Study on Synthesis and NMR Characterization of 2,3-*O*-Hydroxyethyl Cellulose Depending on Synthesis Conditions

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Summary: The synthesis of hydroxyethyl celluloses with regioselective functionalization in position 2 and 3 starting from triphenylmethyl (trityl) cellulose is described. The effects of reaction conditions upon both the degree of substitution and the distribution of the hydroxyethyl moieties were investigated in detail. The interest was not only focused on regioselective functionalization within the anhydroglucose unit but also on the formation of oxyethylene side chains. To avoid the formation of oxyethylene side chains, 2-(2-bromoethoxy)tetrahydropyran was used as etherifying agent in comparison with 2-bromoethanol. By acidic hydrolysis, both protecting groups – trityl at 6 position and tetrahydropyran at the hydroxyethyl substituent – can be simultaneously cleaved off. The hydroxyethyl celluloses were characterized by one- and two-dimensional NMR spectroscopy in order to determine the substitution pattern.

Keywords: cellulose; hydroxyethylation; NMR; protecting group; regioselective functionalization

Introduction

Cellulose ethers like hydroxyalkyl- and mixed ethers with additional methyl moieties, e.g., methylhydroxyethyl cellulose, are important commercial cellulose products that have a broad spectrum of applications in various fields. They are used as stabilizer in food and cosmetic products, or as binder in tablets.[1] Moreover, applications as thickener in latex paints, as water-binder in welding rods or glazes of ceramics, and in building materials are known. Commercial hydroxyethyl cellulose is produced starting from alkali cellulose in a slurry process using ethylene oxide as alkylating agent under pressure. The ether moieties introduced are randomly distributed both within the anhydroglucose unit and along the polymer chain. The newly formed hydroxyethyl functions contain primary hydroxyl groups that are susceptible for etherification as well. As a consequence, the generation of side chains (oxyethylene chains) during the etherification may occur. As a result of the different reactive sites, hydroxyethyl cellulose shows a very complex structure that is difficult to analyze in detail. The characterization of the substitution pattern of commercial hydroxyethyl cellulose is carried out by gas-liquid chromatography in combination with matrix assisted laser desorption ionisation time of flight mass spectroscopy after permethylation and hydrolytical chain degradation.[2,3] It is not possible to get detailed structure information of the intact polymer by means of, e.g., NMR spectroscopy. Therefore,

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regioselective functionalization of cellulose is a promising tool to get model substances very useful for the evaluation of structure property relationships. To reach a regioselective functionalization pattern, the use of protecting groups is the most important approach today.[4-6] By using the thexyldimethylsilyl protecting group at position 2 and 6, 3-mono-*O*-hydroxyethyl cellulose was obtained.[7] One of the most important protecting group in cellulose chemistry is the triphenylmethyl (trityl) moiety. Thus, selective 2,3-*O*-methyl-[8], allyl-[9] and carboxymethyl cellulose[10,11] were successfully synthesized. 2,3-*O*-Hydroxyethyl cellulose was also prepared by the heterogeneous conversion of 6-*O*-(4-monomethoxytrityl) cellulose with ethylene oxide as alkylating agent in 2-propanol/water in the presence of NaOH and tenside with a molecular degree of substitution up to 2.[12]

In this paper, the synthesis of hydroxyethyl cellulose regioselectively functionalized in position 2 and 3 without oxyethylene side chains is discussed. The synthesis and detailed structure characterization of 2,3-*O*-hydroxyethyl cellulose using a protected etherifying agent in comparison with the common reagent is discussed.

Experimental Part

Materials

The cellulose material was wood pulp (Borregaard ChemCell, Blue Bear MV, medium viscosity, 6.6% hemicelluloses, [η] 891 ml/g, degree of polymerization, DP_{cuen} 1323, ISO 5351 and Blue Bear VHV, very high viscosity, 10.5% hemicelluloses, [η] 1223 ml/g, degree of polymerization, DP_{cuen} 1877, ISO 5351). Dimethyl sulfoxide (DMSO) was purchased from Acros. 2-Bromoethanol and 3,4-dihydro-2*H*-pyran were obtained from Merck. Tetrahydrofuran (THF), hydrochloric acid (35%), propionic acid anhydride, and pyridine over molecular sieve were acquired from FLUKA. NaOH, ethanol, methanol and 2-propanol were reagent grade chemicals. 6-*O*-Triphenylmethyl (trityl) cellulose **2a** (degree of substitution, DS 1.17) and **2b** (DS 0.97, from Blue Bear MV and VHV) was synthesized as described previously.[13]

