Carboxymethylation of cellulose in unconventional media *

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Abstract. Carboxymethylation of cellulose in the new and highly efficient aqueous solvent Ni(tren)(OH)$_2$ [tren=tris(2-aminoethyl)amine] and in melts of LiClO$_4 \cdot$ 3H$_2$O or *N*-methyl-morpholine-*N*-oxide (NMMNO), which is now widely applied for cellulose fibre production, was investigated. In case of Ni(tren)(OH)$_2$, a totally homogeneous carboxymethylation of cellulose with sodium monochloroacetate, in the presence of an aqueous NaOH solution is possible for the first time. Structure analysis by means of HPLC and ^{1}H-NMR after chain degradation showed results comparable with findings for CMC obtained by the heterogeneous slurry process, that is, a statistic distribution of substituents along the polymer chain and functionalisation of the hydroxyl groups in the order C-6 $\geq$ C-2 > C-3. The etherification of cellulose in a melt of LiClO$_4 \cdot$3H$_2$O, a new type of cellulose solvent, was shown to be possible and gave products of a statistic functionalisation pattern as well. In contrast, carboxymethylation starting from solutions of cellulose in NMMNO initiated with solid NaOH particles yields polymers with a nonstatistic distribution of functional groups along the chain, as observed for cellulose ethers prepared in reactive microstrctures starting from solutions of cellulose intermediates in dimethyl sulfoxide as well as of unmodified cellulose dissolved in *N,N*-dimethyl acetamide/LiCl.

Key words: cellulose functionalisation, carboxymethyl cellulose, cellulose solvents, homogeneous procedure, reactive microstructure

Introduction

Chemical modification reactions continue to play a dominant role in improving the overall utilisation of cellulosic polymers. Due to the well-recognised significance of accessibility of the hydroxyl groups in affecting reactivity, world-wide research and development activities are devoted to special

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activation procedures yielding highly reactive starting materials. Besides investigations on selected heterogeneous procedures that could guarantee diffusion-free kinetics, interest is focused on cellulose solvents able to provide homogeneous reactions, at least at the beginning of the conversion.

A wide variety of cellulose derivatives has been prepared by applying different protic and aprotic cellulose solvents (Heinze and Glasser, 1998). Usually the goal of these attempts was the destruction of the supramolecular hydrogen bond system and a subsequent complete or regioselective functionalisation of the polymer backbone. In this regard, the distribution of functional groups along the polymer chain was not the centre of interest.

Based on our own work concerning the development of analytical tools for the complete determination of the functionalisation pattern of cellulosics (Heinze *et al.*, 1994) and the ongoing discussion about the state of dissolution of cellulose in solvent systems (Schulz *et al.*, 1998), we are interested in structures of cellulose derivatives resulting in preparation from different stages of activation. Investigations on the etherification of cellulose, starting from solutions of cellulose intermediates (Liebert *et al.*, 1996) to solutions in *N,N*-dimethyl acetamide (DMA)/LiCl (Heinze *et al.*, 1994), showed that these conversions are combined with the formation of a reactive microstructure which determines the pattern of functionalisation (Liebert and Heinze, 1998). The products show a non-statistic content of the different repeating units. Moreover, carboxymethylation reactions of cellulose carried out in the solvent *N*-methylmorpholine-*N*-oxide (NMMNO) are known (Chaudahri *et al.*, 1987). However, no detailed information about the functionalisation patterns of these CMC samples has been published.

In this paper, we wish to report the application of the highly effective aqueous cellulose solvent $Ni(tren)(OH)_2$ [tren=tris(2-aminoethyl)amine] as a reaction medium for the homogeneous carboxymethylation of cellulose. Moreover, the results obtained will be discussed in comparison with conversions starting from cellulose dissolved in melts of $LiClO_4 \cdot 3H_2O$ and NMMNO, respectively, as well as DMA/LiCl.

