CARBOXYMETHYLATION OF POLYSACCHARIDES – A COMPARATIVE STUDY

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Dedicated to Professor Cristofor I. Simionescu,
on his 100th birth anniversary

The present study describes the heterogeneous carboxymethylation of xylan,α-1,3-glucan, glucomannan, pullulan, curdlan, galactoglucomannan, and agarose with sodium monochloracetate (SMCA) using *iso*-propanol as slurry medium in the presence of caustic soda. Using heteropolysaccharides for the carboxymethylation, higher DS values are obtained compared to the DS of homopolysaccharides. The influence of the amount caustic soda in the reaction medium is studied. The characterization of the products obtained is performed by means of ^{13}C-NMR spectroscopy. Carboxymethylation transforms the investigated polysaccharides into water-soluble products.

Keywords: carboxymethylation, polysaccharides, xylan,α-1,3-glucan, glucomannan, pullulan, curdlan, galactoglucomannan, agarose

INTRODUCTION

Biopolymers are an important source of renewable and biocompatible polymers. Especially the highly abundant polysaccharides have come into focusfor the development of new functional polymers, because of increasing environmental concerns. Polysaccharides are divided into two groups.[1] They may belong to the group of homopolysaccharides, like cellulose, starch, chitosan or curdlan, if the polysaccharide consists of one type of repeating unit only, or to the group of heteropolysaccharides, like agarose and glucomannan, containing more than one sugar in the backbone of the polysaccharide.

The chemical modification of polysaccharides is an important tool to change the properties of naturally occurring biopolymers to develop functional polymers. In homogenous modification routes by esterification,[2] novel polysaccharide derivatives, such as polysaccharide tosylates[3-4] or carbonates,[5-10] with interesting properties, could be easily obtained. However, in most cases, the homogenous modification routes are time-consuming and expensive because of low polysaccharide concentration, which can be dissolved due to viscosity reasons, recycling of solvent, and difficult work-up procedures. Therefore, an industrial more interesting modification route is a heterogeneous pathway.

Ethers obtained from polysaccharides, especially those of cellulose, are used in different applications.[11-13] Thepolyanionic carboxymethyl (CM) derivative of cellulose (CMC) is the industrially most important ionic polysaccharide ether. CMC is used, *e.g*., in food,[14] in textile sizing,[15] as detergent,[16] in lithium sulphur batteries,[17] in conductive films,[18] as catalyst,[19] and for drug delivery.[20] Next to the broad investi-gations of CMC, there are a variety of studies about CM starch[21-23] and CM chitosan.[24-27] In contrast to these well-known carboxymethyl polysaccharides, the CM derivatives of other polysaccharides, such as xylan, curdlan, pullulan, glucomannan, or agarose, are certainly known, but significant under-represented.[28-32]

In general, carboxymethylation of polysaccharides is carried out by Williamson ether synthesis with sodium monochloracetate (SMCA) under alkaline conditions heterogeneously.[21,28,33] According to the standard protocol, the reaction is performed mostly in two

steps. The polysaccharide is activated with aqueous NaOH in an alcohol as slurry medium. Then, the nucleophilic displacement reaction with SMCA is carried out.

The CM cellulose, -starch and -chitosan indicate the huge application potential of such polysaccharide derivatives. Therefore, the aim of the present study was to take a comprehensive look at the carboxymethylation of xylan, curdlan, pullulan, glucomannan, galactoglucomannan, agarose, and the biotechnologically produced α-1,3-glucan. Moreover, the products obtained were characterized by means of ^{13}C-NMR spectroscopy to investigate the influence of the polysaccharide backbone on the resulting substituent pattern. Finally, the solubility of the carboxymethylated products was evaluated.

EXPERIMENTAL

Materials

Sodium monochloroacetate (SMCA) was purchased from Alfa Aesar. All other chemicals were obtained from Carl Roth and used as received. Xylan from beech wood was obtained from Lenzing AG (for specifications, see literature).[9] Glucomannan was obtained from Allcura Naturheilmittel GmbH(Wertheim, Germany). Pullulan was purchased from TCI Europe (Lot.: ECRWARI). Galactoglucomannan was kindly provided by the Åbo Akademi (Turku, Finland). Curdlan was obtained from Megazyme. Agarose was purchased from Carl Roth GmbH. α-1,3-Glucan was kindly provided by DuPont. The polysaccharides were dried for 3 h in vacuum at 80 °C prior to use.

Measurements

NMR spectra of polysaccharide derivatives were recorded at 25 °C in deuterium oxide, at concentrations of 60 mg/mL, with a Bruker Avance 250 MHz or a BrukerAvance 400 MHz spectrometer (using 16 scans for ^{1}H- and 20000 scans for ^{13}C measurements).

The degree of substitution (DS) of the carboxymethyl derivatives obtained from xylan, pullulan, curdlan, glucomannan, galactoglucomannan, and α-1,3-glucan was determined by HPLC analysis after hydrolysis using a JASCO device (eluent: 0.005 M H_2SO_4, flowrate: 0.5 mL/min) with a refractive index detector (RI-930), an intelligent pump (PU-980) and an Aminex® HPX-87H column from Bio-Rad Laboratories (length: 300 mm, inner diameter: 7.8 mm).[33] For HPLC analysis, the polymer (ca. 100 mg) was treated with 70% (v/v) $HClO_4$ (2 mL) within 10 minutes at room temperature. After dilution with water (18 mL), the mixture was shaken at 100 °C for 16 hours. The samples were neutralized using a 2 M KOH. Afterwards, the samples were kept at 4 °C for 1 hour to guarantee complete precipitation of $KClO_4$. In a further step, the samples were concentrated to an amount of about 4 mL. In the case of carboxymethyl agarose, a TitroLine 7800 from SI Analytics (Xylem Analytics German Sales GmbH) was used for conductivity titration to determine the DS value. Therefore, a sample (ca. 30 mg) was dissolved in water, followed by the addition of HCl (2 mL, 0.1 M). The titration of the resulting mixture was performed with a NaOH solution (0.01 M).

The degree of substitution of the carboxymethyl derivatives was calculated as follows:

- by the HPLC method:

$$DS = \frac{\sum A\%_{mono}}{\sum A\%} + \frac{2\cdot\sum A\%_{di}}{\sum A\%} + \frac{3\cdot\sum A\%_{tri}}{\sum A\%} \quad (1)$$

where DS – degree of substitution of the carboxymethyl substituent, $\Sigma A\%_{mono}$ – sum of the peak areas of monosubstituted sugar moieties, $\Sigma A\%_{di}$ – sum of the peak areas of disubstituted sugar moieties, $\Sigma A\%_{tri}$ –sum of the peak areas of trisubstituted sugar moieties, $\Sigma A\%$ –sum of the peak areas of the un -, mono -, di - and trisubstituted sugar moiety;

- by conductivity titration:

$$DS = \frac{M_{RU}}{\frac{m_P}{c\cdot V_{NaOH}} - M_{CM} + 1} \quad (2)$$

where c – concentration of NaOH titrant, DS – degree of substitution of the carboxymethyl substituent, M_{CM} – molecular weight of the carboxymethyl substituent (CM), M_{RU} – molecular weight of the repeating unit (RU), m_P – weight of sample taken for titration, V_{NaOH} – consumption of NaOH titrant.

Typical carboxymethylation of polysaccharides using xylan and SMCA (typical example, CMX6)

The reaction was performed by a slightly modified method reported in the literature.[28] Xylan (1 g; 7.56 mmol) was suspended in *i*-PrOH (30 mL). A 15% aqueous sodium hydroxide solution (0.75 g; 18.52 mmol) was added dropwise and the resulting reaction mixture was stirred for 1 hour at room temperature. Sodium monochloracetate (2.64 g; 22.68 mmol) was added subsequently. The reaction mixture was stirred for 5 h at 55 °C. The suspension was decanted and the solid residue was dissolved in water (35 mL). The solution was poured into ethanol (350 mL). The crude product was filtered, washed fourtimes with an ethanol/water mixture (8/2; each 100 mL) and once with ethanol (100 mL), and then dried in vacuum at 40 °C.

Yield: 1.18 g (5.67 mmol) CMX6 (75% of theoretical yield); DS = 1.25.

Elemental analysis found: C% 38.98, H% 3.57; calc.: C% 36.10, H% 4.03.

^{13}C-NMR (250 MHz, D_2O): δ (ppm) = 181.71, 181.23, 180.55 (COOH), 104.48 (C-1), 84.90-75.67 (C-2, C-3, C-4), 73.87 (O-**C**H_2-COOH), 65.61 (C-5).

RESULTS AND DISCUSSION

According to the literature, the carboxymethylation of polysaccharides is performed in twosteps, using sodium monochloracetate (SMCA) and aqueous NaOH.[21,28,33] The polysaccharide is suspended in a slurry medium, *iso*-propanol (*i*-PrOH) is preferred, followed by the addition of aqueous NaOH (w = 15%) in order to swell the polysaccharide. The NaOH also leads to the activation of hydroxyl groups by increasing their nucleophilicity. The nucleophilic displacement reaction at SMCA is performed at 55 °C (Fig. 1). A summary of the results of the experiments can be found in Tables 1-7.

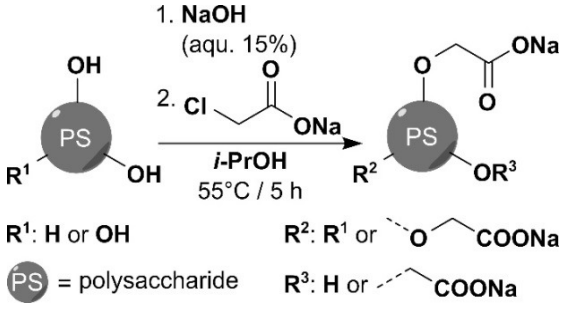

Figure 1: Reaction scheme of carboxymethylation of polysaccharides with sodium monochloracetatein the presence of caustic soda

Table 1
Influence of themolar ratio of sodium monochloracetate (SMCA) and NaOH per mol repeating unit (RU) on the degree of substitution (DS) of carboxymethyl xylan (CMX)

Reaction conditions		Sample	Results	
w_{NaOH}* (%)	Molar ratio RU:SMCA:NaOH		Yield (%)	DS
15	1:0.5:0.5	CMX1	84	0.02
15	1:1.0:1.0	CMX2	71	0.29
15	1:1.0:2.0	CMX3	81	0.43
15	1:2.0:2.0	CMX4	63	0.90
30	1:2.0:2.0	CMX5	53	0.16
15	1:3.0:3.0	CMX6	75	1.25
15	1:10.0:10.0	CMX7	71	1.32

*Mass fraction of added NaOH

Table 2
Influence of themolar ratio of sodium monochloracetate (SMCA) and NaOH per mol repeating unit (RU) on the degree of substitution (DS) of carboxymethyl α-1,3-glucan (CMG)

Reaction conditions		Sample	Results	
w_{NaOH}* (%)	Molar ratio RU:SMCA:NaOH		Yield (%)	DS
15	1:0.5:0.5	CMG1	90	0.03
15	1:1.0:1.0	CMG2	95	0.53
15	1:1.0:2.0	CMG3	77	0.60
15	1:2.0:2.0	CMG4	99	1.21
30	1:2.0:2.0	CMG5	53	0.66
15	1:3.0:3.0	CMG6	98	1.17
15	1:10.0:10.0	CMG7	81	0.83

*Mass fraction of added NaOH

Table 3
Influence of themolar ratio of sodium monochloracetate (SMCA) and NaOH per mol repeating unit (RU) on the degree of substitution (DS) of carboxymethyl glucomannan (CMGM)

Reaction conditions		Sample	Results	
w_{NaOH}* (%)	Molar ratio RU:SMCA:NaOH		Yield (%)	DS
15	1:0.5:0.5	CMGM1	90	0.02
15	1:1.0:1.0	CMGM2	88	0.43
15	1:1.0:2.0	CMGM3	88	0.86
15	1:2.0:2.0	CMGM4	78	1.53
30	1:2.0:2.0	CMGM5	82	0.17
15	1:3.0:3.0	CMGM6	98	1.79
15	1:10.0:10.0	CMGM7	71	1.21

*Mass fraction of added NaOH

Table 4
Influence of themolar ratio of sodium monochloracetate (SMCA) and NaOH per mol repeating unit (RU) on the degree of substitution (DS) of carboxymethyl pullulan (CMP)

Reaction conditions		Sample	Results	
w_{NaOH}* (%)	Molar ratio RU:SMCA:NaOH		Yield (%)	DS
15	1:0.5:0.5	CMP1	88	0.00
15	1:1.0:1.0	CMP2	85	0.26
15	1:1.0:2.0	CMP3	84	0.74
15	1:2.0:2.0	CMP4	39	1.31
30	1:2.0:2.0	CMP5	76	0.14
15	1:3.0:3.0	CMP6	88	1.47
15	1:10.0:10.0	CMP7	100	1.60

*Mass fraction of added NaOH

Table 5
Influence of themolar ratio of sodium monochloracetate (SMCA) and NaOH per mol repeating unit (RU) on the degree of substitution (DS) of carboxymethyl curdlan (CMCu)

Reaction conditions		Sample	Results	
w_{NaOH}* (%)	Molar ratio RU:SMCA:NaOH		Yield (%)	DS
15	1:1.0:1.0	CMCu1	99	0.16
15	1:1.0:2.0	CMCu2	95	0.62
15	1:2.0:2.0	CMCu3	84	0.76
30	1:2.0:2.0	CMCu4	99	0.44
15	1:3.0:3.0	CMCu5	96	0.96
15	1:10.0:10.0	CMCu6	80	1.23

*Mass fraction of added NaOH

In order to study the reactivity of different polysaccharides regarding the carboxymethylation, carboxymethyl xylan (CMX), carboxymethyl α-1,3-glucan (CMG), carboxymethyl glucomannan (CMGM), carboxymethyl pullulan (CMP), carboxymethyl curdlan (CMCu), carboxymethyl galactoglucomannan (CMGGM), and carboxymethyl agarose (CMA) were synthesized.

Influence of molar ratio of sodium monochloracetate on repeating unit

In a set of carboxymethylation reactions, the molar ratio of SMCA per mol repeating unit (RU) varied for all polysaccharides (Fig. 2a). For this investigation, a molar ratio of 1 mol aqueous NaOH per mol SMCA was used.

At a molar ratio of 0.5 mol SMCA per mol RU, the DS values reached almost zero.

Significant carboxymethylation occurred using an equimolar molar ratio of SMCA and RU. Using 1 mol SMCA per mol RU, the CM derivative of curdlan possessed the lowest DS value of 0.16 (CMCu1). At the same molar ratio, the carboxymethylation of xylan, pullulan, and agarose leads to slightly higher DS values in a comparable range of 0.22 to 0.29 (samples: CMX2, CMP2, CMA1). Higher DS values were achieved using glucomannan (CMGM2 DS = 0.43) and α-1,3-glucan (CMGM2 DS = 0.53). At the molar ratio of 1 mol SMCA per mol RU, the carboxymethylation of galactoglucomannan exhibits the highest DS value (CMGGM1).

Table 6
Influence of the molar ratio of sodium monochloracetate (SMCA) and NaOH per mol repeating unit (RU) on the degree of substitution (DS) of carboxymethyl agarose (CMA)

Reaction conditions		Sample	Results	
w_{NaOH}* (%)	Molar ratio RU:SMCA:NaOH		Yield (%)	DS**
15	1:1.0:1.0	CMA1	79	0.22
15	1:1.0:2.0	CMA2	84	0.48
15	1:2.0:2.0	CMA3	83	0.42
30	1:2.0:2.0	CMA4	98	0.49
15	1:3.0:3.0	CMA5	88	1.07
15	1:10.0:10.0	CMA6	97	1.12

*Mass fraction of added NaOH; **Determined via conductivity titration

Table 7
Influence of the molar ratio of sodium monochloracetate (SMCA) and NaOH per mol repeating unit (RU) on the degree of substitution (DS) of carboxymethyl galactoglucomannan (CMGGM)

Reaction conditions		Sample	Results	
w_{NaOH}* (%)	Molar ratio RU:SMCA:NaOH		Yield (%)	DS**
15	1:1.0:1.0	CMGGM1	60	0.83
15	1:1.0:2.0	CMGGM2	99	1.06
15	1:2.0:2.0	CMGGM3	68	1.42
30	1:2.0:2.0	CMGGM4	59	1.59
15	1:3.0:3.0	CMGGM5	63	1.74
15	1:10.0:10.0	CMGGM6	48	1.89

*Mass fraction of added NaOH; **Determined via HPLC

Using a twofold excess of SMCA per mol RU, a significant increase of the DS values was observed in all the cases. The DS of the CMA obtained was 0.48 (CMA2). Higher DS values were observed for xylan (CMX4 DS = 0.90) and curdlan (CMCu3 DS = 0.76). DS values above 1 were obtained in the case of CMG, CMGM, CMP, and CMGGM (samples: CMG4 DS = 1.21, CMGM4 DS = 1.53, CMP4 DS = 1.31, CMGGM3 DS = 1.42). A further increase of the molar ratio yields an increase of the DS values, except in the case of α-1,3-glucan. The CMG derivative obtained possesses a slightly decreased DS value, compared to the product obtained using a twofold excess of SMCA (compare CMG4 DS = 1.21 and CMG6 DS = 1.17).

A strong increase of the molar ratio to 10 mol SMCA per mol RU leads to no significant increase of the DS values of CM derivatives. In contrast to the other polysaccharides studied, the DS values of α-1,3-glucan and galactoglucomannan exhibit a significant decrease (samples: CMG7, CMGGM6). This observation could be explained by a side reaction of the SMCA with the high amount of added aqueous NaOH. At a low molar ratio, the NaOH/water is almost completely bound in the swollen polysaccharide.[34-36] There is more and more free NaOH in the reaction medium in the case of high molar ratio, which could react with the SMCA to glycolic acid. Hence, the SMCA is lost, leading to a decrease of the DS values of the products. These results indicate that the optimal molar ratio with

high DS efficiency is a threefold excess of SMCA per mol RU to prepare CMX, CMP, CMCu, CMGM, CMGGM, and CMA. A maximum of 2 mol SMCA per mol RU should be used for the preparation of CMG.

Comparison of reactivity of the polysaccharides

In order to get a reliable comparison of the reactivity of the polysaccharides, the conversion rate of the available hydroxyl groups was calculated. Therefore, the DS values obtained were normalized to the number of hydroxyl groups present per anhydrosugar unit (Fig. 2b).

Curdlan, pullulan, and agarose exhibit the lowest conversion rates in the range of 5 to 10%. The polysaccharides xylan and glucomannan possess higher reactivity (conversion ≈ 14%). With a conversion rate of 18%, α-1,3-glucan exhibits the second highest reactivity at an equal molar ratio of SMCA to RU. Galactoglucomannan shows the highest reactivity (conversion ≈ 28%) at this molar ratio. The different reactivity of the polysaccharides could be the result of different states of swelling during the activation process. Based on these results, it could be speculated that a higher degree of swelling results in better accessibility of the hydroxyl groups.

Applying a twofold excess of SMCA per mol RU, the polysaccharides studied are more reactive. CMCu and CMA possess the lowest conversion of about 23%. The reactivity of xylan, pullulan, and α-1,3-glucan is comparable, yielding products with higher conversions of around 43%. At the same molar ratio, glucomannan and galactoglucomannan exhibit the highest conversion of about 59%. A further increase of the molar ratio did not significantly affect the conversion of the polysaccharides, except that of agarose – its conversion increased from 21% to 54%.

The results indicate that the reactivity of heteropolysaccharides is high, especially at higher molar ratio of SMCA per mol RU, compared to the homopolysaccharides. The heteropolysaccharides are water soluble and generate gels in the presence of water easily.[37-39] Due to this solubility or at least high swelling in water (in the reaction medium), it could be speculated that the availability of the hydroxyl groups is significantly improved.

Influence of the amount of sodium hydroxide in the reaction medium on the degree of substitution

Due to the decrease of the DS observed at higher molar ratio of SMCA per mol RU, it could be assumed that the amount of NaOH added has an influence on the resulting DS. Furthermore, the swelling behaviour of the polysaccharides may be influenced by the NaOH. Thus, the influence of the molar ratio of NaOH to SMCA was investigated using a molar ratio of 1 mol SMCA per mol RU (Fig. 3a). In contrast to the preceding experiments, a twofold excess of NaOH per mol SMCA was applied.

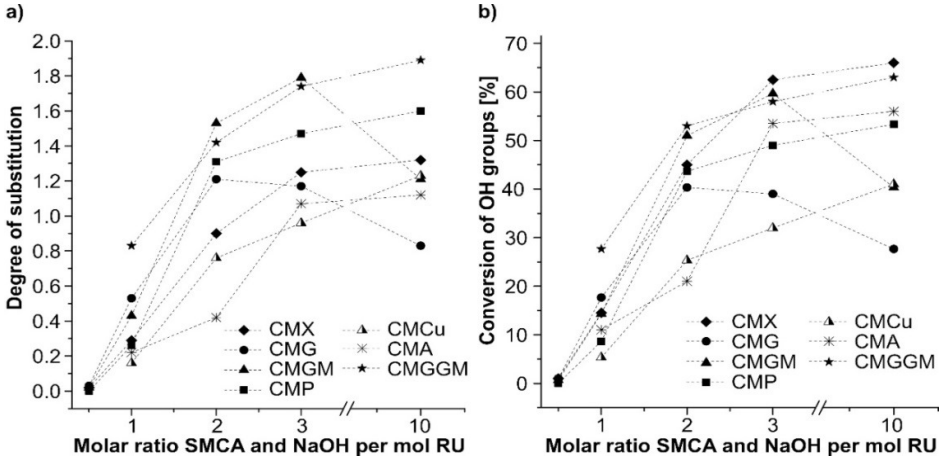

Figure 2: Degrees of substitution of different carboxymethyl (CM) polysaccharides (a) and the conversion of available hydroxyl groups per anhydrosugar unit (b) obtained by the conversion of different polysaccharides with sodium monochloracetate (SMCA) and aqueous NaOH using varying molar ratios (X: xylan, G: α-1,3-glucan, GM: glucomannan, P: pullulan, Cu: curdlan, A: agarose, GGM: galactoglucomannan)

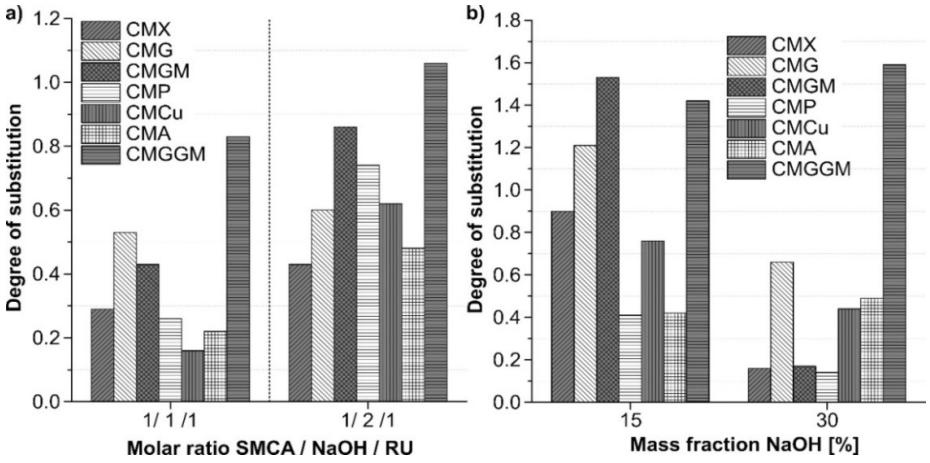

Figure 3: Influence of sodium hydroxide in the reaction medium on the degree of substitution (DS) of carboxymethylated (CM) polysaccharides (X: xylan; G: α-1,3-glucan; GM: glucomannan; P: pullulan; Cu: curdlan; GGM: galactoglucomannan; A: agarose); a) DS values of the obtained CM polysaccharides using 1 mol NaOH per mol sodium monochloracetate (SMCA) or 2 mol NaOH per mol SMCA for a molar ratio of SMCA to repeating unit (RU) of 1:1; b) Influence of a strong increase of the mass fraction of the used aqueous NaOH on the carboxymethylation using 2 mol SMCA per mol RU

For all the polysaccharides studied, a significant increase of the DS could be observed. Curdlan showed the strongest increase, the DS nearly quadrupled from 0.16 to 0.62 (CMCu2).

The reason is obviously the better swelling of the polysaccharides in the presence of a higher amount of NaOH at an equal molar ratio of SMCA to RU, as well as the increased nucleophilicity of the hydroxyl groups. To sum up, at a low molar ratio of SMCA per mol RU, an increased molar ratio of NaOH per mol SMCA leads to products of higher DS values. However, as seen above at high molar ratio of SMCA per mol RU, an excess of NaOH should be avoided, because of a pronounced side reaction of the SMCA.

Further, the influence of the concentration of the aqueous NaOH was investigated. Therefore, the concentration of the caustic soda was increased from 15% to 30% using 2 mol NaOH and SMCA per mol RU (Fig. 3b). Except the conversion of galactoglucomannan, the results indicate clearly that the DS values significantly decreased in all the cases. Inefficient swelling of the polysaccharides may be assumed because of lack of water in the reaction mixture. Thus, the hydroxyl groups are less available. Moreover, the behaviour observed for galactoglucomannan could be traced back to the fact that this polysaccharide is very well water-soluble. Thus, a small amount of water is sufficient for sufficient swelling. Although NaOH and water are important for the success of the carboxymethylation of polysaccharides, the concentration has to be controlled to avoid side reactions of the SMCA, which yield a strong decrease of reaction efficiency.

Characterization

Detailed 2D NMR investigations of the CM polysaccharides were not possible, because the polymers possess short relaxation time. Therefore, the assignment of the signals of the ^{13}C NMR was performed using data from the literature.[28,30,40-43]

The ^{13}C NMR signals related to C=O moieties of the carboxyl group of the CM substituent appear at a chemical shift around 176 ppm for all the CM derivatives (Fig. 4). This signal is split, indicating that the carboxymethylation occurred at different position within the RU of the polysaccharide backbone. The signal of C-atoms of position 1 possessa chemical shift of around 100 ppm. As expected, there are three signals in the case of pullulan caused by three different types of linking of the sugar units. Due to the two different sugars in agarose, there is also a splitting of the signals related to position 1. The splitting of the signals of position 1 caused by the two

different sugars in the backbone is suggested only because of the low resolution of the spectra of the two glucomannans. The ^{13}C NMR signal at a chemical shift of around 70 ppm is assigned to the methylene group of the CM substituent. Unfortunately, these signals overlap with various signals of the backbone of the polysaccharides. Therefore,but also because of the low resolution, no further information about the substitution pattern could be obtained. The signals assigned to the C-atoms of position 6 or 5 of xylan appear at a chemical shift of around 61 ppm. The signal related to position 6 of CMP is split with an additional signal appearing at a chemical shift of 67 ppm.

