

# Characteristics of Carboxymethyl Cellulose Synthesized in Two-Phase Medium $C_6H_6 - C_2H_5OH$ . I. Distribution of Substituent Groups in the Anhydroglucose Unit

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## SYNOPSIS

Carboxymethyl cellulose was synthesized in two-phase medium containing benzene, ethanol, and water. The distribution of substitution of hydroxyl group attached to  $C_k$  Carbons ( $k = 2, 3, \text{ and } 6$ ) in an anhydroglucose unit (AGU) was determined by  $^1H$ -NMR method. It showed that the sequence of distribution of carboxymethyl group of the products in AGU was  $C_6 > C_2 > C_3$ ; and when degree of substitution (DS) was low to 1.0, the approximate value of  $C_2 : C_3 : C_6$  was 1.45 : 1 : 2.15. When DS was higher than 1.0 and increased, the distribution of substitution tends to identical. Through analysis of X-ray diffraction and calculation of crystallinity and interplanar distance of CMC, the principle of distribution of the substituent had been explained. The influence of benzene on distribution of substituent of CMC was also investigated. It was found that distribution of substituent of CMC prepared in medium benzene-ethanol at  $C_6$  position was higher than that prepared in ethanol.

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## INTRODUCTION

Carboxymethylcellulose, one of the important cellulose derivatives, is generally prepared through the reaction of alkali cellulose with monochloroacetate or its sodium salt in organic mediums. CMC possesses many available qualities, such as inspissation, filming, emulsification, suspension, water maintaining, and bind, etc. Since CMC was synthesized by Jansen in 1918<sup>1</sup> and industrialized in the 1940s, CMC has been used for many applications, such as printing and dyeing, medicine, food, textures, toilet, electrical elements, papermaking, etc. Physical and chemical characteristics of CMC are influenced mainly by the degree of substitution, distribution of substitution, degree of polymerization, and its distribution. Among them, DS and homogeneity of distribution of substitution are two important indexes and have influence on dissolubility, rheologic quality of solution, heat durability, salt resistance, and enzyme degradation of CMC, etc. The preparation of CMC with homogeneous distribution of substitution

has been studied by methods of etherifying on several stages<sup>2</sup> or in homogeneous phase.<sup>3</sup> However, the long period of former production leads to low availability of facilities, high consumption of energy, and high cost of product, which make its application limited. The DS of productions prepared by the latter method is very low, which is still in the stage of exploration. Owing to the structure of material cellulose and coexistence of crystalline and amorphous regions, preparations of CMC with homogeneous distribution are very difficult. In this paper, through changing the type of solvent to increase the extent of destroy and transformation of internal crystalline structure of cellulose, we improved the homogeneity of distribution of substitution of CMC. The solvent selected was a two-phase system containing benzene, ethanol, and water, in which CMC was prepared and showed excellent dissolubility and stability.

The method of  $^1H$ -NMR with high resolution has been used for the study of distribution of the substituent at different carbon positions of AGU of cellulose ether (orientation distribution). Characteristics of orientation distribution of CMC prepared in the former medium were also studied and interpreted by X-ray diffraction analysis. At the

same time, we have researched the effect of benzene on orientation distribution of CMC and introduced the method of determination of DS by  $^1\text{H-NMR}$  spectrum.

## EXPERIMENTAL

### Synthesis of Carboxymethylcellulose

100 g industrial cellulose, 320 mL benzene, and ethanol (95%) were added in the kneader. Scission and stirring continued 5 min at  $25^\circ\text{C}$ , a solution of NaOH was added and the reaction lasted longer than 0.5 h, then monochloroacetic acid was added and the reaction proceeded at  $50\text{--}60^\circ\text{C}$  for 0.5 h. Immediately on termination of the reaction, the resultant system was neutralized to pH 7–8 with acetic acid and washed with 80% methanol until  $\text{Cl}^-$  could not be detected by  $\text{AgNO}_3$ . White powder could be obtained after crushing and drying.

