Carboxymethyl Xylan - Control of Properties by Synthesis

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Summary: The hemicellulose xylan is a polysaccharide that occurs in nature in enormous amount in various one year- and perennial plants having different structures and molecular masses. Versatile ways to generate bio-based functional polymers result from the chemical modification of this biopolymer. In our research, xylans from various resources like birch-, beech-, and eucalyptus wood and from oat husk, rye bran, and corn cob were used to investigate the important method of carboxymethylation in detail. Different activation procedures were elaborated to synthesize carboxymethyl xylan. One step reactions lead to products with a degree of substitution (DS) from 0.13 to 1.22 in dependence on the molar ratio of anhydroxylose unit (AXU) to reagent. Two step syntheses yielded DS values up to 1.65. Carboxymethyl xylans are water soluble at a DS of 0.3. The solutions have different clearness depending on the provenience. NMR spectroscopy and HPL chromatography were applied to characterize the carboxymethyl xylans in detail.

Keywords: carboxymethylation; HPLC; NMR; properties; xylan

Introduction

Xylans constitute 25–35% of the dry biomass of woody tissues of dicots and lignified tissues of monocots and occur up to 50% in some tissues of cereal grains. Xylans of all higher plants possess β-(1 → 4) linked xylose units as the backbone, usually substituted with sugar- and *O*-acetyl groups. In the wood of dicots, only the type containing single side chains of 2-linked 4-*O*-methyl-α-D-glucopyranosyl uronic acid units was found. Arabino-(glucurono)-xylan (AGX) types containing side chains of 2-*O*-linked α-D-glucopyranosyl uronic acid units and/or its 4-*O*-methyl derivative and 3-linked α-L-arabinofuranosyl units are typical for lignified tissues of grasses and annual plants. Neutral arabinoxylans (AX) substituted at position 3 and/or at both position 2 and 3 of the anhydroxylose units (AXU) by α-L-arabinofuranosyl residues, represent the main xylan component of cereal grains.[1]

Potential resources for the isolation of xylans are by-products in forestry and the pulp and paper industries (wood chips, wood meal and shavings), where 4-*O*-methylglucuronoxylans (GX) and AGX comprise 25–35% of the biomass as well as annual crops (straw, stalks, husk, hulls, bran), which contain AX and AGX. A typical example is the hemicellulose from the viscose process.[1,2] A new extraction method to isolate xylan from paper pulp uses the complex compound [Ni(tris(2-aminoethyl)amine)$(OH)_2$] (Nitren) in aqueous solution.[3,4]

Carboxymethylation of polysaccharides is one of the most versatile functionalization procedures as it provides access to bio-based materials with valuable properties like metal ion induced gel forming well studied for cellulose and starch.[5,6] Up to now, only a few papers describe carboxymethyl xylan (CMX) using AGX from corn cob, AX from oats and rice, and GX from

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beech wood with a degree of substitution (DS) lower than 1.[7–9] In addition, NMR spectroscopy related CMX as by-product of the carboxymethylation of pulp or lignocellulosic materials.[10,11] The distribution of the substituents in the AXU of commercial carboxymethyl cellulose (CMC) samples from birch Kraft pulp with a content of about 20% CMX was studied by Niemelä and Sjöström by gas-liquid chromatography and mass spectrometry.[12] Details about the reactivity of xylan regarding the carboxymethylation under different conditions and information about structure-property-relationship are still missing.

The present paper describes the carboxymethylation of xylans from different sources applying different reaction conditions. Moreover, the relationship between selected properties of the CMX prepared and the synthesis path are discussed.

