(Received May 21, 1984)

DISTRIBUTION OF SUBSTITUENTS IN CELLULOSE ETHERS PREPARED IN AQUEOUS AND NON-AQUEOUS SYSTEMS

By Akira Isogai, Atsushi Ishizu and Junzo Nakano

(Department of Forest Products, Faculty of Agriculture,
The University of Tokyo, Bunkyo-ku, Tokyo 113)

Synopsis

The distribution of substituents in partially substituted cellulose ethers (methyl-, carboxymethyl-, benzyl- and methallylcelluloses) prepared in aqueous and non-aqueous systems was studied. The reactivity order of three hydroxyl groups in cellulose in aqueous systems was $\text{HO-2} > \text{HO-6} > \text{HO-3}$ with the exception for benzylation. On the other hand, the reactivity order was $\text{HO-6} > \text{HO-2} \approx \text{HO-3}$ for etherifications with powdered sodium hydroxide and etherifying reagents except iodides in a non-aqueous cellulose solvent, SO_2 -diethylamine-dimethylsulfoxide system. The difference in reactivities of the hydroxyl groups in the non-aqueous system were much smaller than those in aqueous systems.

INTRODUCTION

Cellulose ethers have been used in various fields and their properties are known to depend on degrees of substitution (DS), distribution of substituents, molecular weights and so on. Thus, the distribution of substituents in cellulose ethers have been one of important subjects in cellulose chemistry. Studies on the distribution of substituents in partially substituted cellulose ethers prepared from alkalicellulose (aqueous system) revealed that the relative rate-constant of HO-2 was higher than that of HO-3 and the former was comparable to, and in some cases higher than, that of the primary hydroxyl group, HO-6⁽¹⁻⁸⁾. The higher reactivity of HO-2 than that of HO-3 observed for etherifications of both cellulose and its model compounds⁽⁹⁾⁻¹⁴⁾ has been assumed to be due to the higher acidity of HO-2 enhanced by its proximity of the anomeric center, C-1⁽¹⁵⁾. However, the reason for occasional observations of the higher reactivity of HO-2 than that of HO-6 has not been explained clearly yet⁽¹⁵⁾.

Recently, many kinds of non-aqueous cellulose solvents have been found⁽¹⁶⁾, and these findings made it possible to prepare cellulose derivatives in cellulose solutions⁽¹⁷⁾⁻¹⁹⁾. The authors succeeded also in the preparation of many kinds of tri-O-substituted cellulose ethers by the use of a

non-aqueous cellulose solvent (SO_2 -diethylamine-dimethylsulfoxide)⁽²⁰⁾²¹⁾, and some chemical and physical characteristics of these new cellulose derivatives were reported⁽²²⁾.

In this work, the distribution of substituents in several kinds of partially substituted cellulose ethers prepared by the use of aqueous and non-aqueous systems was estimated by modern analytical techniques. The relative reactivities of three hydroxyl groups in anhydroglucose units of cellulose were discussed from a point of the effect of reaction media.

EXPERIMENTAL

Materials

Avicel (Asahi Chemical Ind. Co. Ltd., $\overline{\text{DP}}_v=250$) was used as a cellulose sample. Commercial methylcellulose (Wako Chemical Ind. Co. Ltd., $\text{DS}=1.6$) and commercial carboxymethylcellulose sodium salt (Sunrose; Sanyo-Kokusaku Pulp Co. Ltd., $\text{DS}=1.4$ and 1.8) were used as samples of cellulose ethers prepared in aqueous alkalicellulose systems.

Preparation of cellulose ethers

Cellulose/ SO_2 -diethylamine (DEA)-dimethylsulfoxide (DMSO) solutions were prepared as described in the previous paper⁽²⁰⁾²¹⁾. Methylcelluloses with various DS were prepared by adjusting the amounts of powdered sodium hy-

dioxide and dimethylsulfate or methyl iodide added to the cellulose solutions²¹). The preparative conditions were shown in Table 1. MC were isolated by dialysis and subsequent lyophilization. Carboxymethylcellulose sodium salts (CMC) with various DS were prepared by reacting different amounts of powdered NaOH and sodium chloroacetate, bromoacetic acid or sodium iodoacetate with cellulose in its solution (Table 1). CMC were isolated by dialysis and subsequent lyophilization, and the DS of CMC were determined by the ¹H-NMR method proposed by Ho et al.⁷). Two kinds of benzylcellulose (BC) were prepared by the use of alkalicellulose and the non-aqueous cellulose solution as shown in Table 1. BC were isolated by pouring the reaction mixtures into methanol-water (1:1) and washing the precipitates with methanol and water repeatedly. Their DS were calculated from values of elementary analyses. Methallylcellulose (MAC) was prepared with powdered NaOH and methallyl chloride in the cellulose solution and isolated by the same method as used for BC. The DS of MAC was calculated from the content of double bonds measured by Wijs method²³).