### Determination of Degree of Substitution

DS was determined by ashing.<sup>4</sup> CMC sample was washed several times with ethanol to remove salts. After firing in high temperature, organic substances of CMC were removed while oxidate of sodium salt remained. The quantity of  $\text{Na}^+$  of the remainder could be determined by titration, and the average DS of CMC was calculated.

### X-ray Diffraction Analysis

Absolute dry CMC was placed in the sample container of the X-ray diffractometer and pressed, and the circumference of container was sealed by paraffin. Only samples were exposed to X-rays and scanned by 2308 type X-ray diffractometer (Rigaku Denki Co., Ltd., Japan).

The degree of crystallization of CMC was measured by internal reference method.<sup>5</sup> The interplanar distance was calculated by the Bragg diffraction formula  $2d \sin \theta = n\lambda$ . Here  $n = 1$  (first-order diffraction),  $\theta$  is the diffraction angle, and  $\lambda$  is the wavelength of the X-ray.

### $^1\text{H-NMR}$ Measurement

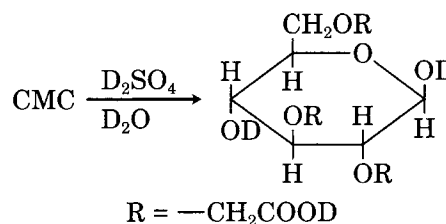
About 50 mg the CMC sample and 0.85 mL  $\text{D}_2\text{O}$  were added in a little heat-resisting glass bottle; CMC was swollen, then added to a 0.85 mL mixture solution of  $\text{D}_2\text{O}$  and  $\text{D}_2\text{SO}_4$  (1 : 1, v/v) and the bottle was shaken. The resulting slurry was heated at  $90^\circ\text{C}$

in oven for 2–4 h (the higher the DS, the shorter time was needed). Yellow, homogenous, and low viscosity solution was obtained at a later period of hydrolysis, 0.4 mL of which was added into 5 $\Phi$ m NMR tube and measured by JE $\Delta$ LF  $\times$  90Q NMR spectrometer. The operating conditions were as follows: 90 MHz; probe temperature,  $25^\circ\text{C}$ ; unipulse; tetramethylsilane, reference substance.

## RESULTS AND DISCUSSION

### $^1\text{H-NMR}$ Peak Assignment of CMC Samples

Substituted glucose can be obtained by hydrolysis of CMC at  $90^\circ\text{C}$  in sulphuric acid solution and analysed by  $^1\text{H-NMR}$ .



The  $^1\text{H-NMR}$  spectra of CMC synthesized in a benzene–ethanol medium with DS of 0.5, 0.65, 0.73, 0.86, 0.95, 1.00, 1.10, 1.28, and 1.37 (1–9) have been determined, respectively, and their shapes are similar. Figure 1 shows that the typical spectra of CMC with DS of 0.65 [Fig. 1(a)] and 1.10 [Fig. 1(b)] (width of spectrum: 5 ppm) double and triple peaks between 3.00–4.00 ppm are caused by protons of  $C_1$  position on AGU. Double peaks (A and B) locates low field and are caused by protons of  $\alpha$ -glucose. Triple peaks (C) locates a higher field and are caused by protons of  $\beta$ -glucose. Peak A is formed owing to attraction of carboxymethyl group at  $C_2$  position with the electric cloud of proton at  $C_1$  position (shift to the lower field). Peak B indicates a hydroxyl group attached to  $C_2$  position not be substituted, which can be verified by increase of strength of peak A when DS improving.

Table I shows that the ratios of  $J_A/J_B$  ( $J_A$  and  $J_B$  are the areas of characteristic peaks of protons at the  $C_1$  position of AGU substituted and unsubstituted at the  $C_2$  position, respectively) increase with improvement of DS. Carboxymethyl groups at other positions except for the  $C_2$  position almost have no influence on the characteristic peak of proton at  $C_1$  position. The integral value of  $A + B + C$  corresponds to proton of the  $C_1$  position. The characteristic peak between 0–2.4 ppm is caused by protons at  $C_2\text{--}C_6$  positions (K), the integral curve of which