Measurements

Elemental analysis was carried out using a Vario EL III (Elementaranalysensysteme Hanau, Germany). FTIR spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer (Thermoelectron, Bremen, Germany) applying the KBr technique. NMR spectra were acquired on a Bruker AVANCE 250 and AVANCE 400 spectrometer (BRUKER, Rheinstetten, Germany). A JASCO size exclusion chromatography system was applied consisting of a degasser DG 980-50, pump PU 980, refractive index detector 930, column oven, a flow rate of 1 mL/min at 40 °C was chosen. Three SDV-Gel columns (10^6, 10^4, and 10^3 Å, Polymer Standards Service, Mainz, Germany) with THF as eluent were used.

Synthesis of 2-(2-Bromoethoxy)-tetrahydropyran (BETHP, According to Arisawa et al.)[14]

3,4-Dihydro-2*H*-pyran (87 ml, 80.2 g, 0.951 mol) und *p*-toluenesulfonic acid (60 mg) were stirred at room temperature for 10 min. 2-Bromoethanol (61 ml, 107.5 g, 0.864 mol) was added slowly over 2 h to maintain the temperature below 20 °C and the reaction mixture was additionally stirred at ambient temperature for 10 min. The reaction was quenched by adding $NaHCO_3$ (6.0 g), and the reaction mixture was stirred for 50 min at room temperature and filtered. The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (n-hexane–acetic acid ethyl ester 30:1∼10:1) to yield 2-(2-bromoethoxy)tetrahydropyran (137.7 g, 77%) as a colourless oil.

Etherification of 6-O-trityl Cellulose

6-*O*-Trityl cellulose **2a** (2.00 g, 4.9 mmol, DS 1.17) was dissolved in 300 ml DMSO. Sodium hydroxide (1.37 g, 34.2 mmol) finely dispersed in 10 ml DMSO was added.

After stirring 1 h at room temperature, BETHP (3.41 g) was added. Further additions of BETHP followed after 2 h, 3 h, and 4 h (0.57 g each case, total 5.12 g, 24.5 mmol). The mixture was allowed to react for 20 h at 70 °C. The product was precipitated in 1500 ml methanol, washed with methanol (3 × 150 ml), and dried under vacuum at 60 °C yielding product **3a**.

Yield: 2.24 g (98%)

Elemental analysis: C 74.62%, H 6.55%

FTIR (KBr, cm^{-1}): 3480 ν(OH), 3058, 3028 $\nu(CH_{Aromatic})$, 2939, 2874 $\nu(CH_{Alkyl})$, 1596, 1491 $\nu(C-C_{Aromatic})$, 1449 δ(C–H), 1208, 1120, 1072 ν(C–O–C).

Deprotection in Ethanol

In a typical procedure, sample **3a** (1.90 g) was suspended in 30 ml ethanol and 2 ml concentrated HCl (37%) and was stirred at room temperature for 20 h. The product was filtered off and washed with ethanol (8 × 100 ml). The process was repeated and the polymer obtained was washed with ethanol (8 × 50 ml) and dried under vacuum at 40 °C yielding **4a**.

Yield: 0.17 g (25%)

Elemental analysis: C 45.47%, H 7.22%

FTIR (KBr, cm^{-1}): 3389 ν(OH), 2929, 2883 $\nu(CH_{Alkyl})$, 1453, 1414, 1372 δ(C–H), 1113, 1063 ν(C–O–C).

Detritylation in THF

In a typical procedure, sample **3g** (2.00 g) was dissolved in 50 ml THF and 2 ml concentrated HCl (35%) were added. After stirring at room temperature for 24 h, the precipitate was filtered off, washed with acetone (4x40 ml), and dried under vacuum at 40 °C yielding product **4g**.

Yield: 0.76 g (93%)

Elemental analysis: C 41.73%, H 6.62%

FTIR (KBr, cm^{-1}): 3438 ν(OH), 2919, 2876 $\nu(CH_{Alkyl})$, 1456, 1372 δ(C–H), 1159, 1066 ν(C–O–C).

