

HOMOGENOUS BENZYLATION OF CELLULOSE – IMPACT OF DIFFERENT METHODS ON PRODUCT PROPERTIES

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Received January 29, 2015

This paper offers an evaluation of different methods for synthesizing benzyl cellulose and of how they affect characteristics such as solubility, degree of substitution, thermal stability and molecular weight of the products. Benzyl celluloses with degrees of substitution between 0.1 and 2.5 were synthesised from microcrystalline cellulose in (1) aqueous NaOH/Urea and (2) dimethyl sulfoxide/tert-butyl ammonium fluoride (DMSO/TBAF) systems in order to evaluate the different properties of the benzyl celluloses of low degree of substitution. In contrast to previous findings in the literature, both systems yielded soluble benzyl celluloses at degrees of substitution <0.5. Also in contrast to the literature, the low degree of substitution benzyl celluloses from both systems showed similar thermal properties. The filtration of the benzyl celluloses in DMSO/TBAF solutions before precipitation gave significantly higher solubility of the products and increased their thermal stability. The molecular weights of the benzyl celluloses of low degree of substitution ($0.4 < DS < 1.25$) were similar between the systems and differed in the range of one order of magnitude from the molecular weights of the higher degree of substitution benzyl celluloses. ^{13}C -NMR data indicated differences in the substitution pattern between the two systems.

Keywords: cellulose and other wood products, functionalization of polymers, benzyl cellulose, solubility, thermal properties, coatings

INTRODUCTION

Cellulose has many uses, one of which is as a polymeric backbone for chemical derivatization. Chemical derivatization of cellulose to either cellulose ethers or esters has been performed for a long time. For example, products containing benzyl cellulose (BC, produced by etherisation of cellulose) were industrially manufactured before the Second World War – at that time BC was used as an electrical insulator and in paint and coatings, for example.¹ BC is still an interesting hydrophobic compound and materials from BC have found modern uses such as haemodialysis membranes due to their unique properties.^{2,3} Furthermore, BCs can potentially be used to modify (normally hydrophilic) cellulose surfaces towards hydrophobicity, as cellulose ethers have been shown to adsorb onto cellulosic surfaces.⁴⁻⁷ This may find applications in packaging and the textile industry.

The benzylation of cellulose can be carried out in several ways. The traditional synthesis of BC is a heterogeneous process where an aqueous suspension of alkali cellulose is reacted with benzyl chloride.⁸⁻¹⁰ For this and similar processes, a high degree of substitution (*DS*) of the formed BC is necessary for obtaining a soluble product. In recent years, many studies have appeared in which homogenous solutions of cellulose are used in the production of cellulose ethers.¹¹⁻¹⁴ Specifically, the production of BC was early studied in homogenous conditions in non-aqueous solvents.^{15,16} In these studies, the authors used a very high excess of benzyl chloride together with long reaction times and high temperatures to achieve high *DS* BCs. Most likely, the reactions to form benzyl alcohol and dibenzyl ether are responsible for the high excess needed.¹

Different synthesis methods yield BCs with different characteristics in *DS*, molecular weight (M_w) and solubility, for example. Ramos *et al.*² found that using aqueous NaOH always gave an insoluble BC. Two studies present two different procedures for BC synthesis: homogenous benzylation of cellulose dissolved in either dimethyl sulfoxide/tetrabutylammonium fluoride (DMSO/TBAF), or in aqueous NaOH/urea. These studies both found that BCs of intermediate *DS* ($DS \approx 0.6$ -1.8) were soluble in different solvents – their specific solubilities were dependent on the conditions during synthesis.^{2,3} For industrial applications, the relatively low cost of NaOH and urea give the aqueous system presented by Li *et al.*³ an economical advantage compared to, e.g., DMSO/TBAF and other more expensive cellulose solvents, but the upscaling possibilities were not attempted in that paper. Furthermore, the soluble low *DS*-range BC from the DMSO/TBAF-system was relatively unexplored.

Different applications demand BCs with different characteristics: for example, to obtain absorption of BC onto cellulose surfaces, cellulose ethers with *DS* from ≈ 0.39 to ≈ 2 have been shown to be necessary.^{4,7} The references given in the previous paragraph are examples of findings in the currently available literature. However, a full, concise investigation of how different synthesis methods impact the characteristics of the BCs being produced has not yet been published. Moreover, the published studies vary quite a lot in method, starting material, *DS* and number of BCs analysed – this makes comparisons difficult. Therefore, in the present study, we evaluate the differences in *DS*, solubility, thermal stability, Molecular Weight Distribution (MWD) and substitution pattern of homogeneously produced BCs made from the same starting material, using DMSO/TBAF and aqueous NaOH/urea as cellulose solvents. Special focus is put on low *DS* BCs because of their potential use for surface modification of cellulosic materials. Furthermore, the methods already published were performed solely on a laboratory scale. However, for industrial uses, upscaling is necessary, and none of the published studies included any such trials or recommendations. We will therefore discuss some aspects of our findings in relation to possible upscaling as well.

