Macromol. Symp. **2010**, 294-II, 107–116 DOI: 10.1002/masy.200900034

Comparison of Benzyl Celluloses Synthesized in Aqueous NaOH and Dimethyl Sulfoxide/Tetrabutylammonium Fluoride

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Summary: Cellulose was benzylated starting from the dissolved polymer in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) and heterogeneously in aqueous NaOH as reaction media. Differences in the distribution of benzyl moieties within the anhydroglucose unit in dependence on the synthesis pathway couldn't be found. However, as revealed by means of ^{1}H-NMR spectroscopy, significant differences in the distribution of substituents along the cellulose chains occurred. Conventionally synthesized samples (in aqueous NaOH), even in the presence of a phase transfer catalyst, possess a block-wise distribution of substituents, while a dissolution of cellulose in DMSO/TBAF prior to the reaction gives products that are uniformly substituted along the cellulose chains.

Keywords: biopolymers; NMR; polysaccharides; structure-property-relations; synthesis

Introduction

Benzyl cellulose (BC) was of technical importance in the 1940s as basic substance for lacquers. It combines resistance against water, strong acids and bases, oil and chemicals with good electrical and thermoplastic properties. After 1945, it was substituted by synthetic polymers with easier handling.[1,2] While BC with very low degree of substitution (DS_{Bn}) of about 0.001–0.079 has found application in hemodialysis,[3,4] BC with other DS_{Bn} values is of scientific interest at present only.

The conventional, heterogeneous benzylation proceeds layer by layer, thus an even distribution of NaOH solution and mechanical agitating (to disrupt the structure of the cellulose) are essential to reach an even reactivity and hence a uniform distribution of substituents.[5] As a consequence, the products are soluble at a DS_{Bn} of 1.7 in organic solvents. Daly et al. discussed a block-like distribution of benzyl groups in samples heterogeneously synthesized as a result of different hydrophilicity and hydrophobicity.[6] The alkali cellulose is hydrophilic while benzyl chloride (BnCl) forms a hydrophobic phase. This makes the diffusion of the reagent into the alkali cellulose, an indispensable prerequisite for etherification, more difficult as compared to other etherification agents like sodium monochloroacetate. Anhydroglucose units (AGU) that already have reacted with BnCl become less hydrophilic, a further reaction in their direct neighbourhood becomes consequently easier and a non-uniform distribution of substituents within the cellulose chain results. It was found that phase transfer catalysts like tetramethylammonium halides could enhance the diffusion of the BnCl into the alkali cellulose and accelerate the reaction, but still a large molar excess of aqueous NaOH and BnCl is needed to achieve DS_{Bn} up to 2.4.[7] Another approach to accelerate the benzylation is the additional use of NaI in the reaction system.[8,9] It is assumed that

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the more reactive benzyl iodide is formed *in situ*. For the conventionally prepared BC, Braun et al. found a ratio of the distribution of substituents within the AGU at positions 2, 3 and 6 of 1.3: 1.0: 1.6.[1]

Alternatively, benzylation of cellulose could be carried out starting from the dissolved polymer. Using *N,N*-dimethyl acetamide (DMA)/LiCl as reaction medium, products of high DS_{Bn} of up to 2.8 could be prepared applying a high molar excess of BnCl and solid NaOH as activating agent. A complete functionalization was achieved applying the cellulose solvents N_2O_4/dimethyl sulfoxide (DMSO) and SO_2/*N,N*-diethylamine/DMSO as the reaction medium for the benzylation.[10,11] The homogeneous reaction in the cellulose solvent SO_2/*N,N*-diethyl amine/DMSO leads to a measured functionalization pattern with a ratio of 0.9 (*O*-2): 1.0 (*O*-3): 1.1 (*O*-6).[12] Recently, the cellulose solvent DMSO/tetrabutylammonium fluoride trihydrate (TBAF) was studied as reaction medium for various functionalization reactions of cellulose including benzylation.[13–20] The BC synthesised with a DS of 1.27 was soluble in DMA, *N,N*-dimethyl formamide, *N*-methyl pyrrolidone and pyridine, i. e. solubility appeared at rather low DS-value. For the heterogeneously prepared samples a DS_{Bn} of at least 1.7 is necessary to reach solubility in these solvents. The required activation of the dissolved cellulose by NaOH, as powder or in aqueous solution, leads to precipitation of the polymer (gelation) resulting in a highly swollen system. Nevertheless, the cellulose bundles are more disaggregated than in the starting cellulose. The reactive sites can be reached more readily and a more uniform reaction should occur. The different solubility of the BCs depending on the synthesis procedure cannot be explained satisfactorily with the results published. Therefore, in the present paper benzylation of cellulose in two different reaction media was studied. The reaction was carried out conventionally as well as starting from cellulose dissolved in DMSO/TBAF. Detailed information about the structure of BC synthesised via the two different paths was obtained by NMR spectroscopy after peracetylation of the samples.