Materials and methods

Materials

Avicel (sample **A**, Fluka, degree of polymerisation, DP = 280) was used without any pre-treatment. Spruce sulfite pulp (sample **B**, DP = 490) was treated with enzymes prior to use (Michels and Meister, 1997). Sodium monochloroacetate, $LiClO_4 \cdot 3H_2O$ and NaOH were purchased from Fluka. For conversions in NMMNO and $LiClO_4 \cdot 3H_2O$ sodium monochloroacetate and

NaOH were treated in vacuum at 105°C for 6 h prior to use. DMSO was distilled over CaH_2.

Dissolution of cellulose in N-methylmorpholine-N-oxide (NMMNO)

After an enzymatic pre-treatment (Michels and Meister, 1997) cellulose sample **B** was dispersed in approximately 60% (w/w) solution of NMMNO in water. The suspension was heated up to 85–90°C. The major part of cellulose dissolved spontaneously after evaporating the required amount of water (to form NMMNO-H_2O). The solution (11% polymer) was kneaded until a light microscopic homogeneousness was achieved.

Homogeneous carboxymethylation

For a typical preparation, 0.50 g of cellulose **A** were dissolved in 5 cm³ Ni(tren)(OH)₂. 3.58 g sodium monochloroacetate in 10 cm³ water and 2.46 g NaOH in 8 cm³ water were added dropwise. During this procedure no precipitation occurred. After 3 h at 80°C, the solution was cooled to room temperature and was precipitated into 100 cm³ methanol. The precipitate was filtered off, dissolved in 20 cm³ distilled water, neutralised with acetic acid and reprecipitated into 80 cm³ ethanol. After filtration, the product (sample **2c**, Table 1) was washed with ethanol and dried in vacuum at 50°C.

DS_{CMC} (HPLC) = 0.54, IR (KBr): 1630, 1410 cm⁻¹ (C=O, carboxylate group).

Carboxymethylation in NMMNO

The dissolved cellulose **B** in NMMNO (11%, w/w) was stored as solidified material at room temperature prior to use. Ten gram of this sample were heated to 85°C and 20 cm³ DMSO were carefully added. After stirring at 80–90°C for about 1 h, a homogeneous system was obtained. In the 20 cm³ DMSO 5.5 g NaOH and in the 10 cm³ DMSO 8.0 g sodium monochloroacetate were added under vigorous stirring. This mixture was kept at 80°C for 2 h. The mixture was carefully precipitated into 400 cm³ of methanol. The precipitate was filtered off, dissolved in 40 cm³ distilled water, neutralised with acetic acid and reprecipitated into 200 cm³ ethanol. After filtration, the product (sample **4b**, Table 3) was washed four times with 200 cm³ aqueous ethanol (10%, v/v) and dried in vacuum at 50°C.

DS_{CMC}(HPLC) 1.26; IR (KBr): 1641, 1412 cm⁻¹ (C=O, carboxylate group).

Carboxymethylation in a melt of $LiClO_4 \cdot 3H_2O$

To a melt (at 95–100°C) of 30 g $LiClO_4 \cdot 3H_2O$, 0.5 g cellulose were added. The cellulose dissolves within a few minutes, (Fischer *et al.*, 1998). The mixture was treated stepwise with 1.23 g solid NaOH and 1.07 g sodium monochloroacetate. During this procedure gelation occurred. The mixture was kept for 4 h at 95–100°C. Isolation was carried out by precipitation in 300 cm^3 methanol, dissolution of the precipitate in 10 cm^3 water, neutralisation with acetic acid and reprecipitation in 100 cm^3 ethanol. The crude product was purified by reprecipitation of an aqueous solution in ethanol, washing with aqueous ethanol (10%, v/v; 3 times with 100 cm^3) and drying in vacuum at 50°C (sample **5**).

DS$_{CMC}$(HPLC) 0.69; IR (KBr): 1646, 1419 cm^{-1} (C=O, carboxylate group).

