Substitution Patterns of Cellulose Ethers – Influence of the Synthetic Pathway

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Summary: Commercial cellulose ethers are usually prepared under heterogeneous reaction conditions. In contrast, this contribution also describes the derivatization under homogeneous conditions in N-methylmorpholine-N-oxide monohydrate (NMMNO*H$_2$O) and under heterogeneous conditions after converting native cellulose to amorphous cellulose. Amorphous cellulose is prepared by dissolving cellulose in NMMNO*H$_2$O followed by precipitation in different media. The degree of order and the porosity of the regenerated cellulose is significantly influenced by the content of water in the precipitating agent. The differences are described by measurements using wide angle X-ray scattering, solid-state ^{13}C-NMR, mercury porosimetry, and water/liquid retention values. Three synthetic pathways (heterogeneous, heterogeneous with amorphous cellulose and homogeneous) are compared regarding the structure-property relationship of the cellulose ethers formed. Carboxymethylation, hydroxyethylation, hydroxypropylation and sulfoethylation are considered in detail. The choice of synthetic pathway has a significant influence on the degree of substitution (DS), the distribution of substituents on the level of the anhydroglucose unit (AGU), solubility behavior, and the viscosity of aqueous solutions. In general an increasing solubility and an increasing viscosity are observed from heterogeneous to heterogeneous with amorphous cellulose to homogeneous reaction conditions. There is a remarkable difference between the heterogeneously produced cellulose ethers with a DS distribution C2 $\geq$ C6 $>$ C3 and the strictly homogeneous etherification in NMMNO*H$_2$O/organic solvent systems with a DS distribution of C3 $>$ C2 $\gg$ C6. This high regioselectivity at the secondary OH-groups of the AGU may be caused by the strong solvation behavior of NMMNO*H$_2$O and thereby a protecting function at the C6-OH-group.

Keywords: cellulose; decrystallization; homogeneous/heterogeneous etherification; NMMNO; regioselectivity

Introduction

Cellulose as a linear polysaccharide is an isotactic β-1,4-polyacetal of cellobiose (4-O-β-D-glucopyranosyl-D-glucose). The actual base unit, cellobiose, consists of two molecules of glucose. Starting with dissolving pulp as a purified raw material, cellulose is converted into cellulose derivatives (ethers and esters) and regenerated materials (fibers, films, food casings, membranes, sponges, among others) by large scale industrial processing.

Nowadays the industrial-scale production of cellulose ethers takes place exclusively under heterogeneous reaction conditions whereby cellulose is initially activated with alkali hydroxide solutions and then reacted with alkyl halides or epoxy alkyl compounds at elevated temperature.[1] Activation is required to loosen the partially crystalline structure of cellulose and to increase the accessibility of the hydroxyl

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groups for the reaction. In order to improve the uniformity of substituent distribution and hence to improve the product properties, the reaction is often carried out in the presence of inert organic solvents such as, e.g. iso-propanol.

Intracrystalline swelling media or decrystallization methods (e.g. NaOH, NH_3,[2,3] orthophosphoric acid,[4] or ball milling[5]) are most effective for the activation of cellulose, especially the regeneration of cellulose or cellulose derivatives from solutions (e.g. cellulose/LiCl/dimethyl formamide (DMAc) or saponification of dissolved cellulose acetate). Because of the high amount of salt, the difficult recovery of the starting compounds, partly high degree of degradation and/or small cellulose concentrations, these processes are currently not used on industrial scale. The production of amorphous cellulose by ball milling is described in literature, but the high degree of degradation is a disadvantage of this method. A special possibility for the decrystallization of cellulose is given by the NMMNO∗H_2O system which is also the only industrialized solvent for spinning of cellulose fibers (Lyocell process) being used in place of the viscose process.[6] For this decrystallization step cellulose is dissolved and regenerated from melt NMMNO∗H_2O solvent system.[7,8]

The comparison of different activation methods (dissolution of cellulose in molten inorganic salts also in NMMNO∗H_2O and the treatment by electron beam irradiation) and their influence on the following derivatization is described by Fischer et al.[9]

Whilst decrystallization is the most important step for increasing cellulose reactivity in heterogeneous reactions, the utilization of cellulose through modification

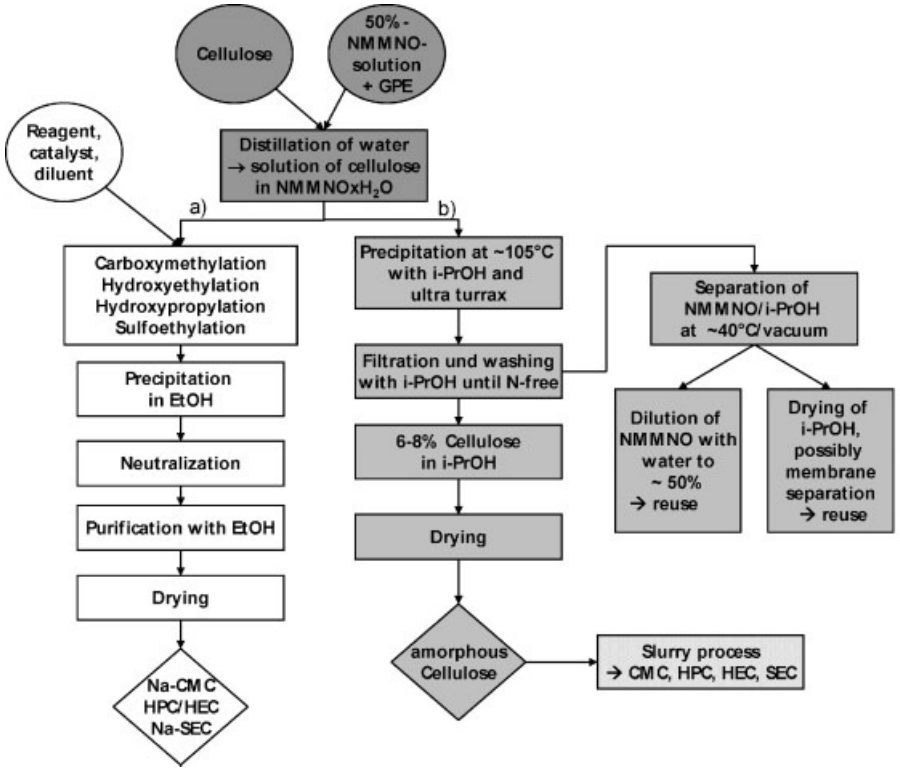

Figure 1.
Flow sheat of synthesized cellulose ethers: dissolution of cellulose in the NMMNO∗H_2O-system followed by a) etherification under homogeneous conditions and b) decrystallization of cellulose with subsequent etherification in a heterogeneous system; GPE: gallic acid propyl ester.

in homogeneous reactions is the ideal way for gaining accessibility of all cellulose molecules and for achieving uniform substituent distributions. Johnson[10] was the first to describe homogeneous etherification reactions of cellulose in melt solutions of cyclic amine oxides, particularly of NMMNO, in the presence of organic solvents, preferably DMSO, as diluent to cyanoethylcellulose or cellulose oxyethyl methyl ketone.

Different inert solvent systems for cellulose and its derivatization have been suggested in the literature[11,12] such as aqueous solutions of quaternary ammonium bases,[13] sodium hydroxide/urea,[14] or Ni(tris(2-aminoethyl)amine](OH)$_2$,[15] non-aqueous mixtures of sulfur dioxide/dimethylamine/dimethyl sulfoxide,[16] dimethyl sulfoxide/ paraformaldehyde,[17] N,N-dimethylacetamide/lithium chloride,[18] 1,3-dimethyl-2-imidazolidinone,[19] or N-methylpyrrolidone/lithium chloride.[20] Also molten inorganic salts[21] and ionic liquids[22,23] are potential solvent systems and reaction media for the derivatization of cellulose.

In this paper, we wish to report on a comparison of three synthetic pathways (homogeneous – see Figure 1 step a) - heterogeneous and heterogeneous with amorphous cellulose - Figure 1 step b)) regarding to the structure-property relationships of cellulose ethers formed, including carboxymethyl (CMC), hydroxyethyl (HEC), hydroxypropyl (HPC), and sulfoethyl cellulose (SEC). These investigations are in relation to our own results on the derivatization of cellulose in the NMMNO∗H_2O/solvent system.[24,25]

Experimental Part

Materials

Three different celluloses were used as starting material (wood pulp Ultraether F from Rayonier Inc. [$DP_{Cuoxam} = 1625$], cotton-linters Temming 500 (T500) from Temming company [$DP_{Cuoxam} = 640$], and wood pulp Borregaard NC from Borregaard [$DP_{Cuoxam} = 580$]). NMMNO was received as a 50% aqueous solution from Degussa. All cosolvents used (dimethyl sulfoxide [DMSO], N-methyl pyrrolidone [NMP], iso-propanol [i-PrOH]); all precipitants and washing media (methanol [MeOH], ethanol [EtOH], iso-propanol, acetone); all bases and catalysts (sodium hydroxide, benzyl trimethylammonium hydroxide [Triton B, 40% aqueous solution], anionic exchanger [AIE; Amberlyst A26]); the stabilizer (gallic acid propyl ester [GPE]); and all reagents (mono chloroacetic acid [MCA], ethylene oxide, propylene oxide, sodium vinylsulfonate) were purchased from Fluka and were used without further purification. The carboxymethyl cellulose CMC 1 (DS = 1.0) and the hydroxypropyl cellulose HPC 1 (DS = 1.58, MS = 1.53) were provided by Wolff Cellulosics GmbH.

Measurements

Wide Angle X-ray Scattering (WAXS)

A Bruker-AXS Kristalloflex 760 X-ray generator and a flat-film camera were used to carry out wide-angle X-ray diffraction (WAXS) experiments. The generator was operated at 40 mA and 40 kV. The X-rays with a wavelength of 0.15418 nm were monochromized by a Ni-filter. The cellulose samples were perpendicularly transmitted by the X-rays. The diffraction patterns were recorded by a flat film (Biomax, Kodak), which was exposed for 1.5 h. The sample-to-film distance was 60 mm.