Experimental Part

Materials

The cellulose samples used were two spruce sulfite pulps; VHVS (**1**) and Super Plast (**2**, both pulps provided by Borregaard ChemCell, Sarpsborg, Norway) and Avicel (**3**, Fluka). Tetrabutylammonium fluoride trihydrate (TBAF, Fluka), benzyl chloride (Merck), acetyl chloride, tetramethylammonium chloride (NMe_4Cl), LiCl, *N,N*-dimethyl acetamide (DMA), ethanol, methanol and dimethyl sulfoxide (DMSO, Merck) were used as received. Sodium hydroxide was dried in vacuum for 24 h and milled before use.

Measurements

The intrinsic viscosity of pulp was determined by capillary viscometry in copper(II)-ethylenediamine using a Lauda PVS 1 according to ISO 5351 (25 °C, Micro Ostwald capillary No. Ic).

Benzyl cellulose possessing a degree of substitution of bezyl groups (DS_{Bn}) below 0.1 were analysed by UV/Vis spectroscopy in cadmium ethylenediamine solution according to Sollinger et al.[21] 3-*O*-benzyl glucose was used as calibration standard.

^{1}H- and ^{13}C-NMR spectroscopic analysis was carried out in $CDCl_3$. The concentration varied with the cellulose used for benzylation (Pulp versus microcrystalline cellulose). It was 50 mg/ml for samples derived from **1,** 30 mg/ml in case of samples derived from **2** and 90 mg/ml for samples derived from **3**.

The ^{1}H-NMR spectra were acquired on a Bruker Avance 250 MHz spectrometer at room temperature collecting 16 scans. The DS_{Bn} was calculated according to the equation (1):

$$DS_{Bn} = \frac{7}{5} * \frac{A_{Aromatic}}{A_{AGU} - \frac{2}{5} * A_{Aromatic}} \qquad (1)$$

$A_{Aromatic}$: Peak area of the aromatic protons ($\delta = 7.2$ ppm)

A_{AGU}: Peak area of the protons of the anhydroglucose unit and the methylene protons of the benzyl moiety between 3.0 and 5.5 ppm.

The spectra of samples synthesised from **1** were acquired on a Bruker Avance 400 MHz spectrometer at room temperature or at 60°C.

Synthesis

Heterogeneous benzylation of cellulose with benzyl chloride in the presence of NMe_4Cl (sample **20**).

30 ml 50% aqueous NaOH (375 mmol) was added to a mixture of 15.0 g cellulose **1** (92.5 mmol) and 0.5 g NMe_4Cl and stirred for 1 h at room temperature under argon atmosphere. 42.5 ml benzyl chloride (369 mmol) was added and the temperature was raised to 100°C within 15 min. After 3.5 h, 150 ml 80% aqueous methanol was added and the mixture was neutralised with aqueous acetic acid (50%). The product was filtered off, washed 2 times with 400 ml ethanol, 3 times with 400 ml water and 2 times with 400 ml ethanol. The sample was dried in vacuum at 60°C.

Yield: 13.49 g.

DS_{Bn} 0.91 (determined by means of ^{1}H-NMR spectroscopy after peracetylation).

Homogeneous benzylation of cellulose in DMSO/TBAF (Sample **21**).

2.00 g (12.3 mmol) Cellulose **3** was stirred in 45 ml DMSO for 1 h at 70°C under argon atmosphere and 6.4 g TBAF was added. The mixture was allowed to cool to room temperature resulting in a clear solution. 1.48 g (37.0 mmol) powdered NaOH and 4.3 ml (37.4 mmol) benzyl chloride were added and the temperature was raised to 70°C. After 5 h, the mixture was cooled to room temperature and 250 ml 80% aqueous methanol was added. The mixture was neutralised with 50% aqueous acetic acid. The product was filtered off and washed once with 200 ml 80% aqueous methanol, 4 times with 200 ml water and 2 times with ethanol.

Yield: 2.58 g.

DS_{Bn} 1.21 (determined by means of ^{1}H-NMR spectroscopy after peracetylation).