Measurements

The HPLC analysis of the CMC samples was carried out as described by Heinze *et al*. (1994). However, the samples were hydrolysed with perchloric acid. 0.1 g of CMC was dispersed in 2 cm^3 $HClO_4$(70%) and after 10 min at room temperature diluted with 18 cm^3 distilled water. This mixture was kept at 100°C for 16 h. The solution obtained was carefully neutralised with 2 M KOH and kept at 4°C for 1 h to guarantee a complete precipitation of the $KClO_4$. The salt was filtered off and washed three times with distilled water. The solution obtained was reduced to approximately 3 cm^3 and diluted with distilled water to give exactly 5 cm^3 sample. Chromatographic experiments were carried out at 65°C with 0.05 M H_2SO_4 as eluent with a flow rate of 0.5 cm^3/min. The column used was a Bio-Rad Aminex HPX-87 H. The ^{1}H-NMR analyses were carried out as described by Baar *et al.* (1994). For this purpose the CMC samples were hydrolysed with a mixture of D_2SO_4/D_2O (25%, v/v) within 5 h at 90°C. The spectra were acquired on a Bruker AMX 400 spectrometer. FTIR spectra were measured on a Bio-Rad FTS 25 PC using the KBr pellet technique. Standard ^{13}C-NMR spectra with proton-decoupling were recorded at 70°C in D_2O (8% polymer) on a Bruker 400 AMX NMR spectrometer. The scan number was between 6000 and 10 000.

Results and discussion

The commercial production of carboxymethyl cellulose (CMC) involves a heterogeneous slurry of cellulose in a liquid that swells but does not dissolve neither the starting polymer nor the CMC obtained. The alkali cellulose

necessary to initiate the reaction is typically prepared with aqueous sodium hydroxide (15–50%). Under these reaction conditions, CMC samples with degree of substitution in the range from 0.4 to 1.3 are formed, which possess a non-uniform distribution of the functional groups within the anhydroglucose unit (AGU) and a statistic distribution of both the differently functionalised carboxymethylated and non-functionalised repeating units (Feddersen and Thorp, 1993; Heinze *et al.*, 1994). In the course of our own studies on cellulosics, one of the most important goals is to develop new synthesis paths and concepts in order to gain products with new unconventional functionalisation patterns and hence with new properties (Heinze, 1997).

Carboxymethylation of cellulose in Ni(tren)(OH)$_2$

An aqueous solution of Ni(tren)(OH)$_2$ [tren=tris(2-aminoethyl)amine] dissolves cellulose, independently of the degree of polymerisation, within one hour completely (Burger *et al.*, 1995). In order to evaluate this new solvent as medium for homogeneous phase reactions, we first studied carboxymethylation of the biopolymer.

Because of the basicity of the system, the first etherification experiments were carried out without addition of an extra base. The conversion of a 10% (w/v) solution of cellulose with 10 mole sodium monochloroacetate per mole anhydroglucose unit (AGU) yielded polymer derivatives with DS$_{CMC}$-values up to 0.22 only which are water insoluble. Thus, the reaction had to be carried out by applying an additional base. As already mentioned, cellulose ethers are typically prepared by initiation of the reaction with aqueous sodium hydroxide solution of a concentration in the range from 15 to 50%. We found that in case of a careful addition of an aqueous NaOH up to concentrations of 31% (w/v) no gelation or precipitation of the polymer occurs. Even during the subsequent addition of 36% (w/v) aqueous sodium monochloroacetate no regeneration was observed. In case of a rapid addition of the reagents precipitation may occur. However, the precipitate redissolves in the course of reaction. This totally homogeneous procedure gives a maximum DS$_{CMC}$ of 0.54 by application of a molar ratio AGU : NaOH : sodium monochloroacetate of 1 : 20 : 10 and a reaction time of 2 h at 80°C (Table 1). Neither the increase of the reagent concentrations nor the prolongation of the reaction times show a significant influence on the total DS$_{CMC}$. In contrast, longer reaction times and especially a higher NaOH concentration (1 : 40 : 20) leads to both an increased hydrolysis of the sodium monochloroacetate and polymer degradation and hence, to lower DS$_{CMC}$ values since highly functionalised oligomeric parts of the sample are removed by the usual work-up procedure, (Table 1, see also Heinze and Pfeiffer, 1998). The stepwise addition of reagents leads to a slight increase of the DS$_{CMC}$ to 0.71 due to a

Table 1. Conditions and results of the homogeneous carboxymethylation of cellulose in Ni(tren)(OH)$_2$

