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Cellulose ethers with a block-like distribution of the substituents by structure-selective derivatization of cellulose

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Native cellulose, especially ground cotton linters, was step-by-step carboxymethylated in alcohol–water medium at low concentrations of NaOH. Using the ^{13}C cross-polarization/magic angle spinning n.m.r. method, it has been found that, under these conditions, initially the non-crystalline regions were selectively etherified; only at higher degrees of substitution were the crystalline regions gradually integrated in the reaction. Therefore, already at relatively low degrees of substitution, the hydrolysates of such cellulose ethers contained higher quantities of di- and trisubstituted glucose units than those of cellulose samples etherified by the conventional method to a comparable degree of substitution. The experimental results confirm the concept of reacting structural fractions proposed for the alkalization of cellulose and indicate the formation of cellulose ethers with a block-like distribution of the substituents along the molecular chains. © 1998 Elsevier Science Ltd. All rights reserved.

(**Keywords: cellulose ethers; structure selective derivatization; ^{13}C n.m.r. spectroscopy**)

INTRODUCTION

Cellulose ethers are amongst the most important water-soluble polymers. They are produced on a large scale and applied in a variety of fields. Accordingly, there are many different types of commercial cellulose ethers varying with respect to the type of substituent as well as to the average degree of polymerization and substitution. However, chemical and physical properties of these materials are determined not only by the averaged substitution, but also by the positions of the substituents at the anhydroglucose units (AGUs) and by the distribution of the substituents along the cellulose chains.

Industrial scale production of cellulose ethers is usually based on a heterogeneous synthesis with alkaline-cellulose-as an intermediate and a subsequent reaction with appropriate reactants[1]. Generally, alkali-cellulose is formed by the interaction of cellulose with sodium hydroxide solutions with $c_{NaOH} \geq 10\%$. Structural changes of cellulose induced by the interaction with alkali depend on alkali concentration and result in different crystalline Na-cellulose modifications[2].

A preferred manufacturing route of carboxymethyl cellulose (CMC), the most important cellulose ether, is given by the so-called slurry method[3]. In the slurry process, cellulose is mostly suspended in an isopropanol–water–NaOH system, with a surplus of isopropanol. The molar ratio of NaOH/AGU is chosen as necessary for the reaction with monochloroacetic acid (MCA), which has to be added to the alkali-cellulose suspension in the desired molar ratio. Yokota[4] carefully investigated the alkalizing effect of a two-phase isopropanol–water–NaOH system used for slurry etherification. Performing wide-angle X-ray scattering and ^{13}C solid-state n.m.r. investigations on wet alkali-celluloses, we found that the effect of a slurry alkalization with the usual aqueous–alcoholic NaOH solution corresponds to that of a highly concentrated aqueous NaOH solution[5]. Summarizing these results with regard to CMC preparation, a highly uniform cellulose ether is obtained from a fully alkalized cellulose characterized by a very low supramolecular order and a lattice type resembling Na-cellulose II. Consequently, a reduced activation of cellulose with NaOH according to the concept of Reacting Structural Fractions (RSF)[6] should result in a selectively substituted cellulose with new properties. As shown by the RSF concept, structural regions of cellulose with different supramolecular order (crystalline and amorphous) can differ with respect to the specific NaOH sorption depending on the NaOH concentration of the alkalizing medium. Thus, we postulated that the reactivity of cellulose to etherification and the distribution of substituents can be adjusted by a controlled activation of the different structural regions.

Starting from the RSF concept of alkalization[6], our goal was to find an experimental method for the synthesis of new cellulose ethers with a controlled distribution of substituents along the cellulose chains, preferentially with a block-like structure. As a model reaction, we investigated the carboxymethylation in an isopropanol–water–NaOH slurry system by adding MCA or its sodium salt (NaMCA). To generate different substitution patterns we used non-selective and structure-selective etherification routes in a conventional and a reverse mode[7], varying the ratios of NaOH/AGU and MCA/AGU.

The resulting products were analysed in the solid state as well as after hydrolysis in solution by appropriate ^{13}C n.m.r. methods. Wide angle X-ray scattering (WAXS) was included for additional cellulose characterization.

It should be mentioned that, independently of our

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suggested route, CMC with a block-like structure has recently been found by Klemm *et al.*[8] to be a reaction product of the regioselective etherification of soluble cellulose intermediates.

EXPERIMENTAL

General

When carboxymethylation is carried out conventionally, using the slurry method, alkali-cellulose is produced in the first stage of the experiment, usually at a ratio of cellulose to water–alcohol medium from 1:20 to 1:25 (w/v). Subsequently, the MCA is added in one step, according to the amount of NaOH used.

In order to limit the derivatization only to the amorphous regions of cellulose, the described structure-selective carboxymethylation was carried out in such a way that a surpassing of the critical NaOH concentration of approximately 9 wt% was avoided in the alkalizing phase of the reaction system during the etherification. Taking into consideration the usual water content (7–8 vol.%) and the ratio of cellulose to the dispersion medium, this was the case at a molar ratio NaOH/AGU < 0.6. These reaction conditions were achieved by:

- adding NaOH and MCA or its sodium salt to the dispersed cellulose at regular intervals,

or according to the reverse method suggested by Pavlov and Petrov[7] by

- periodically adding NaOH to cellulose already impregnated with NaMCA.

In summary, the following methods of etherification were used:

(i) one step, conventional (c);
(ii) one step, reverse (r);
(iii) multi step, structure selective (s);
(iv) multi step, reverse structure selective (r, s).

In the case of an etherification reaction which consumes no alkali, for example the reaction of the hydroxyl groups of cellulose with 1,2-alkylene oxides (epoxides), an appropriate single adjustment of NaOH concentration, which excludes the chemical conversion of the ordered regions, is sufficient. A subsequent derivatization of these remaining unsubstituted regions can be achieved in one step by the well-known application of higher NaOH concentrations.

Starting cellulose

Most of the experiments were carried out using ground cotton linters obtained from Temming Co. In order to be able to make generalizations about the new etherification principle, selected experiments were carried out for comparison with a spruce sulfite dissolving pulp (Borregaard Blue Bear) and a dissolving pulp produced by an alternative method (Organocell). The physical characteristics of interest for the initial celluloses are summarized in *Table 1*.

Carboxymethylation

Cellulose (16.2 g) was suspended in a 500-ml wide-necked reaction vessel with a temperature-controlled jacket in 380 ml of an isopropanol–water mixture. Subsequently, fine-grained NaOH was added under intensive stirring at a reaction temperature of 50 or 70°C. After 15 min, an 80% aqueous solution of MCA was added stepwise. The reaction time between doses was 45 min. Depending on the number of such doses, various $\overline{DS}$ values could be achieved.

In the case of selective carboxymethylation of cellulose, according to the reverse method, the initial cellulose was first charged with sodium chloroacetate and then suspended in an isopropanol–water mixture. After reaching the reaction temperature, NaOH was added gradually without surpassing the critical concentration which would lead to an alkalization of ordered regions.