Before the measurement of i-PrOH-wet amorphous cellulose, the sample was dried in a rotary evaporator at 50 °C/15 mbar and stored in a closed vessel for two weeks.

^{13}C-CP/MAS NMR

The ^{13}C-NMR spectra were recorded using a Varian UNITY 400 NMR spectrometer at a frequency of 100.58 MHz. High-resolution solid-state spectra were obtained with the cross-polarization/magic angle spinning (CP/MAS) method at spinning frequencies of 5–6 kHz. The radio frequency field strength for cross-polarization and decoupling was 50–70 kHz, the contact time

1–2 ms and the repetition time of the experiments 3 s. The never dried i-PrOH wet samples were employed for the ^{13}C-CP/MAS NMR measurements. About 0.1 cm^3 of the activated cellulose were filled into a sample rotor. Depending on the sample and the specific goal the measuring time ranged from 1 to 15 h.

^{13}C-Liquid NMR

For the determination of the degree of substitution and the distribution of substituents in the AGU of derivatized cellulose the samples were hydrolyzed with trifluoroacetic acid, dissolved in D_2O and analyzed with high-resolution liquid ^{13}C-NMR. The measurements were carried out by using a quantitative method without Nuclear-Overhauser effect.[26]

Mercury-porosimetry

About 200 mg of the sample material were weighed and placed into a glass dilatometer. Vacuum was applied in a macroporous Unit Pascal 140 (Thermo Electron Corporation); the dilatometer was filled with mercury to the 10 mm mark and then transferred to the high pressure unit Pascal 440 (Thermo Electron Corporation). Pressure was slowly increased to 400 MPa while recording the drop of the mercury column. Using the Washburn equation for cylindrical pores the pore radius can be calculated.[27]

$$p^{*}r = -2\sigma^{*}\cos\Theta \quad (1)$$

where p = absolute external pressure, r = pore radius, σ = surface tension of mercury and θ = contact angle.

Water/liquid Retention Value (WRV/LRV)

For the determination of the water retention value the sample was first disintegrated in an attrition mill. Then 0.5 g of the sample with known water content was weighed to ±0.1 mg into a 100 ml Erlenmeyer flask and suspended in 50 ml of distilled water. The suspension was shaken for 1 h at 20 °C and then transferred to a G3 sintered-glass disk, applying slight suction to remove the adhering water. The sintered-glass disk was then transferred to a suitably adapted centrifuge beaker with a tight cover and centrifuged at 4000 g (earth gravity acceleration) for 15 min, securing a free efflux from the centrifugate. Subsequently the weight of the moist sample was determined via mass difference before and after careful removal of the sample from the sintered-glass disk. The water retention value was calculated according to

$$\mathrm{WRV}(\%) = \frac{\text{Mass of moist sample} - \text{Mass of dry sample}}{\text{Mass of dry sample}} * 100 \quad (2)$$

or

$$\mathrm{WRV}(\mathrm{cm}^3/\mathrm{g}) = \frac{\text{Mass of moist sample} - \text{Mass of dry sample}}{\text{Mass of dry sample}} * \mathrm{d}_{(liquid)} \quad (3)$$

where $d_{(liquid)}$ = density of the liquid.

Viscosity

The viscosity of a 2% aqueous solution was measured using a rotary viscometer (VT550, Haake) with a conical cylinder (MV-DIN) at 20 °C. The shear viscosity was determined at a shear rate of $\dot{\gamma} = 2.55\ \mathrm{s}^{-1}$.

Determination of the DP (Degree of Polymerization) of Cellulose in Cuoxam Solution

For dissolving the cellulose sample, a brown wide-necked bottle of 100–110 ml capacity was used and the weighed sample was dissolved in 100 ml of Cuoxam solution (aqueous solution of $[Cu(NH_3)_4](OH)_2 \cdot 3H_2O$) at 20 °C. Pieces of metallic copper are used to minimize the air volume above the solution in the bottle. The mixture was kept for 5 min at 20 °C, then vigorously shaken, and then placed again in a water bath of 20 °C. This procedure was repeated until the sample was completely dissolved. The viscosity measurement was performed

in a Doering viscometer.[28] The viscosity was calculated from the efflux time of this cellulose solution and of the blank Cuoxam solution.

The DP was calculated from the specific viscosity

$$\eta_{spec} = \frac{\eta - \eta_0}{\eta_0} \quad (4)$$

according to

$$DP = \frac{2000^* \eta_{spec}}{c^*(1 + 0,29^* \eta_{spec})} \quad (5)$$

where η = viscosity of the cellulose solution; η_0 = viscosity of the solvent; c = concentration of cellulose [g/l].

The determination was always be performed in duplicate.

Preparation of Amorphous Cellulose

Cellulose (53 g Ultraether F [DP 1625], 110 g Temming 500 [DP 640], 110 g Borregaard NC [DP 580] respectively) was suspended in 1700 g of 50% NMMNO solution with 0.01 g GPE/g cellulose as stabilizer and swelled for 24 h at 20 °C. Extraction by suction of the cellulose gave a filter cake with a mass ratio of cellulose to 50% NMMNO of 1: 8. Both the filter cake and the filtrate were dewatered. The filtrate was concentrated in a rotary evaporator at 90 °C/65 mbar to a concentration of about 80%. At the same time the residual NMMNO in the filter cake was dewatered at <85 °C/65 mbar in the reactor. After achieving the desired NMMNO concentration, the warm filtrate was added to the cellulose pulp. The residual small amount of water was distilled off at 110 °C/60-65 mbar until the NMMNO monohydrate concentration was achieved and the cellulose dissolved.

The precipitation was accomplished in two different ways and by using different precipitants, like i-PrOH, H_2O or i-PrOH/H_2O azeotrope. 1) The cellulose solution was added to the precipitant under vigorous stirring in the presence of an ultra turrax (a so called stir-in precipitation). 2) The precipitant was added to the solution slowly under vigorous stirring in the presence of an ultra turrax until the gel point was obtained (T = 105–110 °C). From this point on the addition rate was accelerated until the cellulose was precipitated. The remaining precipitant was added two to four times faster (dispersion precipitation).

Heterogeneous Reactions

Carboxymethylation Under Heterogeneous Conditions (CMC4)

90 g i-PrOH-wet amorphous cellulose (5.9 g cellulose with DP = 830 and 84.1 g i-PrOH)* was stirred with a mixture of 77.3 g i-PrOH/11.6 g MeOH and 22.8 g H_2O in a 250 ml glass reactor equipped with a stirrer, while the first portion of NaOH pellets (0.63 g) was added during 10 min at room temperature. The mixture was tempered to 70 °C during 30 min and MCA and the residual NaOH were added in portions: 1. MCA (0.93 g as a 80% aqueous solution), reaction time: 30 min; NaOH (0.63 g NaOH pellets), reaction time: 10 min; 2. MCA (0.93 g as a 80% aqueous solution), reaction time: 30 min; NaOH (0.63 g NaOH pellets), reaction time: 10 min; 3. MCA (0.93 g as a 80% aqueous solution), rection time: 120 min.

After cool-down to 25 °C, the mixture was washed with 80% (w/w) aqueous ethanol until it was pH neutral and free of chloride ions. Finally the product was dried at 60 °C under vacuum (characterization data see Table 2).

Hydroxyethyl-/Hydroxypropylation Under Heterogeneous Conditions

Using a pressure-vessel reactor, air-dry cellulose (Temming 500), or the corresponding i-PrOH-wet amorphous cellulose (DP = 531; 15 g calculated for the dry product), was suspended in a 1 : 1 mixture of 200 g i-PrOH/t-BuOH (w : w) and 8.4 g H_2O (liquid-to-solid ratio: 18 ml/g)† and

*In the case of native cellulose 5,9 g cellulose was suspended in 161,4 g i-PrOH/11,6 g MeOH and 22,8 g H_2O.

†In the case of i-PrOH-wet amorphous cellulose the liquid-to-solid ratio was increased to 32 ml/g.

was alkalized with 6.0 g NaOH pellets for 80 min at room temperature. After adding 8.2 g of ethylene oxide the mixture was stirred for 40 min at room temperature and then it was heated to 75 °C within 30 min. The mixture was stirred for further 100 min at this temperature, and then neutralized with acetic acid at ~25 °C. After filtration the product was washed with MeOH, and dried at 60 °C under vacuum (characterization data see Table 5). HPC was synthesized by Wolff Cellulosics GmbH under similar conditions.

Sulfoethylation Under Heterogeneous Conditions

Air-dry native cellulose (Ultraether F), or the corresponding i-PrOH-wet amorphous cellulose (DP = 1240; 15 g calculated for the dry product), was suspended in a mixture of 263.8 g i-PrOH and 4 g H_2O (liquid-to-solid ratio: 18 ml/g)[†] in a nitrogen atmosphere, and the mixture was alkalized with 9.9 g NaOH pellets for 24 h at room temperature. After adding 35 g of a 30% aqueous solution of sodium vinylsulfonate the mixture was stirred for 30 min at room temperature before it was heated to 80 °C within 30 min. The mixture was stirred for another 3 h at this temperature and then neutralized with acetic acid at ~25 °C. After filtration the product was washed three times with 70% aqueous MeOH, twice with absolute MeOH, and dried at 60 °C under vacuum (characterization data see Table 7).