Experimental

Materials

Birch xylan (sample **1,** M_w 13000 g/mole) purchased from Roth (Karlsruhe, Germany) was bleached with ClO_2 and washed with methanol. It had a water content of 6%. Paper pulp of birch wood and eucalyptus wood was extracted with Nitren yielding xylan **2** (M_w 13000 g/mole) and **3** (M_w 13000 g/mole). Xylan **4** (M_w 21400 g/mole) was isolated from oat husk (all provided by J. Puls, Federal Research Centre of Forestry and Forest Products, Institute of Wood Chemistry and Chemical Technology of Wood, Hamburg, Germany). Hardwood xylan from beech (**5**, from the viscose process M_w 5300 g/mole) and one year plant xylans from rye bran (**6**, M_w 87800 g/mole), and corn cob (**7**, M_w water insoluble (wis) part 25000 g/mole, M_w water soluble (ws) part 23500 g/mole) were provided by A. Ebringerova, Center of Excellence, Slovak Academy of Sciences, Institute of Chemistry, Bratislava, Slovakia. NaOH and sodium monochloroacetate (SMCA) were obtained from FLUKA. 2-Propanol, ethanol, and methanol were reagent grade chemicals.

Measurements

The DS of the carboxymethyl groups was determined after hydrolytic chain degradation both by ^{1}H NMR spectroscopy (DS_{NMR}) and HPLC (DS_{HPLC}) as known from the carboxymethyl cellulose and carboxymethyl starch analysis.[10,13–15]

The polymers (100 mg) were hydrolyzed with 1.5 ml 25% D_2SO_4 (in D_2O) at 85 °C for 1 h before the ^{1}H NMR measurements. The ^{1}H NMR spectra were measured on a 250 MHz spectrometer (AVANCE 250, BRUKER, Rheinstetten, Germany) at room temperature.

For HPLC, 100 mg polymer was hydrolyzed with 2 ml 70% (v/v) $HClO_4$ within 10 min at 25 °C and after dilution with 18 ml water for 16 h at 100 °C. The samples were carefully neutralized with 2 M aqueous KOH solution. To guarantee a complete precipitation of $KClO_4$, the samples were kept at 4 °C for 1 h and subsequently the solution was reduced to ~4 ml. The samples (20 μl) were analyzed by means of HPLC (KNAUER, Berlin, Germany): column 1 Phenomenex Rezex ROA, column 2 Bio-Rad Aminex HPX-87H, 0.5 ml/min, 0.05 M H_2SO_4, an intelligent pump (KNAUER HPLC pump 64), a differential refractometer (KNAUER), and HPLC software (BOR-WIN).

^{13}C NMR spectra of the intact polymer were acquired in D_2O at room temperature on a BRUKER AVANCE 400 spectrometer.

The rheological investigations of aqueous solutions of the CMX (5%) were carried out with a Rheostress RS 150 (HAAKE, Karlsruhe, Germany).

The surface tension of the aqueous solutions (1%) was detected by a tensiometer K 100 (KRÜSS, Hamburg, Germany) using the plate method with a platinum plate.

The turbitity of the aqueous CMX solutions (1%) were measured with a Turbiquant 3000 IR (MERCK, Darmstadt, Germany).

Complete Heterogeneous Preparation of CMX

For a typical synthesis of CMX, 5 g (37.8 mmole) of xylan was suspended in 150 ml 2-propanol, 10 ml of 15% aqueous NaOH solution (1.51 g, 37.8 mmole) was added and the reaction mixture was vigorously stirred at room temperature for 1 h. 4.39 g (37.8 mmole) SMCA was added and the temperature of the reaction bath was raised to 55 °C. After 5 h, the product was filtered off, suspended in 80% (v/v) aqueous methanol, neutralized with diluted acetic acid and washed 5 times with 100 ml ethanol. The product was dried at 60 °C in vacuum. DS_{NMR} 0.39 (**11**), yield 6.03 g (97%).

For multi-step carboxymethylation, the synthesis procedure was repeated in a similar procedure 2 or 3 times with a molar ratio of 1.0:10.0:10.0 (modified AXU: SMCA:NaOH).

Preparation of CMX Starting with Dissolved Xylan

For a typical synthesis, xylan (5 g, 37.8 mmole) was dissolved in 25 ml of 25% aqueous NaOH (6.25 g, 156.2 mmole). 35 ml 2-propanol were added and the mixture was vigorously stirred for 30 min at 30 °C. 4.39 g (37.8 mmole) SMCA were added and the temperature was raised to 65 °C for 70 min. The reaction mixture was neutralized with diluted acetic acid, the gel-like polymer was precipitated with ethanol, washed with 100 ml 65% aqueous ethanol (v/v), and 4 times with 100 ml ethanol. The product was dried at 60 °C in vacuum. DS_{NMR} 0.49 (**18**), yield 6.08g (93%).