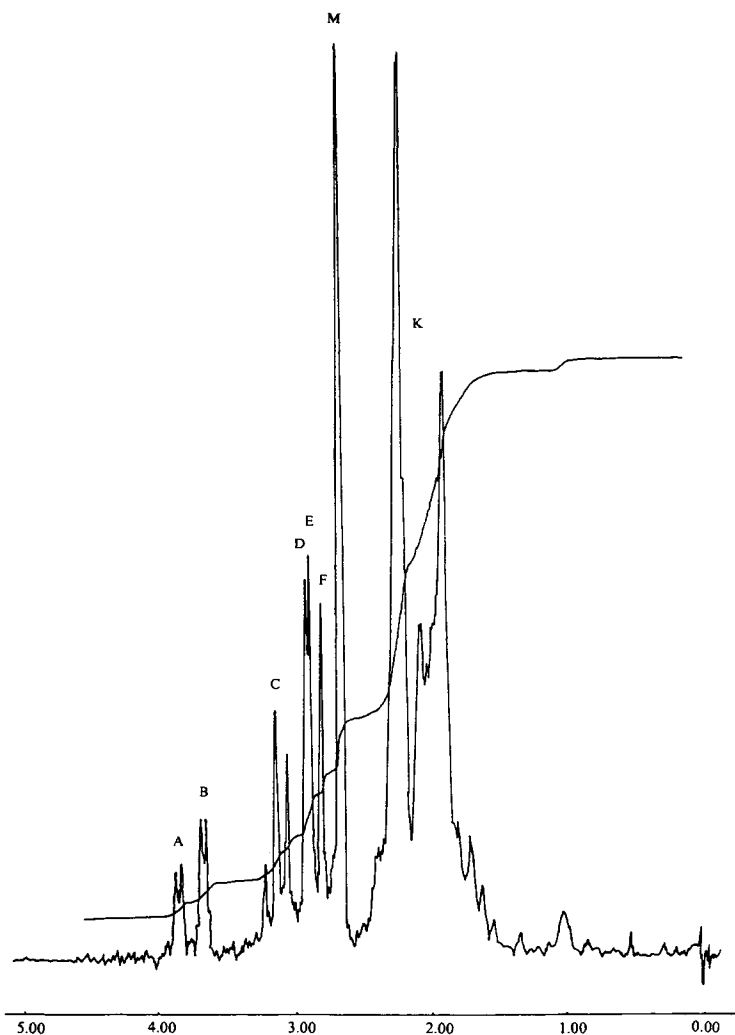


Figure 1  $^1\text{H-NMR}$  spectrum of CMC at 90 MHz.

corresponds theoretically to six protons. The ratios of integral values of  $K$  and  $A + B + C$  ( $J_k/J_{A+B+C}$ ) can be used to determine the degree of acid hydrolysis of CMC. Table I shows that  $J_k/J_{A+B+C}$  are approximately equal to six, which means hydrolysis of the CMC is complete.

Characteristic peaks caused by protons of the  $-\text{OCH}_2\text{COOD}$  group are between 2.5–3.0 ppm, which are signed by  $D$ ,  $E$ ,  $F$ , and  $M$ , respectively.  $D$  is caused by protons of carboxymethyl group at  $C_3$  position, and  $E$  and  $F$  by that of  $\alpha$ - and  $\beta$ -glucose at  $C_2$  position, respectively.  $M$  indicates information of a substituent at the  $C_6$  position and the total integral value of  $D + E + F + M$  corresponds to protons with  $2 \cdot \text{DS}$  in number. Instead of between 0–4.0 ppm, peaks of the unsubstituted hydroxyl group to  $C_2$ ,  $C_3$ ,  $C_6$  position and  $\text{H}_2\text{O}$  absorbed in sample appear in the lower field (about 8 ppm).

#### The Distribution of the Carboxymethyl Groups at $C_2$ , $C_3$ , and $C_6$ Positions

Through analysis of characteristic peaks between 2.5–3.0 ppm, we became aware that the peaks  $D$ ,  $E$ ,  $F$ , and  $M$  are caused by the substituents at  $C_3$ ,  $\alpha C_2$ ,  $\beta C_2$ , and  $C_6$  positions, respectively. The distribution of the carboxymethyl groups at the  $C_2$ ,  $C_3$ , and  $C_6$  positions corresponds to the ratio of integral values of these characteristic peaks ( $\alpha C_2 + \beta C_2 : C_3 : C_6$ ). But Figure 1 shows that the positions of peaks  $D$  and  $E$  approach so closely that it's difficult to read their integral values; for this reason, the following calculation is necessary.