Homogeneous Reactions

Carboxymethylation Under Homogeneous Conditions (CMC11)

A solution of 50 g cellulose (Ultraether F) in 1050 g NMMNO*H_2O melt (0.5 g of GPE as stabilizer) was diluted at 105 °C with 500 g of DMSO. After heating to 65 °C, 14.6 g of MCA dissolved in 53.3 g of DMSO were added within 3 min with intensive stirring. A mixture of 129.1 g of 40% aqueous Triton B and 128.6 g of DMSO were then added dropwise in 30 min and the solution was stirred for 1 h at 65 °C. Then 29.2 g MCA as a solution in 106.6 g DMSO were added within 10 min before a mixture of 322.9 g of 40% aqueous Triton B and 321.4 g of DMSO were added within 10 min. After 2 h stirring the carboxymethyl cellulose was isolated by precipitation in twice the volume of acetone/ethanol (4:1, v/v). After washing three times with ethanol, treatment with 0.5% of NaOH and ethanol containing 10% water for the quantitative conversion to Na-CMC, washing with ethanol until the filtrate was free of chloride, the product was dried at 60 °C under vacuum. The completely water-soluble CMC had a DS = 0.40 with C2 = 0.12, C3 = 0.27, C6 = 0.02 and a solution viscosity in a 2% aqueous solution at 20 °C of $\eta = 26300$ mPa · s with a shear rate of $\dot{\gamma} = 2.55\ s^{-1}$.

Hydroxyethylation Under Homogeneous Conditions (HEC7)

A melt solution of 4.6 g cellulose (Ultraether F) in 96 g NMMNO*H_2O was diluted with 30 ml NMP at 100 °C with stirring and heated to 65 °C. Bead-shaped anion exchanger containing 7.5 g dry matter in suspension in 30 ml NMP was then added and stirred for 15 min. Then 12.5 g ethylene oxide were added to the cellulose solution from a pressure pump within 30 min at 65 °C. The hydroxyethyl cellulose, which is water-soluble after a reaction time of only 10 min, was isolated after 1 h stirring by separating the solid phase catalyst from the polymer solution by centrifugation over a frit, precipitating the derivative by pouring said solution into the 3-fold volume of a 75:25 acetone/ethanol mixture, washing with ethanol and drying.

The completely water-soluble hydroxyethyl cellulose had a DS = 1.02 with C2 = 0.25, C3 = 0.48, C6 = 0.29 and a solution viscosity in a 2% aqueous solution at 20 °C of $\eta = 2500$ mPa · s with a shear rate of $\dot{\gamma} = 2.55\ s^{-1}$.

Hydroxypropylation Under Homogeneous Conditions (HPC7)

A melt solution of 4.6 g cellulose (Ultraether F) in 96 g NMMNO*H_2O with 0.046 g

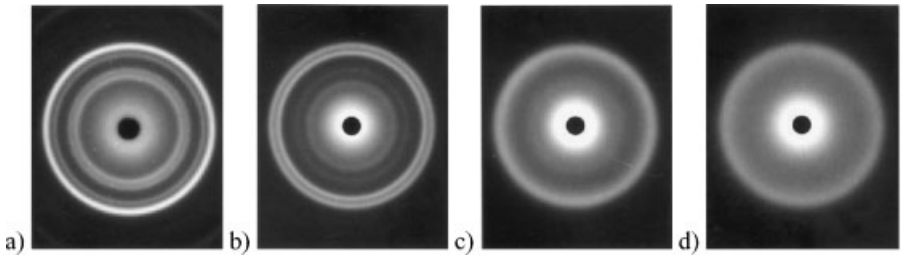

Figure 2.
Wide angle X-ray scattering of a) Temming 500 and after decrystallization and precipitation with b) water, c) aqueous solution of iso-propanol (87.4% i-PrOH), and d) iso-propanol.

propyl gallate as stabilizer was diluted with 20 ml i-PrOH at 85 °C with stirring and heated to 75 °C. A previously prepared suspension of bead-shaped anion exchanger containing 7.5 g dry matter (based on polystyrene with quaternary ammonium groups) in 30 g NMMNO∗H_2O/8 ml iso-Propanol was then added and stirred for 15 min. Then 20 ml of propylene oxide were slowly added to the cellulose solution by way of a dropping funnel within 45 min at 75 °C with intensive stirring, and stirring was continued for 1 h. After separation of the solid phase catalyst, the hydroxypropyl cellulose was precipitated by pouring the polymer solution into the 3-fold volume of a

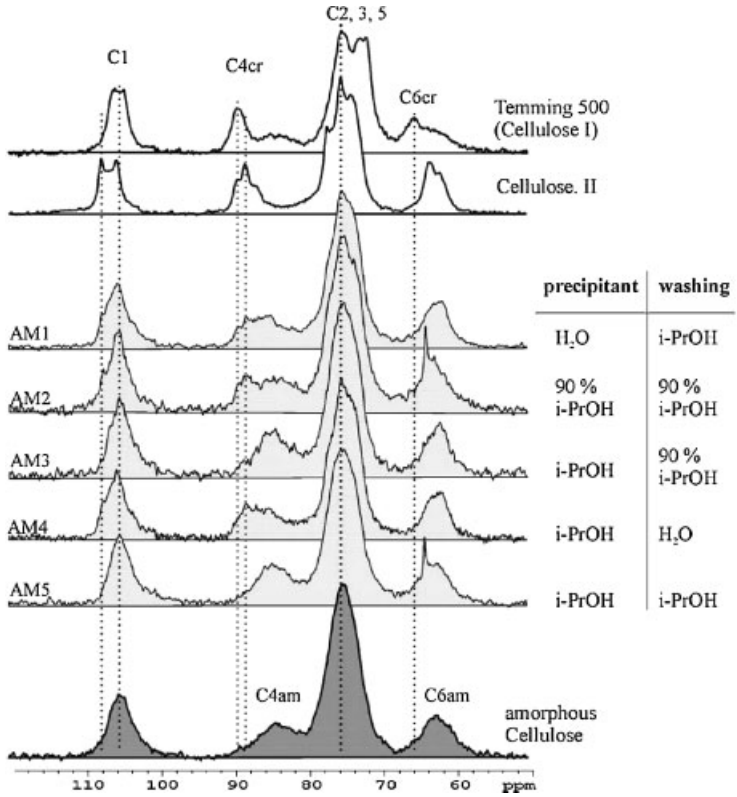

Figure 3.
^{13}C-CP/MAS-NMR spectra of native cellulose, cellulose II, different regenerated cellulose, and ball milled amorphous cellulose (cr: crystalline, am: amorphous).

75:25 acetone/ethanol mixture, washed with ethanol and dried. The completely water-soluble hydroxypropyl cellulose had a MS = 0.93, DS = 0.63 with a substitution distribution of C2 = 0.07, C3 = 0.49 and C6 = 0.07 (determined by means of ^{13}C-NMR spectroscopy); viscosity of a 2% aqueous solution at 20 °C with a shear rate of $\dot{\gamma} = 2.55\ s^{-1}$: $\eta = 14000$ mPa · s. (Instead of i-PrOH DMSO or NMP can be used as a cosolvent in combination with anionic exchanger (AIE) or Triton B as catalyst respectively.)Resd

Results and Discussion

Decrystallization

Wide angle X-ray scattering is still the most important source of information on the supramolecular order of cellulose and its derivatives. Figure 2 shows the flat-film photographs of different precipitated samples in comparison to native cellulose. The Temming 500 with a typical cellulose I structure (a) was dissolved in NMMNO∗H_2O as a 6% solution. Then the cellulose was precipitated under vigorous stirring and dispersing with an ultra turrax by adding water (b), an azeotrope mixture of i-PrOH/water (c), and pure i-PrOH (d) followed by a washing step with i-PrOH. These samples were dried at 50 °C/15 mbar and stored for 2 weeks before they were measured. The comparison of the X-ray flat film photographs shows clearly that with decreasing amount of water in the precipitant the order and the orientation of the regenerated cellulose decrease. While the precipitation with water leads to cellulose with partial cellulose II structure, the precipitation with pure i-PrOH results in amorphous cellulose.

The influence of the precipitant and the washing media on the crystalline structure of cellulose is also pointed up in Figure 3. The ^{13}C-CP/MAS NMR spectroscopic degree of order can be derived from the evaluation of the C-4 signal of the solid state ^{13}C-NMR spectrum of cellulose, which is split into a very sharp crystalline peak at 88–92 ppm and a broader amorphous peak at about 80–90 ppm due to the different electronic environment of this C atom in regions of high and low order as a consequence of different hydrogen-bond systems. A similar inverse change of the peaks of crystalline and amorphous parts is observed in the C-1 and C-6 region of the spectrum.[29]

In comparison with model substances like cellulose I (Temming 500), ordered cellulose II (cellulose beads tempered in boiling water) and amorphous cellulose

Table 1.
Water and liquid (i-PrOH) retention values of native and amorphous cellulose.

Cellulose	Native material		After decrystallization				
	WRV [cm^3/g]	LRV [cm^3/g]		WRV* [cm^3/g]	LRV** [cm^3/g]	WRV-relationship amorph/nativ	LRV-relationship amorph/nativ
Ultraether F DP 1625	0.69	0.18	AM6[a] DP 1270	4.98	6.39	7.2	35.5
Temming500 DP 640	0.60	0.17	AM7[a] DP 558	3.44	5.38	5.7	31.6
Temming500*** DP 640	0.60	0.17	AM2[b] DP 530	4.52	4.82	7.5	28.4
Temming500**** DP 640	0.60	0.17	AM8[c] DP 521	3.95	4.65	6.7	27.4
Borregaard NC DP 580	0.65	0.24	AM9[a] DP 548	3.30	5.27	4.8	22.0

*Solvent exchange of the i-PrOH-wet sample against water;
**Suspension of the i-PrOH-wet sample in i-PrOH;
Precipitation and washing with i-PrOH;
Precipitation and washing with aqueous i-PrOH (87.4%);
Precipitation and washing with water then i-PrOH.