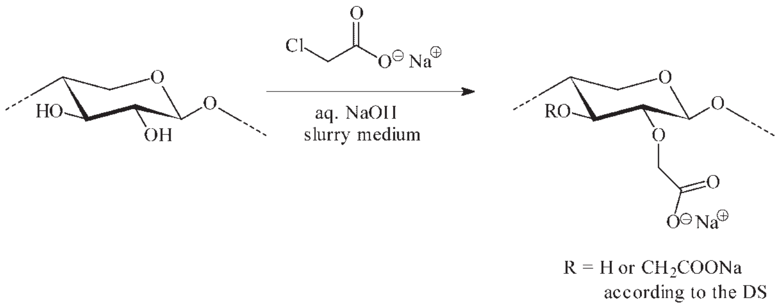
For multi-step carboxymethylation, the synthesis procedure was repeated in a similar procedure 2 or 3 times with a molar ratio of 1.0:4.0:4.1 (modified AXU:SMCA:-NaOH).

Results and Discussion

Completely Heterogeneous Synthesis

For detailed studies of the carboxymethylation of the biopolymer, the ClO_2-bleached birch xylan (GX, **1**) was used. The DS of the CMX was determined by means of ^1H NMR spectroscopy after chain degradation using 25% D_2SO_4. The carboxymethylation was carried out in a typical procedure, i.e., the xylan was slurried in an alcohol or a mixture with toluene (Scheme 1). Aqueous NaOH was used to activate the polymer. The reaction with SMCA was carried out at 55 °C for 5 h.

The DS values reached in this totally heterogeneous reaction depend on the slurry medium (Figure 1). A mixture of ethanol/toluene (1:1) and ethanol as slurry medium leads to comparable DS_{NMR} values of 0.59 (**8**) and 0.58 (**9**) while 2-propanol yields a significant increase of the DS to 0.91 (**10**). Therefore, further studies of the heterogeneous carboxymethylation of xylan under varying conditions were performed with 2-propanol as slurry medium.



Scheme 1.
Carboxymethylation of an idealized xylan structure.

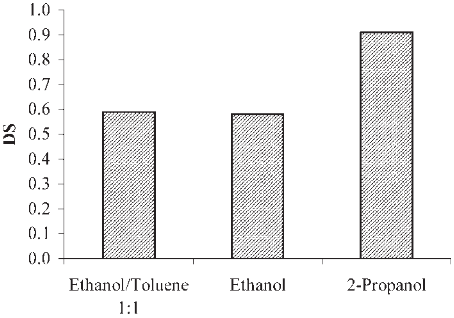


Figure 1.
Degree of substitution (DS) dependent on the slurry medium (heterogeneous carboxymethylation after activation with 15% aqueous NaOH, molar ratio of 1.0:2.0:2.0 (anhydroxylose unit (AXU):sodium monochloroacetate (SMCA):NaOH).

Figure 2 shows the dependence of the DS on the molar ratio AXU:SMCA by using 15% aqueous NaOH and 1.0 mole SMCA per mole NaOH. An increase of the molar ratio SMCA to AXU leads to an increase of the DS. Applying a ratio of 1.0 mole SMCA/mole AXU, a DS_{NMR} of 0.39 (**11**) was realized. At a molar ratio of 1.0:1.5:1.5 (AXU:SMCA:NaOH), the DS decreases to 0.23 (**12**). Most of SMCA does not dissolve in the reaction mixture used to synthesize **12**. An increase of the molar ratio to 2.0 mole and 3.0 mole SMCA/mole AXU leads to products of an increased DS of 0.91 (**10**) and 1.04 (**13**). A further increase of the molar ratio, however, yields no higher DS values.