Molar ratio[a]	Time (h)	Temperature (°C)	Carboxymethyl cellulose		
			Sample	DS_{CMC}	Solubility in water[c]
1:0:10	20	20	–	–	–
–	2	60	**1**	0.22	–
1:5:2.5	3	80	**2a**	0.11	–
1:10:5	3	80	**2b**	0.25	–
1:20:10	3	80	**2c**	0.54	+
1:40:20	3	80	**2d**	0.50	+
1:20:10	24	80	**2e**	0.44	+
1:40:20[b]	4	80	**3**	0.71	+

[a] Mole anhydroglucose unit: NaOH (20% in water): sodium monochloro-acetate
[b] Addition in 4 steps.
[c] + soluble; − insoluble

diminished hydrolysis of the sodium monochloroacetate (an important site reaction) during the etherification.

The samples obtained were water soluble starting from DS_{CMC}-value of 0.4. This is comparable with the solubility behaviour of commercial CMC samples with a statistic distribution of substituents along the polymer chain. FTIR investigations showed the typical signals for CMC (1630 and 1410 cm^{-1}, ν COONa). No evidence for impurities caused by the solvent was found. Moreover, by means of ^{13}C-NMR spectroscopy the molecular structure of CMC was proved. There are the typical signals of the modified AGU in the range from 60 to 105 ppm as well as signals at about 180 ppm which are assigned to the carboxyl groups (sodium salt).

Attempts were made to increase the reactivity of the system by partial liberation of the hydroxyl groups from the solvent co-ordination. Thus, carboxymethylation reactions were carried out in combination with the stepwise addition of ethylene diamine. However, all experiments done in this way showed inhomogeneity of the system during the conversion and yielded water-insoluble polymers.

Structure analysis of CMC samples obtained by homogeneous carboxymethylation was carried out by means of ^{1}H-NMR spectroscopy and HPLC both after complete hydrolytic depolymerisation of the samples. The quantification of the distribution of carboxymethyl groups within the AGUs was possible by means of ^{1}H-NMR measurements (Baar *et al.*, 1994). The hy-

Table 2. Results of the high-performance liquid chromatographic analyses of homogeneously prepared carboxymethyl cellulose (CMC) samples after hydrolytic chain degradation in comparison with statistically calculated data

CMC	Mole fractions of			
No.	Glucose	Mono-	Di-	Tri-O-CMG[a]
1	0.789	0.199	0.012	0
	(0.7957)[b]	(0.1889)	(0.015)	(0.0004)
2a	0.890	0.107	0	0
	(0.8940)	(0.1021)	(0.0032)	(0.0000)
2b	0.765	0.216	0.020	0
	(0.7702)	(0.2101)	(0.0191)	(0.0006)
2c	0.574	0.333	0.072	0.020
	(0.5514)	(0.3631)	(0.0797)	(0.0058)
2d	0.564	0.367	0.070	0
	(0.5787)	(0.3472)	(0.0694)	(0.0046)
2e	0.634	0.310	0.082	0.047
	(0.6214)	(0.3204)	(0.0551)	(0.0031)
3	0.436	0.435	0.128	0.005
	(0.4448)	(0.4137)	(0.1283)	(0.0132)

[a] CMG = carboxymethyl glucose.
[b] Calculated according to the Spurlin statistic, see text.

drolysis was carried out by reacting the samples in D_2SO_4/D_2O (25%, v/v) for 5 h at 90°C. Before hydrolysis, the samples have to be dialysed to remove glycolic acid (one of the main impurities of CMC) which gives a NMR signal at 4.19 ppm, that is in the range of chemical shift of the methylene protons of carboxymethylated *O*-6 within the AGU (Heinze, 1997). From these measurements a distribution of substituents on the level of the AGU in the order C-2 ≥ C-6 > C-3 (e.g. for sample **2e**: DS at *O*-2 = 0.17, *O*-3 = 0.08, and *O*-6 = 0.19; resulting in a total DS = 0.44) was concluded. An analogous distribution of functional groups within the AGU was evaluated for CMC prepared in totally heterogeneous reactions, (slurry process) using different analytical methods (see Baar *et al.*, 1994; Käuper *et al.*, 1998).