Peracetylation of benzyl cellulose (typical example).

0.2 g Benzyl cellulose was stirred in 30 ml DMA for 1 h at 150°C. After cooling to 70°C, 1.5 g LiCl was added and the mixture was allowed to cool to room temperature under stirring. 2 ml acetyl chloride was added and the temperature was raised to 80°C. After 24 h, the product was precipitated in 150 ml 80% aqueous methanol and washed with water until the washing water reacted neutral. Subsequently, the product was washed with ethanol to remove the water. The product was dried in vacuum at 60°C.

Hydrolysis of Cellulose

Samples (100 mg) were suspended in 2.0 ml 70% $HClO_4$ for 10 min at room temperature. Deionised water (18 ml) was added. The hydrolysis was carried out for 16 h at 100°C. The mixture was allowed to cool to room temperature and neutralised with 2 M aqueous KOH. The sample was stored at 4°C for 1 h in order to precipitate the $KClO_4$. The sample was filtrated and the precipitate was washed 3 times with 5 ml water. The solution was reduced to a volume of 3 ml, filtrated into a 5 ml-volumetric flask and water was added to a volume of 5 ml. HPLC measurement was carried out using Phenomenex Rezex ROA- and BioRad Aminex HPX-87H columns, 0.5 ml/min, 0.005 N H_2SO_4 as eluent, an intelligent pump (KNAUER HPLC pump 64), a differential refractometer (KNAUER), and HPLC software (BOR-WIN).

Results and Discussion

Three different cellulose samples (**1**–**3**) were used in this study. Their characteristics are summarised in Table 1. The spruce sulfite pulps **1** and **2** possess a significantly higher intrinsic viscosity [η] and hence a higher degree of polymerization (DP) as sample **3**. Another difference between the

Table 1.
Type, intrinsic viscosity ([η]) and sugar content of the cellulose samples used.

Cellulose		[η]^a [g/ml]	Peak area^b [%]	
Type	No.		Glucose	Other sugars
Spruce sulfite pulp	**1**	672	92.83	7.17
Spruce sulfite pulp	**2**	1315	83.87	15.63
Microcrystalline cellulose	**3**	113	100	-

^{a}Determined by viscometry in copper(II)-ethylenediamine.
^{b}Determined by HPLC after acidic hydrolysis.

cellulose samples used is the content of other sugars than glucose that was evaluated by HPLC after complete hydrolysis. Sample **3**, microcrystalline cellulose, is very pure; only glucose was found. The other samples **1** and **2** contain 7-15% other sugars than glucose that appear from the hemicellulose still present in the pulp.

The dissolution behaviour of the samples in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) proved to be different. While **3** already dissolved when being stirred in DMSO/TBAF at room temperature within 30 min as described,[22] cellulose **2** needed a treatment of at least 12 h in DMSO/TBAF at 60°C. It proved to be faster to activate the pulp in DMSO at 70°C for 1 h before adding the TBAF. A clear solution was achieved while cooling to room temperature. Cellulose **1** could be dissolved by stirring for 30 min at room temperature and 1 h at 60°C. If the pulp was mercerized with aqueous NaOH and dried in vacuum (60°C, 1 h) prior to dissolution, it needed 3 h at 60°C until the pulp was dissolved. Thus, it is obvious that the mercerized and dried pulp needs a more extensive activation to be dissolved. The reason may be the formation of cellulose II as well as the removal of polyoses by aqueous NaOH.[23] The latter are known to be able to act as spacer groups that impede the formation of irreversible hydrogen bonding against rewetting during drying in vacuum.[24,25]

The cellulose samples dissolved in DMSO/TBAF were allowed to react with benzyl chloride (BnCl) in the presence of solid or aqueous NaOH according to the reaction scheme (Figure 1). The benzylation reactions were carried out under argon atmosphere if not mentioned otherwise.

Figure 2 shows the values of degree of substitution (DS_{Bn}) of benzyl celluloses (BC) synthesized from cellulose **1** with a molar ratio of anhydroglucose unit (AGU)/BnCl/NaOH of 1/3/3 at 70°C in dependence on the reaction time (0.5 – 4 h, sample **4a** – **d**). The reaction proceeded fast; after 1 h the highest DS_{Bn} of 1.06 (sample **4b**) was already achieved.