Analyses of distribution of substituents

MC (50 mg) was dissolved in 15 ml of 3% sulfuric acid and was hydrolyzed at 120°C for 1 h. The hydrolyzates were neutralized with barium carbonate, and barium sulfate and excess barium carbonate were removed by centrifugations. The partially methylated glucoses thus obtained were subjected to reduction with sodium borohydride followed by acetylation with acetic anhydride²⁴). The partially methylated glucitol acetates were analysed by GLC^{18,19}).

The distribution of carboxymethyl groups in CMC was estimated by the method proposed by Ho and Klosiewicz⁷).

BC was methylated twice by the Hakomori method. The fully methylated BC (60 mg) was dissolved in dichloromethane (4 ml), and borontrifluoride etherate (0.26 ml) and ethanethiol (1.32 ml) were added to the solution. The mixture was stirred vigorously at 20°C for 9 h to remove benzyl groups. Then, saturated sodium bicarbonate solution was added to the mixture for neutralization. After dichloromethane and ethanethiol were removed by evaporation, the partially methylated

cellulose was isolated by dialysis and subsequent lyophilization. The distribution of methyl groups was analysed by GLC as described above.

MAC was methylated twice by the Hakomori method. The fully methylated MAC (60 mg) and potassium tert-butoxide (20 mg) were dissolved in anhydrous DMSO (0.4 ml), and the mixture was heated at 100°C for 6 h to convert methallyl groups into 2,2-dimethylvinyl substituents. The permethylated 2,2-dimethylvinylcellulose was hydrolyzed successively with 90% formic acid at 100°C for 1 h and with 3% sulfuric acid at 120°C for 1 h to produce partially methylated glucoses. They were analysed as partially methylated glucitol acetates by GLC.

RESULTS AND DISCUSSION

1. Preparation of cellulose ethers

Table 1 shows DS and preparative conditions of cellulose ethers used in this work. The authors have already reported that the addition of sufficient amounts of powdered NaOH and etherifying reagents made it possible to prepare tri-O-substituted cellulose ethers in the case of MC²⁵), BC²⁰) and MAC²¹). In this work, partially substituted cellulose ethers were prepared by adjusting the amounts of powdered NaOH added. Cellulose ethers prepared from alkalicellulose are commercially available ones except BC-1, which was prepared by the method described in the previous paper²⁰).

2. Distribution of substituents in cellulose ethers

2-1. Methylcellulose

Table 2 shows the results of GLC analyses of the substituent distribution (X_n ($n=2, 3$ and 6)) in MC. X_2 , X_3 and X_6 were calculated from molar ratios of glucitol (S_0) and its mono-, di-, tri-derivatives (S_2-S_{236}) which were determined by GLC, and shown in the row of A. These values (X_n) show the distribution of substituents as well as reactivities of hydroxyl groups. The DS represented as the sum of X_2 , X_3 and X_6 coincide well with those shown in parenthesis in the same column, which were calculated from methoxyl contents. Molar ratios of partially methylated glucitols were calculated from X_2 , X_3 and X_6 with the assumption that the reactivity of each hydroxyl group was independent each other within the extents of DS shown in Table 2, and

Table 1 DS and preparative conditions of cellulose ethers.