$J_{D+E}$ ,  $J_F$ , and  $J_M$  (integral values of peaks  $D + E$ ,  $F$ , and  $M$ , respectively) can be obtained through spectrum. Because the proportion of  $\alpha$ - to  $\beta$ -glucose is 36 : 64,<sup>6</sup> the proportion of  $J_E$  to  $J_F$  is also 36 : 64. Then the value of  $J_D$  and  $J_E$  can be calculated, and

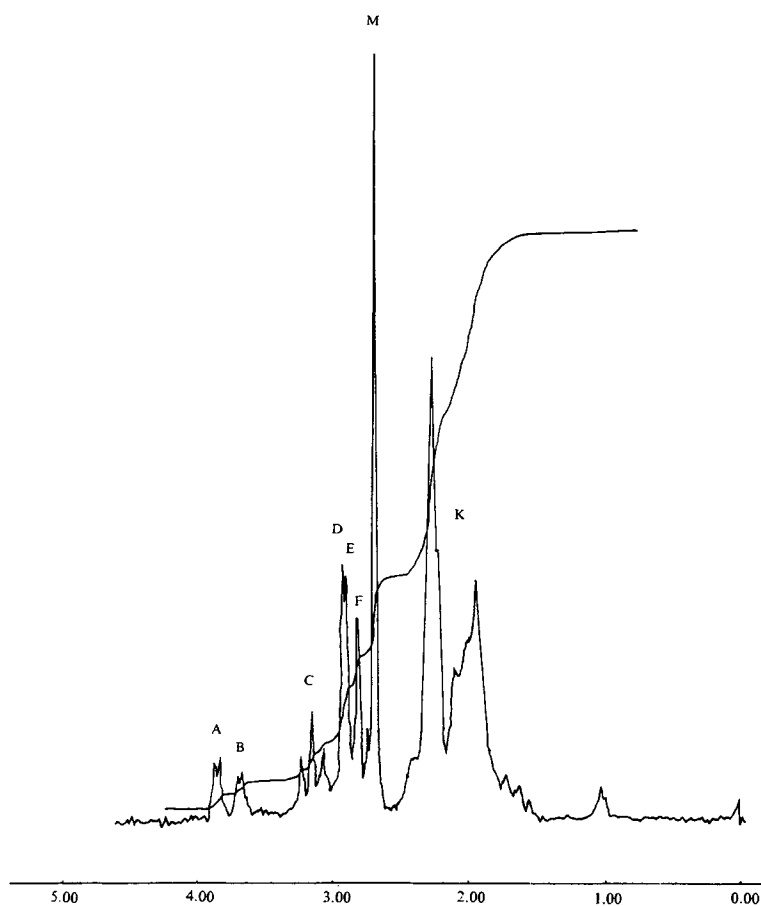


Figure 1 (Continued from the previous page)

the distribution of substituent at the  $C_2$ ,  $C_3$ , and  $C_6$  positions is expressed by  $J_{E+F}$ ,  $J_D$ , and  $J_M$ :  $C_2 = DS \cdot (J_E + J_F) / J_{D+E+F+M}$ ;  $C_3 = DS \cdot J_D / J_{D+E+F+M}$ ; and  $C_6 = DS \cdot J_M / J_{D+E+F+M}$ .

Table II shows that the orientation distribution of substituents of CMC produced in the medium benzene-ethanol-water indicates that the possibility of carboxymethyl substitution of hydroxyl group attached to  $C_6$  is the greatest; the second is that to  $C_2$ ; and the last is that to  $C_3$ . The reason may be that hydroxyl group attached to  $C_2$  is primary alcohol,

which has small steric hindrance and is more easily substituted than secondary alcohol to  $C_2$  and  $C_3$ , while the structure of crystalline regions of cellulose is gravely damaged.