EXPERIMENTAL

Chemicals

Acetic acid (100%, Merck), acetone (Sigma-Aldrich), Avicel® microcrystalline cellulose with a size of $\sim 50 \mu\text{m}$ (PH-101, Sigma-Aldrich), benzene (Scharau), benzyl chloride (99%, Aldrich), chloroform (Sigma-Aldrich), chloroform-D (CDCl₃, 99.8 atom%D, Armar Chemicals), diethylacetamide (DMAc, HiPerSolv CHROMANORM, VWR), 4-dimethylamino pyridine (DMAP, Reagent Plus® ≥ 99 , Aldrich), Dimethyl sulfoxide (DMSO, Sigma-Aldrich), Dimethyl-D₆ sulfoxide (D₆-DMSO, 99.8 atom%D, Armar Chemicals), ethanol (99.5%, Solveco), Lithium bromide (LiBr, ReagentPlus grade, Sigma-Aldrich), methanol (Technical Grade, Sigma-Aldrich), propionic anhydride (Aldrich), 2-propanol (Normapur, VWR Chemicals), pullulan standards (Sigma-Aldrich), pyridine (Baker Analysed, J.T. Baker), tetrabutylammonium fluoride (TBAF·3H₂O, $\geq 97\%$, Aldrich), toluene (AnalR Normapur, VWR) and urea (Merck) were all used without further purification. NaOH (AnalR Normapur, VWR) was pulverised and used immediately or dissolved in degassed (by boiling) MilliQ H₂O. Unless otherwise stated, the chemicals were of pro-analysis grade.

Benylation of cellulose

For the synthesis of the different benzyl celluloses, 9 different methods were used. Some of them are based on procedures from literature, and some modified as described below:

- i. A method based on the work by Li *et al.*³ Briefly, 1 (7) g of cellulose (Avicel) was added to 50 (350) g 1.75/2 M NaOH/urea aqueous solution and vigorously stirred for approximately 5 min. This suspension was cooled to below $-12 \text{ }^\circ\text{C}$, and stirred vigorously while thawing at ambient temperature until a clear cellulose solution was achieved. Benzyl chloride was added under continuous stirring, after which the temperature was increased to $70 \text{ }^\circ\text{C}$. After 4 h, the temperature was decreased to room temperature. The benzyl cellulose polymer was then precipitated by pouring the solution into 4:1 MeOH:H₂O. This final suspension was neutralised with acetic acid. The polymer was filtered off, washed with 4:1 MeOH:H₂O and dried at $50 \text{ }^\circ\text{C}$ for 48 h under reduced pressure.
- ii. As *i*, but benzyl chloride was added a second time after approximately 2 h after the first addition (similar to Okada⁹).

- iii. A method based on the work by Ramos *et al.*,² 1-2 g of cellulose (Avicel) was added to 60 ml/g of DMSO with 11.9 g/g TBAF·3H₂O (6.1 mol/mol) under intense stirring. This was (more gently) stirred for 30 min at room temperature and then for 60 min at 60 °C until the solution was clear. A 1.88 M aqueous NaOH solution and benzyl chloride were then added under increased stirring, after which the temperature was kept constant at 70 °C for 4 h. The precipitation and washing of the precipitated polymer was similar to *i*.
- iv. As in *iii*, but benzyl chloride was added a second time after approximately 2 h after the first addition (similar to Okada⁹).
- v. As *iii*, but the amounts of benzyl chloride and NaOH solutions were divided into several additions (similar to Isogai *et al.*¹⁵), which were added at time intervals dependent on the number of additions (total reaction time 4 h).
- vi. As *iii*, but different concentrations (i.e., 6.3, 13.5 and 20.5 M) of the aqueous NaOH solution were used, and only the fully dissolved product (separated using filtration in a glass filter (P3)) was used for the precipitation.
- vii. As *iii*, but different concentrations (i.e., 3.4 and 13.5 M) of the aqueous NaOH solution were used.
- viii. Cellulose (Avicel) was put in 6.25 M NaOH and kept at 0 °C for 4 h, washed until neutral with MilliQ H₂O and then dried, first at 80 °C overnight, and then again at room temperature under reduced pressure for 24 h. The sample was then treated as in *iii*, but instead of aqueous NaOH, pulverised NaOH suspended in DMSO was added, and only the fully dissolved product (separated using filtration in a glass filter (P3)) was used for the precipitation.
- ix. As *viii*, but a second addition of benzyl chloride was performed after approximately 2 h after the first addition (similar to Okada⁹).

Solubility measurements

The BCs and 1 ml of the solvent per 10 mg of BC were put in glass test tubes with caps. These suspensions were then put in an ultrasonic bath (Brandelin, Sonorex Digitec) for 15 min and then visually inspected for swollen samples. The samples were allowed to rest at 25 °C for a few hours, and the then swollen samples were once more placed in the ultrasonic bath (15 min). The samples then rested overnight at 25 °C and the solubility was determined visually.

Perpropionylation of the benzyl celluloses

An amount of 0.3 g of the dried BC sample was mixed with 5 ml propionic anhydride and 5 ml pyridine with 0.2 g DMAP as catalyst. The reaction mixture was heated to 80 °C and kept isothermal for

>24 h. After cooling to room temperature, the polymer was precipitated in 200 ml 2-propanol and filtered off. The polymer was washed with 2-propanol and then dried under reduced pressure at 70 °C for >2 weeks. The perpropionylated benzyl cellulose was then analysed for the absence of C-OH by the use of FTIR (Bruker IFS 66v/S, diffuse reflectance mode, 128 scans). Upon the existence of OH signal in the range of 3300-3500 cm⁻¹ in the FTIR spectrum, the perpropionylation reaction, the precipitation, washing and drying procedures were repeated. Finally, the FTIR signal was once more checked for the presence of C-OH. Only samples without OH signal were used for further analysis.