Perpropionylation

In a typical synthesis, polymer **4a** (0.16 g) was suspended in a solution of 5 ml pyridine, 20 mg 4-(*N,N*-dimethylamino)-pyridine, and 5 ml propionic acid anhydride. After stirring for 24 h at 80 °C under anhydrous conditions, the polymer was precipitated in 2% aqueous $NaHCO_3$ solution, washed 4 times with water, and dried under vacuum at 105 °C yielding perpropionylated product **4a**.

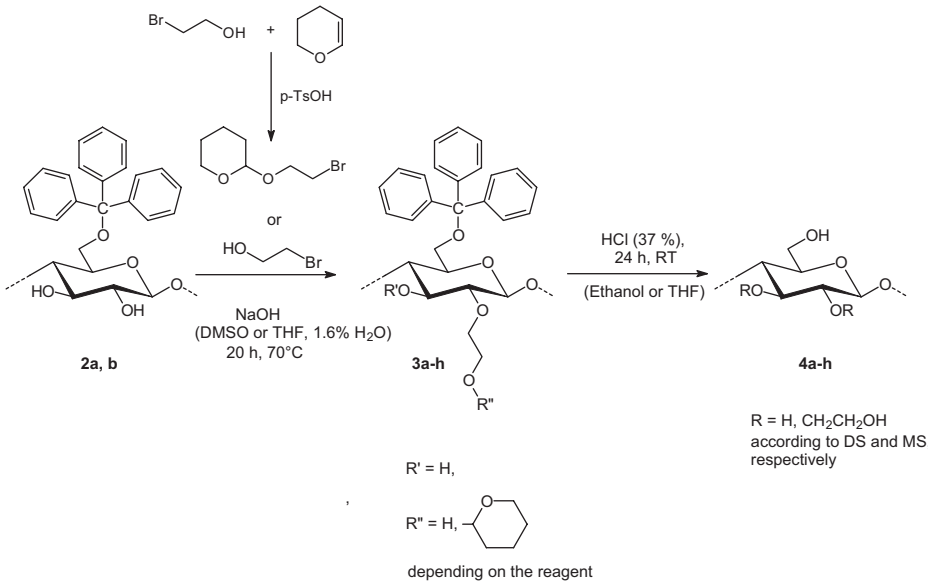
Yield: 0.15 g (40%)

FTIR (KBr, cm^{-1}): 2983, 2946, 2886 $\nu(CH_{Alkyl})$, 1744 ν(C=O), 1463, 1351 δ(C–H), 1188, 1082 ν(C–O–C).

Results and Discussion

To obtain 2,3-*O*-alkyl celluloses, position 6 of the biopolymer must be protected, e.g., by triphenylmethyl (trityl) moiety as shown previously.[8,9,15–17] 6-*O*-Trityl cellulose **2a** (degree of substitution, DS 1.17) was synthesized starting from cellulose **1** dissolved in *N,N*-dimethyl acetamide (DMA)/LiCl by conversion with trityl chloride in the presence of triethyl amine and further reaction of this low tritylated product (DS 0.14) with trityl chloride in *N,N*-dimethyl formamide/LiCl in the presence of triethyl amine. Otherwise, 6-*O*-trityl cellulose **2b** (DS 0.97) was prepared by direct conversion of wood pulp in DMA/LiCl with trityl chloride in the presence of triethyl amine. The 6-*O*-trityl cellulose **2a** was allowed to react with 2-(2-bromoethoxy)tetrahydropyran (BETHP) in the presence of NaOH powder in dimethyl sulfoxide (DMSO) for 20 h at 70 °C to avoid the formation of side chains during the synthesis of 2,3-*O*-(2-tetrahydropyran-2-yloxy)-ethyl)-6-mono-*O*-trityl celluloses **3a–3f** (Scheme 1).

