) giving values of 0.89 (C-6), 0.70 (C-3) and 0.86 (C-2).

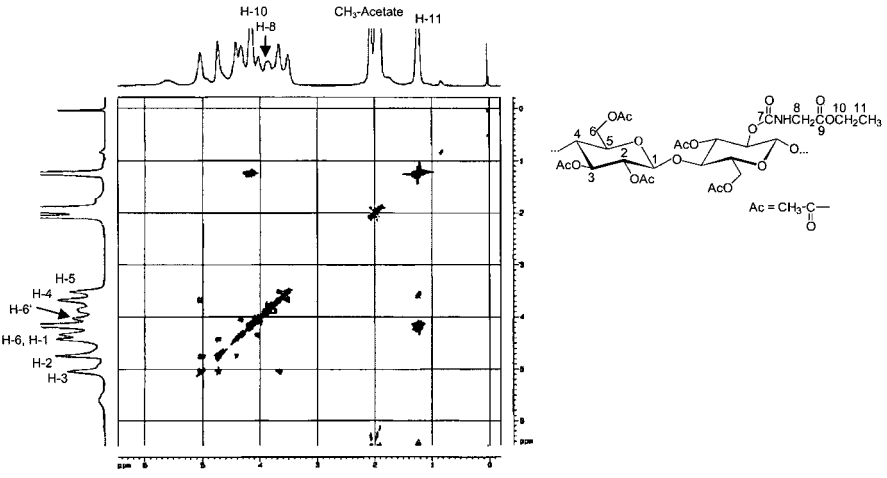

Figure 3. $^1H,^1H$ COSY NMR spectrum of a carbethoxymethylcarbamate of cellulose diacetate ($CDCl_3$, NS 32).

*Phenyl Carbamates of **1***

Complete functionalization of cellulose with phenyl isocyanate and substituted phenyl isocyanates, e.g. 3-(trifluoromethyl)-phenyl or 3-chlorophenyl isocyanate can be achieved by conversion of cellulose suspended in pyridine.[9-14] Completeness of the reaction is an essential prerequisite for studying the molecular weight of the polymer and to investigate structure forming processes in solution state.[11-14] Therefore, the method was applied to investigate the structural features of a commercial cellulose diacetate (**1**). Thus, **1** dissolved in pyridine was allowed to react with phenyl isocyanate at room temperature. Complete derivatization of all free OH groups was confirmed by FTIR spectroscopy.

A ^{1}H NMR spectrum of the mixed derivative **6** is shown in Figure 4. In addition to peaks for the AGU protons and the CH_3 moiety of the acetate (as discussed for the ethyl carbamate, see above), a set of signals corresponding to the aromatic protons of phenylcarbamate moiety appeared at 6.95 - 7.38 ppm. In contrast to the NMR studies of the carbamates **4** and **5** discussed above, the spectrum was acquired in CD_2Cl_2 because the solvent signal of $CDCl_3$ is in the region of the aromatic protons.

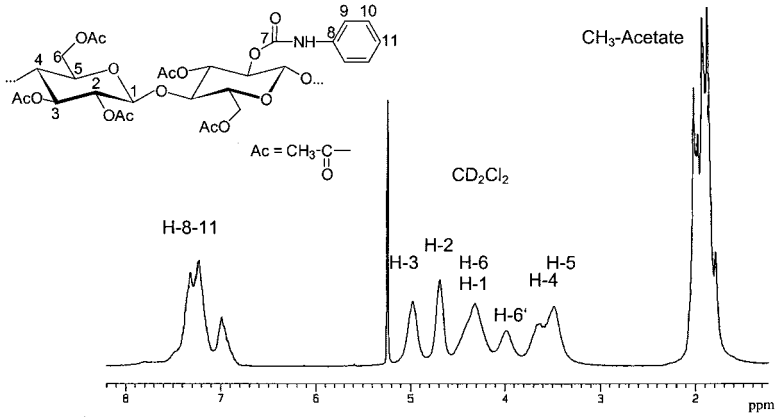

Figure 4. ^{1}H NMR spectrum of a perphenylcarbamoylated cellulose diacetate (CD_2Cl_2, NS 32).

The DS is readily calculated from the ratio of the AGU protons and the phenyl protons or the methyl protons of the acetate moieties. A $DS_{Acetate}$ of 2.31 was calculated, which is in good agreement with propionylation analysis. Calculation of the partial DS values did not yield reasonable results because the signals of the acetyl CH_3 moiety show a more complex splitting, which might be caused by resolution of the different patterns of substitution. An alternative method could be the carbamoylation with a substituted phenyl isocyanate.

Phenylcarbamoylation of Bulky Cellulose Esters

Phenyl isocyanate is the most sterically hindered isocyanate used in this work. Thus, the subsequent conversion of a cellulose derivative functionalized with bulky substituents was carried out to demonstrate the usefulness of the carbamoylation as subsequent step for analysis

of a broad variety of CEs. Subsequent phenyl carbamoylation of adamantanecarboxylic acid ester of cellulose (**2**, cellulose adamantate) was studied. FTIR spectra did not show broad signals in the region of 3600 cm^{-1} for ν (OH). Well resolved ^{1}H-NMR spectra can be recorded. The region from 1.55 to 2.10 ppm corresponds to the protons of the adamantoyl function and the region from 6.89 to 7.26 ppm corresponds to the phenyl moiety. The DS values obtained are summarized in Table 1. All samples (**7**, **8**, **9**) were completely functionalized possessing no free hydroxyl groups. Even in case of a cellulose adamantate with DS 1.24 (**9**, DS determined by NMR after perpropionylation) a phenyl carbamate with DS 1.74 (determined by elemental analysis) was determined.

Table 1. Degree of substitution (DS) of cellulose adamantate and of the phenyl carbamate of cellulose adamantate after carbamoylation.

No.	DS	
	Adamantate	Phenylcarbamate
8	0.65	2.33
7	0.90	2.18
9	1.24	1.74

Application of Subsequent Carbamoylation for HPLC Analysis of CE

Two prerequisites need to be fulfilled to apply the carbamoylation procedures described as subsequent step for the structure determination by means of chromatography. Besides the shown completeness of subsequent functionalization the mixed derivatives need to be depolymerized to the repeating units, which should be preferably soluble in one eluent for the chromatographic measurements. Thus, the hydrolysis and the solubility of the building units were investigated. The hydrolytic degradation of a mixed cellulose ester phenyl carbamate **6** with 1 N trifluoroacetic acid, with 96 % H_2SO_4 and 70 % perchloric acid was studied by means of ^{13}C NMR spectroscopy. An amazing chemical resistance of the polymer backbone against hydrolysis can be concluded from comparison of the signal intensities at 102.3 ppm for C-1 in a glycosidic linkage and the free C-1 at 95.1 and 92.8 ppm of α- and β anomers in ^{13}C NMR spectra. The reason could be the hydrophobic character of the polymers avoiding attack of the protons at the polymer backbone. No complete hydrolysis and therefore no chromatographic experiments were possible.

In contrast, complete depolymerization of the ethylcarbamoylated cellulose acetate (**4**) was achieved with 70 % perchloric acid. The degradation succeeds without splitting of the carbamate function but with complete removal of the acetyl moieties as can be confirmed by elemental analysis and ^{1}H NMR spectroscopy. Nevertheless, no solvent or solvent mixture was found, which dissolves the four units, i.e. glucose, mono-, di- and triethylcarbamoyl glucose. Even different mixtures of water and acetonitrile, as usually applied for the analysis of depolymerized methylcelluloses, were not usable. Therefore, HPL chromatographic investigation of the substitution pattern was not possible via ethylcarbamoylation up to now.

Huseman et al.[16] showed that tris-carbethoxymethylcarbamates of polysaccharides can be selectively converted into the tris-carboxymethylcarbamates. Consequently, acidic treatment of carbethoxymethylcarbamates of cellulose acetates will lead to depolymerization and saponification both of the acetate functions and the ester moiety of the carbamate yielding a mixture of glucose, mono-, di-, and tricarboxymethylcarbamoyl glucoses (Figure 5 and 6), which are collectively soluble in water.

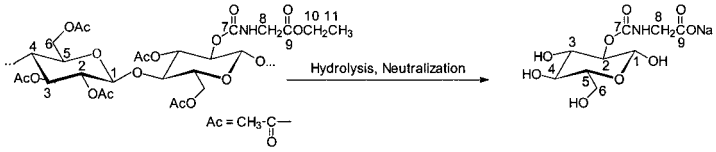

Figure 5. Reaction schema for the hydrolysis of cellulose acetate carbethoxymethylcarbamate.

A ^{13}C NMR spectrum of a cellulose acetate carbethoxymethylcarbamate (**5**, $DS_{Acetate}$ = 2.46 and $DS_{Carbamate}$ = 0.53) before and after hydrolysis with perchloric acid is shown in Figure 2a and b. No carbonyl functions for acetate bound to the polymer backbone and for the ester bound to the carbamate function were determined in the region of 169 - 170 ppm.[17] The signals at 174.5, 178.0 and 181.9 ppm correspond to the carbonyl group of the carbamate, the terminal acid function, and the sodium salt of the liberated acetic acid. The CH_3 group of the sodium acetate is found at 23.7 ppm. A signal for a glycosidic linkage at about 102 ppm is not found. Only peaks for C-1 of glucose can be determined at 92.5 (C-1 of α glucose) and 96.4 ppm (C-1 of β glucose). These results confirm the complete degradation and complete removal of the ester functions.

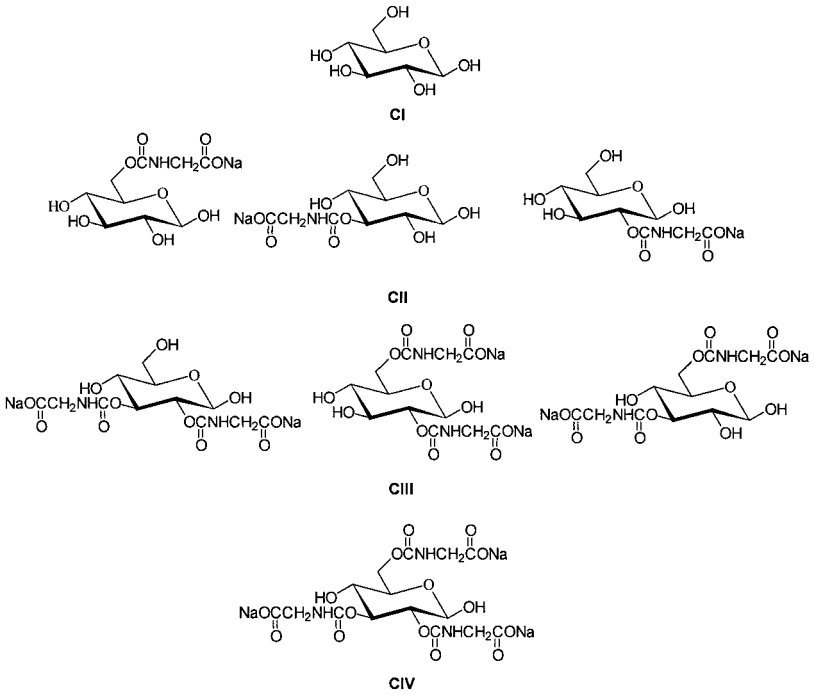

Figure 6. Structure of the main repeating units of a hydrolyzed carbethoxymethylcarbamate of cellulose acetate. Un- (CI), mono- (CII), di- (CIII), and tri-substituted (CIV) glucoses.

HPL chromatographic investigation was possible with a comparable chromatographic system as applied for hydrolyzates of carboxymethylated polysaccharides.[18,19] The chromatograms obtained are almost identical (Figure 7). The retention times of the building units are summarized in Table 2.

The HPLC measurements were evaluated with a diode array detector (DAD) showing pure signals for the carbamoylated glucoses with UV absorptions in the region typical for carbamates at about 286 nm. Moreover, the four peaks were also found with a chiral detector giving evidence for the carbohydrate nature of the material. No glycin was determined in case of the analysis of sample **5**. Besides the signal of the acetate at about 36 min two additional signals appear which could not be assigned up to now. The mole fractions of the building units were

calculated from the chromatogram (Table 3) assuming that the response factor for all signals is 1. $DS_{Carbamate}$ of 0.64 or vice versa a $DS_{Acetate}$ of 2.36 was determined, which is in good agreement with the ^1H NMR studies of **5** and with perpropionylation analysis of the cellulose diacetate **1** (DS 2.36). Comparison of the mole fractions determined by HPLC with statistic calculations, as usually applied for polysaccharide ethers [18], shows no significant deviation, i.e., an even distribution of substituents along the polymer chain was concluded (Table 3).

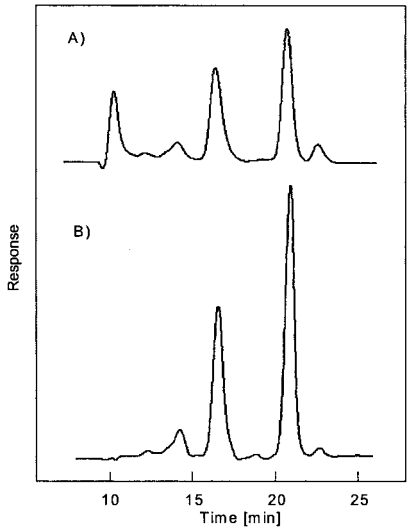

Figure 7. HPL-chromatogram of a hydrolyzed carbethoxymethylcarbamate of cellulose acetate: Curve A) RI- and B) chiral detector.

Table 2. Comparison of the retention times (RT) of hydrolyzed carboxymethyl cellulose (CMC) with hydrolyzed cellulose acetate carbethoxymethylcarbamate (**5**) and the resulting assignment.

Peak No.	RT_{CMC} [min]	RT of sample **5** [min]	Assignment
1	17.96	16.72	2,3,6-Tri-O-substituted glucose
2	18.91	18.20	2,3-; 2,6-; and 3,6-Di-O-substituted glucose
3	20.37	19.73	2-, 3-, and 6-Mono-O-substituted glucose
4	22.30	22.07	Glucose

Table 3. Comparison of the mole fractions of hydrolyzed cellulose acetate carbethoxymethylcarbamate (**5**) determined by means of HPLC with statistic calculations.

Building unit	HPLC	Statistics
Glucose	0.474	0.486
Mono-CMCb*	0.408	0.396
Di-CMCb	0.117	0.107
Tri-CMCb	<0.010	0.009

*CMCb-carboxymethylcarbamate

Unfortunately, this method is up to now only applicable for CE with DS≥1. If a cellulose acetate with DS 0.8 is treated in the same manner, i.e. carbamoylation, degradation and HPLC problems concerning the hydrolysis step appeared. Different hydrolysis conditions were studied. If the samples are treated with 70 % perchloric acid at elevated temperatures in the first step complete degradation occurs but the formation of an unidentified by-product at 28 min and the formation of glycin is observed. This is even more pronounced if H_2SO_4 is applied leading to the assumption that the signal at 28 min is caused by the formation of deoxysugars units. In case of treatment with perchloric acid for 10 min, dilution and heating for 24 h the formation of glycine can be diminished but a remarkable amount of not completely degraded oligomeric material was determined at about 10 min. Optimization of the hydrolysis procedure for the analysis of these low functionalized cellulose acetates is the subject of our ongoing research. Nevertheless, carbethoxymethylcarbamoylation is one of the most efficient tools for the analysis of cellulose esters yielding information on the distribution of substituents both on the level of the AGU and along the polymer chain with one subsequent functionalization step.

Conclusions

Carbamoylation represents a fast, inexpensive and efficient way for the complete subsequent functionalization of cellulose esters. The mixed derivatives obtained can be applied for ^1H NMR experiments because they are well soluble in $CDCl_3$ and guarantee a good spectral resolution. The aliphatic carbamates are especially useful. They allow the calculation of partial DS values at the three reactive sites of the AGU. In case of aromatic carbamates a better spectral resolution could be achieved if substituted derivatives are exploited, which is under investigation.

A new and promising approach for structural analysis of CE was the complete hydrolytic degradation of the mixed ester carbamates and HPLC of the mixture of differently substituted glucoses obtained. Thus, cellulose diacetate was investigated via percarbethoxymethylcarbamoylation, degradation and HPLC yielding DS values of 2.36, which is in good agreement with other methods. From comparison with statistic calculations an even distribution of substituents along the polymer chain was concluded. Consequently, the percarbethoxymethylcarbamoylation of CE can be used to determine the distribution of substituents on the level of the AGU and the same sample can be exploited to acquire information about the distribution along the polymer chain after degradation and HPLC. Up to now this method is limited to highly functionalized esters (DS>1) because of problems with the hydrolysis of the subsequently modified derivative. It seems possible to overcome this shortcoming by optimization of this step.

Because of the efficiency and the low costs this analytic strategy could be applied for a large number of esters and could thereby be the method of choice for the establishment of valuable structure-property relations.

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