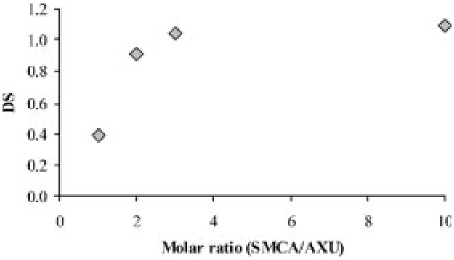


Figure 2.
Dependence of the degree of substitution (DS) on the molar ratio of anhydroxylose unit (AXU):sodium monochloroacetate (SMCA), (heterogeneous carboxymethylation in 2-propanol using 15% aqueous NaOH).

The DS of the CMX could be controlled by the molar ratio of the NaOH/AXU and the concentration of the NaOH. Thus, an increase of the molar ratio of NaOH/AXU to 2.0:1.0 leads to an increase of the DS to 0.49 followed by a decrease of the DS to 0.29 at a molar ratio of 3.0:1.0 (NaOH:AXU) compared to 0.39 (**11**) (NaOH:AXU, 1.0:1.0). The optimal concentration of the aqueous NaOH solution is 15% for the activation of the xylan. An increase of the concentration of the aqueous NaOH to 20% and 30%, respectively, yields a decrease of the DS due to a faster hydrolysis of the SMCA.

Synthesis Starting with the Dissolved Polymer

An alternative synthesis procedure starts with a xylan dissolved in 25% aqueous NaOH followed by the addition of the slurry medium. The reaction was carried out for 70 min at 65 °C. A comparison of different slurry media under these conditions shows that the use of 2-propanol yields CMX with the highest DS value (Figure 3).

The use of ethanol/toluene (1:1) and ethanol as slurry medium or the reaction without any slurry medium leads to comparable DS_{NMR} values of 0.57 (**14**), 0.58 (**15**) and 0.61 (**16**) while 2-propanol results an increase of the DS to 0.68 (**20**) using a molar ratio of 1.0:2.0:4.1 (AXU:SMCA:NaOH). An increase of the molar ratio leads to an increase of the DS in the slurry medium studied. Figure 4 shows the dependence of the DS of the carboxymethylation starting with dissolved xylan on the molar ratio of AXU:SMCA using 2-propanol as slurry medium (CMX **17**–**22**).

A decrease of the concentration of the aqueous NaOH to 15% leads to a decrease of the DS of about 0.1 unit compared with those in the presence of 25% aqueous NaOH independent of the slurry medium.

To get products of higher DS, a consecutive reaction is appropriate. That means the carboxymethylated xylan was reacted again with SMCA. Independently of the reaction procedure, a two time

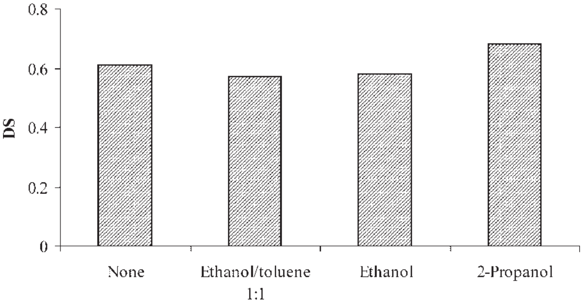


Figure 3.
Degree of substitution (DS) in dependence on the slurry medium as a result of the carboxymethylation starting with a dissolved xylan in 25% aqueous NaOH and a molar ratio of 1.0:2.0:4.1 (anhydroxylose unit (AXU):sodium monochloroacetate (SMCA):NaOH).

carboxymethylation leads with an excess of SMCA to DS values up to 1.66. After 3 reaction steps, nearly a complete functionalized CMX is obtained.

Carboxymethylation of Different Xylan Types

As mentioned, the structure of xylan depends on the source and isolation procedure.[1–4] To get information about the reactivity of different xylans, the carboxymethylation under comparable conditions was investigated. Table 1 shows the results of the heterogeneous reaction and the carboxymethylation starting with the dissolved polymer of xylans from different sources. The xylans studied are GX from hardwood like birch (**1**, **2**), eucalyptus (**3**) and beech (**5**), AGX from corn cob (**7**) and AX from oat husk (**4**) and rye bran (**6**), (Figure 5).