Although the heterogeneous benzylation reaction in aqueous NaOH was carried out applying a different molar ratio AGU/BnCl/ NaOH of 1/0.5/1 at 80°C there are obviously different results. Figure 3 shows the dependence of DS_{Bn} of cellulose **2** on the reaction time (sample **5a** – **e**). To obtain the highest possible DS_{Bn} much longer reaction time was needed compared to the

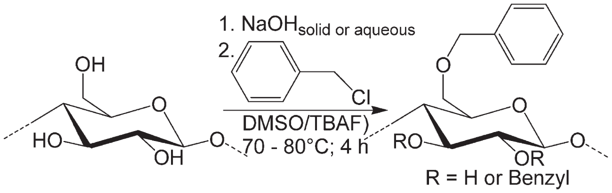

Figure 1.
Reaction scheme of cellulose benzylation in dimethyl sulfoxide (DMSO)/ tetrabutylammonium fluoride trihydrate (TBAF).

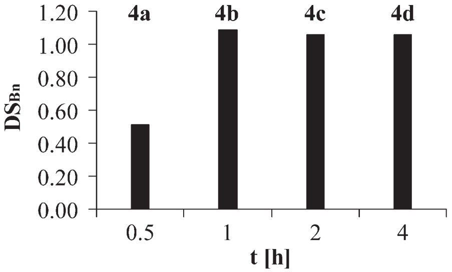

Figure 2.
Degree of substitution (DS_{Bn}) of benzyl celluloses synthesized from cellulose **1** in dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate with a molar ratio anhydroglucose unit/benzyl chloride/NaOH of 1/3/3 at 70°C in dependence on the reaction time.

benzylation starting from dissolved cellulose. The reaction started slowly. After 6 h, a DS_{Bn} of 0.02 only was achieved. After this induction phase, the benzylation became slightly faster; a DS_{Bn} of 0.07 was reached after 10 h. It needed 15 h until the end of reaction, yielding a product with a DS_{Bn} of 0.24. About 50% of BnCl could be reacted under these conditions.

The DS_{Bn} obtained depending on the reaction time applying the 2 different reaction media (DMSO/TBAF versus aqueous NaOH) are consistent with the assumptions of reaction mechanisms mentioned in the introduction. The diffusion of BnCl into the alkali cellulose is difficult because BnCl and the alkali cellulose form hardly miscible phases in the heterogeneous reaction.

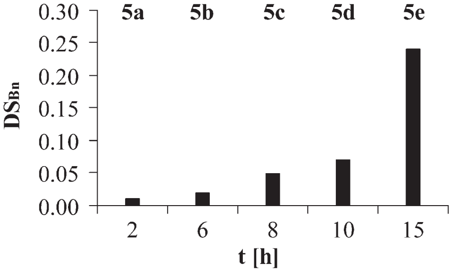

Figure 3.
Degree of substitution of benzyl celluloses (DS_{Bn}) prepared from cellulose **2** depending on reaction time in conventional benzylation in aqueous NaOH at 80°C applying a molar ratio anhydroglucose unit/benzyl chloride/NaOH of 1/0.5/1.

The etherification starts on the surface of the cellulose fibres and becomes faster with decreasing hydrophilic character due to the already introduced benzyl groups. The DS_{Bn} versus time in the homogeneous reaction shows a more regular and uniform reaction progress due to more disaggregated, and consequently more reactive cellulose fibre bundles.

Further experiments to control the DS_{Bn} values in a medium range were carried out in DMSO/TBAF with cellulose **1** applying a molar ratio AGU/BnCl/NaOH of 1/3/3 (Table 2). A mercerization of pulp prior to dissolution reduced the reactivity towards benzylation. Applying a molar ratio AGU/BnCl/NaOH of 1/3/3, samples **11** (DS_{Bn} 0.33) and **9** (DS_{Bn} 0.59) were obtained that have significantly lower DS_{Bn} compared to **8** (DS_{Bn} 0.99) synthesized without mercerization prior to dissolution in DMSO/TBAF. Ramos et al. reached DS_{Bn} values of up to 1.3 using powdered NaOH as base and DS_{Bn} values of 1.1–1.2 with 7% aqueous NaOH using mercerized pulp.[19] In our own experiments untreated pulp was used for all further experiments. Using 7% aqueous NaOH, the cellulose precipitated to a lump instead of a highly swollen system. The accessibility for the BnCl became limited due to the poor mixing of the reaction mixture. Further experiments with aqueous NaOH were carried out with 15% aqueous NaOH because a swollen homogeneous system was obtained.