(ball milled cellulose I), different regenerated cellulose samples were examined. To prepare these products, cellulose was dissolved in molten NMMNO∗H_2O and coagulated by adding a precipitant under vigorous stirring. Then the precipitation was washed NMMNO-free and kept as an i-PrOH-wet sample. These never dried i-PrOH wet samples were employed for the ^{13}C-CP/MAS NMR measurements.

The less ordered form of cellulose was obtained in the case of using iso-propanol as precipitant and as washing medium. This spectrum is very similar to the ball milled cellulose spectrum. The small sharp signal at 64 ppm indicates residues of i-PrOH in the amorphous cellulose structure. An increase of the crystalline C4 and C1 peaks could be observed by using parts of water, either as precipitant or as washing medium, whereas the water from precipitation has a greater influence than from the washing process. The influence of the decrystallization on the water and liquid retention values is shown in Table 1. The water retention value of native celluloses increases in the sequence Temming 500 < Borregaard NC < Ultraether F insignificantly (0.6–0.7 cm^3/g).

As is generally known i-PrOH is a weak swelling medium for native cellulose. While the WRV and LRV values are hardly different for the different cellulose materials, greater changes are recognizable for the relationship amorphous to native. For the samples which are precipitated and washed with pure i-PrOH the relationship of the swelling values amorphous/native increase in the order Borregaard NC < Temming 500 < Ultraether F. The correlation with the DP value is rather coincidental. Related to native cellulose the WRV values of amorphous material increase 5 to 7-fold while LRV values increase 20 to 35-fold.

The comparison of the LRV values of amorphous cellulose (starting from T500) shows an influence on the water content of the precipitant and washing medium. With an increasing amount of water in the precipitant the LRV value is decreasing in the sequence AM7 (i-PrOH) > AM2 (87.4% i-PrOH) > AM8 (water). Water containing precipitants apparently cause not only a recrystallization (Figure 3) but a

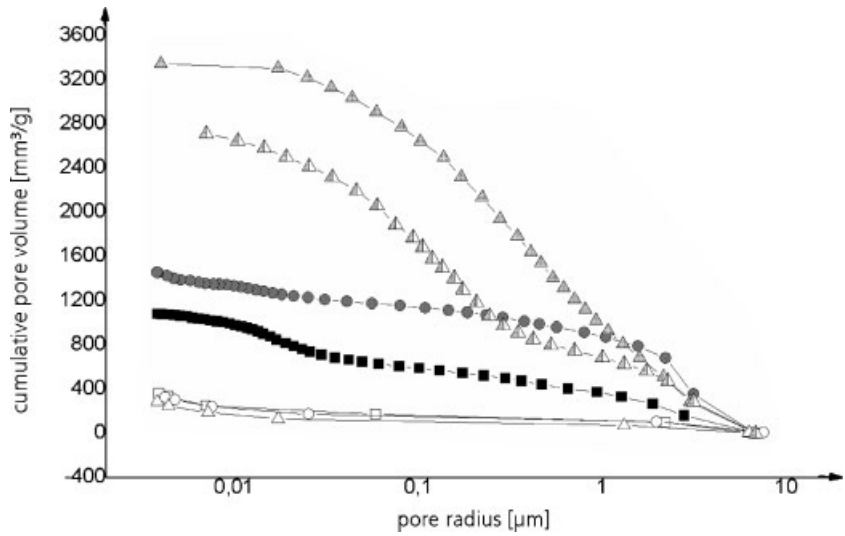

Figure 4.
Cumulative pore volumes of native and amorphous cellulose; □ = Borregaard NC (nativ), ○ = Temming 500 (nativ), △ = Ultraether F (nativ), ■ = Borregaard NC (precipitation with i-PrOH), ● = Temming 500 (precipitation with i-PrOH), ▲ = Ultraether F (precipitation with i-PrOH), ⚠ = Ultraether F (precipitation with water).

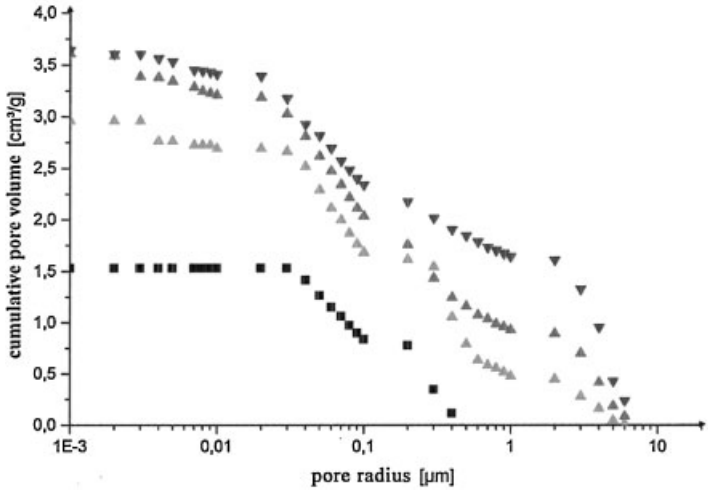

Figure 5.
Influence of the procedure of the precipitation on the pore volume distribution; starting material: Ultraether F, precipitant: i-PrOH, washing medium: 90%i-PrOH; ■ = 3% cellulose solution in i-PrOH (stirring), ▲ = 6% cellulose solution + i-PrOH (ultra turrax), ▼ = 3% cellulose solution + i-PrOH (ultra turrax), ▲ = 3% cellulose solution with i-PrOH until the gel point was obtained then in i-PrOH (stirring).

decrease of the accessible pore system for i-PrOH (Figure 4). Another dependence is given by the WRV values which could already be explained by a reswelling of collapsed pores.

In comparison to the water and liquid retention values Figure 4 shows the pore volumes of native and amorphous celluloses after precipitation with i-PrOH. While the cumulative pore volumes are hardly different for the different cellulose materials, these volumes increase considerably after decrystallization. The total pore volume increases 3-fold in the case of Borregaard NC, 5.4-fold in the case of Temming 500 and 12-fold in the case of Ultraether F. The precipitant employed also has an influence on the pore volume which is demonstrated in the case of Ultraether F. The use of water instead of i-PrOH apparently leads to the collapse of pores in the size area of approx. 2 nm to 1 µm corresponding to the development of organized cellulose II structures.

The pore volume is fundamentally influenced by the precipitation method. There is a differentiation between a dispersion precipitation and a stir-in precipitation. The

Table 2.
Heterogeneous carboxymethylation of Ultraether F (DP = 1625) as native material and after activation with NMMNO*H_2O (DP = 830).

No.	Cellulose	NaOH [mol/mol AGU]	MCA	DS*	Reagent yield [%]	Solubility in water	$\eta(\dot{\gamma} = 2.55\ s^{-1})$ [mPa · s]**
CMC3	pulp	1.3	0.65	0.40	61.5	turbid suspension with gel and fiber particles	1300
CMC4	**amorph**	1.3	0.65	0.46	71	gel paste	19900
CMC5	pulp	2.6	1.3	0.75	57.7	turbid solution with fibers	4360
CMC6	**amorph**	2.6	1.3	0.84	65	solution	6400

*determined by elemental analysis of Na-content;
**2% aqueous solution.

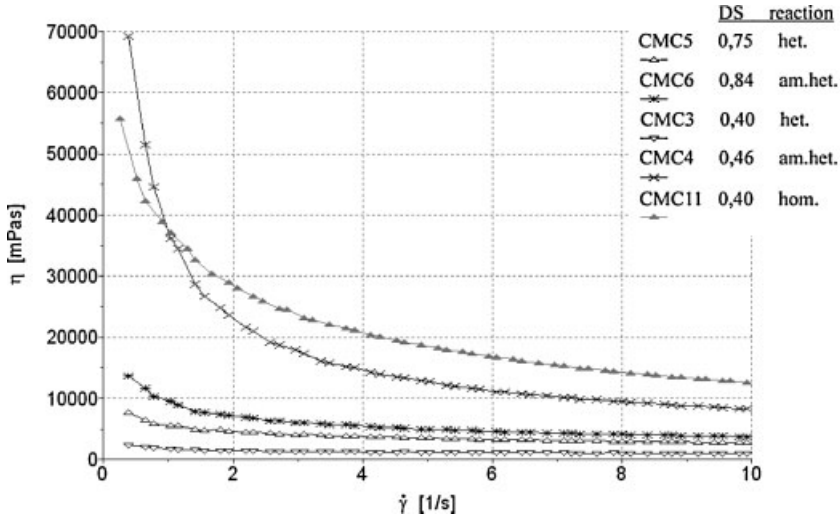

Figure 6.
Viscosity of 2% aqueous solution of CMC vs. shear rate (reaction process, het.: heterogeneous, am.het.: heterogeneous using amorphous cellulose, hom.: homogeneous).

stir-in precipitation was accomplished under different conditions. Firstly the solution of cellulose in NMMNO∗H_2O was added into the precipitant and the performed precipitate was subsequently minced to small pieces. Secondly the solution was added into the precipitant under vigorous stirring and dispersing with an ultra turrax, and thirdly the precipitant was slowly added to the solution under vigorous stirring and dispersing with an ultra turrax until the gel point was obtained. Then this dispersion was added into the precipitant under vigorous stirring with an ultra turrax used additional. By using i-PrOH as a precipitant a decreasing pore volume of decrystallized materials is observed in the order dispersion precipitation > stir-in precipitation of the homogeneous cellulose/NMMNO∗H_2O/i-PrOH mixture > stir-in precipitation of cellulose/NMMNO$^*H_2O$ solution in i-PrOH with ultra turrax (Figure 5).

The highest porosities were obtained by using the dispersion precipitation with a cellulose/NMMNO∗H_2O/i-PrOH mixture. In this case the porosity increased up to 13-fold in comparison to native cellulose. The previous addition of a compatible amount of precipitant to the solution is advantageous for both precipitation methods for getting a high porous material. By doubling the cellulose concentration from 3 to 6% practically no change was observed.