Sample	DS	System	NaOH added (g/lg cellulose)	Etherifying reagent	Reaction conditions (°C , h)
commercial MC-1 ^{a)}	1.6	aq. ^{e)}	-	CH ₃ Cl	-
MC-2	0.1	non-aq. ^{f)}	4	(CH ₃) ₂ SO ₄	60°C , 3h
MC-3	1.0	non-aq.	8	(CH ₃) ₂ SO ₄	60°C , 3h
MC-4	0.4	non-aq.	2	CH ₃ I	20°+60°C , 3h
MC-5	2.2	non-aq.	4	CH ₃ I	20°+60°C , 3h
commercial CMC-1 ^{b)}	1.4	aq.+ iso PrOH	-	ClCH ₂ COOH	-
commercial CMC-2	1.8	aq.+ iso PrOH	-	ClCH ₂ COOH	-
CMC-3	1.2	non-aq.	7	ClCH ₂ COONa	85°C , 12h
CMC-4	1.4	non-aq.	8	ClCH ₂ COONa	85°C , 12h
CMC-5	1.6	non-aq.	9	ClCH ₂ COONa	85°C , 12h
CMC-6	0.7	non-aq.	18	BrCH ₂ COOH	85°C , 9h
CMC-7	0.6	non-aq.	9	ICH ₂ COONa	20°+60°C , 3h
BC-1 ^{c)}	1.5	aq.	6	C ₆ H ₅ CH ₂ Cl	85°C , 12h
BC-2	2.1	non-aq.	4	C ₆ H ₅ CH ₂ Cl	85°C , 12h
MAC ^{d)}	1.5	non-aq.	6	ClCH ₂ C(CH ₃)=CH ₂	70°C , 4h

a) Methylcellulose. b) Carboxymethylcellulose sodium salt. c) Benzylcellulose. d) Methallylcellulose.

e) Aqueous alkaline cellulose was used. f) A SO₂-DEA-DMSO system was used as a medium.

Table 2 Distribution of methyl groups in methylcelluloses.

Samples	DS		Molar ratios (%)								X ₂ , X ₃ , X ₆ ^{e)}		
			S ₀	S ₂	S ₃	S ₆	S ₂₃	S ₃₆	S ₂₆	S ₂₃₆	(X ₂ :X ₃ :X ₆)		
MC-1	1.7 ^{a)} (1.6) ^{b)}	A ^{c)}	10.9	15.8	1.9	12.1	7.5	6.0	23.0	22.8	0.691	0.382	0.639
		B ^{d)}	6.9	15.2	4.3	12.1	9.5	7.5	27.0	16.9	(1.8:1:1.7)		
MC-2	0.1 (0.1)	A:	98.1	0	0	0.2	0.1	0.1	0.3	1.2	0.016	0.014	0.018
		B:	95.3	1.5	1.4	1.7	0	0	0	0	(1.1:1:1.3)		
MC-3	1.1 (1.0)	A:	57.4	3.8	0.7	7.1	2.4	0.7	1.5	26.5	0.342	0.303	0.358
		B:	29.4	15.3	12.8	16.4	6.7	7.1	8.5	3.7	(1.1:1:1.2)		
MC-4	0.4 (0.4)	A:	66.5	9.1	11.9	6.7	3.0	1.2	0.9	0.7	0.137	0.168	0.095
		B:	65.0	10.3	13.1	6.8	2.1	1.4	1.1	0.2	(0.8:1:0.6)		
MC-5	2.1 (2.2)	A:	15.1	4.5	5.6	1.4	11.8	6.1	1.8	53.7	0.718	0.772	0.630
		B:	2.4	6.1	8.0	4.0	20.5	13.7	10.3	34.9	(0.9:1:0.8)		

a) Calculated from yields of glucitol (S₀) and its partially methylated derivatives (S₂~S₂₃₆) determined by GLC, and for example S₂ means the molar ratio of 2-methylglucitol acetate.

b) Calculated from methoxyl content.

c) Data measured by GLC.

d) Data calculated from X₂, X₃ and X₆; S₀=(1-X₂)(1-X₃)(1-X₆)×100, S₂₃₆=X₂·X₃·X₆×100, etc.e) X_n means a ratio of glucitol derivatives substituted at HO-n (n=2, 3 or 6).Ex., X₂=(S₂+S₂₃+S₂₆+S₂₃₆)/100.

these values were shown in the row of B in Table 2. Thus, by comparing the values in the row of A with those in the row of B, it can be deduced whether etherification reactions occurred homogeneously or heterogeneously for cellulose molecules, as discussed later.