BETHP was synthesized by reaction of 2-bromoethanol with 3,4-dihydro-2*H*-pyran in the presence of *p*-toluenesulfonic acid.[14] For comparison, 2,3-*O*-hydroxyethyl-6-*O*-trityl cellulose **3g** (molecular degree of substitution, MS 0.83) was synthesized by reaction of 6-*O*-trityl cellulose with 2-bromoethanol (5 mol/mol anhydroglucose unit, AGU) in the presence of NaOH powder in DMSO for 20 h at 70 °C. Finally in all cases, the trityl moieties and the tetrahydropyran protecting group were



Scheme 1.
Reaction path for the synthesis of 2,3-*O*-hydroxyethyl celluloses via 6-*O*-trityl cellulose.

cleaved by a treatment of the polymer with concentrated HCl either in ethanol or in tetrahydrofuran (THF) to isolate the pure 2,3-*O*-hydroxyethyl celluloses **4a**–**4g**. The DS/MS of the hydroxyethyl substituents was determined by means of ^{1}H NMR spectroscopy after perpropionylation.

As shown in Table 1, the DS of the hydroxyethyl moiety depends on the molar ratio BETHP to anhydroglucose unit (AGU). The DS increases with increasing the molar ratio from 5 mol BETHP/mol AGU (**4a**, DS 0.48) to 10 mol BETHP/mol AGU (**4b**, DS 0.73). No further increase of the DS was determined by increasing of the molar ratio up to 12:1 (**4c**, DS 0.72). In the presence of water at comparable ratio of BETHP:AGU (10:1), an increase of DS was found (compare **4d**, DS 0.81, 1.6% added water, and **4b**, DS 0.73, no added water).

Table 1.
Degree of substitution (DS) and solubility of 2,3-*O*-hydroxyethyl cellulose dependent on the conditions of the etherification of 6-*O*-trityl cellulose **2a** (DS 1.17) with 2-(2-bromoethoxy)tetrahydropyran (BETHP) or 2-bromoethanol (BrEtOH) in DMSO in the presence of NaOH powder for 20 h at 70 °C.

Etherification conditions					2,3-*O*-Hydroxyethyl cellulose		
No.	Reagent	Molar ratio /AGU[a)]		H_2O	No.	DS[b)]	H_2O
		Reagent	NaOH	[%]			Solubility
3a	BETHP	5	7	–	**4a**	0.48	+
3b	BETHP	10	12	–	**4b**	0.73	+/− (NTU 217)[c)]
3c	BETHP	12	15	–	**4c**	0.72	+/− (NTU 350)[c)]
3e	BETHP	5	7	1.6	**4e**	0.72	+
3d	BETHP	10	12	1.6	**4d**	0.81	+
3f	BETHP	12	15	1.6	**4f**	0.87	+
3g	BrEtOH	5	7	1.6	**4g**	0.83[d)]	−

[a)] Anhydroglucose unit.
[b)] Calculated by ^{1}H NMR spectroscopy after perpropionylation.
[c)] +soluble, − insoluble, +/− turbid.nephelometric turbidity units (NTU) of 0.16% solution.
[d)] MS molecular degree of substitution.

Comparable findings were published by Kondo and Gray.[8] Thus, the synthesis of higher alkylated product **3h** was realized by reaction of 6-*O*-trityl cellulose **2b** (DS 0.97), dissolved in DMSO containing 1.6% water, with BETHP in the presence of NaOH (1:10:12, AGU:BETHP:NaOH) for 24 h at 70 °C.

The crude product was separated, suspended in THF (1.6% water) and allowed to react with BETHP and NaOH (1:10:12, AGU:BETHP:NaOH) for 24 h at 50 °C. The hydroxyethyl cellulose **4h** obtained after detritylation possessed a DS of 1.40 and was water soluble.