The arrangement of chains in the cells of natural cellulose (cell I) are parallel. Hydroxyl groups along molecular chains are all embodied in hydrogen bonds. There are intermolecular hydrogen bonds  $[O(3)H \cdots O(5')]$  and  $[O(2')H \cdots O(6)]$  with bond distances of  $2.75 \times 10^{-10}$  and  $2.87 \times 10^{-10}$  m, respectively, along chains. Between two AGU of ad-

Table I The Degree of Hydrolysis of CMC

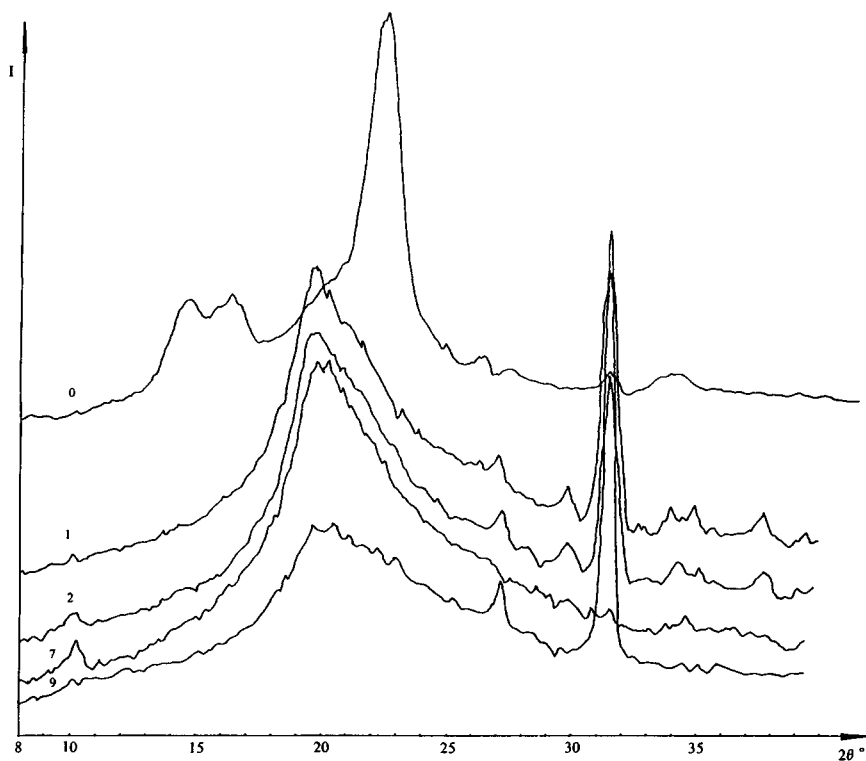
No.	1	3	4	5	6	7	8	9
DS	0.58	0.73	0.86	0.95	1.00	1.10	1.28	1.37
$J_A$	1.8	3.6	4.1	8.0	4.5	4.0	6.6	5.0
$J_B$	3.0	4.0	4.2	6.4	3.5	2.5	3.4	2.0
$J_A/J_B$	0.60	0.90	0.98	1.25	1.29	1.60	1.94	2.50
$J_{A+B+C}$	13.8	16.0	17.9	31.0	20.0	19.0	28.0	16.7
$J_k$	88.0	89.7	87.3	165.2	125	110	168	83.5
$J_k/J_{A+B+C}$	6.38	5.61	4.88	5.33	6.25	5.79	6.00	5.00