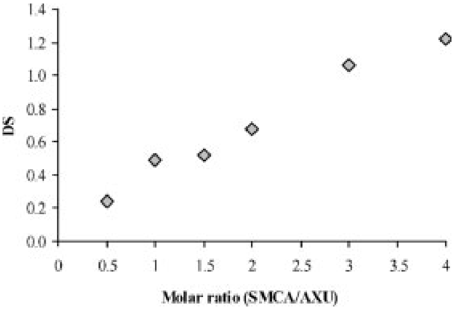


Figure 4.
Dependence of the degree of substitution (DS) on the molar ratio of anhydroxylose unit (AXU):sodium monochloroacetate (SMCA) of the carboxymethylation starting with dissolved polymer and 2-propanol as slurry medium. (CMX **17**: DS_{NMR} 0.24, CMX **18**: DS_{NMR} 0.49, CMX **19**: DS_{NMR} 0.52, CMX **20**: DS_{NMR} 0.68, CMX **21**: DS_{NMR} 1.06, CMX **22**: DS_{NMR} 1.22).

The heterogeneous carboxymethylation leads to products with $DS > 1.0$ independently of the xylan type (Table 1). The functionalization in position 2 is higher than in position 3 in all cases. The highest DS (1.30) was detected for CMX **28** obtained from the water insoluble AGX **7** with a very high content of xylose and a low content of arabinose and uronic acid. Starting with xylan dissolved in 25% NaOH and precipitation with 2-propanol, the obtained CMX have a DS to 1. Mostly the completely heterogeneous conversion yields higher DS values. Figure 6 shows ^{1}H NMR spectra of CMX of different xylans after chain degradation with 25% D_2SO_4. The signals for the protons of the CM substituents in position 2 and 3 can be identified. Additionally, the signals of the protons at C1 (H-1α and H-1β) can be detected in dependence on the sugar unit useful for the DS calculation. In the region of the H-1 signals, the peaks for the H-1 of the arabinose units are found depending on the configuration of the C-1 atom.

Properties

The CMX are water soluble starting at a DS of 0.3 leading to slightly turbid solutions.

5% solutions possess higher nephelometric turbidity units (NTU), (Table 2).

Table 1.
Degree of substitution (DS) and partial DS of carboxymethyl xylan obtained from different sources applying 3 mole sodium monochloroacetate (SMCA) per repeating unit (see Experimental).

Source	Type	Completely heterogeneous reaction				Starting with dissolved xylan			
		$\mathrm{DS}_{\mathrm{NMR}}$				$\mathrm{DS}_{\mathrm{NMR}}$			
		No.	*O*-2	*O*-3	Σ	No.	*O*-2	*O*-3	Σ
Birch **1**	GX[c]	**13**	0.55	0.49	1.04	**21**	0.57	0.49	1.06
Birch **2**	GX[c]	**23**	0.68	0.47	1.15	**30**	0.49	0.40	0.89
Eucalyptus **3**	GX[c]	**24**	0.67	0.52	1.19	**31**	0.51	0.40	0.91
Beech **5**	GX[c]	**25**	0.69	0.57	1.26	**32**	0.52	0.46	0.98
Oat husk **4**	AX[d]	**26**	0.65	0.47	1.12	**33**	0.54	0.29	0.83
Rye bran (wis)[a] **6**	AX[d]	**27**	0.66	0.59	1.25	**34**	0.50	0.38	0.88
Corn cob (wis)[a] **7**	AGX[e]	**28**	0.72	0.58	1.30	**35**	0.59	0.38	0.97
Corn cob (ws)[b] **7**	AGX[e]	**29**	0.64	0.40	1.04	**36**	0.59	0.32	0.91

[a] water insoluble
[b] water soluble
[c] 4-*O*-methylglucuronoxylan
[d] arabinoxylans
[e] arabino-(glucurono)-xylan