Nuclear Magnetic Resonance measurements

¹H Nuclear Magnetic Resonance measurements

The DSs of the BC samples were calculated as DS_{NMR} of perpropionylated samples in accordance with the works by Ramos *et al.* and Li *et al.*^{2,3} The samples were dissolved in CDCl₃ for ¹H NMR measurements (12-14 mg ml⁻¹). The ¹H NMR data were collected on a Bruker (400 MHz, 8 scans) instrument on the NMR core facility at KBC, Umeå University, and the DS_{NMR} was evaluated according to Equation 1:

$$DS_{NMR} = 1.4 \cdot \frac{A_1}{A_2 - 0.4A_1} \quad (1)$$

where A₁ represents the integral of the aromatic peak in the ¹H-NMR spectra (δ≈7.2 ppm), and A₂ – the integral of the area 3.0 ≤ δ ≤ 5.5^{2,3}.

¹³C Nuclear Magnetic Resonance measurements

To analyse the individual substitution of C-6 (<<f₆>>), ¹³C NMR spectra were recorded. Twenty-five (25) mg of the BC sample was dissolved in 0.75 ml of either D₆-DMSO or CDCl₃ (33⅓ mg ml⁻¹). ¹³C NMR spectra were recorded with a Bruker 600 MHz NMR spectrometer at the NMR core facility at KBC, Umeå University. The total number of scans was 70,000, and the temperatures were 70 °C and 25 °C respectively when D₆-DMSO and CDCl₃ were used as solvents.

Thermal analysis

Thermal analysis for determining decomposition characteristics was performed on all samples using a thermogravimetric analyser (TGA, Q5000IR, TA Instruments). Samples of approximately 10 mg were subjected to a heating program in the TGA as follows: 1) drying for 5 min at 105 °C and 2) a heating ramp of 10 °C min⁻¹ to 500 °C. The instrument was purged with N₂ at 50 ml min⁻¹. Data were collected only for part 2), and the weights were normalised to 100% for the dried samples.

A differential scanning calorimeter (DSC, Q1000, TA Instruments) was used to identify events including reaction heats during heat-up and decomposition. Here, the temperature for the samples, approximately 5 mg, was programmed as follows: 1) drying at 105 °C for 5

min, 2) cooling to 0 °C and equilibrating for 5 min, 3) heating at 10 °C min⁻¹. The instrument was purged with N₂ at 100 ml min⁻¹, and part 3) was used for evaluation.

All samples used for thermal analysis were analysed 'as received', meaning no milling or compressing of the particles was performed.

Gel Permeation Chromatography (GPC)

DMSO containing 0.1% (w/w) LiBr was used as eluent. The BCs were dissolved in eluent prior to analysis (1 mg BC ml⁻¹ eluent). The GPC system used consisted of two PLgel MIXED-A 300x7.5 mm columns with a 50x7.5 mm PLgel guard column (Agilent Santa Clara, CA, USA), and a refractive index (RI) detector in a Polymer Laboratories PL-GPC 50 Plus instrument (Agilent). The eluent flow rate was set to 0.5 ml min⁻¹. The system was calibrated using 8 Pullulan standards with molecular masses ranging from 9.6 to 708 kDa. Two subsamples of each BC were taken and analysed in duplicate.

RESULTS AND DISCUSSION

Benylation of cellulose

The appearance of the products varied considerably; they were white or lightly coloured by a yellow by-product. Methods *i-vii* yielded white/pale yellow products, while methods *viii* and *ix* yielded products with intensive yellow colours for the highest addition of NaOH and benzyl chloride.

Any colour strongly indicates that the products are contaminated with by-products. However, the most common by-products are benzyl alcohol and dibenzyl ether, both of which are uncoloured. It is therefore not known what causes the yellow colours, although oxidation might be a significant factor. In fact, the colour was most intensive in BC101 and BC103 (i.e., the BC synthesised in DMSO/TBAF with the highest initial concentrations of solid NaOH). For these two BCs, the molecular weight distribution measurements indicated NaOH-catalysed oxidative degradation of the cellulose polymers. The use of an N₂ atmosphere might have prevented this, but this was not practically possible during our experiments. However, after perpropionylation the traces of colour almost vanished. Furthermore, soluble coloured BCs formed clear (yet slightly coloured) solutions, thus showing that the presence of any contaminations affected neither the solubility nor the DS_{NMR} measurements of the BCs.