DS_{Bn} up to 1.08 (**6**) could be reached using argon as protecting gas and increasing the concentration of cellulose/DMSO to 2.2% (w/v) instead of 1.7% (w/v). The BC (**6**) with highest DS_{Bn} (1.08) still was not soluble in such organic solvents as pyridine, DMSO or *N,N*-dimethyl acetamide. Since a BC with low DS_{Bn} could be interesting for a subsequent etherification to amphiphilic, water soluble ethers as benzyl carboxymethyl cellulose (results of these studies will be published elsewhere), cellulose **2** was used for further studies of benzylation to low DS_{Bn}. The molar ratio AGU/BnCl/NaOH was varied while the other reaction parameters were kept constant.

Table 2.
Benzylation of cellulose in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate, 4 h reaction time.

Cellulose No.	Reaction Conditions							Benzyl cellulose	
	Argon	Mercerization	Concentra-tion [%][a]	NaOH		Molar Ratio[b]	T [°C]	No.	DS_{Bn}[c]
				Type	Concentration [%]				
1	+	–	2.2	solid	–	1/3/3	70	**6**	1.08
1	+	–	2.2	aqueous	15	1/3/3	70	**7**	0.82
1	–[d]	–	1.7	solid	–	1/3/3	70	**8**	0.99
1	–[d]	+	1.7	aqueous	7	1/3/3	70	**9**	0.59
1	+	–	2.2	aqueous	15	1/3/3	70	**10**	0.38
1	–[d]	+	1.7	solid	–	1/3/3	70	**11**	0.33
2	+	–	2.2	solid	–	1/2/3	80	**12**	1.10
2	+	–	2.2	solid	–	1/1/2	80	**13**	0.35
2	+	–	2.2	solid	–	1/0.6/3	80	**14**	0.47
2	+	–	2.2	solid	–	1/0.4/3	80	**15**	0.27
2	+	–	2.2	solid	–	1/0.3/3	80	**16**	0.30
2	+	–	2.2	aqueous	15	1/0.3/3	80	**17**	0.30
2	+	–	2.2	solid	–	1/0.25/3	80	**18**	0.25
2	+	–	2.2	solid	–	1/0.2/3	80	**19**	0.20
3	+	–	4.4	solid	–	1/3/3	70	**21**	1.21
3	+	–	2.2	aqueous	15	1/1.5/3	70	**22**	1.13

[a] (w/v) cellulose/DMSO.
[b] Anhydroglucose unit /NaOH/benzyl chloride.
[c] Determined by means of ^{1}H NMR-spectroscopy after peracetylation.
[d] No protection gas at all.

Decreasing the molar ratio AGU/BnCl/NaOH from 1/2/3 to 1/1/2 led to a product with DS_{Bn} of 0.35 (**13**). Applying a molar ratio of 1/0.6/3 gave a DS_{Bn} of 0.47 (**14**) although the amount of BnCl added was lower. The ratio AGU/NaOH of 1/3 seems to be necessary to achieve an effective reaction of BnCl with the cellulose. Even the use of a ratio AGU/BnCl/NaOH of 1/0.4/3 gave a DS_{Bn} of 0.27 (**15**). Using a lower molar ratio, the reaction became quantitative regarding BnCl, independent of whether the NaOH was used as powder or aqueous solution (compare samples **16** and **17**; **18**). Compared to the conventional benzylation of cellulose to products of low DS_{Bn}, the conversion in DMSO/TBAF is much more effective.

In order to gain detailed information about the distribution of substituents of BCs synthesized in two different reaction media, cellulose **3**, as pure cellulose with low DP, was benzylated heterogeneously in aqueous NaOH and starting from the dissolved polymer in DMSO/TBAF. The activation in DMSO/TBAF was carried out with powdered- or aqueous NaOH. The reaction conditions were chosen to obtain BCs with a DS_{Bn} of about 1 (Table 2). The heterogeneously prepared sample **20** was synthesized using tetramethylammonium chloride as phase transfer catalyst and a molar ratio AGU/BnCl/NaOH of 1/3/3. In this range, it is possible to detect basic differences in the distribution of substituents at the positions 2, 3 and 6 in the AGU as well as the distribution of substituents along the cellulose chain. Structure characterization was carried out by means of NMR spectroscopy after acetylation of the remaining hydroxyl groups. The peracetylation leads to products soluble in $CDCl_3$ and well resolved NMR spectra are obtained due to the decrease of intermolecular interactions that might be caused by hydrogen bonds.