After completion of the reaction, the synthesized Na-CMC was sucked off using a glass frit, washed free from byproducts with methanol–water mixtures and finally air dried.

Analysis

The average degree of substitution ($\overline{DS}$) of the Na-CMC was determined either gravimetrically as Na_2SO_4 (residue from glowing) or after decomposition in concentrated nitric acid with the help of an emission spectrometer, and additionally by solid-state ^{13}C n.m.r. spectroscopy. In contrast to the specific degree of substitution DS_{sp}, to be discussed later, the average degree of substitution refers to the total mass of the cellulose and amounts to the sum of the partial degrees of substitution ($\overline{DS} = \Sigma DS_i$; $i = 2, 3, 6$), which quantify the chemical conversion of the respective hydroxyl groups of the AGU.

N.m.r. spectroscopy

In order to measure the ^{13}C cross-polarization/magic angle spinning (CP/MAS) n.m.r. spectra, approximately 0.2 cm^3 of the respective substance was filled in a sample rotor and rotated under the magic angle (MAS) to the outer magnetic field at 5–6 kHz in a Varian spectrometer (Unity 400). The resonance frequency was 100.58 MHz (^{13}C), the radiofrequency field strength for cross-polarization and decoupling was 50–70 kHz, the time of cross-polarization 1–2 ms and the time of repetition 3 s. The measurement time varied between 1 and 10 h, depending on the sample and acquisition requirements.

The partial substitutions DS_i, i.e. the degree of substitution of the various hydroxyl groups in the glucose unit, was determined by high-resolution liquid-state n.m.r. after the complete hydrolysis of the cellulose ethers with trifluoroacetic acid. The basis for the evaluation was the paper of Reuben and Conner[9].

Table 1 Data for the characterization of initial celluloses[a]

Initial cellulose	DP	LODP	x_c (%)	A (nm^2)	D_{040} (nm)
Temming 500 (T)	2033	150	56	33	10.0
Borregaard Bl. B. (B)	690	176	50	18	8.6
Organocell (OC)	934	156	55	17	10.2

[a] DP, average degree of polymerization; LODP, level-off DP; x_c, crystallinity (X-ray); A, cross-section of crystallites (X-ray); D, length of crystallites along the chain x-ray

Furthermore, the amount of unsubstituted glucose in the hydrolysates was calculated from the spectra in order to obtain the specific degree of substitution $\mathrm{DS}_{\mathrm{sp}}$, which shows the average substitution of the *substituted* cellulose material only:

$$\mathrm{DS}_{\mathrm{sp}} = \frac{\overline{\mathrm{DS}}}{1 - \frac{\%\ \mathrm{glucose}}{100}} \qquad (1)$$

Generally, the glucose part can be calculated by:

$$\%\ \mathrm{glucose} = \frac{\Sigma F_{\mathrm{G}}}{\Sigma F_{\mathrm{G}} + \Sigma F_{\mathrm{subst.G}}} \times 100 \qquad (2)$$

where ΣF_{G} is the sum of all areas of the lines for non-substituted glucose and $\Sigma F_{\mathrm{subst.G}}$ the sum of all areas of lines for substituted glucose.

For practical purposes we used only the well-resolved C-1 lines:

$$\%\ \mathrm{glucose} = \frac{F_{1\alpha(\beta)\mathrm{G}}}{F_{1\alpha(\beta)\mathrm{G}} + \Sigma F_{1\alpha(\beta)i}} \times 100 \qquad (3)$$

where $F_{1\alpha(\beta)\mathrm{G}}$ is the area of the line for C-1, which is assigned to the α (or β) anomers of the unsubstituted glucose, and $F_{1\alpha(\beta)i}$ (i = 2; 3; 6; 2, 3; 2, 6; 3, 6; 2, 3, 6) are areas of lines for C-1 which are assigned to α (or β) anomers of mono-, di- and trisubstituted glucoses.

To determine the glucose portion from the C-1 line, separation of superimposed C-1G and C-1i line components was performed using the VARIAN software.

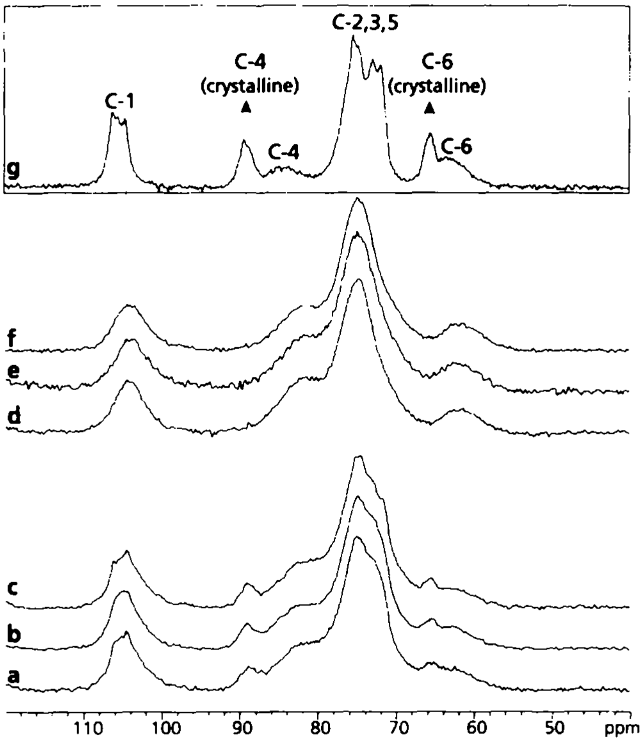

Figure 1 ^{13}C CP/MAS n.m.r. spectra of conventionally and structure selectively prepared CMC. Molar ratio NaOH/AGU = 2(MCA/AGU) = 2.4. (a)–(c) Structure-selective carboxymethylation ($\overline{\mathrm{DS}}$ = 0.80, 0.81 and 0.91, respectively. (d)–(f) Conventional carboxymethylation ($\overline{\mathrm{DS}}$ = 0.93, 0.98 and 0.86). (g) Starting linters for comparison. (a), (d) Dissolving pulp prepared by an alternative method (Organocell). (b), (e) Spruce sulfite dissolving pulp (Borregaard Bl. B.). (c), (f) Linters (Temming)

RESULTS AND DISCUSSION

Figure 1 shows the high-resolution ^{13}C solid-state n.m.r. spectra of conventionally and selectively carboxymethylated cellulose, which demonstrate the main difference between the two derivatization methods. For comparison, the n.m.r. spectrum of the initial cotton linters is shown in the upper part of *Figure 1*. The lines are assigned to the carbon atoms of the AGU, whereby the narrow and wide components of the C-4 and C-6 lines represent the crystalline and non-crystalline regions of the sample, respectively. Comparing the middle and lower parts of the figure, one can see, above all, the change in the intensity of the narrow parts of the lines C-4 and C-6 at 89 and 66 ppm, which are characteristic for ordered cellulose I. From their absence in the middle spectrum group, it can be concluded that, in conventional carboxymethylation, the entire initial cellulose is made accessible to the reaction with MCA due to the conversion of the ordered native cellulose I into alkali-cellulose using concentrated solutions of NaOH. With the gradual addition of NaOH and the etherification reagent, the carboxymethylation occurs scarcely in the

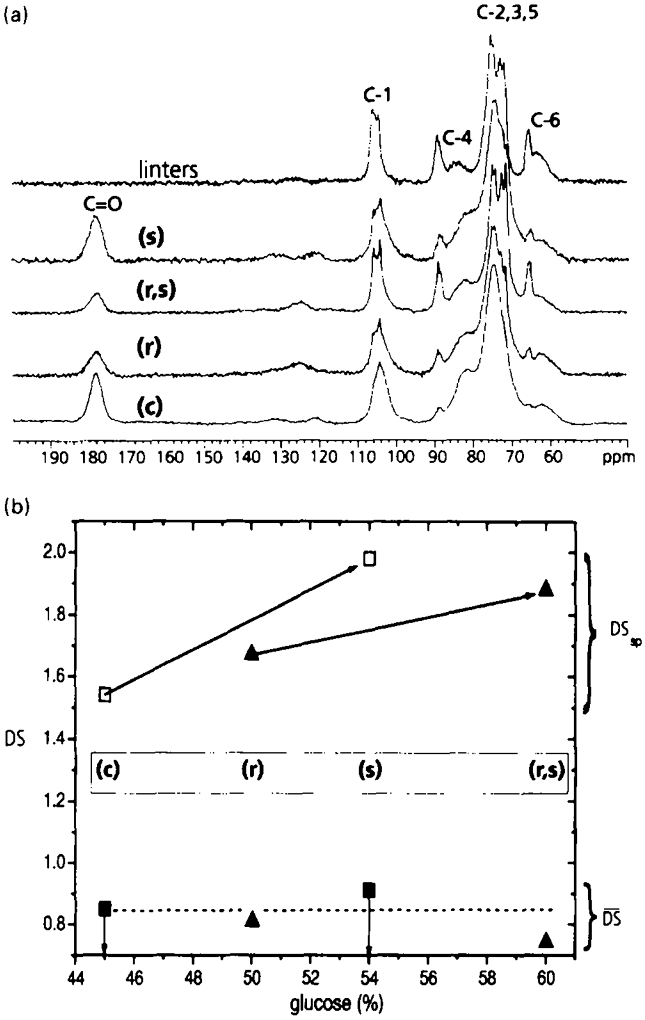

Figure 2 Comparison of CMCs prepared by different methods. (a) ^{13}C CP/MAS n.m.r. spectra of CMC in comparison with linters. (b) Evaluation of the n.m.r. spectrum for glucose, average degree ($\overline{\mathrm{DS}}$) and specific degree ($\mathrm{DS}_{\mathrm{sp}}$) of substitution. c: conventional, molar ratio NAOH/AGU = NaMCA/AGU = 1.2, $\overline{\mathrm{DS}}$ = 0.85; r: overall reverse, molar ratio NaOH/AGU = NaMCA/AGU = 1.2, $\overline{\mathrm{DS}}$ = 0.84; r, s: reverse structure selective, molar ratio ΣNaOH/AGU = ΣNaMCA/AGU) = 1.2, $\overline{\mathrm{DS}}$ = 0.76; s: structure selective, molar ratio ΣNaOH/AGU = 2(ΣMCA/AGU) = 2.4, $\overline{\mathrm{DS}}$ = 0.91

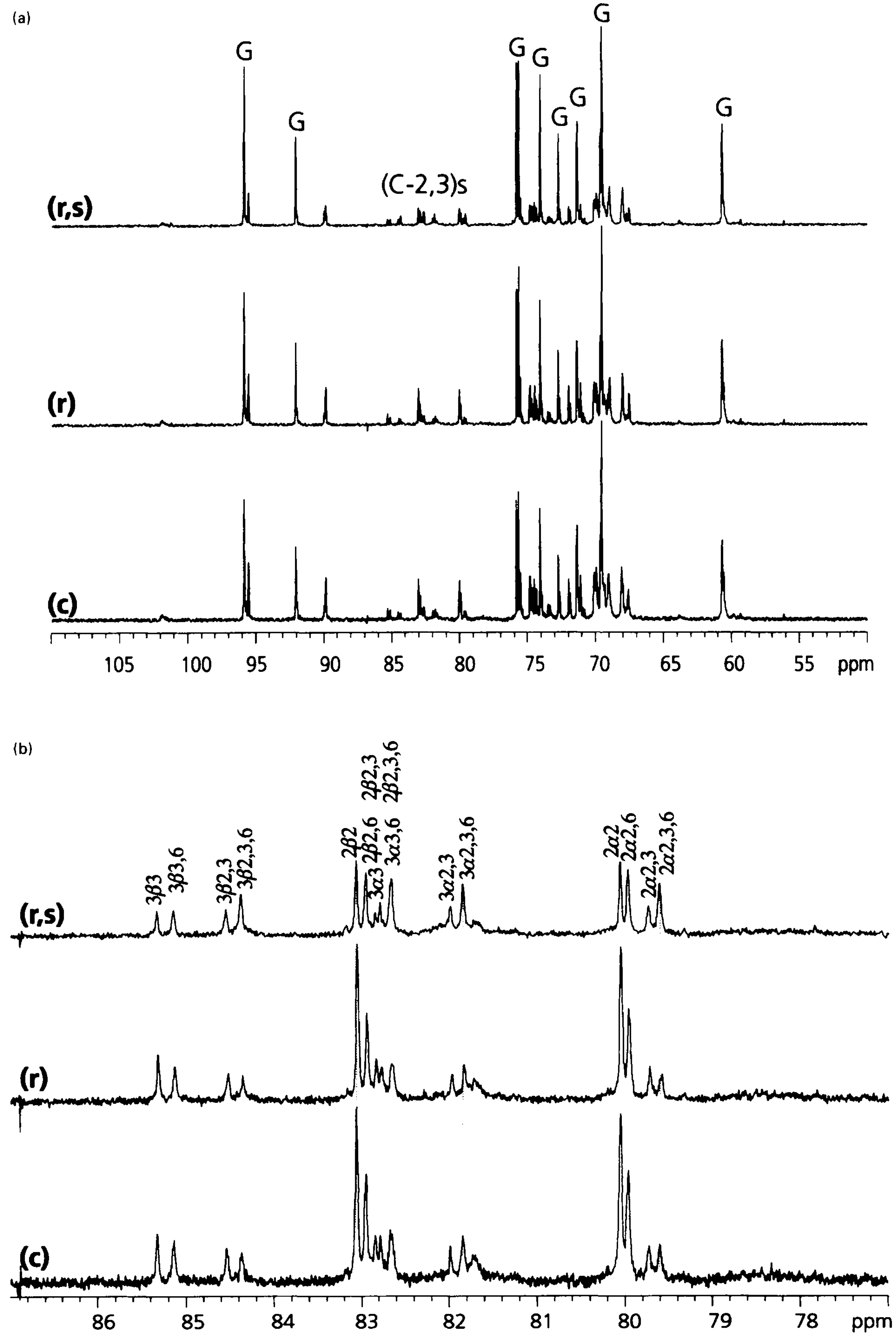

Figure 3 ^{13}C n.m.r. spectra after the complete hydrolysis of the CMCs. (a) General view for part of glucose. (b) Sections of the ^{13}C n.m.r. spectra with details regarding the substitution. c: conventional method, molar ratio NaOH/AGU = NaMCA/AGU = 1.2,$\overline{DS}$ = 0.85; r: overall reverse method, molar ratio NaOH/AGU = NaMCA/AGU = 1.2,$\overline{DS}$ = 0.84; r, s: reverse structure-selective method, molar ratio ΣNaOH/AGU = ΣNaMCA/AGU = 1.2, $\overline{DS}$ = 0.76. For designation of lines see Experimental section, e.g. 3β3, 6: line for C-3 of the β anomer of the disubstituted glucose at C-3 and C-6