For HPLC measurements, the controlled degradation of the polymer chains to the repeating units was achieved by solvolysis with perchloric acid (Liebert and Heinze, 1998). The amounts of the functionalised units (2-, 3-, and 6-mono-*O*-; 2,3-, 2,6-, and 3,6-di-*O*- and 2,3,6-tri-*O*-carboxymethylated glucoses) as well as unmodified glucose, which build up the polymer chains, are given in Table 2. Comparison of these values with statistically calculated

values, (Reuben and Conner, 1983; given in brackets in Table 2) show a good fit of the data. The model assumes that no preference of any of the hydroxyl groups (position 2,3, and 6) exists and that the relative reactivities of the three hydroxyl groups in the AGU are constant throughout the reaction and independent of the DS of the cellulose chain or of the state of functionalisation at the other position within the same AGU. From these assumptions the following binomial distribution results:

$$C_i = \binom{3}{k} \left(\frac{DS}{3}\right)^k \left(1 - \frac{DS}{3}\right)^{3-k},$$

where c_i are the mole fractions of unsubstituted, mono-, di-, and tricarboxy-methylated glucose units, respectively, k is the number of functional groups per AGU ($k = 0, 1, 2, 3$) and DS is the average degree of substitution.

Thus, it can be concluded that the homogeneously prepared CMC samples show a statistical distribution of functional groups along the polymer chain. These results clearly show that both the simple activation of cellulose with aqueous NaOH in a wide range of concentrations, (see e.g. Feddersen and Thorp, 1993; Liebert and Heinze, 1998) and the complete dissolution of the polysaccharide yield a highly reactive polymer with an almost even accessibility of the reactive sites along the polymer chain and, hence, the reaction which is not diffusion controlled.

Carboxymethylation of cellulose in N-methylmorpholine-N-oxide (NMMNO)

In general, the carboxymethylation of cellulose starting from the polymer dissolved in NMMNO is already known (Chaudhari *et al.*, 1987; Kötz *et al.*, 1990). However, no detailed information about the behaviour of the cellulose solution during chemical conversions as well as about the functionalisation patterns of the products obtained are available.

For carboxymethylation of cellulose in NMMNO we used 11% (w/w) solutions of spruce sulfite pulp. In order to obtain a solution of an acceptable viscosity the temperature of the system need to be kept at about 85°C, that is at the melting point of the NMMNO monohydrate which dissolves the cellulose. Both solid NaOH particles and sodium monochloroacetate were added as suspensions in DMSO. Gelation of the reaction mixture was observed during this step. By reacting the polymer with a molar ratio of 20 mole NaOH and 10 mole sodium monochloroacetate for 2 h at 80°C and an usual work-up procedure, a water-insoluble CMC (**4a**) with a DS_{CMC}-value of 0.36 was obtainable (Table 3).

To get a better mixing of the reaction components, the cellulose/NMMNO solution was diluted with dimethyl sulfoxide (DMSO). As is already known, the addition of polar aprotic liquids like *N,N*-dimethyl formamide and DMSO

Table 3. Conditions and results of the carboxymethylation of cellulose in *N*-methylmorpholine-*N*-oxide (NMMNO) and dimethyl sulfoxide (DMSO) for 2 h at 80°C

Molar ratio[a]	DMSO (ml)[b]	Carboxymethyl cellulose		
		No.	DS_{CMC}	Solubility in water[c]
1:20: 10	–	**4a**	0.36	–
1:20:10	2.0	**4b**	1.26	+
1:20:10	2.5	**4c**	1.00	–
1:20:10	3.0	**4d**	0.68	–
1:20:10	2.0	**4e**[d]	0.10	–

[a] Mole anhydroglucose unit: NaOH (solid): sodium monochloroacetate.
[b] Volume of DMSO (in ml/g cellulose) added before reaction.
[c] + soluble; – insoluble.
[d] 5% water (v/w) was added to the reaction medium.

