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Carboxymethylation of cellulose in the new solvent dimethyl sulfoxide/tetrabutylammonium fluoride

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Abstract

The new cellulose solvent dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF) was applied as reaction medium for the carboxymethylation of mercerized cellulose from sisal and cotton linters. The reaction parameters studied were the molar ratio of reagent and NaOH to anhydroglucose unit (AGU) and the addition of the NaOH either as an aqueous solution or as solid particles. Size Exclusion Chromatography results (SEC) indicated that the dissolution medium and/or derivatizing method used in the present work causes a certain depolymerization on the cellulose chains The pattern of substitution within the AGU and along the polymer chains of the carboxymethylcellulose (CMC), which was analyzed by ^{1}H NMR spectroscopy and HPLC after acidic depolymerization of the CMC, is in the order O-6 > O-2 ≥ O-3. With regard to the mole fractions of the different repeating units, samples prepared using aqueous NaOH possess a statistic content, while by using solid NaOH a deviation from statistically calculated values was observed. As a consequence of the non-statistics, the solubility in water of these samples starts at a DS 0.85, while conventionally prepared CMC are water-soluble at a DS as low as 0.4.

Keywords: Carboxymethylcellulose, CMC; Cellulose solvent; Dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate; Sisal; Cotton linters; Pattern of substitution; Size exclusion chromatography

1. Introduction

Carboxymethylcellulose (CMC) represents a widely used water-soluble derivative of cellulose, applied where thickening, suspending, stabilizing, binding, and film-forming properties are important. Commercially, CMC is produced by a so-called slurry process, i.e. by conversion of alkali cellulose in an organic liquid/aqueous NaOH with monochloroacetic acid or its sodium salt as etherifying agent. In this completely heterogeneous reaction, CMC with a degree of substitution (DS) in the range from 0.4 to 1.2 can be formed, which possess a statistic pattern of functionalization (Heinze, Erler, Nehls, & Klemm, 1994; Just & Majewicz, 1985; Reuben & Conner, 1983).

On the other hand, etherification reactions starting with a dissolved polymer were studied (Heinze et al., 1994). McCormick and Shen (1982) first applied *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) as cellulose solvent for etherification reactions. Reports on carboxymethylation have shown that, although this medium presents a number of peculiarities, e.g. the need for a high excess of reagents and a long reaction time, it is possible to prepare CMC in the presence of solid NaOH particles. As shown by Heinze and coworkers the CMC exhibits an unconventional distribution of ether groups and unconventional properties, i.e. the CMC showed a preferred substitution at position O-6, differently from commercial samples, and a block-like distribution of the carboxymethyl groups along the polymer backbone (Heinze, 1998; Liebert & Heinze, 1998a; Saake et al., 2000). Atomic force microscopy (AFM) revealed a network-like system in solution, while commercially prepared samples show 'fringed micelles' (Liebert & Heinze, 2001). These molecular and supermolecular features result in a number of new macroscopic properties, for example, different rheological and colloidal behavior (Kötz et al., 2001).

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It has been reported that the mixture of dimethyl sulfoxide (DMSO) and tetrabutylammonium fluoride trihydrate (TBAF) is a powerful solvent for cellulose. Cellulose with a degree of polymerization as high as 650 can be dissolved without any pretreatment within 15 min (Heinze, Dicke, Koschella, Kull, & Koch, 2000). This solvent has already been tested and adapted for dissolution and acylation of fast growing lignocellulosic materials isolated from sisal and cotton linters (Ass, Frollini, & Heinze, 2004; Ciacco, Liebert, Frollini, & Heinze, 2003). It proved to be more efficient than DMAc/LiCl, which was also used for the dissolution and derivatization of these cellulose samples (Ciacco, Ass, Ramos, & Frollini, 2000; Ramos, Ciacco, Assaf, Seoud, & Frollini, 2002).

In this paper, the new solvent DMSO/TBAF was applied for the carboxymethylation of mercerized sisal and cotton linters starting from a dissolved polymer. Various reaction parameters were studied, such as the molar ratio of reagent and NaOH to AGU and the addition of NaOH either as an aqueous solution or as solid particles. We report the effects of these reaction conditions on total DS, on the pattern of substitution within the AGU and on the formation of different repeating units in the polymer chains.

2. Experimental

2.1. Materials

Sisal cellulose (kindly provided by Lwarcell, Lençois Paulista—São Paulo, Brazil, degree of polymerization, DP = 640) and linters cellulose (kindly provided by Indústria Fibra S/A, Americana, São Paulo, Brazil, DP = 400) were mercerized before use. This consisted of the treatment of the polymer with 20% aqueous NaOH at 0 °C. Sisal cellulose was treated for 1 h and cotton linters for 4 h. After the required time the samples were washed in water until completely neutral and dried in a vacuum at 60 °C for 1 h. Tetrabutylammonium fluoride trihydrate (TBAF, Fluka) and sodium monochloroacetate (Merck) were used as received. Dimethyl sulfoxide (DMSO, Merck) was dried with molecular sieves (4 Å, treated at 150 °C in vacuum for 2 h before use). Sodium hydroxide (NaOH, Merck) was pulverized, dried in a vacuum for 24 h and kept in a desiccator. All reagents were of analytical grade.

2.2. Measurements

2.2.1. Determination of the cristallinity index, I_c

The crystallinity index, I_c, was determined by X-ray diffraction using a RIGAKU Rotaflex model RU-200B diffractometer. The diffractometer was operated at 40 kV, 20 mA and $\lambda(\text{Cu K}\alpha) = 1.5418$ Å. The crystallinity index was calculated using the Buschle-Diller and Zeronian equation $I_c = 1 - I_1/I_2$, where I_1 is the intensity at the minimum (between $2\theta = 18°$ and $19°$) and I_2 is the intensity of the crystalline peak at the maximum (between $2\theta = 22°$ and $23°$) (Buschle-Diller & Zeronian, 1992). The dimensions of the cellulose crystallites were determined by applying the Scherrer equation: $L(hkl) = k\lambda/(B \cos\theta)$, where L is the thickness of the crystal at the (hkl) plane of diffraction, λ is the wavelength of X-ray source, k is Scherrer's constant (=0.9), and B is the peak full-width at the half-height (Awadel-Karim, Nazhad, & Paszner, 1999).