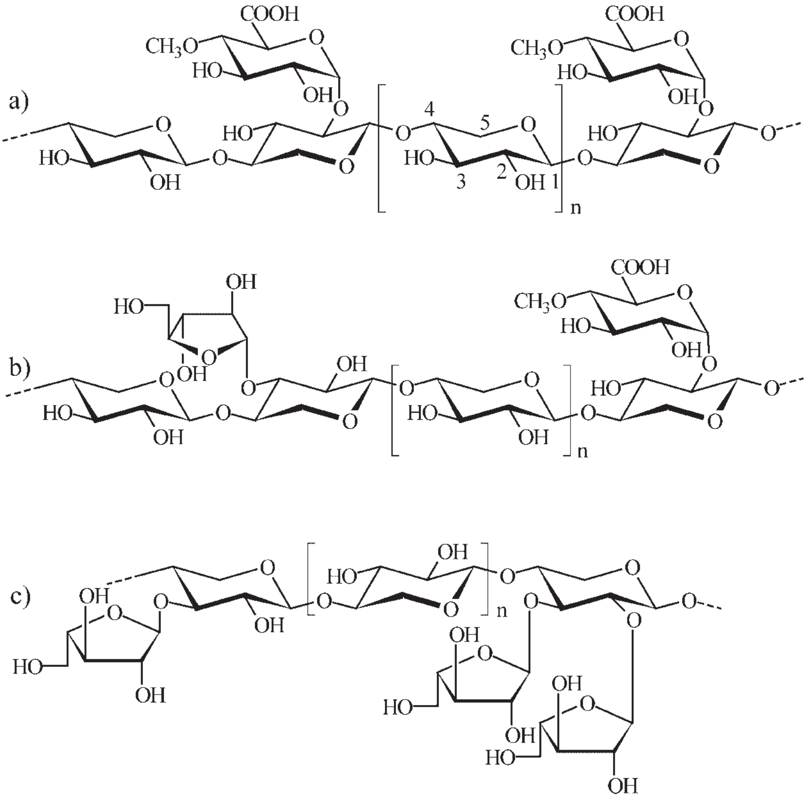


Figure 5.
Structures of xylans: a) 4-*O*-methylglucuronoxylan (GX), b) arabino-(glucurono)-xylan (AGX), c) arabinoxylans (AX).

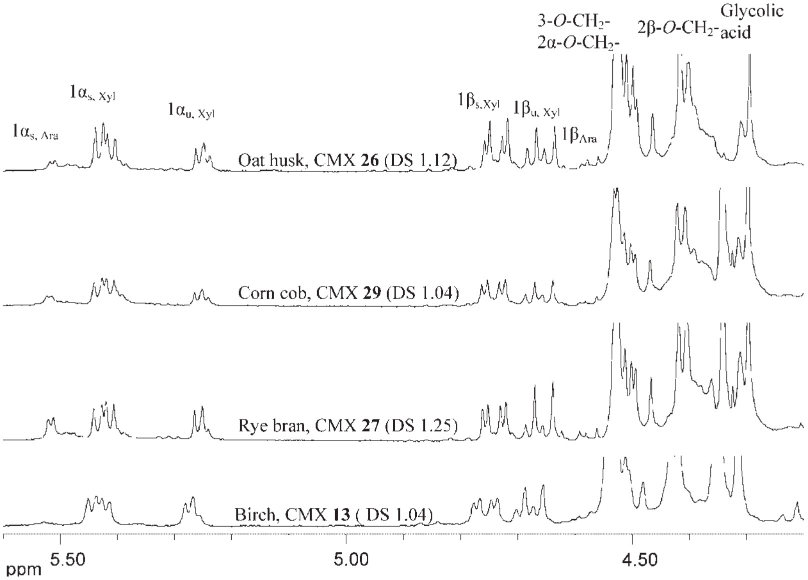


Figure 6.
^{1}H NMR spectra of carboxymethyl xylan (CMX) from different types in D_2SO_4 after depolymerization (s means substituted with carboxymethyl groups in position 2, u means unsubstituted, Ara means arabinose, Xyl means xylose).

The visual turbidity starts at a NTU of 100. With increasing DS, the NTU decreases and the solutions become more clearly. It was possible to separate the insoluble part (about 3%) that was identified by means of FTIR spectroscopy as a "non-sugar" component. Further investigations of the CMX from birch xylan **1** were performed with the polymer after fractionation.