As shown in Table 2, the relative reactivities of hydroxyl groups as estimated by X_n were $\text{HO-2} \approx \text{HO-6} > \text{HO-3}$ for the preparation of MC-1 from alkalicellulose (aq. system). This order of reactivities coincides with that reported for the same etherification by Croon and Lindberg¹⁾²⁾. In contrast, the relative reactivities for the preparation of MC-2 and MC-3 with powdered NaOH and dimethylsulfate in the non-aqueous solution were $\text{HO-6} \approx \text{HO-2} \approx \text{HO-3}$. In the case of methylation with methyl iodide (MC-4 and MC-5), the relative reactivities were $\text{HO-3} \approx \text{HO-2} > \text{HO-6}$ in contrast to those for the preparation of MC-2 and MC-3, and the differences in reactivities were small in these cases, too. In summary, the relative reactivities of hydroxyl groups found for the preparation of methylcellulose in the non-aqueous cellulose solution system (MC-2 ~ MC-5) were quite different from that in an aqueous cellulose solution system (MC-1). Croon and Lindberg²⁾ reported that the order of the relative reactivities for methylation with dimethylsulfate in aqueous cellulose solutions was almost equal to that prepared from alkalicellulose. It should be noted as to their experiment, however, that water was present in both methylations. Therefore, the presence or absence of water may cause the differences in the relative reactivities of hydroxyl groups in the two methylation media.

As noted above, the relative reactivities of hydroxyl groups were different between methylations with dimethylsulfate and with methyl iodide. Joseleau et al.²⁶⁾ prepared methylcelluloses with methylsulfinyl anion and methyl iodide in DMSO (cellulose does not dissolve in this system) and in a cellulose solvent, N-methylmorpholine N-oxide, and reported that the relative reactivities were $\text{HO-2} \approx \text{HO-3} \approx \text{HO-6}$ in both systems. Brederek and Dau²⁷⁾ methylated cellulose and cellulose triacetate with methyl iodide in the presence of sodium methoxide and benzyltetramethylammonium methoxide in a mixture of DMSO and benzene (non-aq.), and found that in both cases the relative

reactivities of hydroxyl groups were $\text{HO-2} > \text{HO-3} \approx \text{HO-6}$. These results together with the author's one (MC-4 and MC-5 in Table 2) indicate that the relative reactivities of hydroxyl groups towards etherifying reagents in non-aqueous systems become similar and the reactivity of HO-6 towards methyl iodide becomes the lowest. These effects found for the methylation with iodide are discussed in the latter section.

2-2. Carboxymethylcellulose

Table 3 shows the results of ¹H-NMR analyses of various CMC. X_2 , X_3 and X_6 are determined directly from the NMR spectra and therefrom the first order relative rate constants k_2 , k_3 and k_6 were calculated with the assumption that the reactivity of each hydroxyl group is independent each other. As shown in the Table, the relative reactivities of hydroxyl groups for the preparation of CMC-1 and CMC-2 from alkalicellulose were $\text{HO-2} > \text{HO-6} > \text{HO-3}$ in agreement with the recent reports⁷⁾⁸⁾. On the other hand, the relative reactivities were $\text{HO-6} > \text{HO-2} \approx \text{HO-3}$ in the case of carboxymethylation with sodium chloroacetate and bromoacetic acid in non-aqueous cellulose solution systems (CMC-3 ~ CMC-6). Interestingly, the use of sodium iodoacetate in the non-aqueous cellulose solution (CMC-7) brought about an increase of the reactivity of HO-3. This effect is also found for the preparation of methylcellulose with CH_3I in the non-aqueous systems (MC-4 and MC-5).

Reuben and Conner⁸⁾ reported that the relative rate constant ($k_2:k_3:k_6$) showed the definite value up to the high DS (2.2). However, there are some differences among the ratios of $k_2:k_3:k_6$ in Table 3. Namely, the reactivities of hydroxyl groups are not found to be independent each other among the samples with various DS shown in Table 3.

2-3. Benzylcellulose and methallylcellulose

The distribution of substituents in partially benzylated and methallylated celluloses were analysed according to the schemes shown in Fig. 1. Although many kinds of catalytic hydrogenolysis have been reported for debenzylation reactions^{28)–31)}, they could not be applied successfully for debenzylation of benzylcellulose. Recently, Fuji et al.³²⁾ reported the combination use of borontrifluoride etherate and ethanethiol

Table 3 Distribution of carboxymethyl groups in carboxymethylcelluloses.

Samples	DS	X ₂ , X ₃ , X ₆ (X ₂ :X ₃ :X ₆)	k ₂ : k ₃ : k ₆ ^{a)}
CMC-1	1.4	0.64, 0.34, 0.46 (1.9:1:1.4)	2.5 : 1 : 1.7
CMC-2	1.8	0.88, 0.46, 0.58 (1.9:1:1.3)	3.4 : 1 : 1.4
CMC-3	1.2	0.36, 0.37, 0.50 (1.0:1:1.4)	1.0 : 1 : 1.6
CMC-4	1.4	0.41, 0.41, 0.57 (1.0:1:1.4)	1.0 : 1 : 1.6
CMC-5	1.6	0.68, 0.59, 0.80 (1.2:1:1.4)	1.2 : 1 : 1.8
CMC-6	0.7	0.14, 0.13, 0.43 (1.1:1:3.3)	1.1 : 1 : 4.0
CMC-7	0.6	0.18, 0.26, 0.13 (0.7:1:0.5)	0.7 : 1 : 0.5

^{a)} Relative rate constants of etherification at HO-2, HO-3 and HO-6, calculated by the use of the following equations;
 $k_2:k_3:k_6 = -\ln(1-X_2):-\ln(1-X_3):-\ln(1-X_6)$.

Fig. 1 Analytical schemes of benzylcellulose (A) and methylcellulose (B).

for debenzilation. In our experiment, the procedure described in the experimental section were first applied to permethylated benzylcellulose, which was prepared from commercial methylcellulose by benzilation with powdered NaOH and benzyl chloride in its DMSO solution, and the benzylmethylcellulose thus prepared was proved to yield partially methylated glucitol acetates in the almost same ratios as original commercial methylcellulose.

The results are shown in Table 4. It is noticeable that in benzilation of alkalicellulose (BC-1), the reactivity of HO-6 is the highest, but the difference in the reactivities of hydroxyl groups is rather small. Furthermore, the order of the reactivities in the aqueous system was the same as that in the non-aqueous system. The steric effect of a benzyl group as compared with methyl and carboxymethyl groups may cause the highest reactivity of HO-6 even in the aqueous system on the analogy

Table 4 Distribution of substituents in benzyl- and methallyl-celluloses.

Samples	DS		Molar ratios (%)								X_2, X_3, X_6		
			S_0	S_2	S_3	S_6	S_{23}	S_{36}	S_{26}	S_{236}	$(X_2:X_3:X_6)$		
BC-1	1.7 ^{a)} (1.5) ^{b)}	A: ^{c)}	14.6	6.4	6.5	8.4	5.9	19.6	16.4	22.2	0.51, 0.54, 0.67		
		B: ^{d)}	7.5	7.7	8.9	15.0	9.2	17.7	15.5	18.4	(0.9:1:1.2)		
BC-2	2.1 (2.1)	A:	9.5	2.7	3.9	11.0	6.2	12.7	6.9	47.1	0.63, 0.70, 0.78		
		B:	2.5	4.2	5.8	8.8	9.8	20.2	14.7	34.2	(0.9:1:1.1)		
MAC	1.4 (1.5)	A:	23.6	5.1	3.4	22.2	6.9	8.4	11.1	19.4	0.43, 0.38, 0.61		
		B:	13.8	10.2	8.5	21.7	6.3	13.4	16.1	9.9	(1.1:1:1.6)		

a) See the footnote 1 in Table 2.

b) Calculated from data of elementary analyses for BC or the content of double bonds for MAC.

c) and d) See the footnote 3 and 4 in Table 2, respectively.

of triphenylmethylation and diphenylmethylation.

For allylation of alkal cellulose with sodium allylsulfonate in an aqueous system³⁾, the relative reactivities were reported to be HO-6 > HO-2 > HO-3. As shown in Table 4, the relative reactivities were HO-6 > HO-2 $\approx$ HO-3 for methallylation in the non-aqueous system.

3. Effect of reaction media on homogeneity of etherifications for cellulose molecules, and on reactivities of hydroxyl groups in cellulose

3-1. Homogeneity of etherifications for cellulose molecules

According to Yamazaki and Nakao³³⁾, cellulose dissolves in a SO₂-DEA-DMSO mixture by forming a complex among a hydroxyl group in cellulose, a SO₂ molecule and a DEA molecule. This complex may be destroyed by addition of powdered NaOH to yield non-crystalline sodium celluloses. This expectation could be supported by our success in the facile preparation of tri-O-alkylcelluloses by the use of a cellulose solvent together with powdered NaOH and alkyl iodides²²⁾²⁵⁾, because alkylations were known to occur at Cell-O⁻ with alkyl iodides (ex. CH₃I) by S_N2 in non-aqueous media³⁴⁾.

As shown in Table 2, the molar ratios of partially methylated glucose residues (A) measured for MC-1 coincide well with those (B) calculated from the values of X₂:X₃:X₆, indicating that this methylation in alkal cellulose system (aqueous) occurs homogeneously for whole cellulose molecules according to the probability. On the other hand, the molar ratios (A) measured for MC-2 ~ MC-5 were different from the calculated ones (B), and the permethylated glucose residue (S₂₃₆) and

the unmethylated residue (S₀) had relatively large ratios for all these samples. Namely, these results show that these methylations occur heterogeneously for cellulose molecules contrary to our expectation when the non-aqueous cellulose solvent was used. Possibly this heterogeneity for methylations may be explained as follows: amorphous sodium cellulosate formed by addition of powdered NaOH into a cellulose/SO₂-DEA-DMSO mixture are so reactive in non-aqueous systems that methylation may proceed immediately at the reaction site.

Also the benzylation of aqueous alkal cellulose was found to proceed more homogeneously than that in the non-aqueous cellulose solution (Table 4).

3-2. Reactivities of hydroxyl groups in non-aqueous system

Studies on the distribution of substituents in partially substituted cellulose ethers prepared in the non-aqueous system revealed that reactivities of hydroxyl groups were generally HO-6 > HO-2 $\approx$ HO-3, and that the differences in reactivities of hydroxyl groups are much smaller than those in the aqueous systems. The highest reactivity of HO-6 may be due to sterical preference to etherifications, and the acidity of HO-3 was almost equal to that of HO-2 in the non-aqueous cellulose solution system.

3-3. Reactivities of hydroxyl groups in aqueous systems

Studies on the distribution of substituents in MC and CMC prepared from alkal cellulose revealed that the reactivities were HO-2 > HO-6 > HO-3, being identical with results of other researchers.

The highest reactivity of HO-2 and the lowest one of HO-3 have been explained to be due to the supposed difference in their acidities. That is, the acidity of HO-2 has been assumed to be higher because of its proximity to the anomeric center¹⁵⁾. However, if such an explanation is true, the difference among reactivity of HO-2 and HO-3 would be much higher in the non-aqueous system, too. In addition to acidities, therefore, factors such as electrostatic, steric, solvating, hydrogen bonding and other effects may be expected to cause the difference among reactivities of hydroxyl groups in aqueous system.

CONCLUSION

Etherifications of cellulose in aqueous (heterogeneous) and non-aqueous (homogeneous) systems showed different characteristics as follows:

- 1) Etherifications in the aqueous systems proceed more homogeneously than those in the non-aqueous system.
- 2) The reactivity orders of three hydroxyl groups in cellulose generally are HO-2 > HO-6 > HO-3 in the aqueous systems and HO-6 > HO-2 $\approx$ HO-3 in the non-aqueous system.
- 3) The differences among the reactivities of hydroxyl groups in the non-aqueous system are much smaller than those in the aqueous systems.

REFERENCES

- 1) I. Croon and B. Lindberg, *Svensk Pappers-tidn.*, **61**, 963 (1958).
- 2) I. Croon and B. Lindberg, *ibid.*, **60**, 843 (1957).
- 3) D. E. Hoiness, C. P. Wade and S. P. Rowland, *Can. J. Chem.*, **46**, 667 (1968).
- 4) O. Ramnas, *Acta Chem. Scand.*, **27**, 3139 (1973).
- 5) E. J. Roberts and S. P. Rowland, *Can. J. Chem.*, **45**, 261 (1967).
- 6) E. J. Roberts and S. P. Rowland, *ibid.*, **47**, 1581 (1969).
- 7) F. F.-L. Ho and D. W. Klosiewicz, *Anal. Chem.*, **52**, 913 (1980).
- 8) J. Reuben and H. T. Conner, *Carbohydr. Res.*, **115**, 1 (1983).
- 9) H. M. Spurlin, *J. Am. Chem. Soc.*, **61**, 222 (1939).
- 10) E. Avela and B. Holmbom, *Acta Acad. Abo. Ser. B*, **31**, p14 (1971).
- 11) A. N. Belder, B. Lindberg and O. Theander, *Acta Chem. Scand.*, **16**, 2005 (1962).
- 12) A. M. Bills and J. W. Green, *J. Chem. Soc.*, B 716 (1967).
- 13) Yu. S. Ovodov and E. V. Evtusenko, *Carbohydr. Res.*, **27**, 169 (1973).
- 14) S. Sato, Y. Takabe and S. Zen, *Bull. Chem. Soc. Jap.*, **45**, 291 (1972).
- 15) A. H. Haines, *Advan. Carbohydr. Chem.*, **33**, 11 (1976).
- 16) S. M. Hudson and J. A. Cuculo, *J. Makromol. Sci.-Rev., Makromol. Chem.*, **C18**, 1 (1980).
- 17) T. Ishii, A. Ishizu and J. Nakano, *Carbohydr. Res.*, **59**, 155 (1977).
- 18) A. Isogai, A. Ishizu and J. Nakano, *Sen-i Gakkaishi*, **37**, T363 (1981).
- 19) A. Isogai, A. Ishizu and J. Nakano, *Cellulose Chem. Technol.*, **17**, 123 (1983).
- 20) A. Isogai, A. Ishizu and J. Nakano, *J. Appl. Polym. Sci.*, **29**, 2097 (1984).
- 21) A. Isogai, A. Ishizu and J. Nakano, *ibid.*, in press.
- 22) A. Isogai, A. Ishizu and J. Nakano, *ibid.*, in press.
- 23) J. A. Wijs, *Chem. Ber.*, **31**, 750 (1898).
- 24) P. Albersheim, D. J. Nevis, P. D. English and A. Karr, *Carbohydr. Res.*, **5**, 340 (1967).
- 25) A. Isogai, A. Ishizu, S. Eda, K. Katō and J. Nakano, *ibid.*, in press.
- 26) J. P. Joseleau, G. Chambat and B. C.-Hermoza, *ibid.*, **90**, 339 (1981).
- 27) K. Brøderek and T. B. P. Dau, *Angew. Makromol. Chem.*, **89**, 167 (1980).
- 28) C. H. Heathcock and Y. Ratcliffe, *J. Am. Chem. Soc.*, **93**, 1746 (1971).
- 29) J. S. Bibdra and A. Grodski, *J. Org. Chem.*, **43**, 3240 (1978).
- 30) G. M. Anantharamaiah and K. M. Sivanandaiah, *J. Chem. Soc., Perkin Trans.*, **1**, 490 (1977).
- 31) A. M. Felix, E. P. Heimer, T. J. Lambros, C. Tzougraki and J. Meienhofer, *J. Org. Chem.*, **43**, 4194 (1978).
- 32) K. Fuji, K. Ichikawa, M. Noda and E. Fujita, *ibid.*, **44**, 1661 (1979).
- 33) S. Yamazaki and T. Nakao, *Sen-i Gakkaishi*, **30**, T234 (1974).
- 34) I. Ciucanu and F. Kerek, *Carbohydr. Res.*, **131**, 209 (1984).

水系および非水系で調製したセルロース エーテル類の置換基分布

東京大学農学部 磯貝 明, 石津 敦, 中野準三

非水系セルロース溶剤の一種である、 SO_2 -ジエチルアミン-ジメチルスルホキシドを用い、粉末苛性ソーダとエーテル化剤により合成したセルロースエーテル類（メチル-, カルボキシメチル-, ベンジル-, メタリル-セルロース）の置換基分布を測定し、アルカリセルロースから合成したセルロースエーテル類のそれと比較した。

アルカリセルロースのエーテル化における各水酸基の反応性が $\text{HO-2} > \text{HO-6} > \text{HO-3}$ であったのに対して、非水系セルロース溶剤を用いた場合には $\text{HO-6} > \text{HO-2} \approx \text{HO-3}$ となり、さらに各水酸基の反応性の差は水系の場合に比べて小さいことが見出された。