**Table II** The Distribution of CMC's Substituents on C<sub>2</sub>, C<sub>3</sub>, and C<sub>6</sub> in AGU

No.	DS	Integral Value						Content of Substituents			Distribution of Substituents			C <sub>2</sub> : C <sub>3</sub> : C <sub>6</sub>
		J <sub>D+E+F+M</sub>	J <sub>D+E</sub>	J <sub>F</sub>	J <sub>E+F</sub>	J <sub>D</sub>	J <sub>M</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>6</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>6</sub>	
1	0.58	18.1	6.0	3.7	5.78	3.92	8.4	0.319	0.217	0.464	0.185	0.126	0.269	1.47 : 1 : 2.14
2	0.65	25.5	8.2	5.0	7.81	5.39	12.3	0.306	0.211	0.482	0.199	0.137	0.313	1.45 : 1 : 2.29
3	0.73	23.5	8.0	4.5	7.03	5.47	11.0	0.299	0.233	0.468	0.218	0.170	0.342	1.29 : 1 : 2.01
4	0.86	27.0	8.5	5.5	8.59	5.41	13.0	0.309	0.210	0.481	0.266	0.192	0.414	1.39 : 1 : 2.16
5	0.95	52.0	18.0	12.0	18.75	11.25	22.0	0.360	0.216	0.423	0.325	0.195	0.419	1.67 : 1 : 2.15
6	1.00	39.8	14.1	9.8	14.31	8.99	16.0	0.359	0.226	0.402	0.359	0.226	0.402	1.59 : 1 : 1.78
7	1.10	41.7	13.5	8.5	13.28	8.92	19.7	0.318	0.235	0.447	0.350	0.259	0.492	1.35 : 1 : 1.90
8	1.28	68.5	25.5	15.5	24.22	16.78	27.5	0.354	0.245	0.401	0.453	0.314	0.514	1.44 : 1 : 1.64
9	1.37	41.0	20.0	11.0	17.29	13.81	20.0	0.419	0.337	0.487	0.574	0.461	0.668	1.25 : 1 : 1.45

adjacent chains also exist intermolecular hydrogen bonds [O(6) ··· O(3)], with a bond distance of  $2.79 \times 10^{-10}$  m which is on (020) crystal face.<sup>7</sup> In crystalline regions, linkage depends mainly on a large quantity of intermolecular hydrogen bonds. During carboxymethylation of cellulose, crystalline structure of cell I is gravely destroyed by the aquated Na<sup>+</sup> and the medium benzene-ethanol. Through X-ray diffraction analysis of natural cellulose and CMC, we can see that no characteristic peak of cell I exists;

there is only a diffraction peak of amorphous cellulose at  $2\theta = 20^\circ$  (Fig. 2), which indicates that the crystalline structure of the original cellulose has been damaged almost completely. The data of interplanar distance and crystallinity in Table III shows that the crystallinity of CMC decreases largely, while  $d_{101}$ , increases. The increase of interplanar distance of (101) is due to the damage of hydrogen bonds on (020) and the formation of the etherification center (cell-ONa).<sup>8</sup> Rapid decrease of

**Figure 2** X-ray diffraction of cellulose and CMC.

**Table III The Analysis of the X-ray Diffraction of Nature Cellulose and CMC**

No.		Crystallinity	$d_{101}$ ( $10^{-10}$ m)
0	Cellulose	0.565	6.010
1	CMC	0.433	7.306
2	CMC	0.388	7.366
7	CMC	0.229	8.835
9	CMC	0.134	9.012

crystallinity means that most of the intermolecular bonds [O(6)H · · · O(3)] on (020) have been opened; the resulting improvement of accessibility of hydroxyl group to  $C_6$  carbon leads to high reactivity.

Table II shows that the distribution of carboxymethyl groups  $C_2 : C_3 : C_6$  is approximately equal to 1.45 : 1 : 2.15. However, when DS is higher than 1.0 and increases, and the degree of increase of substituents at  $C_2$  and  $C_3$  positions is higher than at  $C_6$  position, we offer the following explanation. The higher the degree of activation of the hydroxyl group attached to  $C_6$  carbon (accessibility), the smaller the quantity of hydroxyl groups without being activated, which leads to a decrease of the rate of reaction of hydroxyl group attached to  $C_6$  position and increase of probability of activation of hydroxyl groups at  $C_2$  and  $C_3$  positions. The distribution of substituent at  $C_2$ ,  $C_3$ , and  $C_6$  positions become homogeneous when DS of CMC is higher than 1.0.

Generally, the reactivity of hydroxyl group attached to the  $C_2$  position is higher than that to  $C_6$  and  $C_3$ ;<sup>9-13</sup> however, the former discussions indicate that the sequence of distribution of the substituent is  $C_6 > C_2 > C_3$  and shows a certain extent regularity. The reason may be that, on the one hand, it's related to the raw material used; on the other hand, the different types of reaction mediums lead to different destroyed extents of crystalline structure of CMC and different reactivity of hydroxyl group.