In Table 3, a comparison of NTU of 1% solutions of CMX of different sources shows low NTU values and consequently the solutions are visually clear. Only the CMX solution from oat husk is turbid. Visual tests indicate that the solutions of the CMX at higher concentrations become turbid. However, the solutions of the CMX (**32**, **35**, **36**) from beech (**5**) and corn cob (**7**) remain clear.

The shear viscosity of the CMX samples is low (8–140 mPas, 5%) independent on the xylan type.

The CMX samples decrease the surface tension of water, however, the adjustment of the equilibrium is rather slow. The surface tension values were taken after

Table 2.
Nephelometric turbidity units (NTU) of solutions of carboxymethyl xylan (CMX) (from birch **1**) in water.

Carboxymethyl xylan				NTU
No.	Synthesis procedure	DS[a]	Concentration (%)	
11	Heterogeneous	0.39	1	1350
			5	>1750
13	Heterogeneous	1.04	1	136
			5	570
19	Starting with dissolved xylan	0.52	1	253
			5	1533
21	Starting with dissolved xylan	1.06	1	108
			5	1040

[a] Degree of substitution

Table 3.
Nephelometric turbidity units (NTU) of a 1% solution of carboxymethyl xylan (CMX) from different sources in water.

Carboxymethyl xylan			NTU
No.	Source	DS[a]	
30	Birch (Nitren) (GX)[b] **2**	0.89	8.6
31	Eucalyptus (GX)[b] **3**	0.91	3.6
32	Beech (GX)[b] **5**	0.98	4.5
33	Oat husk (AX)[c] **4**	0.83	102.0
34	Rye bran (AX)[c] **6**	0.88	24.0
35	Corn cob (wis)[d] (AGX)[e] **7**	0.97	11.6
36	Corn cob (ws)[f] (AGX)[e] **7**	0.91	13.4

[a] Degree of substitution
[b] 4-*O*-methylglucuronoxylan
[c] arabinoxylans
[d] water insoluble
[e] arabino-(glucurono)-xylan
[f] water soluble

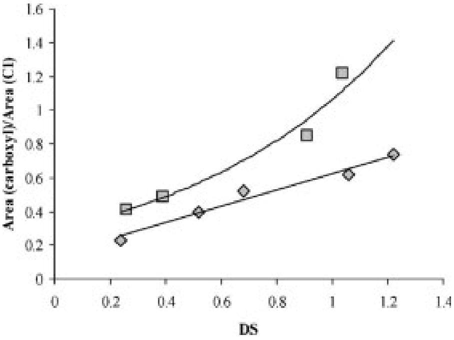


Figure 7.
Relationship between the quotient of the integral of the carboxyl peaks (173–178 ppm) and the integral of the C1 signal (95–102 ppm) and the degree of substitution (DS) depended on the synthesis procedure. (■ complete heterogeneous carboxymethylation, ◇ starting with dissolved xylan).

6 h. Surprisingly, the decrease of the surface tension of water (72.7 mN/m) depends on the procedure used for the CMX synthesis (Table 4). The CMX synthesized by carboxymethylation starting with dissolved xylan causes only a minor decrease of the surface tension to values of 57.4 and 61.2 mN/m. In contrast, the CMX synthesized completely heterogeneous lead to a significant decrease of the surface tension down to 45.5 mN/m at a DS of 0.39 (CMX **11**). These differences may be explained by a different functionalization pattern (see below).

To get information about the DS and the substitution pattern of the polymeric CMX, the samples were studied by means of ^{13}C NMR spectroscopy in D_2O consequently under identical conditions.

In Figure 7, the quotient of the integral of the carboxyl peaks (173–178 ppm) and the integral of the C1 signal (95–102 ppm) is plotted in relationship to the DS_{NMR} determined by ^{1}H NMR spectroscopy after hydrolytic chain degradation and the synthesis procedure.

According data acquisition conditions (0.4 s to acquire the FID and 0.8 s relaxation delay) applied, the longitudinal relaxation (T_1) of the AXU carbons was complete, whereas the carboxyl carbons were not fully relaxed. It becomes apparent that the course of the curve is different according to the synthesis path. The curve of the samples synthesized completely heterogeneous proceeds in a nonlinear manner. This strong increase of the integral ratios with growing DS can be explained by a noticeably decrease of the T_1 of the carboxyl carbons indicating that the carboxyl groups are embedded in a more rigid environment in the case of the CMX from the heterogeneous carboxymethylation than the CMX from the procedure starting

Table 4.
Surface tension of a 1% solution of carboxymethyl xylan (CMX) (birch, **1**) in water.

Carboxymethylation starting with dissolved xylan			Heterogeneous carboxymethylation		
No.	DS[a]	Surface tension (mN/m)	No.	DS[a]	Surface tension (mN/m)
17	0.24	61.2	**12**	0.23	49.4
19	0.52	57.4	**11**	0.39	45.5
22	1.22	60.0	**13**	1.04	52.6

[a] Degree of substitution

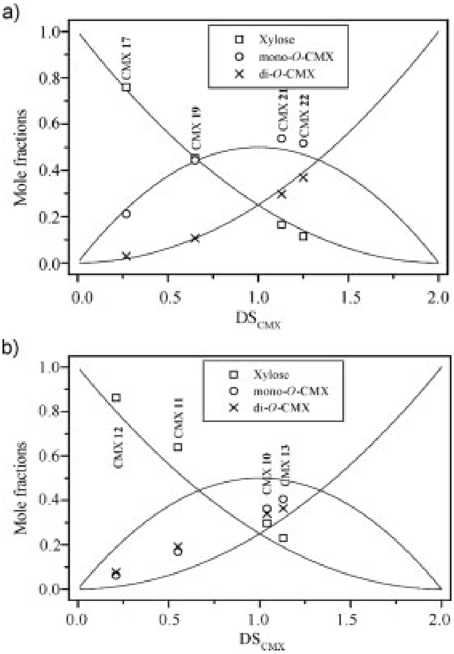


Figure 8.
Mole fractions of the repeating units (xylose, mono-*O*-carboxymethyl xylose, di-*O*-carboxymethyl xylose) of carboxymethyl xylan (CMX) samples synthesized a) starting with dissolved xylan and b) heterogeneously as a function of the degree of substitution (DS) (detected by HPLC after acidic chain degradation with $HClO_4$). The curves were calculated by $c_u = (1\text{-}DS/2)^2$, $c_{mono} = DS(1\text{-}DS/2)$, $c_{di} = (DS/2)^2$ with $k2 = k3$.

with the dissolved polymer. These differences may be explained by a different functionalization pattern, too (see below).

The CMX were studied by HPLC after chain degradation. The sugar units obtained can be separated from the un-, mono-, and di-*O*-substituted units employing an cation exchange column. Figure 8a presents the mole fractions of the CMX synthesized starting with dissolved xylan. The mole fractions fit with the theoretical calculated curves.[14,16] In contrast, the mole fractions of the CMX prepared by a complete heterogeneous procedure (Figure 8b) do not follow the calculated curves. The polymers contain more unsubstituted and di-*O*-carboxymethylated units and less mono-*O*-carboxymethylated units indicating a non-uniform distribution of the CM functions within the polymer chains.

Conclusion

The xylans used from different sources showing various side chains can be carboxymethylated with SMCA in the presence of aqueous NaOH under heterogeneous conditions in 2-propanol as slurry medium or starting with dissolved xylan. The DS and the partial DS at the different positions in the sugar units can be determined by ^{1}H NMR spectroscopy after hydrolytic chain degradation.

The CMX from birch (**1**) shows a dependence of the properties on the synthesis pathway resulting from a different substitution pattern as revealed by HPLC after hydrolytic chain degradation. Thus, the properties of CMX can be controlled by the reaction procedure. Further investigations will include carboxymethyl ethers of other hemicelluloses (galactomannan, glucomannan) in view of the reactivity and the substitution pattern as well as the properties.

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