is not combined with regeneration processes (Lang *et al.*, 1986; Godsay, 1993). Thus, 20 cm³ DMSO were added to 10 g of the 11% (w/w) solution at 85°C obtaining a clear mixture. Analogous reaction conditions (see Table 3) were applied, as mentioned above, yielding a CMC (**4b**) with DS_{CMC} 1.26. By increasing the amount of co-solvent DMSO the accessible DS_{CMC} decreases. For example after addition of 25 cm³ DMSO and carboxymethylation a polymer (**4c**) with DS 1.0 was isolated. In case of 30 cm³ DMSO the DS_{CMC} was found to be 0.68 only (**4d**).

Moreover, an influence of the water content on the DS_{CMC} reached was found. Thus, solutions were converted which contained up to 5% additional water. In this case, the achievable DS_{CMC} was below 0.1. This is due to a regeneration of the cellulose during addition of water, yielding a rubber-like product. Hence, the reaction takes place at the surface only.

FTIR investigations showed typical signals for the carboxymethyl groups (1617 and 1426 cm⁻¹, ν COONa). The products contain no impurities from the solvent after the work-up procedure. However, as usual for CMC samples, hydrolysis products of the sodium monochloroacetate were determined. Results of HPLC studies of CMC prepared in NMMNO in comparison with statistic calculations are shown in Figure 1. As can be seen, the data obtained by HPLC have a characteristic deviation from the calculated values, that is the conversion of cellulose in NMMNO yields polymers with a nonstatistic content of the differently functionalised repeating units and of glucose. The deviation of these values from the statistical values are in the same range as observed for CMC samples prepared in DMA/LiCl or via organo-soluble cel-
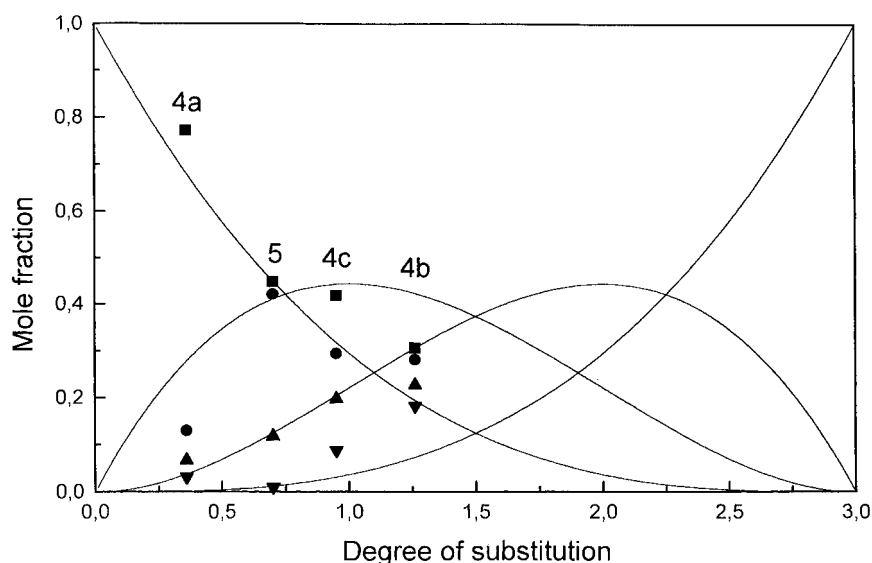
Figure 1. The mole fractions of glucose (■), mono-*O*-carboxymethyl glucose (●), di-*O*-carboxymethyl glucose (▲), and tri-*O*-carboxymethyl glucose (▼) of completely de-poylmerised carboxymethyl cellulose samples (prepared in NMMNO, sample **4** or melted LiClO$_4$, sample **5**) plotted as function of total DS. The curves are calculated (see text).

lulose intermediates like cellulose formates, cellulose trifluoroacetates, and trimethylsilyl celluloses in dimethyl sulfoxide via an induced phase separation (Heinze *et al.*, 1994; Liebert *et al.*, 1996; Liebert and Heinze, 1998).