The structure characterization of the 2,3-*O*-hydroxyethyl celluloses was carried out by NMR spectroscopy after propionylation of the remaining OH groups to get products soluble in chloroform that yield well resolved NMR spectra. The assignment of the peaks was carried out by different two dimensional NMR techniques. Figure 1 shows a comparison of the ^{1}H,^{1}H COSY NMR spectra of the perpropionylated 2,3-*O*-hydroxyethyl celluloses **4f** (DS 0.87, synthesized with BETHP) and **4g** (MS 0.83, synthesized with 2-bromoethanol) along with structures of repeating units observed in the polymer. The peaks for H-6a and H-6b were found at 4.33–4.39 ppm and 4.09–4.10 ppm, respectively, independent of the substitution in position 2 and 3. No evidence of a hydroxyethylated position 6 was detected. The signal for H-5 appeared at 3.47 ppm for perpropionylated **4f** and at 3.57 ppm for perpropionylated **4g**, respectively. It should be mentioned, that the peaks for H-4 split off depending on the substitution pattern at neighboured position 3. In case of a hydroxyethylated position 3, the signal of H-4 (assigned as H-4 and H-4″) was detected at 3.53 ppm (**4f** propionate) and 3.56 ppm (**4g** propionate), respectively. Due to a propionylation in position 3, the peak of H-4 (assigned as H-4′ and H-4*) was found at 3.59 ppm (**4f** propionate) and 3.69 ppm (**4g** propionate). In both spectra, the expected peaks for the 2,3-di-*O*-(2-(propionyloxy)ethyl-6-*O*-propionyl unit were identified. For perpropionylated **4f**, the peaks for H-2 and H-3 were found at 2.95 ppm and 3.23 ppm, respectively, in case of hydroxyethylation in positions 2 and 3. For perpropionylated **4g**, these signals were detected at 3.02 ppm (H-2) and 3.33 ppm (H-3). H-1 was identified at 4.10 ppm (**4f** propionate) and at 4.14 ppm (**4g** propionate). In case of a hydroxyethylation in position 2 only, namely the 2-mono-*O*-(2-(propionyloxy)ethyl-3,6-di-*O*-propionyl unit, the H-1′ signal was found at 4.30 ppm (**4f** propionate) and 4.24 ppm (**4g** propionate), respectively. As a consequence of the hydroxyethylation, the signal for H-2′ was determined at 3.06 ppm (**4f** propionate) and 3.12 ppm (**4g** propionate), whereas H-3′ appeared at 5.01 ppm (**4f** propionate) and 5.05 ppm (**4g** propionate) as a result of propionylation in position 3.

The signal of H-1″ of the 3-mono-*O*-(2-(propionyloxy)ethyl-2,6-di-*O*-propionyl unit was found at 4.39 ppm (**4f** propionate) and 4.48 ppm (**4g** propionate), H-2″ was detected at 4.69 ppm (**4f** propionate) and 4.78 ppm (**4g** propionate) due to a propionylation in position 2. In contrast, H-3″ was found high field shifted to 3.32 ppm (**4f** propionate) and 3.44 ppm (**4g** propionate) as a consequence of a hydroxyethylation in position 3. According to the incomplete hydroxyethylation of positions 2 and 3, peaks for 2,3,6-tri-*O*-propionyl units appeared. For **4f** propionate, signals were detected for H-1* at 4.37 ppm, for H-2* at 4.75 ppm, and for H-3* at 5.01 ppm with a down field shift due to the esterification in positions 2 and 3. Comparable results were found for **4g** propionate. H-1* was determined at 4.44 ppm, H-2* was found at 4.78 ppm, and H-3* was detected at 5.13 ppm.

It is not possible to assign of the signals of the hydroxyethyl substituent only with COSY NMR spectra. A comparison of the ^{1}H NMR spectra at the horizontal axis of the COSY NMR spectra in Figure 1 shows that the relation of the peak intensities and peak distribution differ depending on the hydroxyalkylation agent used. By using HSQC-DEPT NMR spectroscopic technique, it is possible to differentiate the

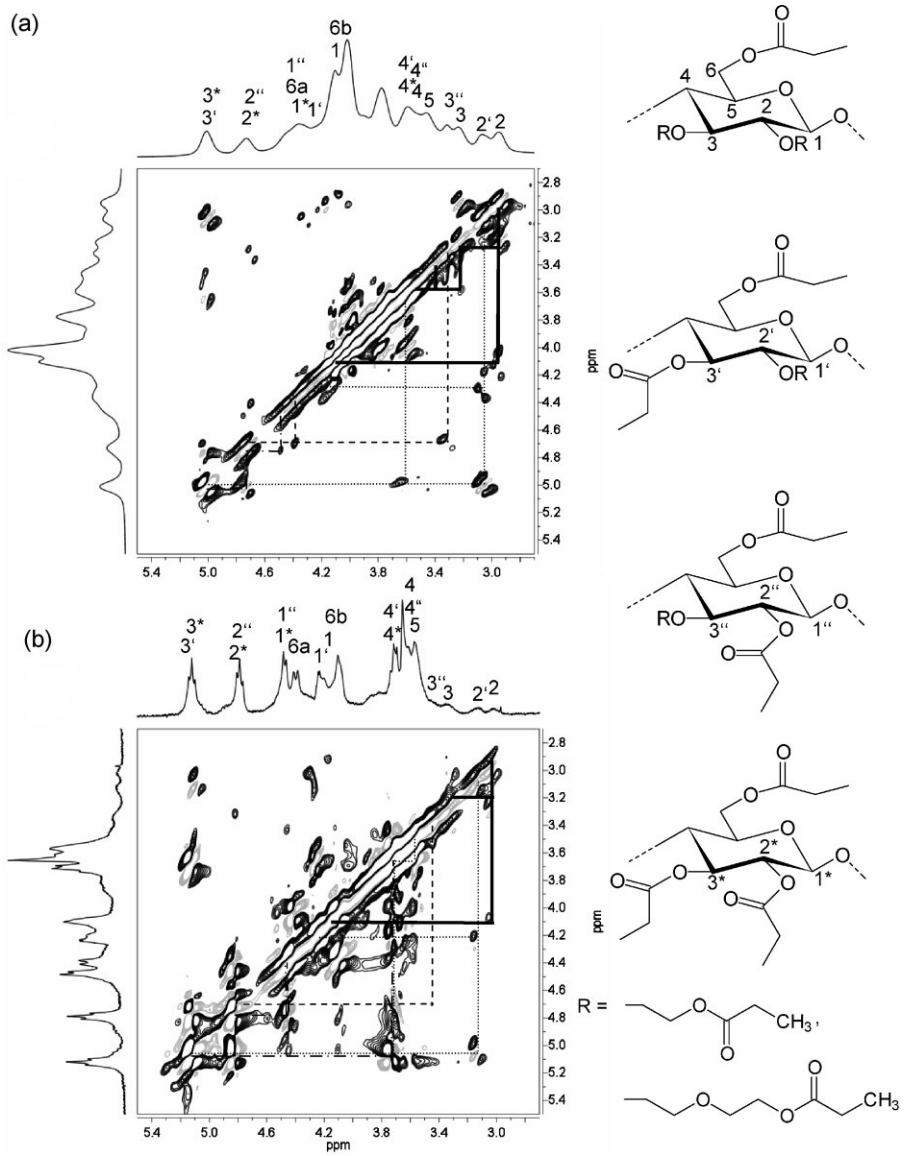


Figure 1.
$^{1}H,^{1}H$ COSY NMR spectra of a) perpropionylated **4f** (degree of substitution 0.87, synthesized with 2-(2-bromoethoxy)tetrahydropyran) and b) perpropionylated **4g** (molecular degree of substitution 0.83, synthesized with 2-bromoethanol) in $CDCl_3$; assigned cross-peaks: — cross-peaks of the unit 2,3-di-*O*-(2-(propionyloxy)ethyl-6-mono-*O*-propionyl, ···· cross-peaks of the unit 2-mono-*O*-(2-(propionyloxy)ethyl-3,6-di-*O*-propionyl, positions are marked with ', ——— cross-peaks of the unit 3-mono-*O*-(2-(propionyloxy)ethyl-2,6-di-*O*-propionyl, positions are marked with '', —·— cross-peaks of the unit 2,3,6-tri-*O*-propionyl, positions are marked with *.

peaks for the hydroxyethyl substituent (Figure 2). In Figure 2a, the product **4f** obtained by synthesis with BETHP as hydroxyethylation agent, two clear peaks were distinguished for C7 at 70.5 ppm and C8 at 63.3 ppm with cross-peaks in grey to H-7a (3.77 ppm) and H-7b (3.60 ppm), and H-8a (4.09 ppm) and H-8b (4.01 ppm), respectively, of the methylene groups of the substituent in the HSQC-DEPT

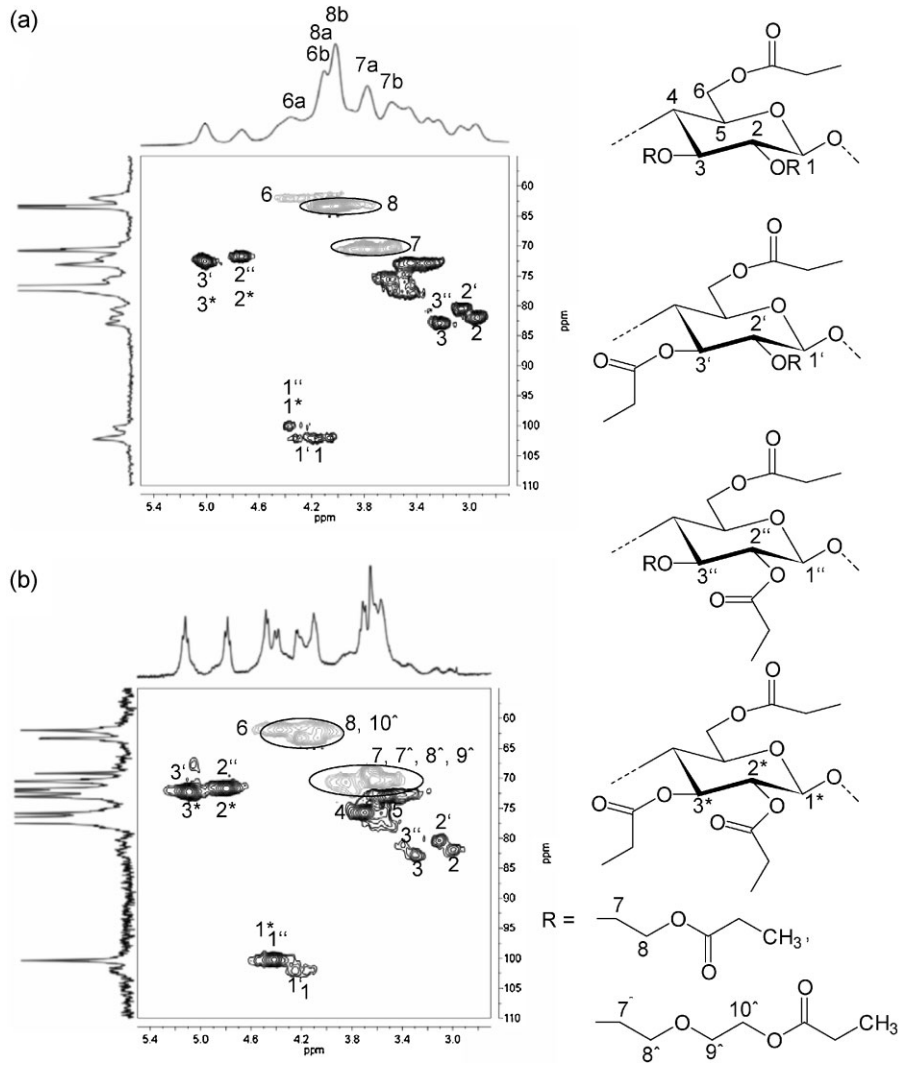


Figure 2.

HSQC-DEPT spectra of a) perpropionylated **4f** (degree of substitution 0.87, synthesized with 2-(2-bromoethoxy)-tetrahydropyran) and b) perpropionylated **4g** (molecular degree of substitution 0.83, synthesized with 2-bromoethanol) in $CDCl_3$; negative signals scaled in grey.

spectrum of **4f** perpropionate. No evidence for the formation of oxyethylene side chains appears. 2-Bromoethanol as alkylating agent yields product **4g** (perpropionate) showing peaks for methylene groups of oxyethylene side chains (Figure 2b). In the region of the carbons of the methylene groups of the substituent in neighbourhood of ether functions (68.3–72.01 ppm), signals for C-atoms were detected, which were assigned to C7, C7^, C8^, C9^, whereas, peaks for C8 and C10^ (61.3–63.9 ppm) were determined in the region of the signals of the methylene protons in neighbourhood of ester functions. Indicated by the cross-peaks, the signals of the protons at C7, C7^, C8^, C9^ were detected at 3.56 to 3.87 ppm as a result of an ether function in the neighbourhood. The protons at C8 and C10^ were observed at 4.09–4.21 ppm. However, a clear assignment of the protons of the methylene groups along the

oxyethylene side chains was not possible. Due to the short transversal relaxation time of the protons of the AGU, it is not possible to use long-range NMR techniques, which are necessary for the correct assignment of the signals of the oxyethylene side chains.

The molecular masses of the products and in conclusion the degree of polymerization (DP) were measured by size exclusion chromatography using the perpropionylated products in THF.

The DP of **4f** perpropionate is 992 and **4g** perpropionate has a DP of 67. Surprisingly, the chain degradation of resulting 2,3-*O*-hydroxyethyl cellulose seems to be stronger by using 2-bromoethanol as alkylating agent with the possibility of the formation of oxyethylene side chains.

The formation of side chains has an influence on the properties of the 2,3-*O*-hydroxyethyl celluloses. The 2,3-*O*-hydroxyethyl cellulose **4f** (DS 0.87) with etherification at the cellulose backbone only is soluble in water, whereas, 2,3-*O*-hydroxyethyl cellulose **4g** (MS_{HE} 0.83), which contains oxyethylene side chains is insoluble in water. As known, the properties of hydroxyethyl celluloses depend on the synthesis conditions, too. A 2,3-*O*-hydroxyethyl cellulose, which was synthesized using 6-*O*-(4-monomethoxytrityl) cellulose and ethylene oxide in 2-propanol/water, is water soluble starting with an MS 0.3.[12]

Conclusion

Novel 2,3-*O*-hydroxyethyl cellulose samples (HEC) without oxyethylene side chains were synthesized and compared with 2,3-*O*-hydroxyethyl cellulose with side chains. The 6-*O*-trityl cellulose was allowed to react with the protected etherifying agent 2-(2-bromoethoxy)tetrahydropyran on the one hand and with 2-bromoethanol on the other. One- and two-dimensional NMR spectroscopy could be efficiently used for the characterization of the substitution pattern of the repeating units of the 2,3-*O*-hydroxyethyl celluloses after perpropionylation of the remaining OH groups. Additionally, differences between the oxyethylene chain containing HEC and the HEC without side chains could be clearly evaluated by peak assignment of the carbon- and proton signals of the substituents using the cross peaks in the two dimensional NMR spectra. The formation of oxyethylene side chains influences the properties of the HEC like the solubility of the products.

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[1] T. G. Majewicz, T. J. Podlas, in: *Kirk-Othmer Encyclopaedia of chemical technology*, M. Howe-Grant, Ed., 4th Edn. Volume 5, Wiley Inter-Science, New York **1993**, p. 541 ff.
[2] R. Adden, R. Müller, G. Brinkmalm, R. Ehrler, P. Mischnick, *Macromol. Biosci.* **2006**, *6*, 435.
[3] R. Adden, W. Niedner, R. Müller, P. Mischnick, *Anal. Chem.* **2006**, *78*, 1146.
[4] T. Heinze, K. Petzold, in: *Monomers, oligomers, polymers, composites from renewable resources*, M. N., Belgacem, A. Gandini, Eds., Elsevier, Oxford **2008**, p 343 ff.
[5] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, *Angew. Chem. Int. Ed.* **2005**, *44*, 3358.
[6] T. Heinze, in: *Polysaccharides: structural diversity and functional versatility*, S. Dumitriu, Ed., 2nd Edn., Chap. 23, Marcel Dekker, New York, Basel, Hong Kong **2004**, p. 551 ff.
[7] D. Fenn, T. Heinze, *Cellulose* **2009**, *16*, 853.
[8] T. Kondo, D. G. Gray, *Carbohydr. Res.* **1991**, *220*, 173.
[9] T. Kondo, *Carbohydr. Res.* **1993**, *238*, 231.
[10] T. Heinze, K. Röttig, I. Nehls, *Macromol. Rapid Comm.* **1994**, *15*, 311.
[11] U. Heinze, J. Schaller, T. Heinze, S. Horner, B. Saake, J. Puls, *Cellulose* **2000**, *7*, 161.
[12] J. Schaller, T. Heinze, *Macromol. Biosci.* **2005**, *5*, 58.
[13] K. Petzold-Welcke, M. Kötteritzsch, T. Heinze, *Cellulose* **2010**, *17*, 449.
[14] M. Arisawa, C. Kato, H. Kaneko, A. Nishida, M. Nakagawa, *J. Chem. Soc., Perkin Trans.* **2000**, *1*, 1873.
[15] J. A. Camacho Gomez, U. W. Erler, D. O. Klemm, *Macromol. Chem. Phys.* **1996**, *197*, 953.
[16] T. Kondo, C. Sawatari, R. S. Manley, D. G. Gray, *Macromolecules* **1994**, *27*, 210.
[17] T. Kondo, *J. Polym. Sci. B: Polym. Phys.* **1994**, *32*, 1229.