### The Effect of Benzene on the Orientation Distribution of the Substituent of CMC

Figures 3 and 4 show 90 Hz  $^1\text{H-NMR}$  spectrum of the CMC sample prepared in an ethanol medium with DS = 0.53, and in benzene-ethanol with DS = 0.55, respectively. Analytical results of the orientation distribution of substituent are arranged in Table IV.

The data of the distribution of the substituent of CMC produced in benzene-ethanol have been compared with that in ethanol. Results dicte that the quantity of the substituent at the  $C_6$  position of the

former CMC is higher than the later under same DS; that at the  $C_3$  position is similar. It is related to the existence of benzene, which improves the extent of destruction of the crystalline region of CMC and increased the break of intermolecular bond [O(6)H · · · O(3)] formed at  $C_6$  position, which leads to an increase of the accessibility of hydroxyl groups at the  $C_6$  and  $C_3$  positions.

### Determination of the Degree of Substitution by NMR

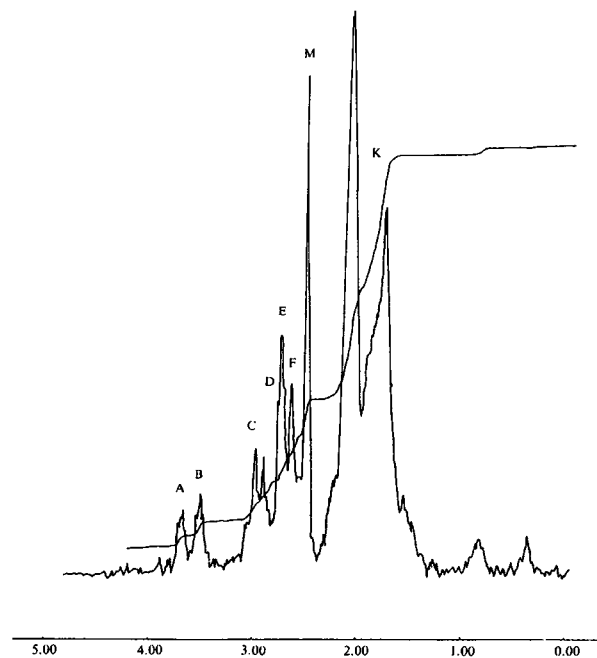
DS of CMC can be determined by a number of analytical techniques, such as the former related ashing or acid washing method.  $^1\text{H-NMR}$  is also capable of providing DS.

After analysis of the  $^1\text{H-NMR}$  spectral, the principle of measuring DS of CMC by NMR is clear. DS is the ratio of area of characteristic peaks of substituents (between 2.5–3.0 ppm) to that of AGU (between 3.0–4.0 ppm or 0–2.4 ppm):