The homogeneities of the syntheses were estimated from observations of the experiments. All the experiments started with fully dissolved

cellulose, in other words, homogenous solutions. For the experiments performed according to methods *iii* and *iv*, the addition of an aqueous NaOH solution immediately caused gelling of the mixture, thus allowing the benzyl chloride to react with this Na-cellulose gel. When a large volume of aqueous NaOH was added (>10 ml), the precipitation of a solid (possibly regenerated cellulose) was very evident. The reaction between the benzyl chloride and the alkaline forms of the regenerated cellulose is *not* homogenous. These methods, especially when large volumes of aqueous solution are added, are thus not fully homogenous. Furthermore, this problem was also seen when the addition of the NaOH (aq) was divided into smaller portions (method *v*), but seemed to decrease when the concentration of the NaOH solution was increased (methods *vi* and *vii*). The aqueous solution methods (*i* and *ii*) were initially the most homogenous methods. There, no gelling of the solution occurred, and the poor solubility of benzyl chloride was compensated by the stirring. However, as the *DS* of the formed benzyl cellulose increased, the insolubility of BCs in the aqueous solvent led to the precipitation of BCs, with a completely heterogeneous continuation of the reaction. Similarly, gelling did not occur in the experiments where solid NaOH (suspended in DMSO) was used (methods *viii* and *ix*). However, the very poor solubility of NaOH in the solvent caused undissolved pulverised NaOH(s) to circle around in the reaction vessel for hours. Nevertheless, the cellulose was always in homogenous solution, so this method of reaction was quite homogenous.

To sum up, ordered from the most homogenous to the least, the synthesis paths were as follows: *viii* and *ix* > *i* and *ii* > *vi* and *vii* (with emphasis on high concentration of the NaOH solutions) > *v*, *iv* and *iii*.

The yield was 0.4-0.7 g of BC per g of starting material except for methods *vi*, *viii* and *ix*, where much of the cellulosic material was lost in the filtration step. For several of these samples, the yield was very low. In fact, the yield in several experimental trials was beneath the amount necessary for analysis and perpropionylation (i.e., 0.3 g for the latter), and the synthesis was therefore scaled for most of these samples so that the yield would be enough. Synthesis path *i* was upscaled 7 times for testing (6 mol benzyl chloride mol⁻¹ of AGU). The yield in that experiment was much higher, almost 1.2 g benzyl cellulose /g cellulose.

Solubility and degree of substitution

The DS_{NMR} resulting from benzylation in the different solvents is shown in Fig. 1 as a function of added benzyl chloride and ordered according to the use of filtration. Although a very high excess of benzyl chloride (28 mol/mol) was used, the highest resulting DS_{NMR} was only 0.95 for the aqueous solutions. The results indicate that there is a limit in the DS of benzyl cellulose produced in the NaOH/urea aqueous system, in agreement with Isogai *et al.*, who reported that H_2O disturbs the benzylation of cellulose in non-aqueous solvents.¹⁵ From the present study, it is clear that high DS is very difficult to achieve with high H_2O presence. This is possibly caused by the insolubility of the formed BC in the aqueous solvent, resulting in heterogeneous reaction conditions. The accessibility of cellulose for benzyl chloride during heterogeneous reactions is considerably inhibited by the strongly limited diffusion of the hydrophobic benzyl chloride in cellulose, and the control of the reaction in heterogeneous production of cellulose ethers is problematic.^{1,17} Therefore, it is very likely that any formed insoluble cellulose-based material reacts only on the surface, which would result only in an extremely low increase of DS .

Since a hydrated salt ($TBAF \cdot 3H_2O$) was used in the DMSO/TBAF solvent system, H_2O was always present there and could hence disturb the benzylation. Additionally, when aqueous NaOH was used as a base, even more H_2O was present. However, the DS_{NMR} was not generally lower for the samples with low concentration of added aqueous NaOH; it rather seemed that filtration of the product was more important for their solubility. Nonetheless, for the non-filtered samples, and when a high amount of aqueous NaOH was added, the resulting DS_{NMR} was very low (cf. Fig. 1). The reason for this might be the following: H_2O acts as an anti-solvent for cellulose, and the addition of aqueous NaOH causes regenerated cellulose to precipitate. Precipitated cellulose reacted heterogeneously, and achieving high DS from heterogeneous conditions was difficult (cf. above). Since the lack of filtration gave a significant contribution of regenerated (very low DS) cellulose to the precipitated BC, the measured DS_{NMR} of these samples became very low. Furthermore, since the perpropionylated samples of some BCs prepared inhomogeneously were forming cloudy suspensions rather than clean solutions in $CDCl_3$, it must be considered that the DS_{NMR} of these BCs may be an overestimation.

Table 1
Method, ratios of reagents (synthesis conditions), DS_{NMR} and solubility properties

Sample name	Method	$DS_{\text{NMR}} \pm \sigma$	Solubility* (10 mg/ml) in 24 h at 25 °C				
			DMAc	Acetone	Benzene	9:1**	$CHCl_3$
BC32	i	0.17 ± 0.12	i	n.d.	sw	sw	sw
BC33	i	0.54	p	n.d.	p	p	sw
BC34	i	0.73	s	i	p	p	sw
BC35	ii	0.45	i	n.d.	i	i	i
BC36	ii	0.38	i	i	i	i	i
BC37	ii	0.92	s	i	i	sw	i
BC90	ii	0.95	s	i	n.d.	n.d.	n.d.
BC82	vi	0.81	s	n.d.	i	n.d.	i
BC84	vi	0.58	s/p	n.d.	n.d.	i	i
BC83	vi	0.47	i	i	i	sw	i
BC61	vi	2.24	s	n.d.	n.d.	p	n.d.
BC81	vi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BC60	vii	1.42	sw/p	sw	n.d.	sw	sw/p
BC62	vii	2.41	p	sw	p/n	n.d.	sw
BC70	v	1.59	n.d.	n.d.	n.d.	n.d.	n.d.
BC71	v	1.54	n.d.	n.d.	n.d.	n.d.	n.d.
BC72	v	1.23	sw	i	n.d.	i	i
BC56	v	1.65	sw	n.d.	i	sw	sw