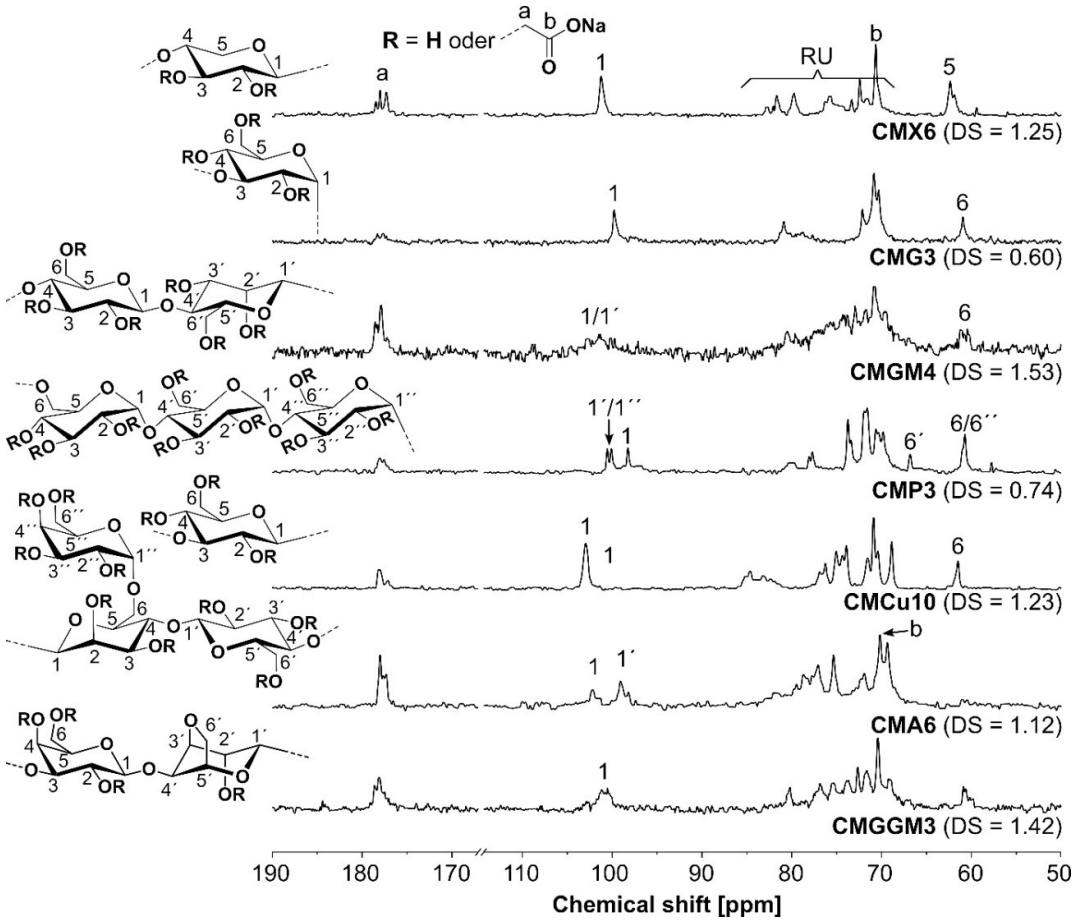

Figure 4: ^{13}C-NMR spectra of carboxymethyl (CM) polysaccharides recorded in D_2O (X: xylan; G: α-1,3-glucan; GM: glucomannan; P: pullulan; Cu: curdlan; A: agarose; GGM: galactoglucomannan)

Table 8
Starting degree of substitution (DS) of solubility in water of carboxymethyl polysaccharides

Polysaccharide backbone	Starting DS
Xylan	0.3
α-1,3-Glucan	0.8
Glucomannan	0.7
Pullulan	-*
Curdlan	0.3
Galactoglucomannan	0.6
Agarose	1.3

*Soluble even unmodified

The introduction of the CM substituent significantly improves the solubility of the polysaccharides in water (Table 8). CMX and CMCu are water-soluble starting at a DS of 0.3. The CMGGM possess water-solubility starting from a DS value of 0.6. At slightly higher DS value, CMGM (DS = 0.7) and CMG (DS = 0.8) become soluble in water. CMP is equally soluble as unmodified pullulan. Thus, all the CMP derivatives are water-soluble. Using agarose for the carboxymethylation, the water-solubility only starts at a DS value of 1.3. Due to the gel forming properties of agarose, the CMA derivatives form gels below this DS value.

The water-solubility of CMX and CMCu is slightly enhanced compared with the well-known CMC, whose water-solubility starts at a DS value of 0.4.[44] Due to the natural water-solubility of pullulan, the solubility of CMP is significantly better than that of the cellulose derivative. The other polysaccharide investigated possesses a significantly worse water-solubility than that of CMC.

CONCLUSION

The studies about the carboxymethylation of different polysaccharides conducted in the present work indicate that heteropolysaccharides possess higher reactivity under heterogeneous reaction conditions using 2-propanol as slurry medium. There is a significant effect of the concentration of the aqueous NaOH in the reaction medium on the DS values obtained. The CM polysaccharides are water-soluble and will be studied in terms of their viscosity profile in aqueous solution. Moreover, it turned out that the carboxymethylation of the polysaccharides studied may be carried out on a larger scale, providing novel functional bio-based polymers with properties controlled by the backbone for a wide range of applications, which is under investigation now.

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