$$DS = \frac{J_{D+E+F+M}/2}{J_{A+B+C}}$$

or

$$DS = \frac{J_{D+E+F+M}/2}{J_K/6}$$



**Figure 3** NMR spectra of a CMC sample (produced in ethanol medium) with DS = 0.53.

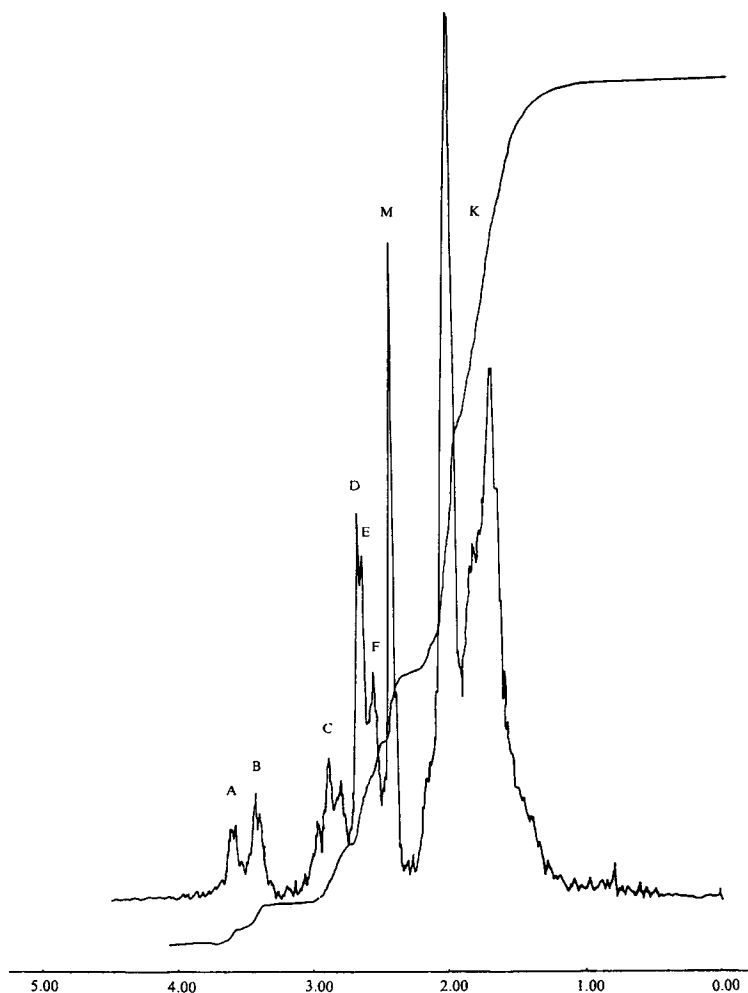


Figure 4 NMR spectra of a CMC sample (produced in benzene-ethanol) with  $DS = 0.55$ .

Table V shows the  $DS$  ( $DS_1$ ) calculated through the method of averaging  $J_{A+B+C}$  and  $J_K/6$ :

$$DS = \frac{J_{D+E+F+M}}{J_{A+B+C} + J_K/6}$$

which approximate the value of  $DS$  determined by the ashing method ( $DS_2$ ). The results indicate that the NMR method is feasible and isn't influenced by weight of the samples and impurity, such as NaCl,  $Na_2CO_3$ , and  $HOCH_2COONa$ .

## CONCLUSIONS

1. Four characteristic peaks between 2.5–3.0 ppm in the NMR spectra are caused by protons of the carboxymethyl groups at the  $C_2$ ,  $C_3$ , and  $C_6$  positions.
2. The sequence of distribution of substituent on AGU is  $C_6 > C_2 > C_3$ . When  $DS < 1.0$ ,  $C_2 : C_3 : C_6$  is equal approximately to 1.45 : 1 : 2.15. When  $DS$  is higher than 1.0 and im-

Table IV The Effect of Medium Benzene on the Distribution of Substituents of CMC

DS	Medium	Content of Substituents			Distribution of Substituents			
		$C_2$	$C_3$	$C_6$	$C_2$	$C_3$	$C_6$	$C_2 : C_3 : C_6$
0.53	ethanol	0.470	0.149	0.389	0.249	0.077	0.202	3.15 : 1 : 2.59
0.55	benzene-ethanol	0.360	0.209	0.431	0.203	0.115	0.237	1.72 : 1 : 2.06

**Table V DS Determination of CMC Samples**

No.	1	3	4	5	6	7	8	9
$J_{D+E+F+M}$	18.1	23.5	27.0	52.0	39.8	41.7	68.5	41.0
$J_{A+B+C}$	13.8	16.0	17.9	31.0	20.0	19.0	28.0	13.9
$J_{k/6}$	14.7	14.95	14.55	27.5	20.8	18.3	28.0	13.9
DS <sub>1</sub>	0.635	0.759	0.832	0.889	0.975	1.118	1.223	1.339
DS <sub>2</sub>	0.58	0.73	0.86	0.95	1.00	1.10	1.28	1.37

proves, the degree of an increase of substituent at C<sub>2</sub> and C<sub>3</sub> positions is higher than C<sub>6</sub> positions, and the distribution of substitution at C<sub>2</sub>, C<sub>3</sub>, and C<sub>6</sub> positions tend to identical.

- