Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Liebert, Tim , Klemm, Dieter and Heinze, Thomas(1996) 'Synthesis and Carboxymethylation of Organo-Soluble Trifluoroacetates and Formates of Cellulose', Journal of Macromolecular Science, Part A, 33: 5, 613 — 626
To link to this Article: DOI: 10.1080/10601329608010882
URL: http://dx.doi.org/10.1080/10601329608010882

J.M.S.—PURE APPL. CHEM., A33(5), pp. 613–626 (1996)

SYNTHESIS AND CARBOXYMETHYLATION OF ORGANO-SOLUBLE TRIFLUOROACETATES AND FORMATES OF CELLULOSE

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ABSTRACT

Soluble cellulose intermediates are converted into carboxymethyl cellulose (CMC) with a high degree of substitution (DS_{CMC}) of up to 2.2 by removing the solubilizing ester groups in an one-step synthesis in dimethylsulfoxide (DMSO) with suspended solid NaOH powder as a base and monochloroacetate within 4 hours at 70°C. The reaction is a pseudohomogeneous conversion, i.e., it proceeds under temporary inhomogeneity of the substrate (cellulose). As confirmed by means of HPLC analysis, these CMCs contain a significantly higher amount of both 2,3,6-tri-*O*-carboxymethylated and unsubstituted units in the polymer chain than those obtained in a slurry of cellulose in isopropanol/water (totally heterogeneous conversion) at comparable DS_{CMC}. In contrast to heterogeneously prepared samples, the CMCs show a distribution of carboxymethyl groups within the anhydroglucose unit in the order O-6 > O-3 > O-2 as revealed by means of ^{13}C- and ^{1}H-NMR studies. As intermediates for subsequent carboxymethylation, organo-soluble cellulose trifluoroacetates (CTFA) and cellulose formates (CF) have been synthesized and studied. The CFs were obtained by a new, convenient synthesis method consisting of the acylation of cellulose with mixtures of formic acid and phosphorus oxychloride within 4 hours at room temperature. The CFs with a degree of substitution (DS_{CF}) of 2.2 are soluble in DMSO and DMF, and they show a complete substitution of the primary OH groups as confirmed by ^{13}C-NMR studies and HPLC analysis after

permethylation and chain degradation. The CTFAs (DS_{CTFA} = 1.5) prepared by acylation of cellulose with a mixture of trifluoroacetic acid/trifluoroacetic anhydride also show a preferred substitution of the C-6 position.

INTRODUCTION

Various kinds of nonaqueous solvents for cellulose have been found and investigated in terms of their abilities as reaction media for homogeneous cellulose modification [1, 2]: *N*,*N*-dimethylformamide/N_2O_4 [3]; *N*,*N*-dimethylacetamide/LiCl [4]; *N*-methylmorpholine-*N*-oxide [5], and so on. An alternative way to dissolve cellulose involves the formation of intermediates which can be isolated, purified, and dissolved in common organic solvents and which can be easily regenerated. Typical examples are cellulose trimethylsilyl ethers [6] as well as lower cellulose esters that are unstable toward hydrolysis.

As early as 1956, Geddes reported the dissolution of cellulose in trifluoroacetic acid (TFA) to form hydrolytically instable cellulose trifluoroacetates (CTFAs) [7]. We recently showed that the acylation of cellulose with mixtures of TFA/trifluoroacetic anhydride (TFAA) represents a convenient synthesis method for organo-soluble CTFAs which are free of impurities [8]. Furthermore, cellulose reacts with formic acid (FA) to yield the well-known cellulose formate ester (CF) [9]. The synthesis of CFs is usually carried out by dissolution of cellulose in pure FA or in a combination with catalysts like H_2SO_4 and HCl, respectively [10, 11]. On the other hand, up to now the behavior of both CTFAs and CFs as organo-soluble cellulose intermediates in subsequent etherification reactions has not been investigated. At appropriate reaction conditions, a simultaneous removal of the solubilizing ester groups should be possible.

In continuation of our studies on the synthesis and characterization of carboxymethyl cellulose (CMC) having a controlled nonstatistic distribution of substituents [12, 13], our interest was focused on the use of CTFAs and CFs as starting materials for alternative carboxymethylation reactions. At present, CMC is the most important ionic cellulose ether commercially produced in a heterogeneous slurry of cellulose in a solvent that swells but does not dissolve the polymer [14]. Under these reaction conditions, CMCs with an average degree of substitution (DS) in the range from 0.4 to 1.3 are formed which possess a statistical distribution of substituents [12, 15]. In contrast, the carboxymethylation of cellulose in *N*,*N*-dimethylacetamide/LiCl as a cellulose solvent leads to CMC samples which contain a significantly higher amount of both 2,3,6-tri-*O*-carboxymethylated and unsubstituted units than those obtained in a slurry of cellulose in isopropanol and water at comparable DS values [12].

In this context we wish to report our results of the carboxymethylation of CTFAs and CFs as part of ongoing research about the behavior of such esters as protected or activated intermediates in cellulose functionalization. The CMCs obtained are characterized by means of FT-IR and ^{13}C-NMR spectroscopy and, after hydrolytic chain degradation, by means of both high-performance liquid chromatography (HPLC) and ^{1}H-NMR spectroscopy. Preliminary results of polarized-light microscopy and viscometric measurements are presented as well.

EXPERIMENTAL

Materials

Spruce sulfite pulp (DP = 680) was used after drying at 105°C for 5 hours (synthesis of CTFA) or used in the air-dry state (synthesis of CF). Trifluoroacetic acid (TFA), trifluoroacetic anhydride (TFAA), and formic acid (FA) were purchased from Fluka. Water-free FA used was obtained by distillation over phthalic anhydride.

Cellulose Trifluoroacetate (CTFA), 2

One gram cellulose was swollen in 20 mL TFA at room temperature for 20 minutes. Ten milliliters TFAA was added to the slurry. The cellulose dissolved completely after stirring for 4 hours at room temperature. The solution was stirred for an additional 2 hours and was precipitated into 200 mL diethyl ether. The precipitate was filtered off, washed with 100 mL diethyl ether, and dried under vacuum (80 Pa) at 25°C for 20 hours. In order to remove traces of both diethyl ether and trifluoroacetic acid, the sample was kept at 150°C for 40 minutes under vacuum (80 Pa).

Yield 1.78 g (94.2%). Degree of substitution, DS_{CTFA} = 1.5. IR (KBr): 1790 cm^{-1} ($\nu_{C=O}$ ester). ^{13}C-NMR data: See Ref. 8.

Cellulose Formate (CF), 3

One gram cellulose was swollen in 30 mL FA at room temperature for 15 minutes. Phosphorus oxychloride (2.7 mL) was added to the slurry at 5°C. The cellulose dissolved completely after stirring for 5 hours at room temperature. The solution was precipitated into 100 mL diethyl ether, filtered off, and washed three times with 350 mL acetone. After drying at room temperature, the polymer was washed again with 200 mL acetone and then dried under vacuum (80 Pa) at 25°C for 24 hours.

Yield 1.26 g (94%). DS_{CF} = 2.2. IR (KBr): 1728 cm^{-1} ($\nu_{C=O}$ ester). ^{13}C NMR: see Fig. 1.

Carboxymethyl Cellulose Samples (CMC), 4

For a typical preparation, 1 g each CTFA and CF was dissolved in 17.5 mL dimethyl sulfoxide (DMSO) under nitrogen. A suspension of dried pulverized NaOH (2.5 g, dried under vacuum at 45°C, 5 hours) in 7 mL DMSO was added to the solution within 10 minutes, followed by 3.6 g sodium monochloroacetate (dried under vacuum at 45°C) under vigorous stirring. The temperature was raised to 70°C. After various reaction times (see Table 3), the reaction mixture was cooled down to room temperature and precipitated into 75 mL methanol. The precipitate was filtered off, dissolved or suspended (in dependence on DS_{CMC}) in water, neutralized with acetic acid, and reprecipitated into 100 mL of 80% (v/v) aqueous ethanol.

DS_{CMC} are given in Table 3. IR (KBr): 1620, 1410 cm^{-1} ($\nu_{C=O}$, carboxylate group). ^1H and ^{13}C NMR: see Figs. 5 and 6.

Measurements

The determination of the total DS values of both CTFAs and CFs was carried out by the backtitration method after saponification of the samples [16]. Determination in the case of CMC was gravimetrically by the uranyl method [17].

FT-IR spectra were measured on a Bio-Rad FTS 25 PC.

For HPLC analysis according to Ref. 12, the CMCs were hydrolyzed with 80% (v/v) sulfuric acid within 12 hours at 25°C and after dilution with a tenfold amount of water for 5 hours at 100°C. After neutralization, the chromatographic experiments were carried out at 65°C with 0.01 N sulfuric acid as the eluent with a flow rate of 0.5 mL/min. The column used was a Bio-Rad Aminex HPX-87A (H^+ form). HPLC analysis after permethylation and chain degradation of CF samples was carried out as described previously for CTFAs [8] and trialkylsilyl celluloses [18].

For ^1H-NMR spectroscopy, the CMCs were dialyzed against running water (resulting polymer content 100%) and hydrolyzed with a mixture of D_2SO_4/D_2O (25%, v/v) within 5 hours at 90°C. The spectra were acquired on a Brucker AMX 400 spectrometer [19].

Standard ^{13}C-NMR spectra with proton-decoupling were recorded at 70°C in DMF-d_7 (CTFA and CF samples) solution and D_2O (CMC samples) solution on a Varian Unity 400 NMR spectrometer. The scan number was between 6000 and 17,000.

Viscometric measurements were carried out with a rotational rheometer Rheolab (Physica, Germany) at 25 ± 0.1°C. The measuring container (Z1 DIN) had a total volume of 17 mL [20].

Polarized-light microscopy was carried out with a Jenapol Interphako microscope.

RESULTS AND DISCUSSION

Synthesis and Characterization of Organo-Soluble Cellulose Intermediates

According to our experience, organo-soluble cellulose intermediates represent valuable and promising alternatives to solutions of unmodified cellulose for a controlled modification of the biopolymer [21]. Interesting intermediates (e.g., lower cellulose esters) are instable toward hydrolysis.

Thus, cellulose trifluoracetates (CTFA) were prepared by acylation of the polymer with a mixture of trifluoroacetic acid and trifluoroacetic anhydride (33% v/v) at room temperature within some hours and subsequent treatment of the crude polymer at elevated temperature under vacuum. The CTFAs used had a degree of substitution (DS_{CTFA}) of 1.5 and a degree of polymerization (DP) of 460. By means of ^{13}C-NMR spectroscopy and HPLC on permethylated and degraded samples, complete substitution of the O-6 atom was determined [8].

Cellulose formates (CF), on the other hand, were obtained by a new and effective esterification reaction applying formic acid (FA) in combination with phosphorus oxychloride. The advantage of this synthesis pathway consists in the activation of the FA via the known formation of mixed anhydrides with $POCl_3$ [22]. Furthermore, it may be assumed that the dehydrating behavior of the HCl and polyphosphorus acids liberated increases the rate of reaction. In addition, the partially hydrolyzed $POCl_3$ and phosphoric acid formed are effective swelling agents for cellulose. Finally, a partial esterification directly with $POCl_3$ cannot be excluded, which makes the cellulose hydroxyls accessible to the formylation agent, too. However, phosphorylation reactions of cellulose with $POCl_3$ proceed only to a very small extent without an organic base like triethyl amine [23].

The CF's obtained are phosphorus-free (determined by ultimate analysis) after reaction of cellulose (spruce sulfite pulp, not thermally dried) with FA in the presence of 3–12 mol $POCl_3$/mol anhydroglucose unit (AGU), precipitation in diethyl ether, and repeated careful washing with acetone. The IR spectra of the CFs show the typical peaks of the cellulose backbone as well as the characteristic ester peak at 1728 cm^{-1} ($\nu_{C=O}$). Further evidence for the absence of potential stable side products (e.g., chlorodeoxy groups) was gained by means of HPLC analysis of CF samples after saponification with aqueous NaOH and degradation of the polymer chain with sulfuric acid. The elution pattern obtained was identical with those measured for pure degraded cellulose.

The synthesis potential of this pathway was examined by variation of both the amount of the dehydrating reagent $POCl_3$ (molar ratio $POCl_3$/AGU from 3.0 to 12.0) and reaction time (from 2 to 10 hours). A maximum DS_{CF} of 2.2 ± 0.1 was reached by applying 4 mol $POCl_3$/mol AGU and a reaction time of 4 hours. Practically no change in DS_{CF} was found by prolonging the reaction time up to 10 hours and by increasing the molar ratio of $POCl_3$/AGU up to 12. The products with a DS_{CF} of 2.2 ± 0.1 were soluble in DMSO and DMF and thermally stable up to 280°C. The DP value of a CF sample prepared from spruce sulfite pulp was determined by a viscometric method after saponification and dissolution of the cellulose obtained in cuoxame [24]. It was found to be 280, i.e., the formylation and probably the saponification yields a decrease in DP of about 60%. This degradation is higher than in the case of the trifluoroacylation method (about 32% degradation).

Standard ^{13}C-NMR experiments with proton-decoupling reveal complete substitution of the O-6 position. In a typical spectrum (Fig. 1) only one signal for the substituted C-6 position at 61.9 ppm was observed. In comparison with pure cellulose, a further new signal at about 79.9 ppm indicates O-2 subtitution. Furthermore, the splitting of the peak of the C-1 carbon atom (C-1″) demonstrates substitution at C-2, too. A C-3 substitution, however, is not unambiguously detectable because the signal which would indicate such a substitution overlaps with the peaks of the C-4 and C-5 atoms. Splitting of the C-4 signal is not clearly visible, which indicates a substitution at the C-3 position.

To gain further information about the distribution of formyl groups in the AGU, HPLC analysis was employed [18]. For this, the samples were permethylated with methyl trifluoromethane sulfonate in the presence of 3,5-di-*tert*-butylpyridine to convert the pattern of substitution of CFs into an inverse pattern of the methyl cellulose ether (MC). After total saponification and degradation of the resulting MC with aqueous TFA, the mixture of different methyl glucoses obtained could be

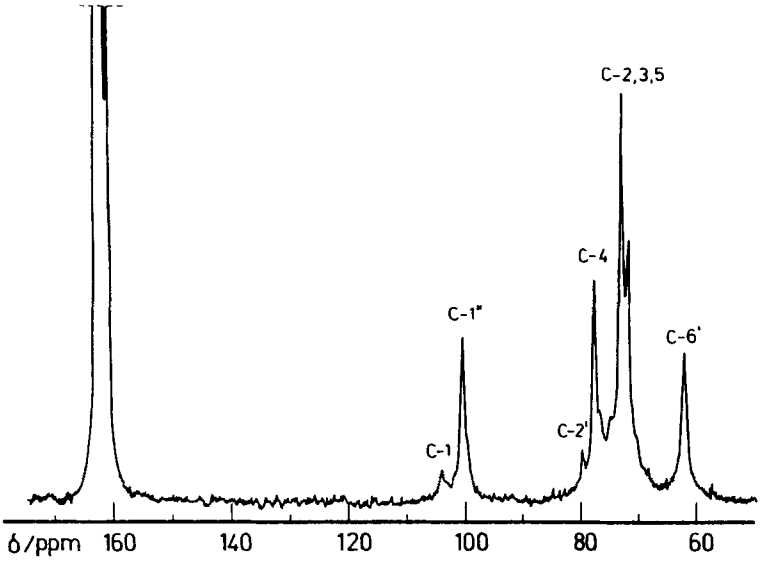

FIG. 1. ^{13}C-NMR spectrum of cellulose formate 3 (DS_{CF} = 2.2) dissolved in *N,N*-dimethylformamide-d_7 (a single prime means substituted; a double prime means influenced by an adjacent substituent).

separated by a chromatographic run on a reversed-phase column. The results obtained for CF 3 (Table 1) confirm the preference of O-6 formylation as already concluded from the NMR examinations. Furthermore, C-2 and C-3 substitutions were detected, which agrees with the total $DS_{CF} > 2$. The DS_{MC} determined was 0.69, and consequently the calculated DS_{CF} is 2.31, which agrees quite well with the value determined by the backtitration method (DS_{CF} = 2.2 ± 0.1).

TABLE 1. Signal Assignment and Quantification of HPL Chromatogram of Methylglucose Samples by Methylation, Saponification, and Degradation of Cellulose Formates (DS_{CF} = 2.2 ± 0.1)

Methylglucoses		Starting cellulose formate substitution pattern
Substituent pattern	mol%	
2,3,6-tri-*O*	4.37	Unsubstituted
2,3-di-*O*	13.28	6-mono-*O*
2,6- and 3,6-di-*O* as traces		3- and 2-mono-*O*
3-mono-*O* as main product	28.70	2,6-di-*O*
2-mono-*O*		3,6-di-*O*
6-mono-*O* as trace		2,3-di-*O*
Unsubstituted	53.64	2,3,6-tri-*O*

Carboxymethylation of Intermediates

In a first series of experiments, CTFA (DS_{CTFA} = 1.5, DP = 460) and CF (DS_{CF} = 2.2, DP = 280) were converted to carboxymethyl cellulose (CMC) by using solid NaOH powder and sodium monochloroacetate which were slurried in a solution of the polymers in DMSO (5.7% polymer, w/v). During the addition of NaOH in order to obtain the alkali cellulose to initiate the etherification reaction, the homogeneous solution is transferred to a highly swollen gel-like state. To elucidate the reasons for this behavior, the course of reaction was studied. The immediately formed species (after the addition of the NaOH suspended in DMSO) was isolated by precipitation into diethyl ether because a continuous spectroscopic observation was not possible. By means of FT-IR studies of the isolated material, regenerated cellulose without any ester functions (disappearance of the signals at 1790 and 1728 cm^{-1}) and the sodium salt of the corresponding acid were found. The deconvolution of the absorbance range of the cellulose OH valency vibrations [25] reveals cellulose mainly in crystal modification II, as expected. In comparison with the starting cellulose I (Fig. 2, Curve a), the typical signals at 3282 and 3315 cm^{-1} disappear (Fig. 2, Curves b and c).

An alternative way to study structural changes during this first stage of reaction was found to be the application of polarized-light microscopy. The solution of

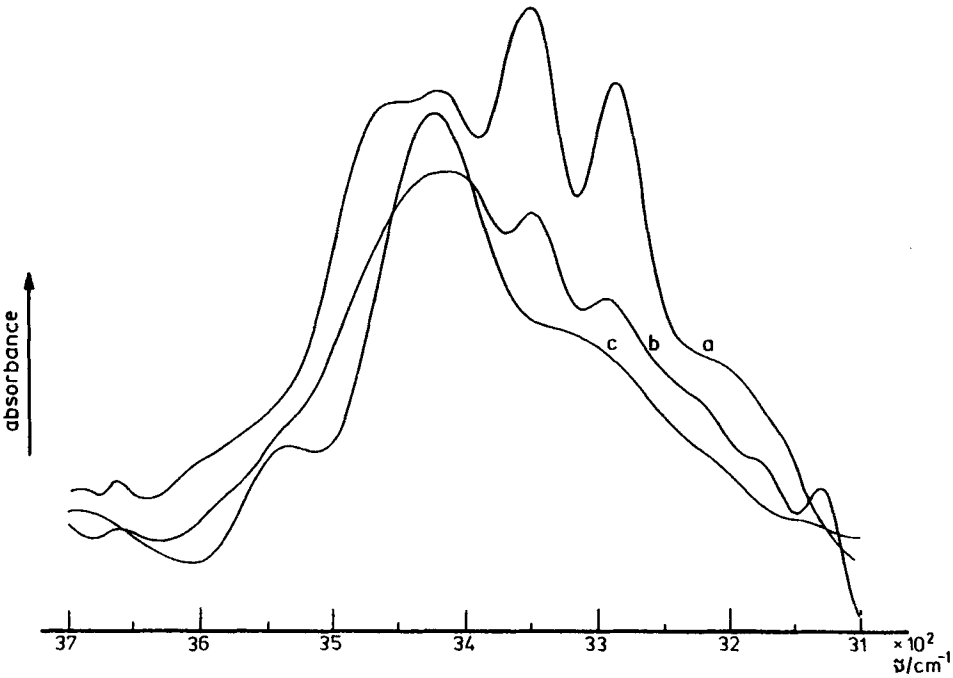

FIG. 2. Deconvoluted FT-IR spectra of cellulose which was regenerated from a 5.0% solution of unmodified cellulose in *N,N*-dimethyl acetamide/LiCl (b) and from a 5.7% solution of cellulose trifluoroacetate **2** (c) in dimethylsulfoxide by addition of NaOH powder. For comparison, the spectrum of untreated cellulose I (spruce sulfite pulp, a) is shown.

both CF and CTFA represents a homogeneous system. Some small particles of undissolved polymer could be detected by means of polarized-light microscopy (Fig. 3a). After addition of the NaOH/DMSO suspension, a growth of crystals (sodium salts of formic and trifluoroacetic acids) was observed (Fig. 3b). The regenerated insoluble cellulose II is not detectable as a polymeric particle. Consequently, we think that the polymer has to be fixed on solid NaOH.

Concentrations and reaction times were varied to evaluate the accessible range of DS_{CMC}. Regarding the results (Table 2), it has to be underlined that in comparison with a totally heterogeneous synthesis in isopropanol and water, samples with considerably higher DS values were obtained in a single-step synthesis. The products

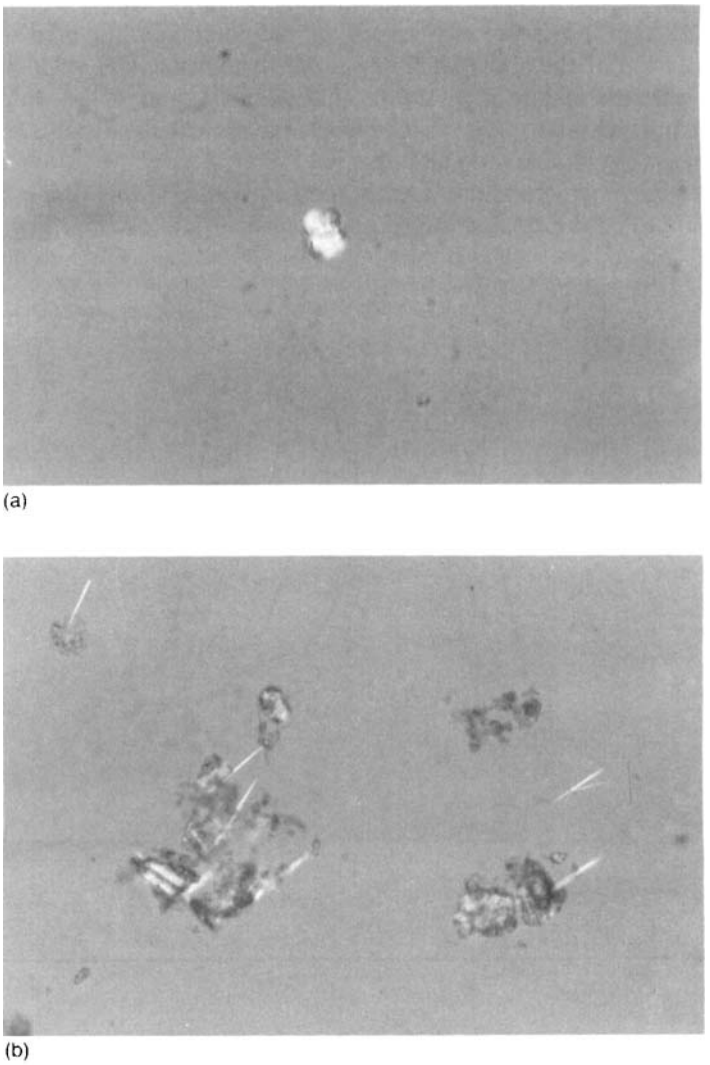

FIG. 3. Polarized-light micrographs of cellulose formate 3 dissolved in dimethylsulfoxide without (a) and after addition of solid NaOH powder (b).

TABLE 2. Conditions and Results of the Carboxymethylation of Cellulose Trifluoroacetate (CTFA) **2** and Cellulose Formate (CF) **3** in Dimethylsulfoxide (5.7%, w/v of **2** and **3**, respectively)

Starting intermediate	Molar ratio[a]	Reaction time, hours[b]		Carboxymethyl cellulose degree of substitution		
				Gravimetric[c]	^{1}H NMR	HPLC
2 CTFA	1:5:10	2.0	**4a**	0.07	–	–
	1:5:10	2.0	**4b**	0.11	–	–
	1:10:20	0.5	**4c**	1.17	1.32	1.60
	1:10:20	1.0	**4d**	1.48	1.62	1.62
	1:10:20	2.0	**4e**	1.34	–	1.92
	1:10:20	4.0	**4f**	1.69	1.66	1.86
	1:10:20[d]	4.0	**4g**	0.88	–	1.36
	1:10:20	16.0	**4h**	1.38	–	1.54
3 CF	1:5:10	2.0	**4i**	0.12	–	–
	1:10:20	2.0	**4k**	1.18	–	1.46
	1:15:30	2.0	**4l**	1.18	–	1.79
	1:20:40	2.0	**4m**	1.97	–	2.21
	1:10:20	4.0	**4n**	1.60	–	1.91

[a]Molar ratio: Modified anhydroglucose unit: $ClCH_2COONa$:NaOH
[b]Reaction temperature, 70°C.
[c]Uranyl method [17].
[d]First addition of $ClCH_2COONa$.

contain no residual ester groups, i.e., the synthesis and/or the workup succeed by complete removal of the ester groups, and pure CMCs are obtained. It should be mentioned, however, that significantly higher amounts of etherification agent have to be employed.

In general, the sodium salt of CMC is water soluble at a DS of about 0.4–0.5. The limiting DS value for solubility in water of samples obtained via CFs and CTFAs was found to be 1.2. This solubility behavior might be caused by an unconventional distribution of substituents. In order to gain detailed information about the substituent pattern of the CMC obtained, ^{13}C and ^{1}H NMR as well as HPLC studies were carried out after hydrolytic chain degradation.

For HPLC analysis, the controlled degradation of the polymer chain to the monomeric units was achieved by solvolysis with sulfuric acid. The samples contained a significantly higher amount of both 2,3,6-tri-*O*-carboxymethylated and unsubstituted glucose units in the polymer chain than those obtained in a slurry of cellulose in isopropanol and water at comparable total DS values [12], as shown in Fig. 4. The 2-, 3-, and 6-mono-*O*- as well as the 2,3-, 2,6-, and 3,6-di-*O*-substituted units are formed in a smaller amount. This means that the mole fractions of the repeating units of CMC synthesized under the chosen reaction conditions do not

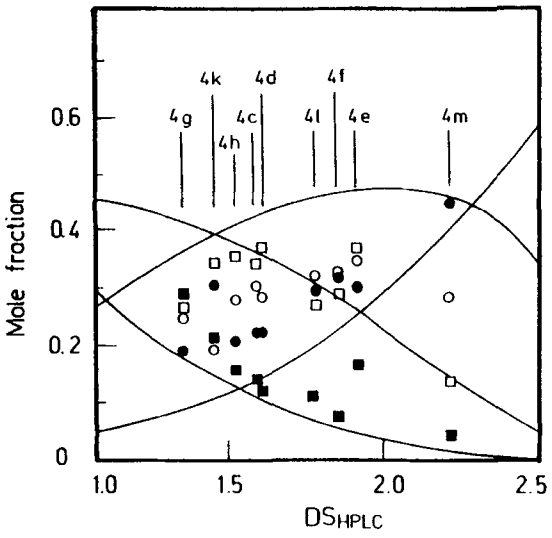

FIG. 4. The mole fractions of glucose (■), mono-*O*-carboxymethyl glucoses (□), di-*O*-carboxymethyl glucoses (○), and 2,3,6-tri-*O*-carboxymethyl glucose (●) in hydrolyzed CMC samples plotted as function of DS_{HPLC}. The curves are calculated [26].

agree with the calculated amounts using the statistical model of Spurlin [26] and found for heterogeneously synthesized samples [12].

Figure 5 shows a representative standard ^{13}C-NMR spectrum with proton decoupling (8% CMC **4f** in D_2O) as well as the assignment of the peaks according to Refs. 19 and 27. A comparison of the intensity of the peak at 60.99 ppm (unsubstituted O-6) with that at 69.48 ppm (substituted O-6) reveals a high degree of substitution at this position. The signals for a C-4 adjacent to the substituted ($4_{2,3,6}$; $4_{2,6}$; $4_{3,6}$, compare Fig. 5) and unsubstituted (4_C) O-3 positions show comparable intensities. The weak shoulder on the signal for the C-1 atom at 102.91 ppm (chemical shift of a C-1 atom without a substitution at O-2) indicates a relatively small extent of O-2 carboxymethylation. From this estimation it is concluded that the distribution of carboxymethyl groups within the anhydroglucose units is in the order O-6 > O-3 > O-2.

Complete quantification of the distribution of substituents within the AGUs was possible by means of ^{1}H NMR measurements of hydrolytically degraded CMC samples [19]. The hydrolysis was carried out by treating the samples in D_2SO_4/D_2O (25%, v/v) for 5 hours at 90°C. Before hydrolysis, the samples have to be dialyzed to remove glycolic acid (one of the main impurities of CMC) which gives a NMR signal at 4.19 ppm (range of chemical shift of the carboxymethylated C-6 position within the AGU). A typical spectrum (CMC **4c**) is shown in Fig. 6. The results obtained confirm those of ^{13}C-NMR spectroscopy. For Samples **4c** and **4f**, partial DS values at positions O-2, O-3, and O-6 of 0.18, 0.47, 0.67 and 0.25, 0.60, 0.81 were determined. That means there is a significant difference in the distribution of substituents compared to heterogeneously synthesized CMC (O-3 < O-6 < O-2). In the course of heterogeneous cellulose modification, the reactivity of the three

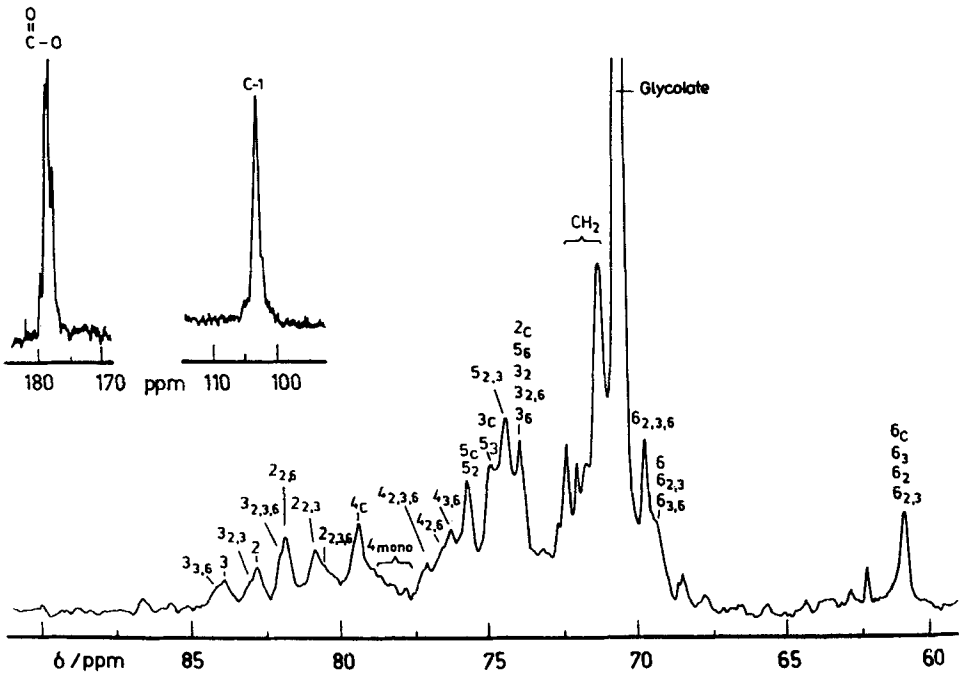

FIG. 5. ^{13}C-NMR spectrum of carboxymethyl cellulose **4f** (DS_{CMC} = 1.66) dissolved in D_2O. Numbers indicate positions of carbon atoms, unsubstituted anhydroglucose resonances are indicated by subscript c, and other subscripts indicate substituent pattern as positions 2, 3, and 6.

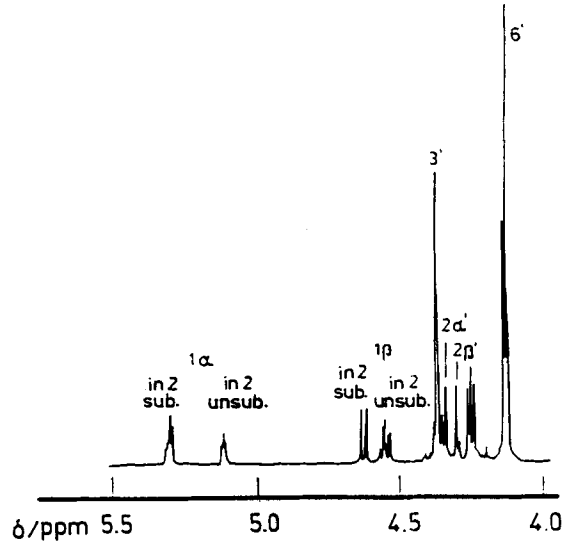

FIG. 6. ^{1}H-NMR spectrum of carboxymethyl cellulose **4f** (DS_{CMC} = 1.66) after hydrolytic chain degradation in D_2SO_4/D_2O (25%, v/v).

TABLE 3. $CaCl_2$-Salt Tolerance of Carboxymethyl Cellulose (CMC) Samples Prepared by Different Synthesis Paths

CMC sample synthesis path	DS[a]	Molar ratio Ca^{2+}/COO^- (mol/mol)	Salt tolerance,[b] η_S/η_0
Via CTFA **4f**	1.69	0.12	1.000
		0.30	0.875
In DMA/LiCl [12]	1.84	0.12	0.941
		0.30	0.855
Heterogeneous [12]	1.44[c]	0.12	0.745
		0.30	0.564
	2.32[c]	0.12	0.794
		0.30	0.618

[a]Degree of substitution.
[b]η_0 represents the viscosity before and η_S after the salt addition.
[c]Two- and three-step synthesis.

different OH groups is mainly determined by their inclusion in the strong H-bond system. CFs and CTFAs, on the other hand, possess a less supramolecular order. Therefore, they are, e.g., soluble in common organic solvents. Due to the homogeneous start of the reaction and the formation of the gel structure as a result of the NaOH addition, an altered accessibility of the reaction centers exists. This may explain the preferred carboxymethylation of the primary OH groups found. Detailed studies regarding the reason for such a distribution of substituents within both the AGU and the polymer chain are in progress using other cellulose intermediates with different stabilities (e.g., trialkylsilyl celluloses).

In order to gain further information about the properties of the CMC synthesized, the salt tolerance (Ca^{2+} ions) of aqueous solutions was studied [20]. Preliminary results are summarized in Table 3. In comparison with data obtained from heterogeneously synthesized samples, a lower decrease of viscosity as a result of ion addition occurs, i.e., the CMCs obtained via the organo-soluble intermediates possess a higher salt tolerance.

CONCLUSIONS

Organo-soluble CFs and CTFAs synthesized in a convenient way represent useful intermediates for etherification reactions of the biopolymer as exemplified by carboxymethylation. The synthesis path includes simultaneous removal of the solubilizing ester groups to yield pure CMCs with a new, interesting distribution of substituents at both the AGU and polymer chain level. A reasonable mechanism which would explain our findings includes the assumption that the alcoholate is formed on the polymer-base interface during the addition of NaOH. These polymer segments are the centers for the subsequent reaction. This is accompanied by splitting of the ester functions and the formation of crystalline sodium salts of trifluoro-

acetic and formic acid. CMC is formed in this way, and it exhibits regions with a high content of both tri- and unsubstituted units. The process is not determined by the supramolecular structure of the cellulose, and an unconventional substitution pattern within the AGU (O-6 > O-3 > O-2) is obtained.

Comparable results were obtained by carboxymethylation of cellulose dissolved in the nonderivatizing cellulose solvent DMA/LiCl [12]. The unusual distribution of substituents seems to be caused by the homogeneous starting conditions and the formation of a gel as a result of the addition of solid NaOH.

Carboxymethylation experiments will be carried out with other cellulose intermediates of different stabilities. The biodegradability of the synthesized samples will be examined.

ACKNOWLEDGMENTS

The general financial support of the German "Bundesministerium für Forschung und Technologie" is gratefully acknowledged. One of us (Th.H.) thanks the German "Otto-Ritter-Stiftung" of the "Stifterverband für die Deutsche Wissenschaft" for generous financial support.

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