Carboxymethylation in melts of LiClO$_4$·3H$_2$O

Very recently it was reported that different melts of inorganic salts may act as efficient solvents for a number of polymers including cellulose (Fischer *et al.*, 1998). It was shown that cellulose is not extensively degraded in these systems and that even the acquisition of NMR spectra in these media is possible. A still open question was the use of salt melts for the chemical modification of the polysaccharide. Thus, we applied a melt of cellulose in LiClO$_4$ · 3H$_2$O for the carboxymethylation of cellulose. A solution of cellulose (1.7%, w/v) was converted with solid NaOH and sodium monochloroacetate (molar ratio AGU : NaOH : sodium monochloroacetate was 1 : 10 : 3) at the melt temperature of the salt (95°C) for 4 h. During this time gelation occurred. This may be partially caused by the high reagent concentrations and the regeneration of the cellulose on the NaOH particles.

The carboxymethyl cellulose isolated was water soluble. FTIR studies confirmed that the product obtained is a pure CMC. Signals at 1646 and

$1419\,cm^{-1}$ were found. These are characteristic of the carboxylate groups. The result of the HPLC-analysis, after complete chain degradation in comparison with the statistical values is shown in Figure 1 (sample **5**). As can be seen, the CMC had a DS_{CMC} of 0.69 and does not show a deviation from the statistical value in contrast to findings for carboxymethylation reactions which succeed under comparable cellulose regeneration processes, that is in a reactive microstructure (Liebert and Heinze, 1998). The reason for the occurrence of a statistically functionalised polymer in this process should be the high amount of co-ordination water. The solid NaOH does partially dehydrate the salt and thereby the expected reactive microstructure on the NaOH surface is destroyed. The drastic influence of water on this type of reaction has already been demonsatrated by us for reactions starting from solutions of cellulose derivatives in DMSO.

From these preliminary studies we can state that the melt of $LiClO_4 \cdot 3H_2O$ can be applied as medium for the chemical modification of cellulose as exemplarily shown for the carboxymethylation of the polysaccharide. Reaction of cellulose in the melts of $LiClO_4 \cdot 3H_2O$ with aqueous reagents, (aqueous solutions of NaOH), are under investigation. These conversions seem to be problematic because of the high temperatures (95°C) necessary for melting the salt. Further studies will deal with reactions of cellulose and other polysaccharides in salt melts and in aprotic organic solvents such as DMSO.

Conclusions

It is possible to use the cellulose solvent $Ni(tren)(OH)_2$ for the totally homogeneous etherification of cellulose. In this way carboxymethyl cellulose can be prepared in a one-phase-reaction. Structure analysis showed that both the distribution of functional groups on the level of the repeating unit as well as on the level of the polymer chain is comparable with products synthesised in a conventional slurry process using aqueous NaOH, that is the OH groups at positions 2 and 6 were more reactive than those at position 3. The mole fractions of the different carboxymethylated repeating units as well as those of unmodified glucose follow the simple statistical pattern first proposed by Spurlin. The application of homogeneous conditions does not influence the regioselectivity significantly compared to the totally heterogeneous process since products with the same functional patterns are obtained. This is a very important finding, especially from a scientific point of view. This is because it is further proof that the etherification of cellulose in the presence of aqueous NaOH, of mercerisation concentration, is not controlled by diffusion processes.

Carboxymethylation of cellulose in a salt melt of $LiClO_4 \cdot 3H_2O$ has been successfully carried out for the first time. Although, up to now we have only synthesised CMC with structural features comparable to commercial products, a number of new synthesis capabilities, including regeneration processes, arises from these systems. At present, the influence of a dilution of the salt melts with aprotic organic solvents is under investigation.

Conversions starting from a solution of cellulose in pure NMMNO or NMMNO/DMSO mixtures yield CMC samples with a nonstatistical distribution of functional groups along the polymer chain. This is comparable with our earlier findings that etherification reactions starting from a solution of cellulose in DMA/LiCl or from cellulose intermediates in DMSO, for example via an induced phase separation, give cellulose ethers with new unconventional functionalisation patterns. Thus, an analogous course of reaction including the formation of a reactive microstructure can be concluded.

Acknowledgement

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