BC57	v	1.16	sw	n.d.	n.d.	sw	i
BC58	v	2.53	sw	sw	i	i	i
BC63	iii	1.42	n.d.	n.d.	n.d.	n.d.	n.d.
BC64	iii	0.69	n.d.	n.d.	n.d.	n.d.	n.d.
BC65	iii	0.10	n.d.	n.d.	n.d.	n.d.	n.d.
BC66	iv	1.88	p	i	i	i	p
BC67	iv	0.51	sw	i	n.d.	i	i
BC68	iv	0.28 ± 0.12	i	i	i	n.d.	i
BC3	viii	0.50 ± 0.04	n.d.	n.d.	i	i	i
BC100	viii	1.86	s/p	n/sw	n.d.	p/sw	sw
BC101	viii	0.94 ± 0.03	s	i	n.d.	i	i
BC8	ix	1.29	s	n.d.	i	i	i
BC102	ix	2.50	s	s	s	s	s
BC103	ix	2.23	s	p	p	p/s	i

* s = soluble, p = partly soluble (turbid 'solution') or highly swollen benzyl cellulose, sw = strongly turbid suspension or partly swollen benzyl cellulose, i = insoluble, and n.d. = not determined; ** 90% benzene, 10% ethanol

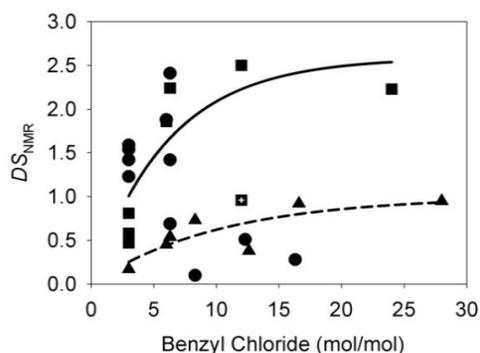


Figure 1: DS_{NMR} of benzyl chlorides produced in aqueous NaOH/urea solution (▲, dotted line), and DMSO/TBAF solution precipitated from non-filtered (●) and filtered (■, solid line) solutions. The lines show regressions according to the general equation $y = a(1 - e^{-bx})$ and are intended to guide the eye towards 'max' DS_{NMR} . BC101 is marked with a '+' sign, and is not included in the regression line calculation

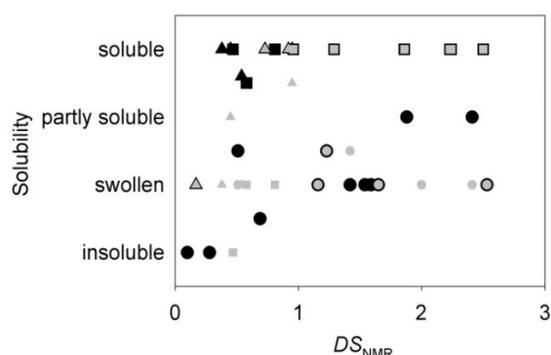


Figure 2: Solubility (10 mg/ml) as a function of DS_{NMR} for BCs precipitated from aqueous NaOH/urea solution (▲), and non-filtered (●) and filtered (■) DMSO/TBAF solutions; the solubility in DMSO (black) and pyridine (grey)

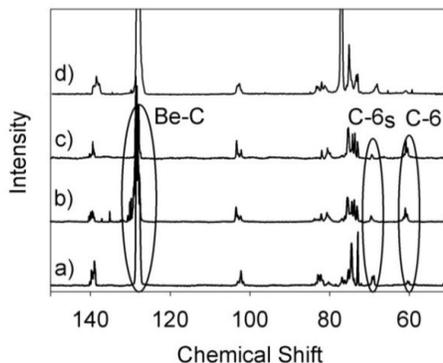


Figure 3: ^{13}C NMR spectrum of a) BC102 ($DS_{NMR} = 2.50$), b) BC37 ($DS_{NMR} = 0.92$), and c) BC82 ($DS_{NMR} = 0.81$) in D_6 -DMSO at 70 °C, and d) BC102 in $CDCl_3$. The number of scans was 70,000

In accordance with the study by Isogai *et al.*,¹⁵ some of the data indicated that more than one

addition of benzyl chloride often gave higher DS_{NMR} . In addition to their results, it was seen that

dividing a quite small addition of benzyl chloride/NaOH (aq) into even smaller additions in one case gave a much higher DS_{NMR} than a single addition did (cf. BC58 in Table 1). However, our data show that no general increase of the solubility of the BCs was achieved by dividing the additions into two or more additions.