2.2.2. Determination of the degree of polymerization, DP, and α-cellulose content

DP was measured by viscometry using an Ostwald shear dilution viscometer. The cellulose was dissolved in copper ethylene diamine (CUEN)/water (1:1, v/v) (TAPPI Press, 1990). The α-cellulose content was determined from masses of cellulose before and after treatment with 17.5% NaOH solution (1:20, w/v) according to Browning (1967).

2.2.3. Size exclusion chromatography, SEC

The average molecular weight ($\overline{M_w}$) and molecular weight distribution (MWD) of the CMC samples (0.2% polymer solution) were analyzed in a Shimadzu SCL-10A system equipped with a refractive-index detector, RID-6A. A Shodex OHpak KB-g guard column and two Shodex OHpak 806 column (300×8 mm) packed with highly cross-linked polyhydroxymetacrylate (Polymer Laboratories) were used. As mobile phase and solvent were used solutions 0.1 N $NaNO_3$ (pH = 5.7), 0.1 N $NaNO_3$ (pH = 11.5) and an acetate buffer (0.2 M sodium acetate/0.2 M acetic acid, pH = 4.5). The analyses were carried out at 35 °C, flowing at 1 mL/min under 25 kg f/cm^2. Pullulan was used as calibration standard (M_w = 1,600,000, 380,000, 212,000, 100,000, 48,000, 23,700, 12,200, 5800, 738 and 180 g/mol).

2.2.4. Characterization of CMC

HPLC analysis of the CMC samples was carried out as described by Heinze et al. (1994), but the samples were hydrolyzed with perchloric acid. CMC (0.1 g) were dispersed in 2 mL of $HClO_4$ (70%) at room temperature. After 10 min, 18 mL of distilled water were added and the mixture maintained at 100 °C for 16 h. The solution obtained was carefully neutralized with 2 N KOH and kept at 4 °C for 1 h to precipitate the $KClO_4$. The salt was filtered off and rinsed three times with distilled water. The solution obtained was reduced to approximately 3 mL and diluted with distilled water to give an exactly 5 mL sample. Chromatographic experiments were carried out at 65 °C with 0.01 N H_2SO_4 as eluent with a flow rate of 0.5 mL/min. The column used was a Bio-Rad Aminex HPX-87 H.

^{1}H NMR analyses were performed as described by Gronski and Hellmann (1987). For this purpose, the CMC samples were hydrolyzed in a mixture of 25% (v/v) D_2SO_4/D_2O (50 mg/mL) overnight at 90 °C. The spectra were acquired on a Bruker AMX 250 spectrometer at room temperature. The scan number was 16.

^{13}C NMR spectra of CMC samples were recorded in D_2O (80 mg/mL) at 70 °C on a Bruker AMX 400 spectrometer The scan number was between 20,000 and 70,000.

FTIR spectra were measured on a Bio-Rad FTS 25 PC using the KBr pellet technique (0.1%, w/w).

2.3. Synthesis

2.3.1. Dissolution of cellulose in DMSO/TBAF

Cellulose (1.0 g) was suspended in a mixture of 60 mL of DMSO and 6.6 g of TBAF (9%, w/w). The mixture was stirred for 30 min at room temperature and then for 60 min at 60 °C, resulting in a clear solution of cellulose.

2.3.2. Carboxymethylation of cellulose in DMSO/TBAF

To the solution of cellulose either a suspension of NaOH in 10 mL of DMSO or a 20% aqueous NaOH (see Table 2) was added. In a typical preparation, for sample **11** for example (Table 2), 4.94 g (123.4 mmol) of NaOH suspended in 10 mL of DMSO and subsequently 10.78 g (92.55 mmol) of sodium monochloroacetate were added under vigorous stirring leading to gelation and partly precipitation of the cellulose. The temperature was raised to 70 °C. After 4 h the mixture was cooled to room temperature and put into 300 mL isopropanol. The solid product was filtered off, dissolved in 40 mL of distilled water, neutralized with acetic acid, and precipitated into 300 mL of ethanol. After filtration the product was washed with 90% (v/v) ethanol and dried in a vacuum at 50 °C.

Degree of substitution, $DS_{HPLC} = 2.17$, was determined by HPLC analysis after complete acidic depolymerization.

The mol fractions of glucose = 0.06; 2-,3-, and 6-mono-*O*-CMG = 0.18; 2,3-,2,6-, and 3,6-di-*O*-CMG = 0.24; and 2,3,6-tri-*O*-CMG = 0.45 were determined from the HPLC as well.

^{1}H NMR (after hydrolysis in 25% D_2SO_4/D_2O) revealed partial percentage of substitution at O-6, O-2 and O-3 positions. (O-6 = 27%; O-2 = 26%; O-3 = 47%).

FTIR (KBr): 1600 cm^{-1} (ν, C=O) 1420 cm^{-1} (ν, C=O).

^{13}C NMR (D_2O): $\delta = 178$–180 ppm (C=O), 60–105 ppm (cellulose backbone).

3. Results and discussion

The characteristics of the cellulose samples (sisal **1** and cotton linters **2**) are listed in Table 1. These samples contain almost the same percentage of α-cellulose due to an alkali treatment. In the case of the sisal sample (**1**), hemicelluloses and in the case of cotton linters **2** mainly wax and pectins are extracted by this procedure.

The accessibility of solvent and/or reagent to the reactive hydroxyl groups of cellulose is determined by various structural parameters such as degree of polymerization (DP), crystallinity index (I_c), and crystallite size by a different extent (Buschle-Diller & Zeronian, 1992; Heinze, 1998; Isogai & Atalla, 1998; Lai, 1996; Heinze & Liebert, 2001). To achieve dissolution of cellulose it is necessary to disrupt the intermolecular hydrogen bonds between adjacent cellulose chains in the crystalline domains. The cellulose samples used in the present work exhibited a degree of polymerization (DP) of about 400 (**2**) and 600 (**1**), respectively. Moreover, the content of crystalline regions and the size of the crystallites are significantly different (see Table 1). The higher the I_c and crystallite size, the more difficult it is to disrupt such intermolecular bonds. However, although cotton linters has a higher I_c and crystallite size than sisal, the solubility in DMSO/TBAF of both cellulose samples was similar. In addition, no influence of the DP on the solubility appeared. This behavior confirms again the efficiency of the new solvent DMSO/TBAF. Besides, it seems that the solvent/cellulose interaction also happens to the same extent for both cellulose samples, since the reactivity under comparable reaction conditions is similar as will be shown.

As revealed by means of ^{13}C NMR spectroscopy, the dissolution of cellulose in DMSO/TBAF occurs without derivatization of the polymer. In the spectrum, exactly 6 signals for the polymer backbone appear in the range from 59.9 to 102.7 ppm at the expected chemical shift (Heinze et al., 2000). The same spectral data were obtained for cellulose dissolved in the typical non-derivatizing cellulose solvent DMAc/LiCl (Nehls, Wagenknecht, Philipp, & Stscherbina, 1994) although the spectrum of cellulose is much better resolved in DMSO/TBAF. From the comparable results it is obvious that cellulose is dissolved in DMSO/TBAF without any covalent interactions.

3.1. Carboxymethylation

The carboxymethylation of cellulose in DMSO/TBAF was carried out in a conventional way, i.e. sodium hydroxide for activation and monochloroacetate as etherifying agent were applied. In a first series of experiments, the sodium hydroxide was added as an

Table 1
Degree of polymerization (DP), content of α-cellulose, crystallinity index (I_c) and crystallite size (L_{002} and $L_{10\bar{1}}$) of mercerized cellulose samples used

Cellulose		Characteristics				
No.	Source	DP	α-Cellulose (%)	I_C	L_{002} (Å)	$L_{10\bar{1}}$ (Å)
1	Mercerized Sisal	574	97.0	0.64 ± 0.02	27 ± 2.0	31 ± 3.0
2	Mercerized Linters	400	96.0	0.73 ± 0.02	39 ± 2.0	36 ± 3.0

Table 2
Conditions and results of carboxymethylation of cellulose dissolved in dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate (9%, w/w)

Cellulose	Reaction conditions		Carboxymethylcellulose	
	NaOH	Molar ratio[a]	No	DS[b]
Sisal	Dissolved	1:5:10	**3**	1.53
Sisal	Dissolved	1:10:15	**4**	1.45
Linters	Dissolved	1:5:10	**5**	1.63
Linters	Dissolved	1:10:15	**6**	1.51
Sisal	Solid	1:1:2	**7**	0.26
Sisal	Solid	1:2.5:5	**8**	1.24
Sisal	Solid	1:5:10	**9**	1.95
Sisal	Solid	1:10:15	**10**	2.05
Sisal	Solid	1:15:20	**11**	2.17
Linters	Solid	1:1:2	**12**	0.29
Linters	Solid	1:2.5:5	**13**	0.85
Linters	Solid	1:5:10	**14**	1.87
Linters	Solid	1:10:15	**15**	2.02
Linters	Solid	1:15:20	**16**	2.01

[a] Anhydroglucose unit: $ClCH_2COONa$:NaOH.
[b] Degree of substitution (DS) determined by HPLC after hydrolytic chain degradation.

aqueous solution. From the results (Table 2, samples **3**–**6**) it is obvious that the carboxymethylation occurs very efficiently. In a one-step procedure, DS values as high as 1.6 can be realized independent of the cellulose used. In contrast, a two-step procedure is necessary to get these high DS values applying the conventional heterogeneous preparation. On the other hand, a rather high excess of etherifiying agent in the range of AGU to monochloroacetate from 1 to 5 must be applied as in the case of etherification reactions in DMAc/LiCl.

Excepting samples **7** and **12** (Table 2), insoluble in the experimental conditions considered in the present work, all the CMC samples were analyzed by SEC. The analyses were carried out using ionic aqueous solutions as eluents (aqueous 0.1 N $NaNO_3$, pH = 5.7; 0.1 N $NaNO_3$, pH = 11.5 and a buffer 0.2 M sodium acetate/0.2 M acetic acid, pH = 4.5). The eluents were changed, and also the pH value, looking for optimal experimental conditions to analyze the polyelectrolytic CMC samples. However, it can be observed that no significant differences were found, considering the results obtained using the different eluents (Figs. 1 and 2, Table 3).

It must be emphasized that a direct comparison of the molecular weight of celluloses and those of their derivatives is nor possible, due to the differences between the techniques and solvents used in each case. Viscometry/CUEN and SEC/aqueous salt solutions were chosen for celluloses and CMCs, respectively, due to lab facility.