The assignment of signals of cellulose acetate and of tri-*O*-BC in the ^{13}C-NMR spectra is known[10,26,27] and was used for assigning the signals of our own samples. Moreover, to assign the signals of the mixed derivatives two-dimensional NMR measurements proved to be very useful (Figure 4). The assignment is exemplarily

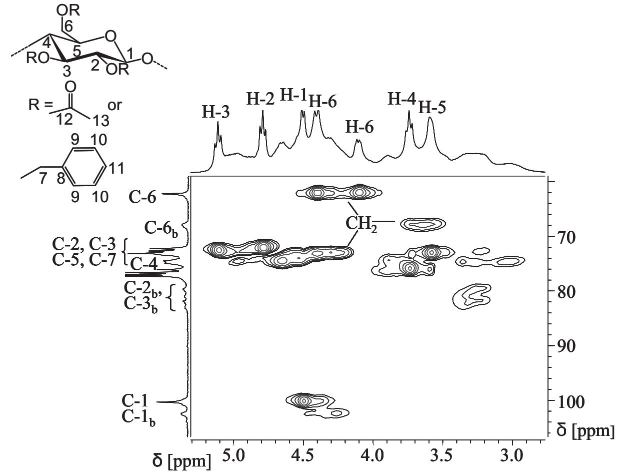

Figure 4.

HSQC/DEPT NMR spectrum of peracetylated **20**, (degree of substitution 0.91), recorded at 60°C in $CDCl_3$. The index $_b$ refers to benzyl substituted moieties.

shown with sample **20**, synthesized heterogeneously in NaOH.

The sharp, well recognizable signals of the AGU between 2.8 ppm and 5.3 ppm in the ^{1}H-NMR spectrum of **20** correspond to the typical signals of cellulose acetates. Those peaks of the protons of the acetyl-substituted positions without influence of any benzyl moieties appear at 5.11 ppm (H-3), 4.79 ppm (H-2), 4.51 ppm (H-1), 3.74 ppm (H-4) and 3.59 ppm (H-5). Two signals are observed for H-6 at 4.41 ppm and 4.11 ppm due to the neighbouring chiral carbon atom at position 5. The modification of the AGU with benzyl moieties leads to an upfield shift of the signals, depending on the substitution pattern (Figure 5). H-2 and H-3 of AGUs that are dibenzylated in position 2 and 3 or tribenzylated appear at 3.2 and 3.3 ppm. H-4 is found at 3.0 ppm and H-6 appears at 3.65 ppm.

The broader signals of the AGUs resulting from benzyl moieties are overlapping and make it impossible to calculate

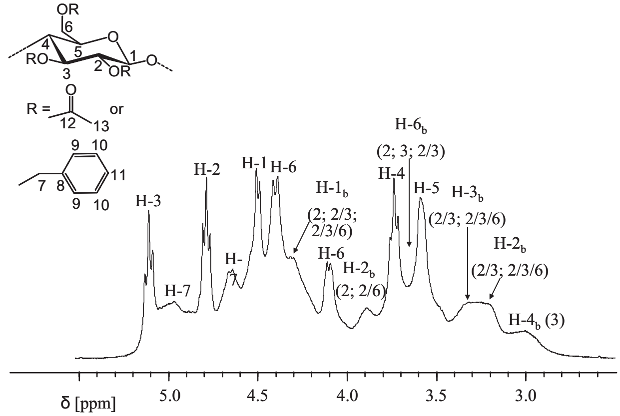

Figure 5.

Assignment of signals of the anhydroglucose unit (AGU) in the ^{1}H-NMR spectrum of peracetylated **20**, recorded at 60°C in $CDCl_3$. The index $_b$ refers to benzyl moieties. 2, 3 and 6 indicate the position of the benzyl group within the AGU.

partial DS-values from the ^{1}H-NMR spectrum. Further information was gained by ^{13}C-NMR spectroscopy. A typical spectrum of sample **20** is shown in Figure 6 (spectrum A). The signals of the AGU appear between 60 and 105 ppm. The peaks of the acetylated AGUs without benzyl groups are found at 62.2 ppm (C-6), 72.2 ppm (C-2), 72.6 ppm (C-3), 73.1 ppm (C-5), 74.9 ppm (C-4) and 100.3 ppm (C-1). C-7 appears at 74.9 and 73.2 ppm. The signals at 83.3 ppm and 82.2 ppm are assigned to C-3$_b$ and C-2$_b$ of tribenzylated AGUs. Two further peaks (C-2$_b$ and C-3$_b$) of repeating units dibenzylated in positions 2 and 3 are found around 80 ppm. Further signals of AGUs with benzyl moieties appear at 77 ppm (C–2$_b$, benzyl groups at 2 or 2 and 6, overlapped with the $CDCl_3$ signal), C-4$_b$ under C-7 (74.5 ppm) and C-6$_b$ at 68.3 ppm.

All three peracetylated BCs contain triacetylated as well as tribenzylated AGUs as can be seen in the ^{13}C-NMR spectrum from 79 to 83 ppm (Figure 6). In order to gain more insight to the distribution of the acetyl groups and consequently for the distribution of the benzyl moieties within the single AGUs, Figure 7 shows the ^{13}C-NMR signals of the carbonyl group and the ^{1}H-NMR signals of the methyl group of the acetyl moieties.

The substitution took place at all 3 possible positions. The peaks of the carbonyl groups at position 2, 3 and 6 appear at 168.3, 169.5 and 170.0 ppm. The signals of the benzyl cellulose acetates synthesized in DMSO/TBAF are broader compared to the benzyl cellulose acetate benzylated in NaOH. In the ^{1}H-NMR spectra, the signals at the 3 positions 2, 3 and 6 are observed at 2.00, 1.90 and 2.08 ppm. They are overlapping too much. It is not possible to calculate partial DS_{Bn} values, even although the spectra of **20** and **22** were recorded in DMSO to eliminate the water signal that appears between 1.6 and 1.9 ppm in $CDCl_3$ (Figure 7, spectrum B). **22** (spectrum C) shows additionally fine structures that

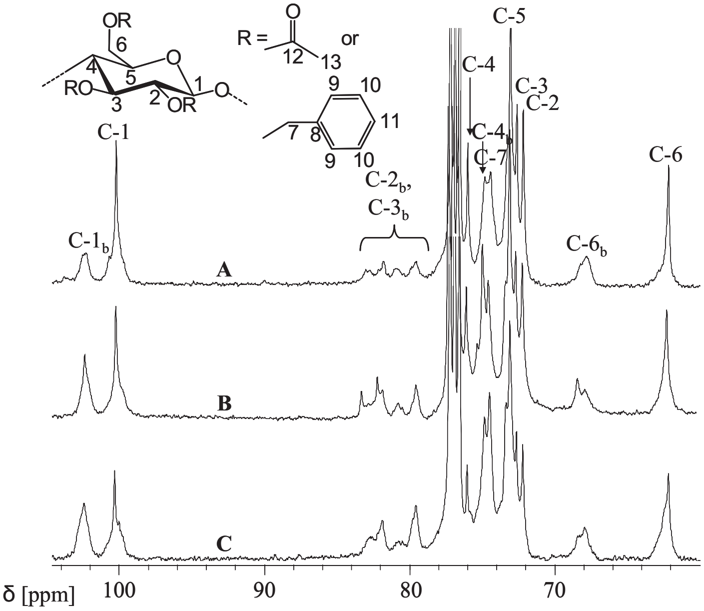

Figure 6.
^{13}C-NMR spectra of benzyl cellulose peracetates (from **3**) recorded at 60°C in $CDCl_3$, A = **20** (synthesized in aqueous NaOH, degree of substitution, DS_{Bn} 0.91), B = **21** (synthesized starting from a dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) solution using powdered NaOH for activation, DS_{Bn} 1.21), C = **22** (synthesized starting from a DMSO/TBAF solution using aqueous NaOH for activation, DS_{Bn} 1.13). The index $_b$ refers to benzyl substituted moieties.

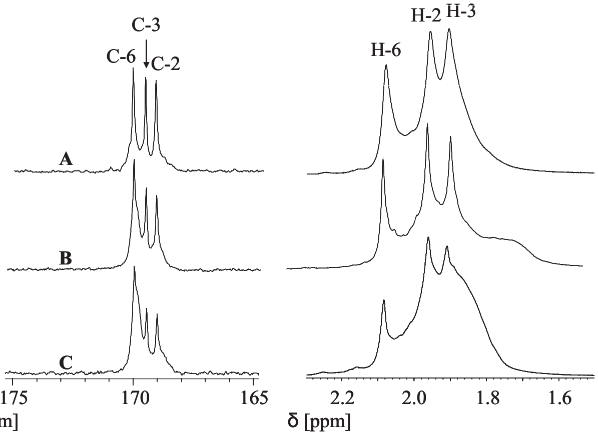

Figure 7.
^{13}C-NMR spectra of the carbonyl group (left) and ^{1}H-NMR spectra of the methyl protons (right) of benzyl cellulose acetates (from **3**) recorded at 60°C. A = **20** (synthesized in aqueous NaOH, degree of substitution, DS_{Bn} 0.91, in DMSO-d_6), B = **21** (synthesized starting from a dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) solution using powdered NaOH for activation, DS_{Bn} 1.21, in $CDCl_3$), C = **22** (synthesized starting from a DMSO/TBAF solution using aqueous NaOH for activation, DS_{Bn} 1.13, in DMSO-d_6).

contribute to the failure of the determination of partial-DS_{Bn}.