Table 3.
Compatibility of 3–5% cellulose solutions with cosolvents (T = 85 °C).

Solvent	Mass ratio cell. sol.: solvent	Solution state	Color of cellulose solution
DMSO	1:1	homogeneous	orange
DMAc	1:0.5	homogeneous	orange
NMP	1:0.5	homogeneous	orange
morpholine	1:0.5	homogeneous	yellow
N-methylmorpholine	1:0.5	2 liquid phases	orange
tetramethylurea	1:0.5	homogeneous	yellow
iso-propanol	1:0.15	homogeneous, foamy	orange
iso-propanol	1:0.5	caogulation	orange
ethylmethylketone	1:0.5	homogeneous	orange
dimethylglycole	1:0.5	2 liquid phases	orange

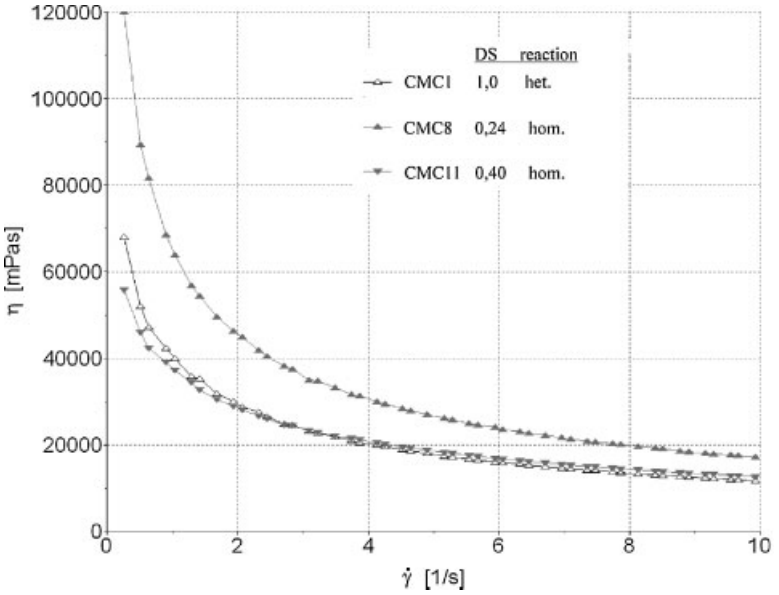

Figure 7.
Viscosity of 2% aqueous solution of CMC vs. shear rate (reaction process, het.: heterogeneous, hom.: homogeneous).

Carboxymethyl Cellulose

The carboxymethylation of native cellulose and cellulose after decrystallization in a slurry process was investigated and the DS, yield, solubility and viscosity of synthesized CMC samples were compared. For the evaluation of the influence of the decrystallization step on the properties of the products the wood pulp Ultraether F was carboxymethylated with and without an activation as described above. In Table 2 the results of these investigations are shown. They reveal a considerable influence of the activation with NMMNO on the properties of carboxymethyl cellulose.

By comparison the decrystallization leads to non-activated cellulose under suitable reaction conditions a) to a clearly better solubility of CMC and higher DS values (compare CMC3 with CMC4 and CMC5 with CMC6 respectively), b) to about 10% higher reagent yields, c) to clear-dissolvable, gel-forming or paste-like CMC in dependence of the amount of

Table 4.
DS and DS distribution of homogeneous synthesized CMC in comparison to a commercial available sample.

	Mol Triton B per AGU	DS (^{13}C-NMR)	Distribution			
			DS_2	DS_3	DS_6	$\%DS_3$
Sequence: **R**eagent+**B**ase+**B**+**R**						
CMC7	6	0.23	0.07	0.07	0.09	30
Sequence: **R**+**B**+**R**+**B**						
CMC8	4	0.22	0.1	0.12	0	55
CMC9	3.5	0.34	0.1	0.33	0	77
CMC10	3.5	0.39	0.12	0.26	0.01	67
CMC11	3.5	0.41	0.12	0.27	0.02	66
CMC12	4*	0.58	0.21	0.3	0.07	57
Reference Sample						
CMC1		1.02	0.45	0.21	0.36	21

*using Na-MCA as reagent.

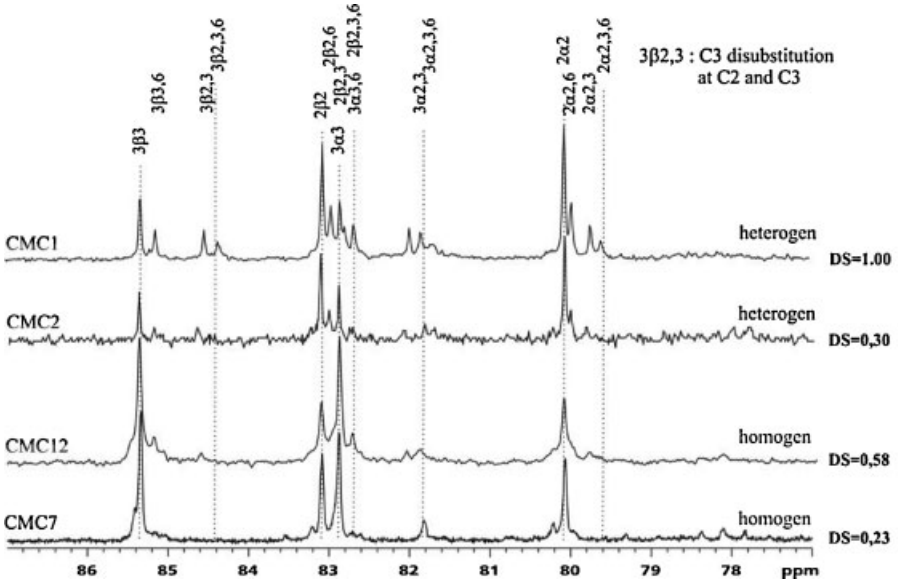

Figure 8.
^{13}C-NMR spectra in the range of C2 and C3 signals of heterogeneous and homogeneous synthesized CMCs; the products were totally hydrolyzed with trifluoro acetic acid and dissolved in D_2O (∼5%).

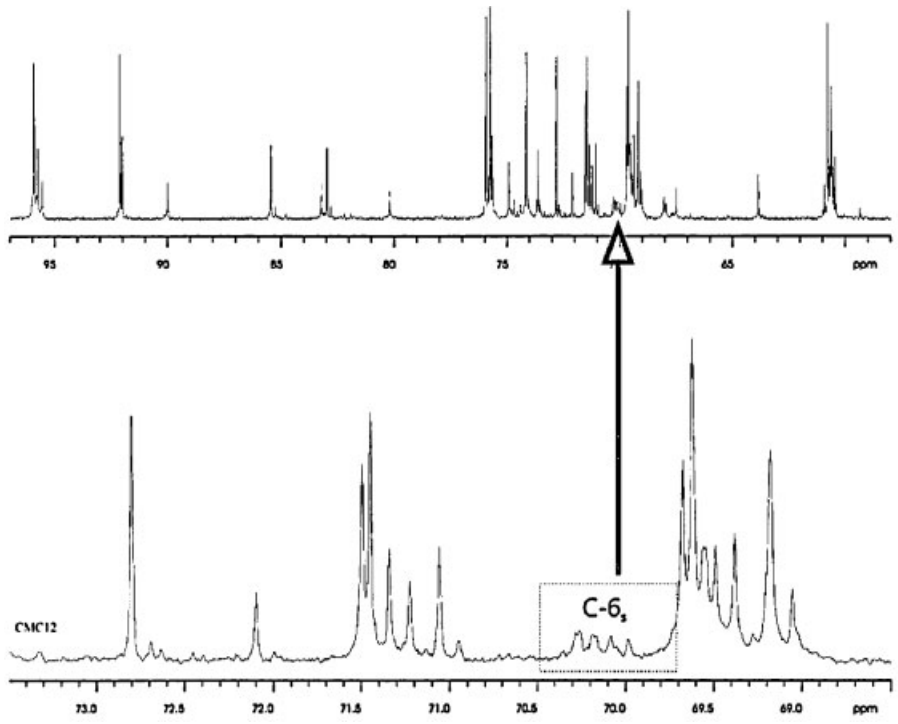

Figure 9.
Focus of C6 position in ^{13}C-NMR spectra of $CMC_{homogen}$ (DS = 0.6); the product was totally hydrolyzed with trifluoro acetic acid and dissolved in D_2O (∼5%).

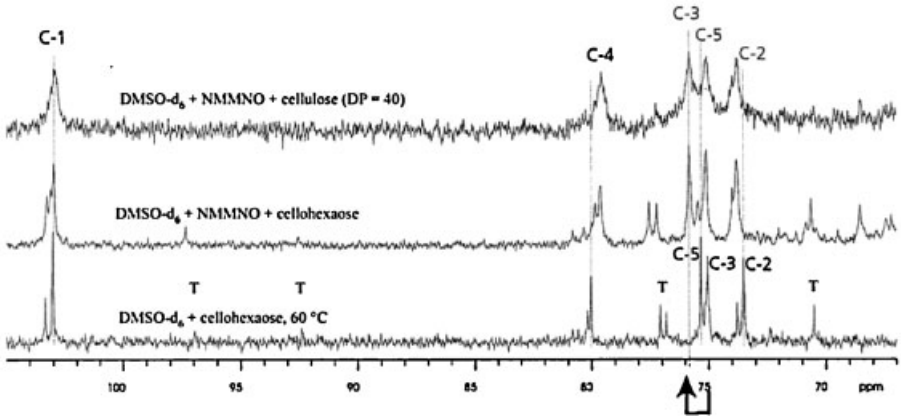

Figure 10.
^{13}C-NMR spectra of level off DP cellulose and cellohexaose in DMSO/NMMNO*H_2O and cellohexaose in DMSO (T: terminal group).

reagent. The positive influence of decrystallization on the product characteristics is especially strong by using a low amount of reagent (DS around 0.45). In comparison with that the homogeneous carboxymethylation in NMMNO∗H_2O/DMSO described in the following chapter leads to a clearly dissolvable product (DS = 0.40) with high viscosity and distinctive structural viscosity (see Figure 6).

Basically the solubility of cellulose and the emerging cellulose derivative is important in the homogeneous conversion during the total reaction time. It appeared that a coagulate was formed by the addition of NaOH to a solution of cellulose in NMMNO∗H_2O, therefore some preliminary tests were carried out to different solubilities and compatibilities in the solution. Alkali cellulose (DP = 350), consisting of 40% cellulose, 15% NaOH and 45% of water, did not dissolve under the standard conditions. Commercially available sodium carboxymethyl cellulose, which was made under heterogeneous conditions with DS of 0.9 dissolved under analogous conditions only incompletely and viscous systems containing swelled particles were received. In all probability, the quantitative solubility in NMMNO∗H_2O is not only dependent on the DS, but rather also on the type of the counterion and the regularity of the sub-

Table 5.
Hydroxyethylation of native and amorphous cellulose; slurry in i-PrOH/t-BuOH, 5 mol H_2O and 2 mol EO/mol AGU, reaction at 75 °C, 100 min.

No.	Cellulose/ precipitation medium	mol NaOH/ mol AGU	Alkalization	$\eta(\dot{\gamma} = 2.55\ s^{-1})$ [mPa · s]*	Solubility [%]**	MS***
Native						
HEC1	Temming 500	1.6	80 min, 25 °C	10	37 suspension	0.44
HEC2	Temming 500	0.8	160 min, 10 °C	5	19 suspension	n.d.
Decrystallization						
HEC3	i-PrOH	1.6	80 min, 25 °C	700	96	1.11
HEC4	i-PrOH	1.6	160 min, 25 °C	640	95	1.15
HEC5	i-PrOH	0.8	160 min, 10 °C	1150	93	1.35
HEC6	i-PrOH	0.6	160 min, 10 °C	775	92	1.45

2% aqueous solution;
**solubility: soluble part after centrifugation;
***MS (molar substitution) determined by the method of Zeisel.[33]

stitution in connection with the amount of water in the system.

With investigations to the preparation of 5% Temming 500-solutions in NMMNO∗H_2O after pre swelling in 0.3 to 2 mol NaOH/AGU containing 50% NMMNO it appeared that already > 0.3 mol NaOH/AGU prevent the formation of optically clear cellulose solutions.

Furthermore the compatibility of the cellulose solution in NMMNO∗H_2O with organic cosolvents, different bases and different reagents were investigated. Their melt temperature can be lowered by mixing of cellulose solutions in NMMNO∗H_2O with suitable organic solvents by which derivatization reactions are practicable at lower temperatures as 85 °C. For exploratory analysis, 3 to 5% cellulose solutions were diluted slowly under intensive stirring at 85 °C with the solvent amounts given in Table 3 and their compatibility was judged visually. As a result it was found that several polar media are suitable as diluents and so it is possible to reduce the melt temperature of the mono hydrate system NMMNO.

The results of the compatibility analysis with different bases can be summarized with: a) alkalihydroxides and -alcoholates cause strong coagulation, b) the quaternary base benzyl trimethylammonium hydroxide is more compatible with the cellulose solution, c) a non-soluble pear-like anionic ion exchanger is completely compatible in combination with the mentioned solvent after prior dehydration, d) 60–80% aqueous NMMNO, DMSO, DMAc or NMP are applicable as diluting media for the quaternary bases, and e) tertiary amines like e.g. tri-n-butylamine or triethylamine indeed cause no coagulation, but fail to lead to a carboxymethylation reaction.

The reagents MCA and Na-MCA dissolved in 50% aqueous NMMNO can be added homogeneously into the reactions system. DMSO is applicable only for MCA. In addition i-PrOH can only be of limited use because of the coagulation effect at higher concentrations. From these pre-examinations, the reaction conditions for homogeneous carboxymethylation described in the experimental part were developed.

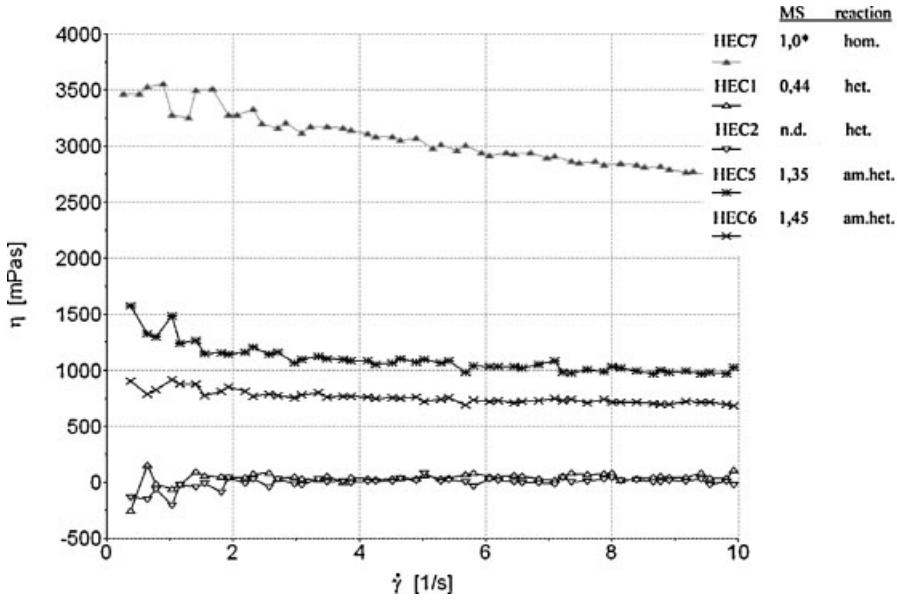

Figure 11.

Viscosity of 2% aqueous solution of HEC vs. shear rate (reaction process, het.: heterogeneous, am.het.: heterogeneous using amorphous cellulose, hom.: homogeneous); * DS instead of MS.

By investigations regarding to carboxymethylation, a certain addition sequence of the reagents in the system cellulose/NMMNO/DMSO/MCA/Triton B succeeded, and this produced a homogeneous synthesis of clearly water soluble products already by a DS > 0.2. This was never found for any other homogeneous carboxymethylation reactions in cellulose solvent systems. By decreasing the reaction temperature from 85 to 65 °C the reaction yield increased from 10 to 33%. Samples taken after 5 to 15 min were already water soluble, which indicates a high reaction rate. High resolution ^{13}C-NMR-spectroscopy after total hydrolysis shows a substituent distribution within the AGU of C3 > C2 ≫ C6 for the DS- range from 0.3 to 0.6, and this is anomalous for cellulose derivatives and it contrasts the results described by Heinze et al.[30] A functionalization of the hydroxyl groups in the order C6 ≥ C2 > C3 was found by using sodium monochloroacetate as reagent and NaOH as base in different cellulose solvent systems.

At strictly homogeneous systems without NaOH we found an uniform distribution of the substituents along the polymer chains without multiple substitution in the AGU. High solution viscosities e.g. of 41500 mPa · s (DS = 0.24, $\dot{\gamma} = 2.55\ s^{-1}$) indicate a low depolymerization when gallic acid propyl ester was used as stabilizer. In comparison, a commercially available reference sample, produced by a heterogeneous process (CMC1, DS = 1.0), has a substituent distribution of C2 ≥ C6 > C3, and the viscosity of a 2% aqueous solution is 28000 mPa · s (Figure 7).

^{13}C-NMR Spectroscopic Analysis Regarding DS and DS-distribution

This chapter demonstrates the exceptional substituent distribution of the homogeneously synthesised CMC-samples, whose results are combined in Table 4, and whose

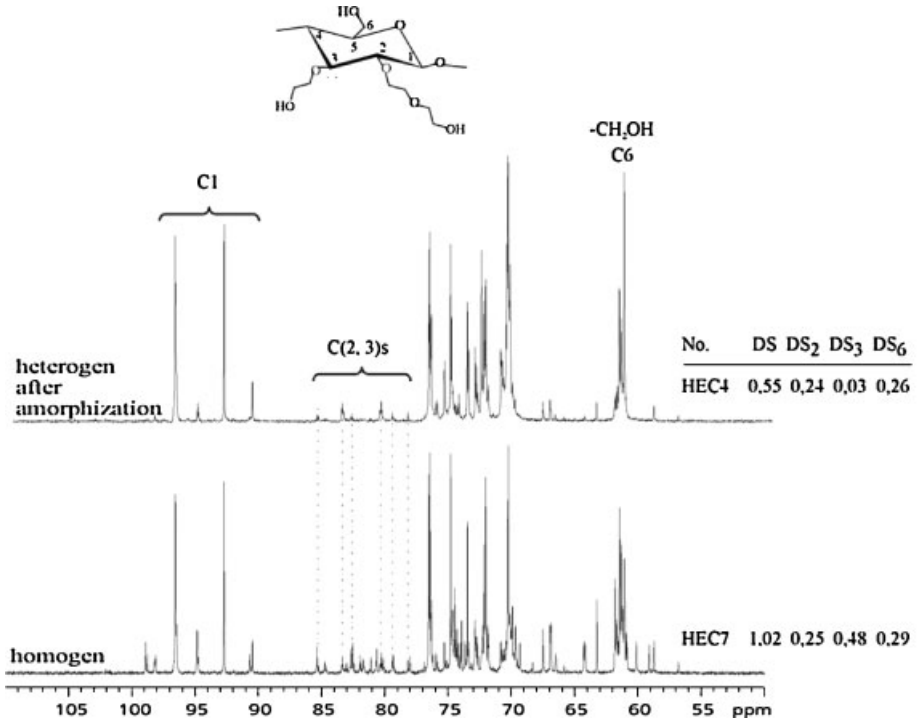

Figure 12.
^{13}C-NMR spectra of hydrolyzed hydroxyethyl cellulose dissolved in D_2O; s: substituted.

spectra are given in Figure 8 in comparison to commercial reference samples.

Typical substituent distributions of heterogeneously produced carboxymethyl celluloses with partial-DS-values of C2 > C6 > C3 in the DS-range of 0.33 to 1.0 are shown in Figure 8. This DS-range indicates non-uniformities caused by multiple substitutions in the AGU to di- and trisubstituted units already by low DS values, which increase with higher DS. The comparison of the spectra of insoluble CMC2 (heterogeneous, DS = 0.33) with CMC7 (homogeneous, DS = 0.24) and CMC1 (heterogeneous, DS = 1.0) with CMC12 (homogeneous, DS = 0.6) demonstrate the high equality of homogeneous carboxymethylation, because of none or only marginal multiple substitution (C3/C6) within the AGU.

Apparently the DS-distribution is influenced by the reaction conditions (see Table 4). The primary C6-OH-Gruppe is surprisingly widely blocked, and this is evidenced by detailed analysis of the ^{13}C-NMR spectrums in the range of 69.8 to 70.5 ppm by a DS = 0.6 (Figure 9).

Investigations of the Mechanism:

In order to understand the phenomenon of the preferential substitution of the C3-position of the AGU, ^{13}C-NMR spectroscopic studies were undertaken. The interaction of cellulose with NMMNO and DMSO was explored using cellohexaose (DP = 8) and microcrystalline cellulose (DP = 40) as model substances under comparable concentration conditions. Temperature was kept constant at 60 °C. The spectra of Figure 10 reveal that the addition of NMMNO∗H_2O results in (a) no shift for C1, (b) modest and significant shifts for C2 and C3, respectively, and (c) significant and modest upfield shifts for C4 and C5, respectively. C4 apparently interacts with C3. C6-signals overlap strongly and cannot be interpreted. The strong downfield shift of C3 indicates a possible anion formation caused either by the strong interactive demand for this OH-group by NMMNO, or by the preservation of the intramolecular H-bond to the O-atom of the C6-position of the adjacent AGU. The H-atom of the latter is sterically favored to interact with NMMNO. The last-mentioned explanation

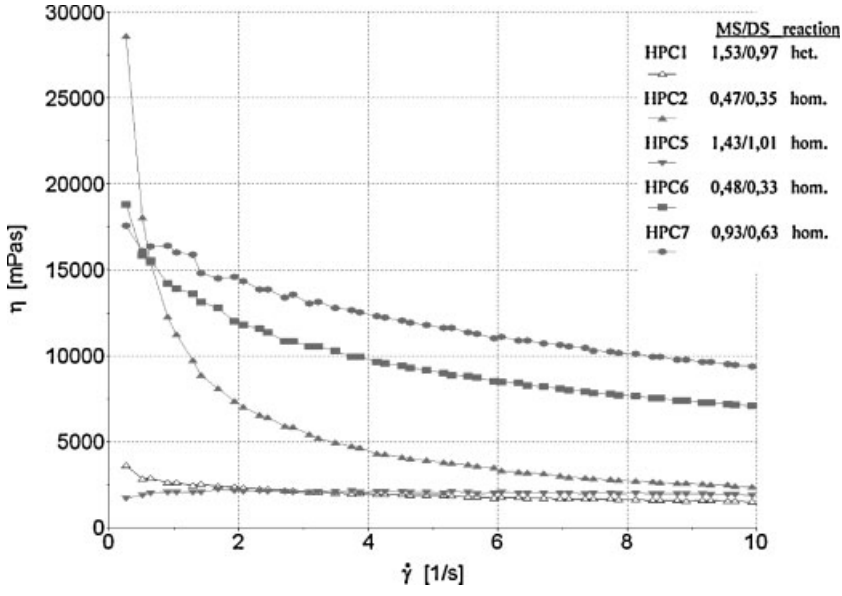

Figure 13.
Viscosity of 2% aqueous solution of HPC vs. shear rate (reaction process, het.: heterogeneous, hom.: homogeneous).

is consistent with published mechanistic suggestions of Berger, Keck, and Philipp.[31,32]

The experimental results for the determination of substituent distributions, which reveal a sequence of preference in the order of C3 > C2 ≫ C6, is consistent with a progressively increasing protection of OH-groups by NMMNO in the sequence of C6 ≫ C2 > C3.

Hydroxyethyl Cellulose

A comparison of the HEC-syntheses under heterogeneous (before and after decrystallization of cellulose) and homogeneous reaction conditions was done in reference to product properties like DS, yield, solubility and viscosity. The main results of the two heterogeneous pathways are shown in Table 5. In the case of decrystallized cellulose, precipitated and purified with i-PrOH, the reagent yield is 2.5-times higher in comparison to native cellulose (see HEC1 and 3) and the water solubility increases considerably.

A reduction of the amount of NaOH (1.6 to 0.8 or even 0.6 mol/mol AGU) is possible and yields nearly completed water soluble products with high viscosities (HEC5 and 6). This was obtained in combination with lowering the temperature for alkalization (25 °C to 10 °C) by concurrent increasing the time for alkalization.

Flow curves for selected heterogeneously synthesized HEC samples and one homogeneously prepared product (HEC7) are presented in Figure 11. All products hardly ever showed any structural viscosity.

It is remarkable that the viscosity of the homogeneously manufactured product is considerably higher than the viscosities of the samples prepared heterogeneous.

Figure 12 shows the ^{13}C-NMR spectra of HEC7 homogeneously synthesized in NMMNO∗H_2O/NMP under AIE-catalysis (DS = 1) and of HEC4 heterogeneously etherified amorphous cellulose (DS = 0.55). The marked difference among these two samples is the unequal substituent distribution. On the one hand a distribution of C2 ≅ C6 > C3 was detected for the hydroxyethylation of amorphous cellulose and on the other hand C3 > C2 ≅ C6 was observed after homogeneous reaction. This is in contrast to the results described for the NaOH/urea solvent system in the literature.[34,35] There a functionalization was found of the hydroxyl groups in the order C6 > C2 > C3, an analogous functionalization pattern as HEC obtained by the heterogeneous slurry process.

Hydroxypropyl Cellulose

First investigations using the cellulose/NMMNO∗H_2O-system at 85 °C without any cosolvent into homogeneous hydroxypropylation were not successful. Thereupon the use of different diluents for lowering the melting point and the use of different catalysts instead of NaOH were examined. It was found that DMSO is an excellent cosolvent, and catalytic amounts of Triton

Table 6.
^{13}C-NMR determination of MS, DS, and DS distribution of HPC after homogeneous synthesis by using DMSO as cosolvent in comparison with commercially available material.

No.	MS	DS	DS-distribution	
		(MS/DS)	DS_{2+3}	DS_6
Commercial HPC heterogeneously synthesized				
HPC1	1.53	0.97 (1.58)	0.58	0.39
Benzyl trimethylammonium hydroxide as catalyst				
HPC2	0.47	0.35 (1.34)	0.29	0.06
HPC3	0.49	0.36 (1.36)	0.19	0.17
HPC4	1.75	1.35 (1.30)	1.13	0.18
Anion exchanger as catalyst				
HPC5	1.43	1.01 (1.40)	0.72	0.09
HPC6 (with NMP)	0.48	0.33 (1.45)	0.32	0.01
HPC7 (with i-PrOH)	0.93	0.63 (1.48)	0.56	0.07

B can be used instead of NaOH. A catalyst molar ratio of 0.5 mol Triton B per mol AGU and a reaction temperature of 70 °C are advantageous reaction conditions to get soluble products. Alternatively an insoluble strong basic quaternary anion exchanger was used in the homogeneous cellulose/NMMNO/DMSO system to produce completely soluble HPC with high viscosity. The MS/DS-range of water soluble HPC manufactured so far is between 0.27/0.2 and 1.45/1.0 (HPC5, with AIE) and 1.75/1.35 (HPC4, with Triton B). It is an advantage using an anion exchanger that no bases and salts need to be eluted from the product. It was found that for homogeneous hydroxypropylation, which gave products with high degree of etherification (HPC4 und HPC5) the 2% aqueous solutions did not coagulate at elevated temperatures up to 100 °C as well as it is known from commercially available HPC.

Besides DMSO other organic co-components in combination with AIE as catalyst were examined. By adding DMSO, NMP, i-PrOH or n- BuOH the reaction resulted in products completely water soluble with MS values up to 1.75. The compatibility with the cellulose solution decreases in the above order and so does the amount of solvent which is necessary for lowering the melting point. For a successful

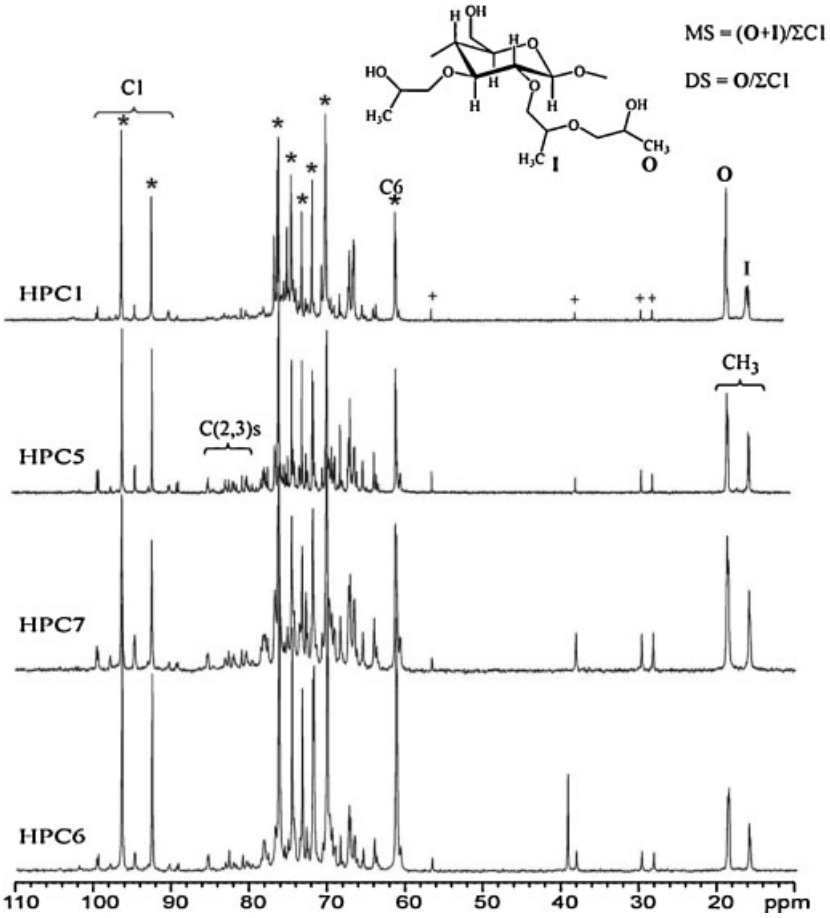

Figure 14.
^{13}C-NMR spectra of hydrolyzed hydroxypropyl cellulose; *: glucose signals, +: impurities, I: interior methyl group, O: outer methyl group, s: substituted.

Table 7.
Heterogeneous sulfoethylation of native and amorphous cellulose (Ultraether F.

No.	Precipitant	NaOH/ AGU NaVS/AGU	DS_{SEC}	η ($\dot{\gamma} = 2.55\ s^{-1}$) [mPa·s]*	Reagent yield [%]
Native					
SEC1	–	2.4/0.8	0.48	4200 remaining fibers	60
SEC2	–	0.6/0.8	0.21	turbid suspension	26
Decrystallization					
SEC3	i-PrOH	2.4/0.8	0.19	32000 turbid	24
SEC4	i-PrOH	1.2/0.8	0.46	firm gel	57.5
SEC5	H_2O	1.2/0.8	0.43	14800	54
SEC6	i-PrOH	0.6/0.8	0.18	turbid suspension	22.5
SEC7	H_2O**	1.2/0.6	0.32	960 gel paste	53

*2% aqueous solution;
**starting material Temming 500.

reaction a certain solvent concentration is necessary depending on properties of the organic cosolvent.

In Figure 13 the rheological characteristics of some synthesized HPCs are compared with a commercially partially soluble heterogeneously manufactured HPC. The low substituted product (e.g. HPC2) displayed a pronounced structural viscosity. The higher substituted sample (HPC5) prepared by AIE-catalysis to $MS = 1.4$ showed no structural viscosity, whereas the structural viscosity for the partially soluble reference sample (HPC1) with comparable MS was slightly pronounced. Remarkably higher viscosities of $\eta = 11300$ and 14000 mPa·s at a shear rate of $\dot{\gamma} = 2.55\ s^{-}1$ were achieved by adding GPE as a stabilizer for the NMMNO-system and using NMP (HPC6) or i-PrOH (HPC7) as cosolvents.

NMR results in terms of DS, MS, and DS-distribution for the HPC samples are given in Table 6. The derivatives, which were made homogeneously show a lower substitution at C6 for the complete DS-range from 0.2 to 1.35 and a strong preference of the 2/3-position up to 90% of the over all substitution. The substitution pattern follows the order $C3 > C2 \gg C6$, which is regioselective and anomalous.

The low MS/DS-ratio for homogeneous reaction with 1.3 to 1.4 compared with 1.5 to 1.7 for heterogeneous reaction indicates a more evenly derivatization pattern which was corroborated by the solubility behavior of the samples. These differences are clearly seen in the comparative NMR-spectrum (Figure 14). They are indicated by the ratio O/I of the outer to the interior CH_3-groups, the ratio of unsubstituted to substituted C6 signals, and the signals in the range of substituted C2 and C3. The comparison of the used two catalysts shows that the catalysis of the hydroxypropylation at the surface of the anion exchanger (0.4–0.5 mol OH- /AGU) leads to nearly the same substituent distribution as the catalysis with the soluble quaternary base (0.25–0.5 mol Triton B/AGU).

Sulfoethyl Cellulose

The large number of investigations for homogeneous sulfoethylation with sodium vinylsulfonate for the $NMMNO^{*}H_2O$ and DMSO containing system under broad variation of reaction time and temperature, concentration and type of the basic component, as well as the dosage sequence of the reagents indicate that there are in principle hurdles for a successful reaction. Therefore are several possibilities such as an adverse reaction equilibrium, the deactivation of NaVS caused by to strong interactions with NMMNO or DMSO and/or the deficient electronegativity of the cellulosic hydroxyl groups. The water content of the system can be of further importance.

Therefore only the heterogeneous SEC-syntheses before and after decrystallization of cellulose were compared regarding

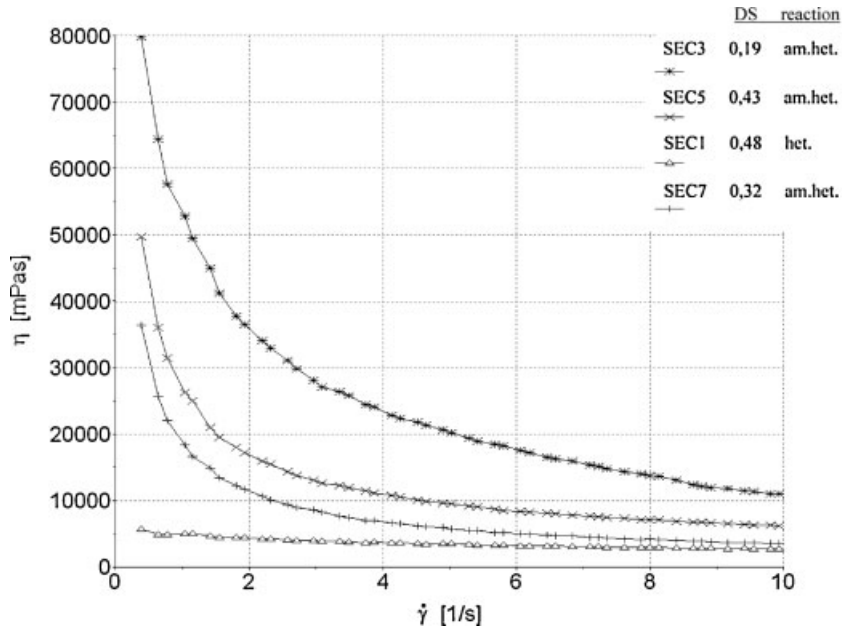

Figure 15.
Viscosity of 2% aqueous solution of SEC (reaction process, het.: heterogeneous, am.het.: heterogeneous using amorphous cellulose, hom.: homogeneous).

product properties like DS, yield, solubility and viscosity. The DS was determined by elemental analysis of sulfur and sodium content of the purified Na-salts of the sulfoethyl cellulose (Na-SEC). The basic results are given in Table 7. The sulfoethylation of native Ultraether F led to water insoluble products in the DS-range of 0.2–0.5, indicating inaccessible pulp components (SEC1 and SEC2). For comparable DS a considerable improvement of the viscosity properties can be found after decrystallization (SEC4). Reducing the amount of NaOH from 2.4 to 1.2 mol/mol AGU an increase of DS and reagent yield was observed under this reaction conditions whereas a further reduction to 0.6 mol/mol proved to be unfavorable (SEC6).

Varying the precipitation conditions during the decrystallization and the molar ratio of reagents sulfoethyl celluloses were obtained with different viscosity properties like high viscous solutions (SEC5) to gel pastes (SEC7).

Figure 15 shows the flow curves of SECs with very high viscosity and structural viscosity in the case of sulfoethylated amorphous cellulose (SEC5) in contrast to SEC1 based on native cellulose at nearly equal DS of 0.45. The highest viscosity was found for products with low DS $\sim$ 0.2 which is nearly the limit value of solubility (synthesized from amorphous cellulose; SEC3). Decreasing the DS to 0.3 (SEC7, Temming 500 amorphous, precipitation in water) a pasty shear thinning SEC is produced.

This indicates that besides the decrystallization the amount and distribution of NaOH inside the polymer matrix can control the rheological product properties.

Conclusion

In order to explore the broad potential of cellulose synthesis and understand structure-property relationships, etherification reactions of native cellulose, decrystallized cellulose and homogeneously dissolved cellulose were compared. A method was developed for decrystallization of cellulose under very low degradation by precipitation in NMMNO$*$$H_2O$-system. Native cellulose with its typical low porosity

was turned into highly porous structure. Varying the precipitation conditions the degree of crystallinity could be adjusted to the desired level. In general an improvement of the solution qualities and an increasing viscosity of synthesized cellulose derivatives were observed from heterogeneous to heterogeneous with amorphous cellulose to homogeneous reaction conditions. It is also recognized that the substitution along and between the polymer chains is more equal with the homogeneous conversion compared to classical procedures. There is a remarkable difference between the heterogeneously produced cellulose ethers with a DS distribution C2 > C6 > C3 and the homogeneous etherification in NMMNO∗H_2O/organic solvent systems with a DS distribution of C3 > C2 ≫ C6. This high regioselectivity at the secondary OH-groups of the AGU may be caused by the strong solvatation behavior of NMMNO∗H_2O thus protecting the C6-OH-group. Another important point for the homogeneous reaction is the correct choice of the base or the catalyst because NaOH forms an undesired coagulate with the dissolved cellulose. Both the homogeneous derivatization and the activation in NMMNO with subsequent heterogeneous conversion yield new products with new qualities.

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