ordered structural regions. This is shown clearly by the remaining crystalline C-4 and C-6 line components and by the form of the line for C-1 at 105 ppm in the lower part of *Figure 1*. Obviously, in this case primarily the non-crystalline regions have been derivatized. The high reactivity of the non-crystalline regions becomes clear from the resulting average degree of substitution ($\overline{DS}$ = 0.8–1.0), which is approxymately equal to that of the conventional carboxymethylation using the same amounts of chemicals.

The decisive influence of the NaOH concentration present during the etherification on the location of substitution in the cellulose chain also becomes clear in the application of an equimolar amount of NaMCA as etherifying agent. To reach comparable degrees of substitution, it requires only half of the amount of NaOH applied to the samples of *Figure 1*. Additionally, the sodium chloroacetate allows the undisturbed process of etherification according to the reverse method. For this reason, CMCs were synthesized from ground cotton linters (molar ratio of NaOH/AGU = 1.2) according to different variants of the slurry method: the conventional method (c), the reverse method (r), the structure-selective method (s) and the reverse structural-selective method (r, s). *Figure 2a* shows the solid-state n.m.r. spectra which were measured for these samples. A comparison of the two lower spectra with that of the linters shows that, using the conventional slurry method, a molar ratio of NaOH/AGU = 1.2 is apparently not sufficient for the carboxymethylation of the cellulose throughout its chains, since residual characteristic lines for cellulose I (see the auxiliary lines) point to an incomplete alkalization of the ordered regions. This finding stands in agreement with the results of previous structural investigations of the alkalization of native cellulose with various NaOH concentrations[5]. The complete conversion of the crystalline cellulose I regions into reactive Na-cellulose I can only be attained at higher NaOH concentrations.

On the other hand, the n.m.r. spectra of the samples CMC(r, s) and CMC(s) illustrate very clearly the effect of selective etherification: in comparison to the linters spectrum, the characteristic lines of crystalline cellulose remain clearly visible.

If, however, NaOH is added in one portion, using the non-selective reverse method, a competition obviously arises between the direct carboxymethylation of the non-crystalline structural regions and the substitution reaction which occurs in the crystalline regions through the partial intermediate formation of alkali-cellulose. This means a parallel run of selective and conventional etherification, as the spectrum for CMC(r) proves. The areas of narrow lines for C-4 and C-6 are, in comparison to CMC(r, s), notably smaller. In addition, the high field shoulder of the line group C-2,3,5 is heavily flattened, which clearly shows the transition towards a conventionally carboxymethylated cellulose.

Figure 2b contains these results in a quantified form, by figuring the average as well as the specific degree of substitution in terms of their dependence on the glucose portion of the etherification products. The glucose portion of the CMC samples increases, at equal $\overline{DS}$, proportionally to the cellulose I portion in *Figure 2a*, from 45% for the conventional to 54% using the structural-selective method, and in the case of the reverse method from 50% to 60%, respectively. The DS_{sp} amounts to significantly higher values, corresponding to the respective selective variant.

The highly resolved ^{13}C n.m.r. spectra of the CMC hydrolysates in aqueous solution are shown in *Figure 3a* as an overview (but without the lines of the carboxyl groups). In *Figure 3b*, sections of these spectra can be seen in an interval of 77–87 ppm, allowing a detailed discussion regarding mono-, di- and trisubstitution of the AGUs.

The spectra in *Figure 3a* are also suitable to recognize the unsubstituted glucose portion, which increases proportionally to the cellulose I portion of the sample CMC(c) via the CMC(r) to the CMC(r, s). All lines marked with G correspond to glucose, whereby the lines located at 60.5, 92 and 96 ppm are well resolved. Percentages of glucose were calculated according to equation (3); data are given in *Figure 2b*.

From the different glucose portions of the samples with $\overline{DS}$ values between 0.76 and 0.85, at approximately equal average, it follows that the substituent distribution of the respective samples must also be different. The substituent distribution of the sample CMC(r, s), shown in *Figure 3b*, is significantly changed in favour of di- and trisubstituted glucoses. The comparison of line intensities at 79.6, 80, 81.8, 82.7 and 83 ppm (see line assignment in upper spectrum), between CMC(r, s) and CMC(c) spectra, clearly shows the changed proportions. According to the widely accepted two-phase model of the physical structure of cellulose, it was initially assumed that, if the degree of crystallinity x_c of the highly molecular cotton cellulose used in our experiments amounts to 56%, the preferred carboxymethylation of unordered regions, achieved through the applied reaction conditions, could only lead to $\overline{DS}$ rates of approximately 1.5. However, the systematic preparative and analytical work has shown that a continuation of successive etherification can lead to $\overline{DS}$ values higher than 2. The ^{13}C CP/MAS n.m.r. spectra shown in *Figure 4* give an insight into structural changes which thereby occur in the solid state with increasing total NaOH/AGU and MCA/AGU ratios, respectively. From the intensity of the narrow lines for C-4 and C-6, it is apparent that with increasing molar NaOH/AGU ratio (i.e. increasing $\overline{DS}$), more crystalline cellulose is included in the reaction. Cellulose I

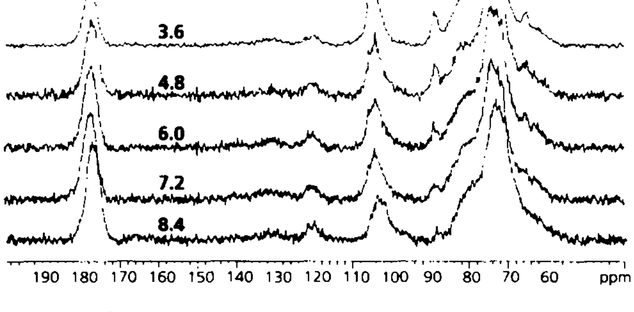

Figure 4 ^{13}C CP/MAS n.m.r. spectra of structure selectively carboxymethylated linters. Number at the spectrum is the molar ratio ΣNaOH/AGU = 2(ΣMCA/AGU); values of DS from top to bottom are 0, 0.30, 0.91, 1.11, 1.37, 1.75, 2.00 and 2.13, respectively

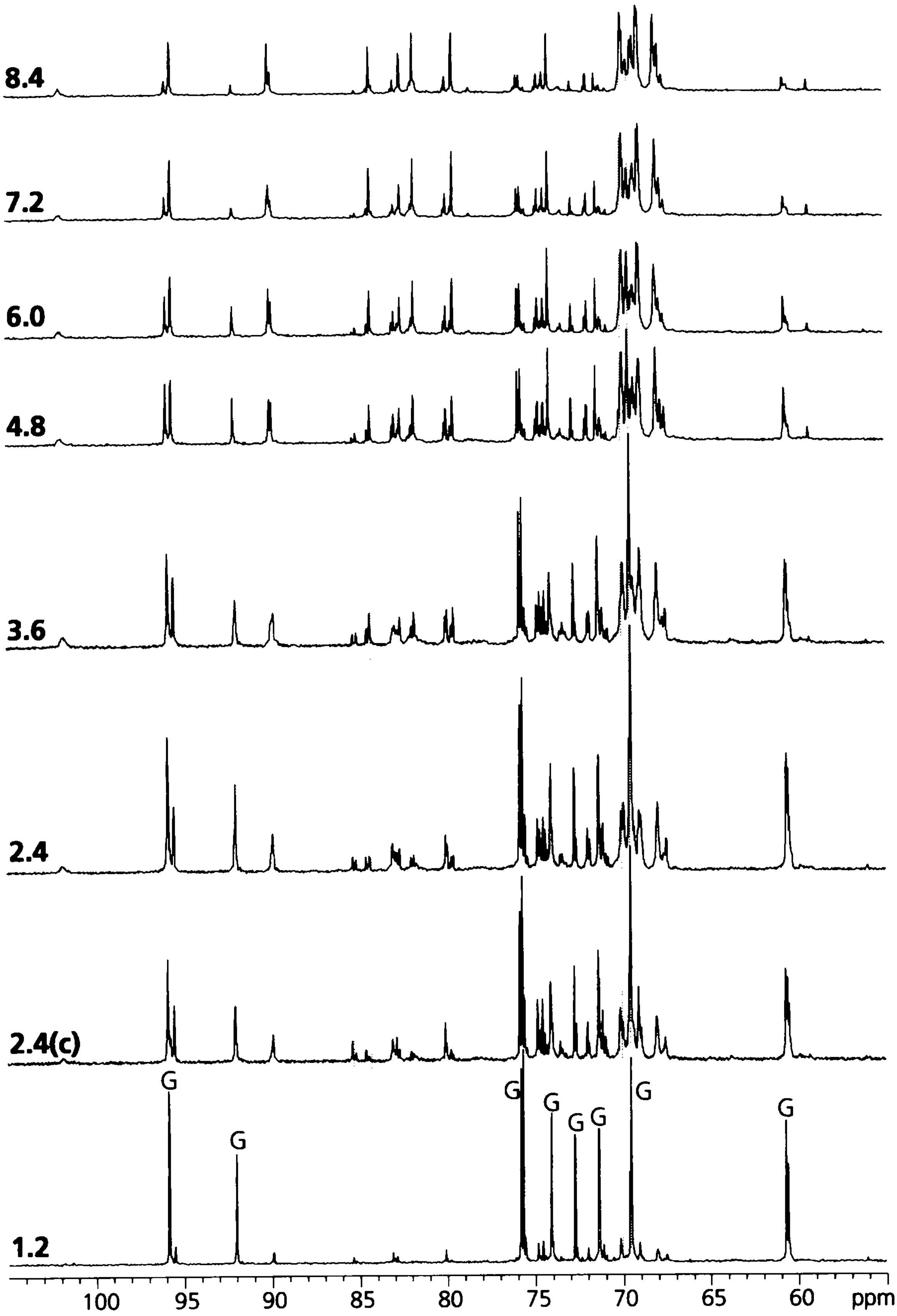

Figure 5 ^{13}C n.m.r. spectra of the hydrolysates of structure-selective synthesized CMC samples. Number at the spectrum is the molar ratio ΣNaOH/AGU 2(ΣMCA/AGU), as in *Figure 4*. c: conventional method for comparison, $\overline{DS}$ = 0.84

crystallites are still present in relatively high quantities in the CMC at values up to 1.4. However, only a very small amount is detectable above $\overline{DS} = 2$. The structural changes are also reflected in the lines for C-1 and C-2,3,5.

These findings can be explained on the basis of the two-phase amorphous–crystalline model, with extended cellulose chains passing a number of ordered and unordered regions. With increasing substitution of the non-crystalline regions, crystalline anhydroglucose units of the interface between crystalline and non-crystalline regions become accessible to the etherification without previous formation of alkali-cellulose.

To prove this idea and to obtain a more detailed insight into the process of structure-selective carboxymethylation, the CMC samples according to *Figure 4* were also hydrolysed with trifluoroacetic acid. After dissolving the hydrolysates in D_2O, the various structural units of the CMC samples were detected using ^{13}C n.m.r. spectroscopy. The results of these investigations are shown in *Figures 5–7* and *9*.

Figure 5 shows a decreasing amount of unsubstituted glucose with increasing NaOH/AGU ratio (i.e. increasing $\overline{DS}$), corresponding to the changing amount of crystalline cellulose I in *Figure 4*.

The quantitative evaluation of the glucose from the spectra of *Figure 5* is described in *Figure 6*, and shows a non-linear decrease in the glucose content of the samples with increasing degree of derivatization.

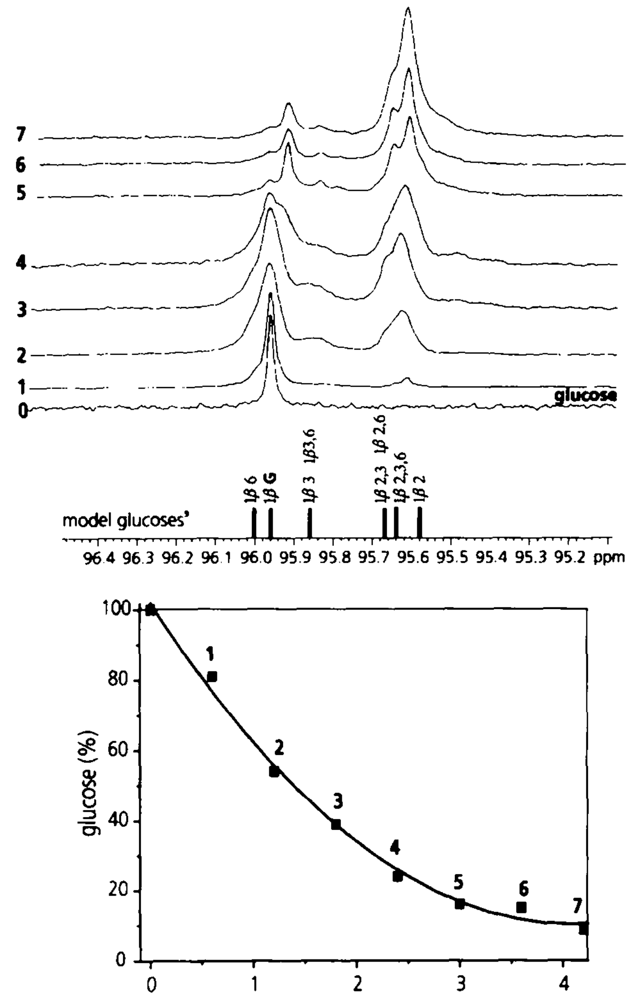

Figure 6 C-1β line region of the ^{13}C n.m.r. spectra of the hydrolysed CMC samples from *Figure 5* and the evaluated amounts of glucose (bottom). Values of $\overline{DS}$ from spectra 0 to 7: 0, 0.30, 0.91, 1.11, 1.75, 2.00 and 2.13, respectively

Further evidence of structure-selective derivatization is obtained from the number of mono-, di- and trisubstituted AGUs for structure selectively and conventionally synthesized CMC, at an average of $\overline{DS} \approx 1$. If the substitution up to this $\overline{DS}$ level were uniform throughout all structural regions, then one would detect mostly monosubstituted glucose in the hydrolysate. For structure-selective derivatization, we would expect a considerable amount of di- and trisubstituted glucose, at least greater than using the conventional method. The parts of spectra in *Figure 7*, with the labels 2,4(c), 2,4 and 3,6, allow the evaluation of the substitution of conventional and selective derivatization in the $\overline{DS}$ range of 0.84–1.15. Using the designation at the upper border of *Figure 7*, one can see that with approximately equal $\overline{DS}$, the derivatized portions of the conventionally prepared sample 2,4(c) are mostly mono- and disubstituted, while those of the selectively derivatized samples 2,4 and 3,6 are considerably more di- and trisubstituted. This is further proof of the intended structure-selective or non-uniform etherification.

The block-like distribution of the substituents of selectively carboxymethylated cellulose also becomes evident in dissolving experiments: conventionally synthesized CMC is either completely soluble in water (e.g. $\overline{DS} \approx 1$, concentration of CMC = 2% by weight), or it gives soluble and insoluble parts. Under the same conditions, on the other hand, samples of selectively carboxymethylated cellulose exhibit only more or less swollen particles as detected by microscopic investigations. We conclude that in this case numerous unsubstituted crystalline network junctions prevent the transition into the solution state.

Figure 8 displays the $\overline{DS}$ values reached respectively in terms of dependence upon the total mole ratio MCA/AGU for the structure-selective experimental series, with successive increases in NaOH and MCA. The resulting curve shows a continuous increase, with gradual flattening at higher degrees of substitution (maximum possible $\overline{DS} = 3$). Additionally, it can be concluded from the values in the diagram that the reagent yield in the etherification amounts to at least 50%.

In *Figure 9*, the amounts of glucose are given as a function of both conventional and structure-selective CMC syntheses. The curves of the conventional synthesis (full lines without symbols) are taken from the paper of Reuben and Conner[9]. The upper diagram of *Figure 9* shows the dependence of the residual glucose portion $X_{glucose}$ upon the obtained average degree of substitution $\overline{DS}$ of the hydrolysed CMC samples. The structure-selective reaction in the experimentally studied $\overline{DS}$ range can be recognized by the respectively higher proportion of glucose. The difference is especially significant at a $\overline{DS}$ value of approximately 1, and decreases inherently as the non-crystalline phase becomes completely substituted. These differences become especially apparent when one correlates the specific degree of substitution DS_{sp} with $X_{glucose}$, as can be seen in the lower diagram of *Figure 9*.

The proof of specific structural changes, as shown by ^{13}C CP/MAS n.m.r. spectroscopy, during the structure-selective carboxymethylation of cellulose, is supported by the results of WAXS measurements of some of the samples.

N.m.r. spectroscopic investigation also showed that, after a further alkalization and subsequent regeneration of the selectively synthesized CMC, the remaining

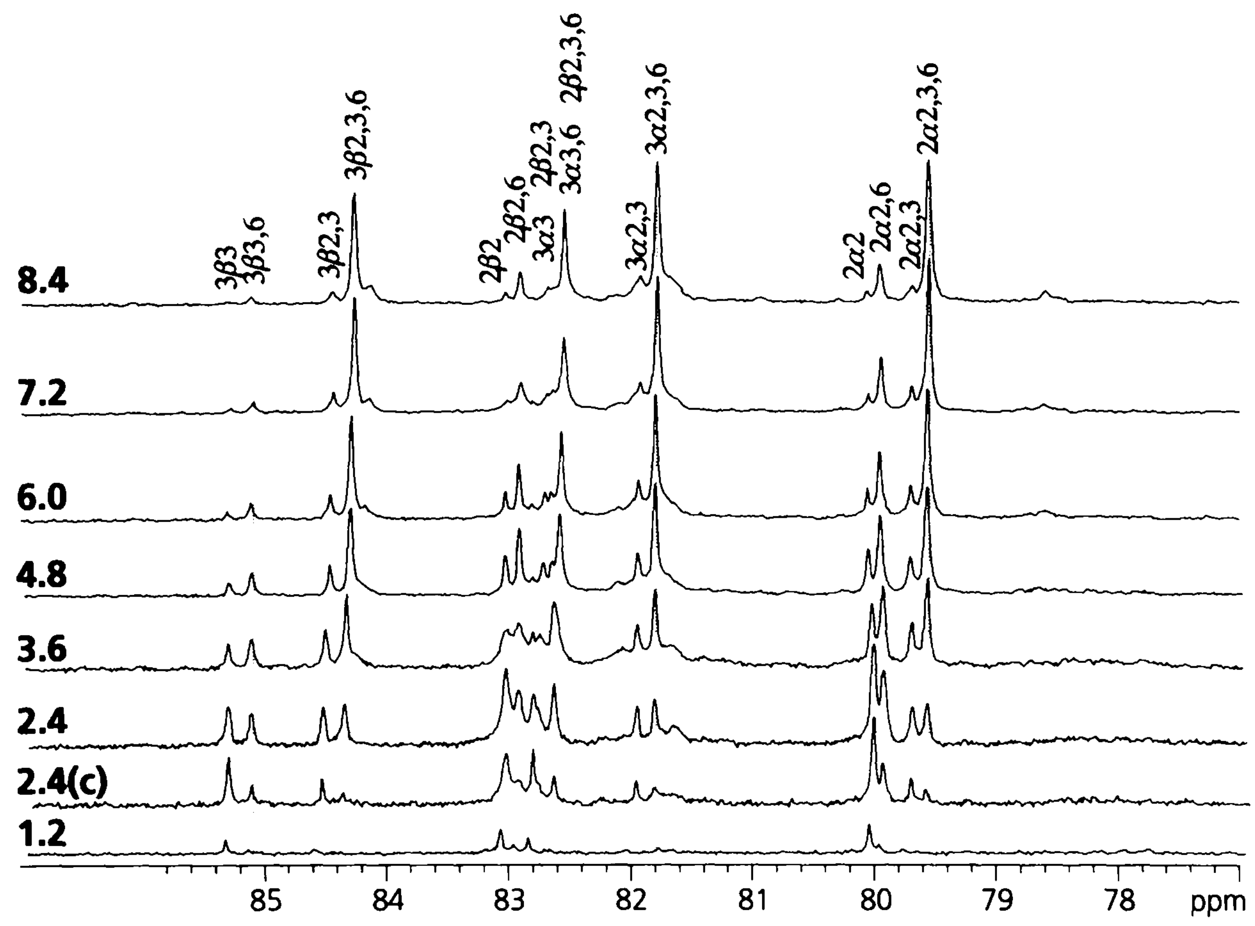

Figure 7 Sections of the ^{13}C n.m.r. spectra with details regarding substitution. Number at the spectrum is the molar ratio ΣNaOH/AGU = 2(ΣMCA/AGU), as in *Figures 4 and 5*. c: conventional method for comparison

cellulose I crystallites of the original CMC sample are converted to crystalline cellulose II, as shown in *Figures 10* and *11*.

CONCLUSIONS

It has been shown, by systematic investigations of carboxymethylation in alcohol-water medium, that even at low NaOH concentrations high degrees of substitution can be achieved by means of a step-by-step etherification reaction. However, the CMC synthesized in this way shows a different microstructure compared to conventionally prepared products, as revealed by solid-state ^{13}C n.m.r. investigations. In the new type of CMC, with a $\overline{DS}$ of up to 2, crystalline regions of cellulose I are still present. From this result we concluded that a structurally selective substitution of cellulose chains occurs under the given conditions, namely through the initial etherification of mainly non-crystalline chain segments. The course of this reaction is determined by its deliberately low alkalinity, which practically excludes the alkalization of crystallites as the necessary prerequisite for their derivatization. Thus, the RSF concept of alkalization[6] has been proven at least qualitatively and extended to a subsequent derivatization.

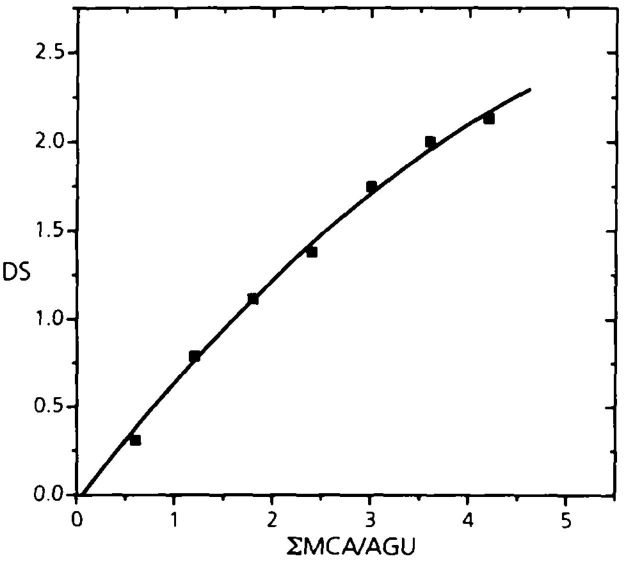

Figure 8 Average DS via molar ratio of MCA/AGU for the structure-selective cargboxymethylation

More detailed insights into the structure-selective etherification of cellulose are provided by n.m.r. spectroscopic examinations of the hydrolysates of products synthesized under these conditions. It follows from the spectra that the proportion of the unsubstituted glucose units diminishes more slowly with increasing $\overline{DS}$ than during conventional etherification. Additionally, starting with a $\overline{DS}$ of 0.5, the spectra already show substantial portions of di- and trisubstituted AGUs.

By multiple carboxymethylation, it is possible to achieve $\overline{DS}$ values up to 2.5. Taking into account a degree of crystallinity of 56% of the starting linters material, it may be concluded that during progressive substitution even crystalline chain segments present in the native cellulose are included in the reaction. This experimental finding can be explained by reasoning that substituted non-crystalline AGUs near crystallite surfaces—especially the frontal areas—are able to disrupt hydrogen bonds of ordered chain segments and to make their hydroxyl groups accessible to etherification.

Summarizing our investigations, it has been clearly shown that the applied etherification method leads to retention of non-substituted crystalline regions of cellulose I. Cellulose molecules are generally assumed to be stiff and extended in the crystalline state. The average chain length (350–1000 nm) of our samples is much larger than the average crystallite length of approximately 10 nm (cf. D_{040} in *Table 1*), which is in good agreement with the well-known idea that cellulose chains run through several adjacent crystalline and non-crystalline regions. Thus, a block-like distribution of substituents along the cellulose chains is strongly indicated. Its characteristics can be controlled through the choice of the etherification reagent, by the adjusted degree of substitution and by various pre- and post-treatments. An interesting modification of selectively synthesized cellulose ethers with a $\overline{DS} < 1.8$ should be a subsequent substitution of the hydroxyl groups of the ordered regions by a conventional etherification or esterification reaction. This obviously makes it possible to synthesize block-like mixed cellulose ethers or cellulose etheresters with alternating hydrophilic and hydrophobic as well as various ionic chain segments. The experimental proof of these ideas will be the subject of further preparative work in this field.

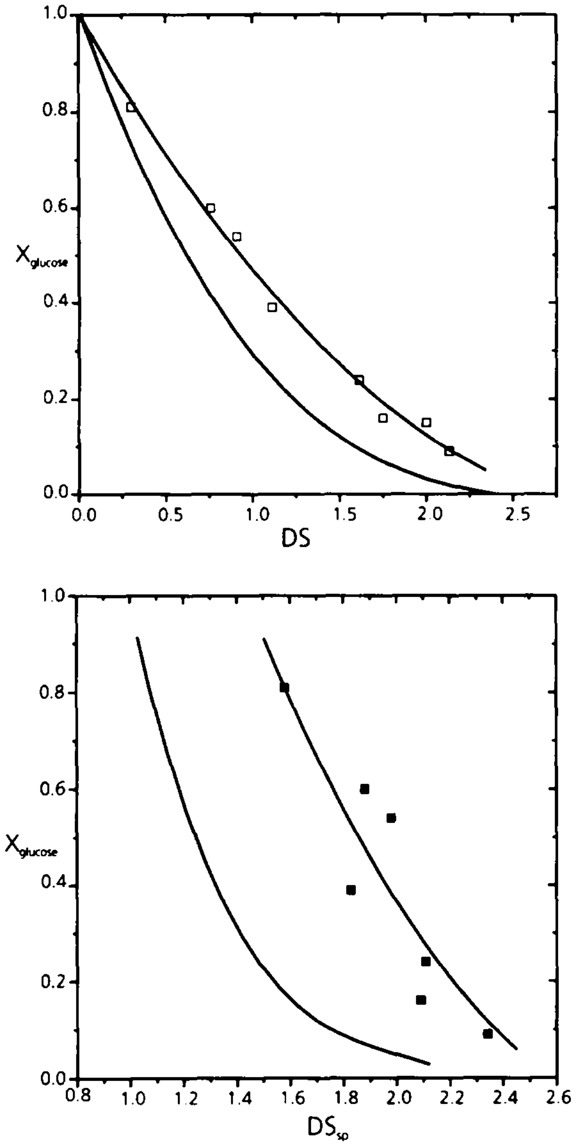

Figure 9 Amounts of glucose via average (top) and specific (bottom) DS for conventional[9] and structure-selective carboxymethylation. Structure selective: with symbols

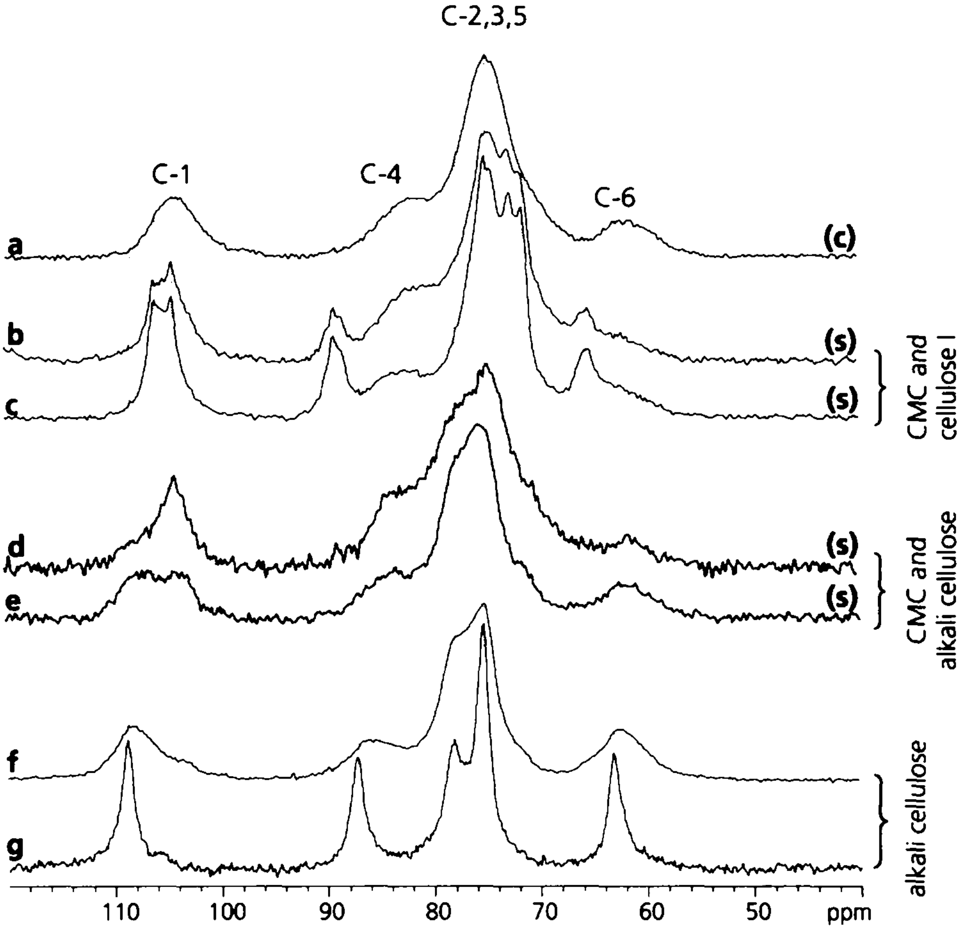

Figure 10 ^{13}CP/MAS n.m.r. spectra of CMC before and after alkalization. c, s: conventional and structure-selective carboxymethylation, respectively. (a) CMC; NaOH/AGU = 2.4, $\overline{DS}$ = 0.77, for comparison. (b), (c) CMC; ΣNaOH/AGU = 3.6, $\overline{DS}$ = 1.11 and ΣNaOH/AGU = 1.2, $\overline{DS}$ = 0.30, respectively. (d) and (e) are (b) and (c) after alkalization. (f), (g) Alkaline cellulose prepared by steeping (aqueous lye: 16 wt% NaOH) and slurry alkalization (molar ratio NaOH/AGU = 1.2), respectively

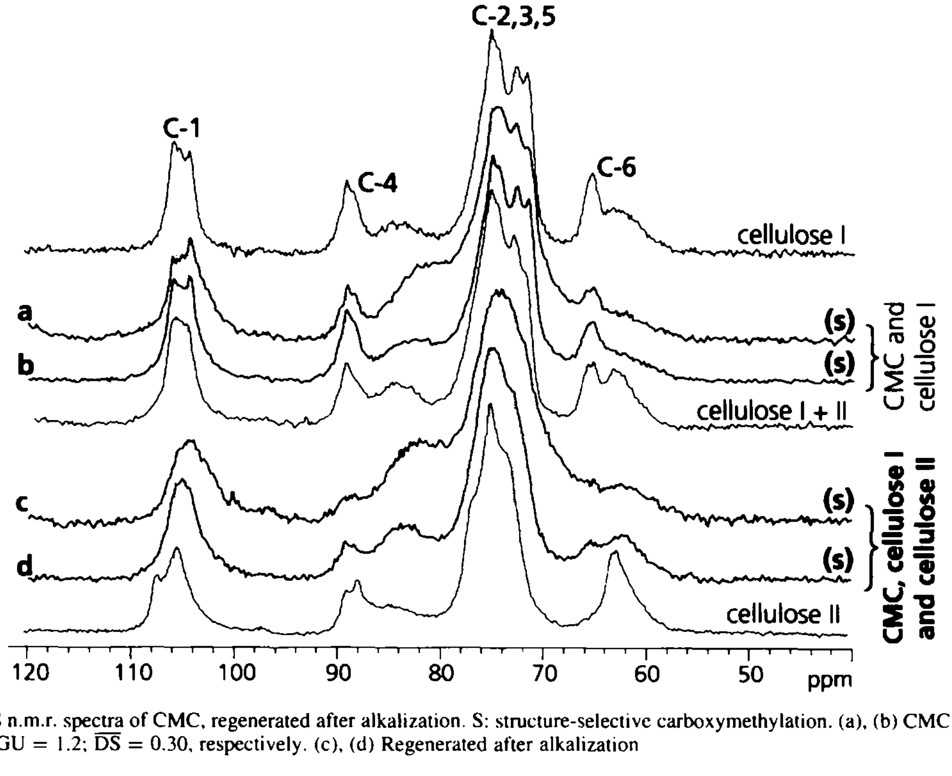

Figure 11 ^{13}CP/MAS n.m.r. spectra of CMC, regenerated after alkalization. S: structure-selective carboxymethylation. (a), (b) CMC; ΣNaOH/AGU = 3.6, $\overline{DS}$ = 1.11, ΣNaOH/AGU = 1.2; $\overline{DS}$ = 0.30, respectively. (c), (d) Regenerated after alkalization

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