Comparing the ^{13}C-NMR spectrum of the heterogeneously synthesized BC with the spectra of BCs synthesized starting from DMSO/TBAF solution (Figure 6, spectra B and C), no other differences were found than those resulting from the slightly different DS_{Bn}. On the contrary, the ^{1}H-NMR spectra of the three samples

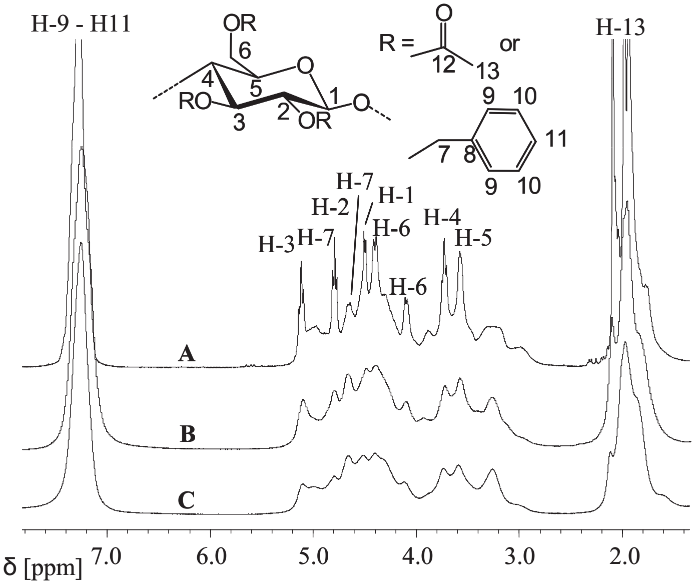

Figure 8.
^{1}H-NMR spectra of benzyl cellulose peracetates (from **3**), recorded at 60°C in $CDCl_3$, A = **20** (synthesized in aqueous NaOH, degree of substitution, DS_{Bn} 0.91), B = **21** (synthesized starting from a dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) solution using powdered NaOH for activation, DS_{Bn} 1.21), C = **22** (synthesized starting from a DMSO/TBAF solution using aqueous NaOH for activation, DS_{Bn} 1.13).

synthesized heterogeneously or starting from DMSO/TBAF solution show some characteristic differences (Figure 8).

The ^{1}H-NMR spectrum of **20**, synthesized in a conventional way with additional use of tetramethylammonium chloride as phase transfer catalyst shows broad, not too well dissolved peaks of the AGUs bearing benzyl moieties superimposed by sharp peaks of the acetyl substituted hydroxyl groups as if there was a mixture of two different polymers. This behaviour is typical for block-wise substituted polymers or polymers with a bimodal distribution of molecular mass. A bimodal distribution could be excluded by a spin-echo experiment and an experiment using a diffusion filter.

The samples **21** and **22** synthesized starting from DMSO/TBAF solution show only broad peaks, indicating a regular distribution of benzyl moieties along the cellulose chains.

Conclusion

The benzylation of cellulose starting from the dissolved polymer in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) is significantly faster than the conventional synthesis applying aqueous NaOH as medium. At low amount of benzyl chloride (BnCl) a quantitative conversion occurred concerning the BnCl. A difference in the distribution of benzyl moieties within the anhydroglucose unit of the products in dependence on the reaction medium couldn't be found. However, as revealed by means of ^{1}H-NMR spectroscopy, significant differences in the distribution of substituents along the cellulose chains occurred. Conventionally synthesized samples (in aqueous NaOH) even in the presence of a phase transfer catalyst possess a block-wise distribution of substituents, while a dissolution of cellulose in DMSO/TBAF prior to reaction gives products that are more uniformly substituted along the cellulose chains.

Acknowledgements: The financial support of Borregaard ChemCell, Sarpsborg, Norway is gratefully acknowledged. The authors thank Dr. W. Günther, Institut für Organische Chemie und Makromolekulare Chemie, Friedrich Schiller Universität Jena, for the discussion and the efforts to acquire well-resolved NMR spectra.

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