As seen, the solubility of the homogeneously produced BCs was not strongly correlated to their DS_{NMR} values (Fig. 2 and Table 1). However, the solubility of the BCs in several solvents was dependent on the synthesis of the BCs. In particular, the removal of any solid material before the precipitation in 80% methanol was very important for the BCs synthesised in DMSO/TBAF, which is illustrated in Fig. 2. Our data indicate that BCs have a complicated solubility. Most obviously, several of our BCs were soluble in DMSO, but dissolved, or swelled, only partly in pyridine. Many of the traditionally prepared BCs studied by Okada⁹ were soluble in benzene, and benzene-ethanol mixtures with up to approximately 15% ethanol. Also, some traditionally produced BCs with low DS (≤ 1.5) were insoluble, while high DS benzyl chloride ($DS \approx 2$) was found to be soluble in several organic solvents such as CHCl_3 , for example.^{1,8} However, the high DS_{NMR} BCs synthesised by Ramos *et al.* were only partially soluble in organic solvents such as CHCl_3 .²

In our study, only one BC did dissolve in these solvents (BC102), which is in contrast to the

findings of other authors. It is likely that this high solubility is due to the combination of a very high DS and low molecular weight (cf. below).

In Fig. 2, the solubility (10 mg/ml) in DMSO and pyridine is shown as a function of DS_{NMR} for the three types of BCs. The importance of filtration of the DMSO/TBAF solution before precipitation in 2-propanol is obvious. Also, it is clear that the difference alleged by Li *et al.*³ in solubility between BC synthesised in aqueous NaOH/urea and DMSO/TBAF was non-existent, at least when the same starting material was used for the two systems. In Table 1, the solubility of the samples in other solvents is given. The BC produced in the upscaling of method *i* had a DS_{NMR} of 0.65 and was soluble in DMSO (10 mg/ml).

¹³C Nuclear Magnetic Resonance measurements

It is also interesting to evaluate whether different synthesis conditions gave different distribution of the substituents on the hydroxyl groups on cellulose. Braun and Meuret used a very laborious method that included hydrolysis and gas chromatography.¹ ¹³C NMR of the BC gives an indication of the substitution distribution with much less effort. However, since C-2 and C-3 give rise to ¹³C NMR signals that are hard to interpret, the only carbon that we easily get an understanding of is C-6.

Table 2

DS_{NMR} of three BCs, and $\langle\langle f_6 \rangle\rangle$, the degree of substitution of C-6 in the glucose unit, and the relative importance of C-6 for the DS_{NMR} for three BC samples

Name	DS_{NMR}	$\langle\langle f_6 \rangle\rangle$	$3 \cdot \langle\langle f_6 \rangle\rangle =$
BC37	0.92	0.20	87%
BC82	0.81	0.12	44%
BC102	2.50	0.66	80%

Fig. 3 shows four spectra and the assignments of the carbons of three of them ($T = 70^\circ\text{C}$ in D_6 -DMSO) are made according to Ramos *et al.*²

A separate DS of C-6 ($\langle\langle f_6 \rangle\rangle$) can be calculated from the integrals of the relative importance of C-6, to the sum of C-6 and C-6_s by Equation (2).

$$\langle\langle f_6 \rangle\rangle \approx \frac{\int \text{C-6}_s}{\int \text{C-6}_s + \int \text{C-6}} \quad (2)$$

For the three samples, this is shown in Table 2. BC102 was chosen since it had a high DS_{NMR} and was soluble in both DMSO and CHCl_3 . BC37 was chosen since it was of intermediate DS_{NMR} and prepared in aqueous urea/NaOH solution, and BC82 was chosen since it had a DS_{NMR} close to BC37, but was prepared in the DMSO/TBAF solvent system.

In this table, the last column indicates the relative importance of C-6 for the total substitution. A value of 100% represents that one third of the substituents are attached to C-6, a value of < 100% indicates that less than one third of the substituents are attached to C-6, and so on. From these data, it seems obvious that BC82 had a much lower importance for the substitution on C-6 than the other samples had. BC102 was almost fully substituted, and thus it was expected that C-6 was also almost fully substituted. Thus, comparing BC37 and BC82 indicates that the aqueous solution yielded BC samples with more homogenous distributions for the substituents. The solubility of the low DS_{NMR} BCs from both systems was similar, so there seems to be no tight connection between the solubility and the C-6 substitution ratio.

Thermochemical properties of the benzyl celluloses

Thermal stability

The decomposition onset temperatures were difficult to analyse since there was evidence of a lighter fraction, possibly a contaminant or by-products in the samples, evaporating at temperatures overlapping with those of the main thermal degradation. Therefore, the relative thermal stability was determined by comparing the temperatures of maximum weight loss rates (using the temperature at peak maximum value of the time derivative, TDG, of the TGA curve) of

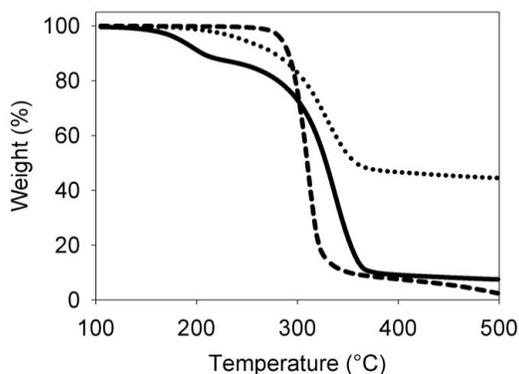


Figure 4: TGA curves of BC37 (solid line), BC66 (dotted line), and the original cellulose (dashed line)

In Fig. 5, the decomposition temperatures estimated from DTG curves are plotted against DS_{NMR} . In the data, a slight separation between the BCs precipitated from filtered and non-filtered

the main decompositions of the samples, which gave information that was considered more accurate and related to the BC properties. Fig. 4 shows weight loss for BC37 and BC66 used as examples. BC37 especially shows the early weight loss (150-200 °C) mentioned above. This weight loss may have been the result from the loss of a minor component and showed that the BCs were not completely pure.

Besides different decomposition profiles, there were also considerable differences in the amounts of solid residues remaining after heating. There are several possible explanations for that, and inorganic residues, in other words, Na-containing compounds from the benzylation, may still be in the sample contributing to the increased mass of residues. That, however, cannot account for the entire mass remaining. It is known from the literature that secondary reactions of volatiles leaving the samples are important for the char formation reactions.¹⁸ Therefore, physical properties of the sample and the conditions of the atmosphere surrounding it during decomposition will determine to a high degree both gas composition and the amount of char residue formed. Large, dense particles, as observed for some of the samples in this study, can therefore be expected to generate high and varying amounts of solids upon decomposition. The chemical effect of cellulose benzylation on char formation is unknown, (to the authors' knowledge) and is outside the scope of this study.

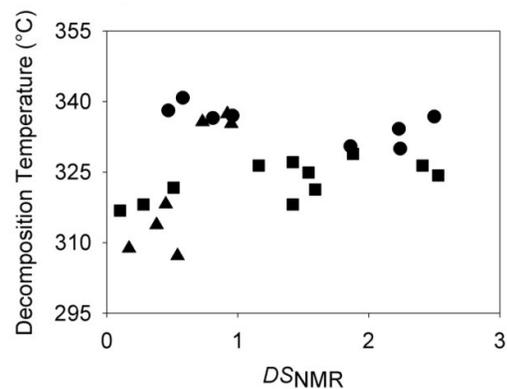


Figure 5: Decomposition temperature, estimated from the peak in the DTG curves, against the DS_{NMR} for BCs precipitated from aqueous NaOH/urea solution (▲), non-filtered (●), and filtered (■) DMSO/TBAF solutions

DMSO/TBAF can be seen. In contrast to this, the BCs made in aqueous solution show decomposition temperatures that are more scattered.

The thermal stability of low DS BCs precipitated from non-filtered DMSO/TBAF solutions had lower thermal stability than low DS BCs precipitated from filtered DMSO/TBAF solutions. This was possibly due to a mixture of moderately substituted BC and low (surface on particles only) substituted cellulose, which did not have as strong interactions as the more homogenous materials had. However, the increase in thermal stability with increasing DS_{NMR} for these samples was evident. Also, for the BCs produced in aqueous NaOH/urea solution, the decomposition temperature seemed to increase with the DS_{NMR} .

Differential scanning calorimetry and melting point measurements

DSC was used to find detailed information on phase transitions in the samples. No distinct endothermic or exothermic events were identified in the temperature range of the corresponding TGA measurements. A broad and weak endothermic event ranged over the temperature region between drying and decomposition for most of the samples. This can be interpreted as the softening (melting) of the material, but it can also be a slow evaporation of solvents or other

volatiles trapped in the sample structure. The decomposition reactions varied quite a lot in reaction heat, ranging from overall endothermic to exothermic, with evidence of competing reactions. This is, however, not surprising and probably to a great extent related to the physical properties of the sample and the char formation reactions already mentioned. If there is any effect of the benzylation on the heat from decomposition reactions, it cannot be easily separated from other events contributing to the DSC signal.

All samples with DS_{NMR} above 2.0 (BC58, BC61, BC100, BC102 and BC103) were investigated in a melting point apparatus (Electrothermal). No melting was detected for either BC58 or BC100; however, BC61 ($mp = 255\text{ }^\circ\text{C}$), BC102 ($mp = 205\text{ }^\circ\text{C}$) and BC103 ($mp = 260\text{ }^\circ\text{C}$) all melted. The melting of these BCs was very gradual, with a continuous softening under a long temperature interval (approximately $100\text{ }^\circ\text{C}$), after which a clear melting of the semi-melted soft material was seen. This behaviour could possibly explain why no distinct melting points were found in the DSC curves for these materials. Since the DSC data were not found to contribute any new information, they were not analysed or quantified in more detail.

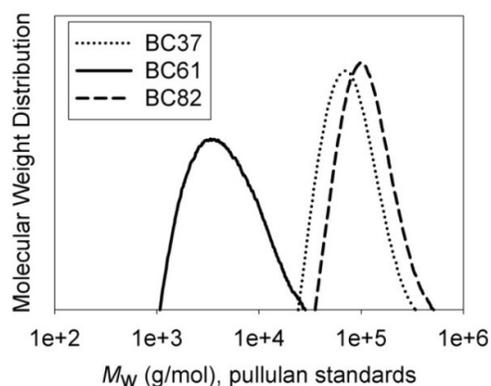


Figure 6: Molecular weight distribution (Pullulan standards) for BC37, BC61 and BC82 (chosen for mid, low, and high M_w respectively) according to the GPC analysis

Molecular weight estimations (gel permeation chromatography)

No peaks indicating aggregation of particles could be seen in the chromatograms. However, as illustrated in Fig. 6, the chromatograms varied both in elution times (molecular weights) and