Figs. 1 and 2 show sisal CMC curves, considering the samples prepared using 5 mol NaOH (sample **8**, Table 2) and 20 mol NaOH (sample **11**, Table 2), respectively. It can be observed, for all eluents considered, a main peak corresponding to a higher $\overline{M_w}$ fractions (retention time between 14 and 19 min, Figs. 1 and 2, Table 3). The fractions eluting in the time interval between 19 and 21 min correspond to oligomeric fragments ($\overline{M_w}$ smaller than

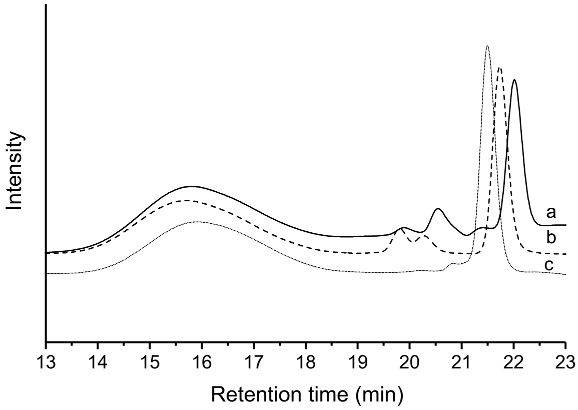

Fig. 1. Chromatograms of CMC sisal samples, in different eluents, prepared using 5 mol solid NaOH (sample **8**). The chromatograms *a*, *b* and *c* were obtained using 0.1 N $NaNO_3$ (pH = 5.7), 0.1 N $NaNO_3$ (pH = 11.5) and acetate buffer (pH = 4.5), respectively.

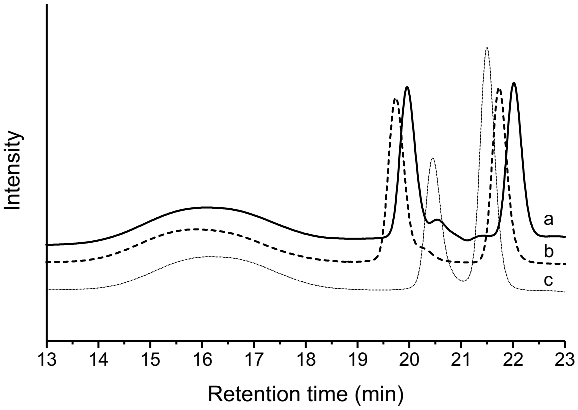

Fig. 2. Chromatograms of CMC sisal samples, in different eluents, prepared using 20 mol solid NaOH (sample **11**). The chromatograms *a*, *b* and *c* were obtained using 0.1 N $NaNO_3$ (pH = 5.7), 0.1 N $NaNO_3$ (pH = 11.5) and acetate buffer (pH = 4.5), respectively.

Table 3
Average molecular weight ($\overline{M_w}$), and polydispersity $\overline{M_w}/\overline{M_n}$ for sisal and linters CMC samples

Sample no	Peak (retention time from 14 to 19 min)								
	NaNO$_3$ 0.1 N (pH=5.7)			NaNO$_3$ 0.1 N (pH=11.5)			Acetate buffer (pH=4.5)		
	$\overline{M_w}$ (g/mol)	$\overline{M_w}/\overline{M_n}$	%	$\overline{M_w}$ (g/mol)	$\overline{M_w}/\overline{M_n}$	%	$\overline{M_w}$ (g/mol)	$\overline{M_w}/\overline{M_n}$	%
Sisal samples									
8	368,000	2.8	68	374,000	3.3	62	309,000	2.3	60
9	218,000	2.5	63	204,000	2.6	62	106,000	1.9	41
3	143,000	2.1	62	132,000	2.2	61	119,000	2.3	57
10	398,000	2.9	59	428,000	3.4	56	336,000	2.9	54
4	235,000	2.5	60	227,000	2.6	55	194,000	2.6	57
11	317,000	2.8	43	330,000	3.1	40	264,000	2.8	38
Linters samples									
13	244,000	2.4	78	240,000	2.5	68	216,000	2.6	72
14	114,000	3.9	66	109,000	3.0	63	94,000	3.4	59
5	178,000	2.3	65	165,000	2.3	60	148,000	2.4	59
15	395,000	2.5	68	426,000	2.9	64	328,000	2.6	54
6	240,000	2.3	55	230,000	2.5	54	198,000	2.5	49
16	473,000	3.4	53	534,000	3.2	53	400,000	2.6	42

1500 g/mol). This last result can be seen as an indication that the dissolution medium and/or derivatizing method causes a certain depolymerization on the cellulose chains. The higher the NaOH concentration (solid or aqueous) used during the CMC synthesis the higher the extension of depolymerization, as observed by the percentage of the main peak compared to the other ones (Table 3). The sisal and linters CMC prepared in the same reaction conditions (Tables 2 and 3) presented the same elution pattern (figures not shown).

The molecular structure of the CMC was analyzed by means of ^{13}C NMR spectroscopy of the intact polymer. A representative spectrum (Fig. 3) shows the typical peaks of the modified AGU in the range from 60 to 105 ppm as well as peaks assigned to carboxymethyl groups from 178 to 180 ppm (C=O). No hint for any side reaction can be seen.

The DS values were determined by HPLC analysis after complete acidic depolymerization. Moreover, this analytical tool reveals the mol fraction of the different repeating units, i.e. the substituted units (2-,3-, and 6-mono-; 2,3-,2,6-, and 3,6-di- and 2,3,6-tri-*O*-carboxymethylated glucoses) and unmodified glucose. Fig. 4 shows a typical chromatogram of the hydrolytically degraded CMC sample **6** as well as the assignment of the peaks.

The mol fractions analyzed by HPLC are compared with a statistic model (Fig. 5), which simulates the amount of the different repeating units. The model assumes that no preference for any OH groups exists and that the relative reactivity of the three OH groups in the AGU are constant throughout the reaction and independent of the DS of the cellulose chain or of the state of substitution at another position within the same anhydroglucose unit (Spurlin, 1939).

The good agreement between the mol fractions analyzed and the statistics indicates that the aqueous NaOH activates the polymer chain evenly. Obviously there is no reactivity variation between regions of the polymer dissolved in DMSO/TBAF.

Earlier studies show that both a totally heterogeneous reaction (alkali cellulose suspended in organic liquid) and

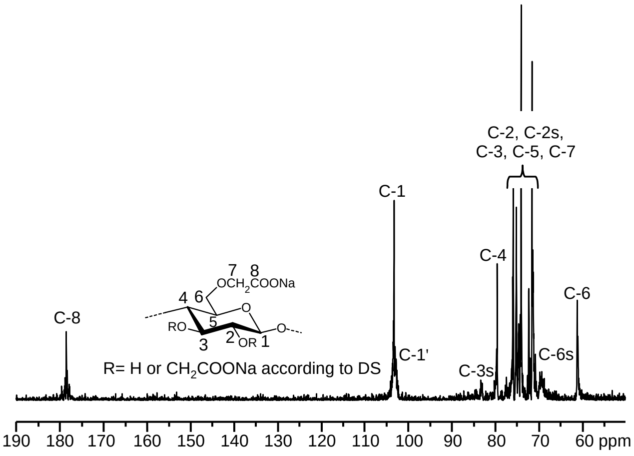

Fig. 3. ^{13}C NMR spectrum of carboxymethyl cellulose (**9**) recorded in D_2O (number of scans 23,000). The index *s* refers to substituted hydroxyl group and C-1′ means influenced by carboxymethylation at O-2.

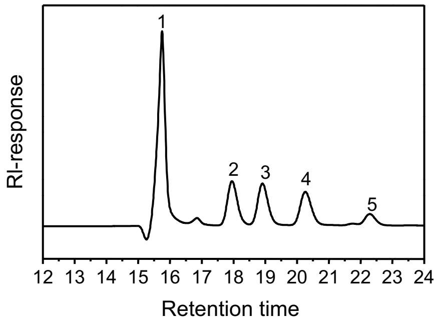

Fig. 4. Chromatogram of carboxymethyl cellulose (**6**) hydrolytically depolymerized. Peak assignment: (1) inorganic salts; (2) 2,3,6-tri-*O*-carboxymethylglucose; (3) 2,3-,2,6-,3,6-di-*O*-carboxymethylglucose; (4) 2-,3-, and 6-mono-*O*-carboxymethylglucose; (5) glucose.

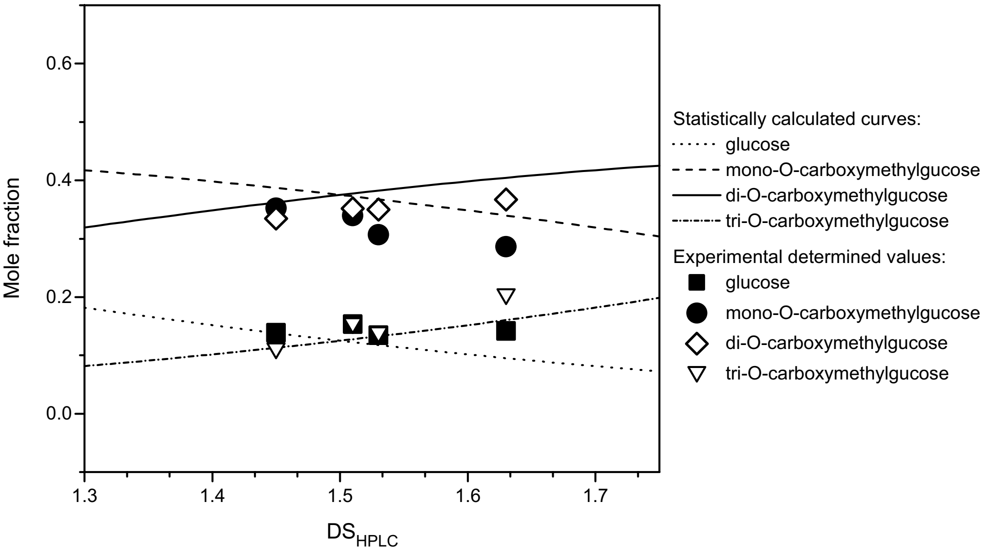

Fig. 5. Mol fraction of glucose (calculated: ⋯; found: ■); 2-,3-,6-mono-*O*-carboxymethylglucose (calculated: - - -; found: ●); 2,3-,2,6-,3,6-di-*O*-carboxymethylglucose (calculated: —; found: ◇); and 2,3,6-tri-*O*-carboxymethylcellulose (calculated: –·–·–; found: ▽) of hydrolytically depolymerized CMC samples synthesized in DMSO/TBAF using aqueous NaOH, plotted as a function of DS. The curves are calculated (see text).

a totally homogeneous reaction (cellulose dissolved in Ni[tris(2-aminoethyl)amine]$(OH)_2$) or a conversion in DMAc/LiCl using solid NaOH in the presence of water lead to products with comparable structural features, i.e. the polymers contain statistic amounts of the different repeating units (Heinze, Liebert, Klüfers, & Meister, 1999).

On the other hand, derivatization via so-called induced phase separation may produce polymers with unconventional structural features. This kind of reaction has been described for conversions starting with cellulose dissolved in DMAc/LiCl as well as with solutions of cellulose derivatives with limited hydrolytic stability (cellulose trifluoroacetate and cellulose formate) in common organic solvents, e.g. DMSO (Heinze, 1998). It is characterized by the addition of a solid water-free catalyst or reagent to the solution of the polymer in the first step, resulting in the formation of a highly reactive solid reagent/polymer interface called a 'reactive microstructure'. The conversion of the cellulose is favored in the microstructure.

In this light, the carboxymethylation reaction of cellulose dissolved in DMSO/TBAF was carried out applying sodium hydroxide as solid water-free particles. The reaction conditions and DS values (obtained by HPLC of the depolymerized samples) of the CMC samples are summarized in Table 2 (samples **7–16**).

In any case, the DS of the CMC samples obtained applying this unconventional procedure depends on the molar ratio. Applying a molar ratio of AGU: $ClCH_2COONa$ of 1:1, a DS of about 0.3 can be realized, which increases with increasing molar ratio up to 2.2. Only slight differences of the reactivity between the two different cellulose materials are found.

With regard to the substitution pattern concerning the different repeating units, comparison of the mol fractions of the various repeating units with their statistically calculated values for samples **7–16** shows a deviation from the statistics (Fig. 6). In particular for samples with DS values below 1.5 (**7**, **8**, **12**), a significantly higher amount of mono-CMG was found. Samples with DS above 1.5 possess a smaller amount of di-CMG, while the other repeating units meet the statistics, mainly those related to glucose and mono-CMG. In order to get detailed information, the synthesis and characterization of further samples with DS values up to 1.5 must be carried out. No tendency for a block-like functionalization was found, as seen in the carboxymethylation of cellulose in DMAc/LiCl using solid NaOH (Heinze, 1998; Heinze et al., 1994). The more random distribution of carboxymethyl functions along the polymer chain explains the finding that these CMC samples gave clear solutions in water for DS ≥ 0.85. In contrast, CMC with a block-like structure, synthesized in DMAc/LiCl or via hydrolytically instable cellulose intermediates, is soluble starting at a DS as high as 1.5. It is important to point out that conventionally prepared CMC with a statistic content of repeating units and an even distribution of the functional groups within the polymer chain are soluble in water at a DS as low as about 0.4. Consequently, the different functionalization pattern of CMC obtained in DMSO/TBAF applying solid, water-free NaOH influence the solubility and may have an influence on other properties, like the rheological behavior or the interaction with polycations as well, which will be investigated in further studies.

It is worth emphasizing that the reaction mixture DMSO/TBAF contains a rather large amount of water (62.7 mmol) present in the trihydrated TBAF used, which has obviously a strong influence on the pattern of substitution. It is known that cellulose dissolved in this medium is able to incorporate this water so that a special

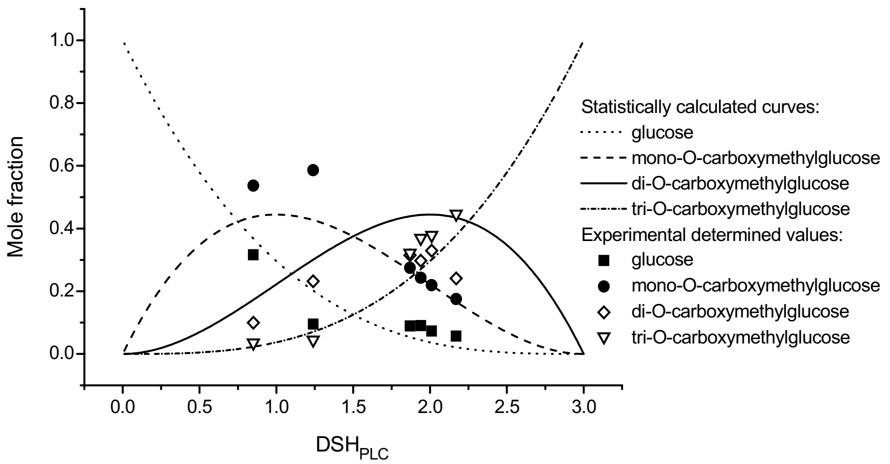

Fig. 6. Mol fraction of glucose (calculated: ···; found: ■); 2-,3-,6-mono-*O*-carboxymethylglucose (calculated: - - - found: ●); 2,3-,2,6-,3,6-di-*O*-carboxymethylglucose (calculated: — found: ◇); and 2,3,6-tri-*O*-carboxymethylcellulose (calculated: –·–·– found: ▽) of hydrolytically depolymerized CMC sample synthesized in DMSO/TBAF using solid NaOH, plotted as a function of DS. The curves are calculated (see text).

reactive microstructure can be formed by addition of solid NaOH. In contrast, traces of water can lead to products with a completely statistic distribution of ether functions along the chain synthesized under comparable etherification conditions starting with organo-soluble cellulose derivatives or cellulose dissolved in DMAc/LiCl as mentioned above.

The dependence of the total DS on the molar ratio of reagent $ClCH_2COONa$ and NaOH to AGU, either using solid NaOH or aqueous NaOH, illustrated in Fig. 7 indicates that a rather steep increase of DS appears up to a ratio of 1:5 (monochloroacetate) corresponding to 1:10 for NaOH. A further increase leads only to a small increase of DS. When using up to 10 mol of solid NaOH and up to 5 mol of monochloroacetate, a DS below 2.0 was obtained. By using 15 and 20 mole of solid NaOH and 10 and 15 mol of etherifying agent, a DS between 2.0 and 2.17 was attained in samples **10**, **11**, **15**, and **16**, which is similar to that obtained with another source of cellulose (Avicel) in the same solvent and reaction conditions (Heinze et al., 2000). These results indicate that it would be possible to control the DS by adjusting the molar ratio of reagents and NaOH to the AGU in the reaction mixture, up to a DS of 2.0 (Fig. 7).

Cellulose in DMSO/TBAF proved to be more reactive when solid NaOH was used compared to reactions either in heterogeneous slurry medium (maximum DS 1.3) or dissolved in DMSO/TBAF using aqueous NaOH (maximum DS 1.63). Therefore, addition of aqueous NaOH, instead of solid NaOH, led to lower DS when comparing with samples produced using the same molar ratio (see DS values to samples **3** and **9**; **4** and **10**; **5** and **14**; **6** and **15**, Table 2 and Fig. 7). When aqueous NaOH is added to the reaction medium, the OH^- anions are surrounded by hydration layers. Then, the access of these anions to the hydroxyl groups, in order to act as bases and then increases the nucleophilic power of the cellulose oxygen atom, requests an extra effort, since the OH^- anions are strongly interacting with the water molecules of the hydration layer. Besides, the presence of water in higher amount can facilitate the development of hydrogen bonds between cellulose hydroxyls and water, which in turns can block the interaction between OH^- and cellulose hydroxyls. Both factors can lead to a less nucleophilic site and hence to a decreased DS.

The partial substitution on the three reactive sites of the AGU is accessible by ^1H NMR spectroscopy after acidic depolymerization. A typical ^1H NMR spectrum is shown in Fig. 8. Due to the cleavage of the glycosidic linkage, the α and β anomers of the glucose and modified glucose units are generated. The two sets of doublets in the spectral region between 4.6 and 5.5 ppm are assigned to the proton at C-1 of the α-anomer (at the lower field) and to the proton at C-1 of the β-anomer (at the higher field) coupled with the single proton at C-2. Protons from the carboxymethyl group are

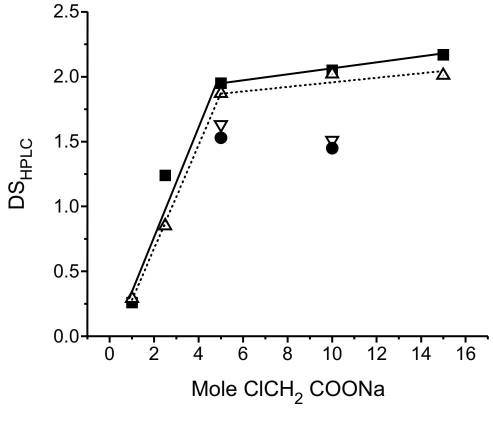

Fig. 7. Dependence of degree of substitution (DS) of carboxymethyl cellulose (CMC) on the molar ratio of $ClCH_2COONa$/anhydroglucose unit (AGU). (■) CMC from sisal/solid NaOH; (●) CMC from sisal/aqueous NaOH; (△) CMC from linters CMC/solid NaOH; (▽) CMC from linters/aqueous NaOH.

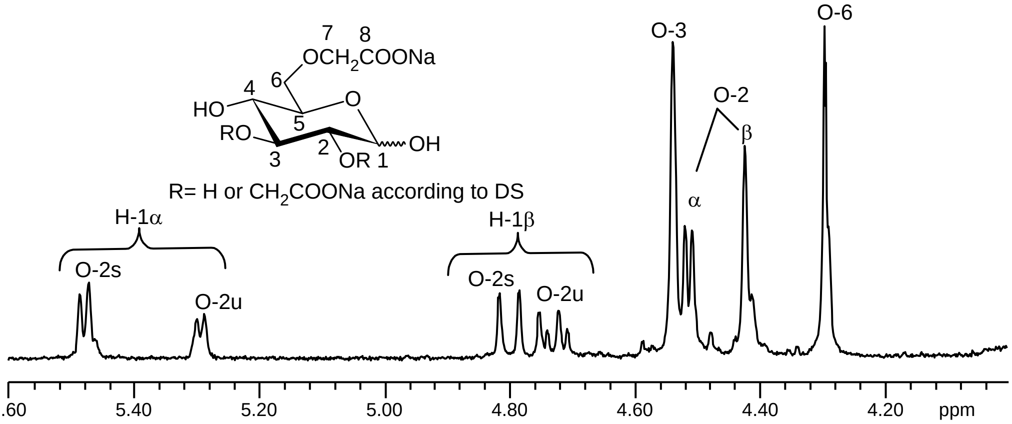

Fig. 8. ^{1}H NMR spectrum of carboxymethyl cellulose (**9**) depolymerized in D_2SO_4/D_2O. The index *s* and *u* of the signals refers to substituted and unsubstituted hydroxyl group.

observed in a spectral region between 4.2 and 4.6. The determination of the partial percentage of substitution was carried out according to Gronski and Hellmann (1987). A distribution of substituents at the level of the AGU in the order O-6 > O-2 ≥ O-3 was found. Typical results are listed in Table 4. A comparable distribution of substituents within the AGU was obtained for CMC samples prepared from a dissolved state after the induced phase-separation technique in DMAc/LiCl or using cellulose intermediates with limited hydrolytic stability in DMSO (Liebert & Heinze, 1998b). As well-known, this reactivity order is a consequence of the higher steric accessibility of the primary hydroxyl group at position 6, while the secondary OH groups show a lower reactivity due to steric reasons and may be stronger involved in interactions of the solution complex.

Table 4
Partial degree of substitution (DS) determined by ^{1}H NMR analysis after depolymerization

Sample no[a]	Partial percentage of substitution at each position (%)		
	O-2	O-3	O-6
3	29	13	58
4	35	11	54
5	36	19	45
6	32	18	50
7	32	18	50
8	31	30	39
9	30	24	46
10	27	27	46
11	27	26	47
12	27	17	56
13	33	21	46
14	26	26	48
15	30	29	41
16	29	24	47

[a] See Table 2.

4. Conclusion

It can be concluded that although linters has a higher I_c and crystallite size than sisal, the solubility in DMSO/TBAF of the two cellulose samples is similar, confirming the efficiency of this solvent. The solvent interacts to the same extent with both cellulose samples since the DS values obtained under comparable reaction conditions are almost equal.

The total DS could be controlled by varying the molar ratio of reagents and NaOH to AGU. CMC with DS values as high as 2.2 are accessible in a one-step synthesis. Besides, using solid NaOH attained a higher reactivity of cellulose in DMSO/TBAF.

The amount of the different repeating units within the polymer chain and the distribution of the carboxymethyl groups within the AGU show an order at the level of the AGU O-6 > O-2 ≥ O-3 as often found after modification of cellulose starting from a dissolved polymer. With regard to the polymer chain, the mol fractions of the different repeating units in samples prepared using solid NaOH showed a deviation from statistically calculated values to a certain extent. On the other hand, using aqueous NaOH, a statistic content of the different repeating units was obtained. Thus, it is possible to control the pattern of substitution of CMC within the polymer chain applying the new solvent DMSO/TBAF by the choice of the use of aqueous or solid NaOH.

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References

Ass, B. A. P., Frollini, E., & Heinze, Th. (2004). Studies on the homogeneous acetylation of linters cellulose in the novel solvent system tetrabutylammonium fluoride trihydrate/dimethyl sulfoxide. *Macromolecular Bioscience*, *4*, 1008–10013.

Awadel-Karim, S., Nazhad, M. M., & Paszner, L. (1999). Factors affecting crystalline structure of cellulose during solvent purification treatment. *Holzforschung*, *53*, 1–8.

Browning, B. L. (1967). *Methods of wood chemistry*, vol. 2. New York: Wiley. 499–500.

Buschle-Diller, G., & Zeronian, S. H. (1992). Enhancing the reactivity and strength of cotton fibres. *Journal of Applied Polymer Science*, *45*, 967–979.

Ciacco, G. T., Ass, B. A. P., Ramos, L. A., & Frollini, E. (2000). Acetylation of cellulose under homogeneous reactions conditions. In L. H. C. Mattoso, A. Leão, & E. Frollini (Eds.), *Natural polymers and composites* (pp. 139–145). Sao Paulo, Brazil: EMBRAPA-USP-UNESP, 139–145.

Ciacco, G. T., Liebert, T. F., Frollini, E., & Heinze, Th. (2003). Application of the solvent dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate as reaction medium for the homogeneous acylation of sisal cellulose. *Cellulose*, *10*, 125–132.

Gronski, W., & Hellmann, G. (1987). NMR-spektroskopische Charakterisierung von Carboxymethylcellulose. *Papier (Darmstadt)*, *41*, 668–672.

Heinze, T., Dicke, R., Koschella, A., Kull, A. H., & Koch, W. (2000). Effective preparation of cellulose derivatives in a new simple cellulose solvent. *Macromolecular Chemistry and Physics*, *201*, 627–631.

Heinze, Th. (1998). New ionic polymers by cellulose functionalization. *Macromolecular Chemistry and Physics*, *199*, 2341–2364.

Heinze, Th., Erler, U., Nehls, I., & Klemm, D. (1994). Determination of the substituent pattern of heterogeneously and homogeneously synthesized carboxymethyl cellulose by using high-performance liquid chromatography. *Angewandte Makromoleculare Chemie*, *215*, 93–106.

Heinze, Th., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, *26*, 1689–1762.

Heinze, T., Liebert, T., Klüfers, P., & Meister, F. (1999). Carboxymethylation of cellulose in unconventional media. *Cellulose*, *6*, 153–165.

Isogai, A., & Atalla, R. H. (1998). Dissolution of cellulose in aqueous NaOH solutions. *Cellulose*, *5*, 309–319.

Just, E. K., & Majewicz, T. G. (1985). Cellulose Ethers. In H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menger, & J. I. Kroschwitz, *Encyclopedia of Polymer Science and Engineering* (vol. 3) (pp. 226–269). New York: Wiley, 226–269.

Kötz, J., Bogen, I., Heinze, Th., Heinze, U., Kulicke, W.-M., & Lange, S. (2001). Peculiarities in the physico-chemical behaviour of non-statistically substituted carboxymethylcelluloses. *Colloids Surfaces A: Physicochemical Engineering Aspects, 183-185* , 621–633.

Lai, Y.-Z. (1996). Reactivity and accessibility of cellulose, hemicellulose, and lignins. In D. N.-S. Hon, *Chemical modification of lignocellulosic materials* (pp. 35–96). Hong Kong: Marcel Dekker, 35–96.

Liebert, T., & Heinze, Th. (1998a). Induced phase separation: a new synthesis concept in cellulose chemistry. In Th. Heinze, & W. G. Glasser (Eds.), *Cellulose derivatives: modification, characterization and nanostructures. ACS Symposium Series 688*, 61–72.

Liebert, T., & Heinze, Th. (1998b). Synthesis path versus distribution of functional groups in cellulose ethers. *Macromolecular Symposia*, *130*, 271–283.

Liebert, T. F., & Heinze, Th. (2001). Exploitation of reactivity and selectivity in cellulose functionalization using unconventional media for the design of products showing new superstructures. *Biomacromolecules*, *2*, 1124–1132.

McCormick, C. L., & Shen, T. S. (1982). Cellulose dissolution and derivatization in lithium chloride/*N*,*N*-dimethylacetamide solution. In R. B. Seymour, & G. S. Stahl (Eds.), *Macromolecular solutions: Solvent-property relationships in polymers* (pp. 101–107). New York: Pergamon Press, 101–107.

Nehls, I., Wagenknecht, W., Philipp, B., & Stscherbina, D. (1994). Characterization of cellulose and cellulose derivatives in solution by high resolution ^{13}C-NMR spectroscopy. *Progress in Polymer Science*, *19*, 29–78.

Ramos, L. A., Ciacco, G. T., Assaf, J. M., Seoud, O. A., & Frollini, E. (2002). Studies on dissolution and acetylation of microcrystalline, sisal, and cotton linter celluloses in DMAc/LiCl solvent system. In L. H. C. Mattoso, E. Frollini, & A. Leão (Eds.), *Natural polymers and composites IV* (pp. 42–50). Sao Paulo, Brazil: EMBRAPA-USP-UNESP, 42–50.

Reuben, J., & Conner, H. T. (1983). Analysis of the carbon-13 N.M.R. spectrum of hydrolyzed *O*-(carboxymethyl)cellulose: Monomer composition and substitution patterns. *Carbohydrate Research*, *115*, 1–13.

Saake, B., Horner, S., Kruse, Th., Puls, J., Liebert, T., & Heinze, Th. (2000). Detailed investigation on the molecular structure of carboxymethyl cellulose with unusual substitution pattern by means of an enzyme-supported analysis. *Macromolecular Chemistry and Physics*, *201*, 1996–2002.

Spurlin, H. M. (1939). Arrangements of substituents in cellulose derivatives. *Journal of American Chemical Society*, *61*, 2222–2227.

TAPPI Press—Viscosity of pulp (capillary viscosimeter method). (1990)*TAPPI test methods 1991*. (1990). Atlanta: Tappi Press. 1, Ref. T230 om-89.