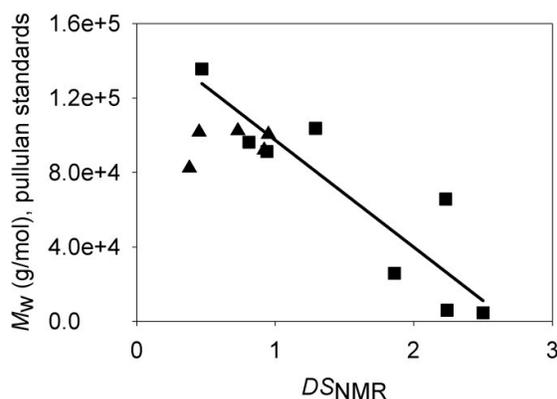


Figure 7: M_w as a function of DS_{NMR} for the soluble (10 mg ml^{-1} in DMSO) BCs, precipitated from aqueous NaOH/urea solution (\blacktriangle), and filtered DMSO/TBAF (\blacksquare) solutions. The solid line represents a linear regression (of the latter) and is added to guide the eye

width of the peaks (polydispersity). In Fig. 7, the measured M_w is plotted vs. the DS_{NMR} for the soluble (10 mg ml^{-1} in DMSO) BCs. For the samples in the figure, the M_w seemed to decrease with increasing DS_{NMR} . This was probably due to an increased harshness (more NaOH) in the

methods for synthesizing the BCs with increased DS_{NMR} , which in turn degraded the cellulose and hence resulted in lower M_w s.

As seen in these figures, the molecular weights varied considerably. According to the analysis, there was a difference of at least one order of magnitude between the low DS_{NMR} BCs (10^4 - 10^5 g mol⁻¹) and the higher DS_{NMR} BCs (10^3 - 10^4 g mol⁻¹).

The BCs with the lowest measured M_w were outside the calibration range, but within the linear range of the columns. Moreover, the pullulan standards used for the determination of the molecular weight are more similar to cellulose than to 3-O-benzylcellulose ($DS = 3$). The interactions between the hydrophobic gel of the column and the sample molecules increased with their hydrophobicity (elution time: H₂O 2,470 s; acetone 2,860 s; toluene 3,510 s). Since the hydrophobicity of the BCs increased with increasing DS_{NMR} , the elution time was expected to increase with increasing DS_{NMR} too. Because the hydrophobicity of all the BCs is not equal, a GPC system (column, eluent and calibrations standard) that suits all BCs is hard to find. Thus, the M_w numbers given in this investigation must therefore be considered to be relative, but not absolute.

The measured differences in molecular weight were too great to be explained solely by differences in hydrophobicity. Thus, we claim that there were significant differences in the molecular weights of the BCs.

Interestingly, BC102 ($DS_{\text{NMR}}=2.50$) had a much higher solubility than BC103 ($DS_{\text{NMR}}=2.23$) (cf. Table 1); although the DS_{NMR} is nearly the same, the (approximately) one order of magnitude lower M_w for BC102 could have made it much easier to dissolve. The stronger colour of BC103 also indicates that this BC is more heavily oxidized, with a significant loss in molecular weight as a result. As previously mentioned, this could possibly have been prevented by using an N₂ atmosphere during the experiments. The high DS_{NMR} of both of these BCs will affect the error in M_w in the same way (seemingly lower M_w), and the relative difference remains (although it is not certain that the numbers are correct).

CONCLUSION

An investigation of how different synthesis methods impact the product characteristics of BCs was conducted. We could propose that, using the

same starting material, BCs produced in aqueous media are soluble at lower DS_{NMR} than BCs produced in DMSO/TBAF solution. Furthermore, we found that the molecular weight (M_w) of the samples decreased with the DS_{NMR} , possibly due to the increasing amount of NaOH in the reaction. Also, the thermal stability showed a similar behaviour for the two systems with an increasing stability with the degree of benzylation for most of the samples.

We showed that soluble BCs can be produced in DMSO/TBAF solutions with aqueous NaOH as a base if filtration is applied before the precipitation. However, the low yield of such a procedure makes it less useful. If homogeneously produced soluble intermediates to high DS BCs are desired, a DMSO/TBAF system with NaOH(s) as a base is advisable. At the conditions applied, the DS_{NMR} of the BC produced in aqueous solution was always below 1, although a very high excess of benzyl chloride was applied. Nonetheless, if a DS below 1 is the target, aqueous solutions of cellulose have economic advantages. Based on our findings, it is advisable to apply this aqueous system with a benzyl chloride to cellulose ratio of approximately 6 mol mol⁻¹. Our results also allow us to recommend this system for further investigation on upscaling the production of low DS BCs, since we found that it works with a high product yield, in addition to the cellulose solvent system being considered relatively inexpensive and environmentally friendly.

ACKNOWLEDGEMENTS: We thank Bio4Energy, a strategic research environment appointed by the Swedish government, and Kungliga Skogs- och Lantbruksakademien (Royal Swedish Academy of Agriculture and Forestry), Sweden, (H12-0007-CFH) for supporting this work. Additionally, Mattias Hedenström, Department of Chemistry, Umeå University, is acknowledged for helping record ¹³C NMR spectra.

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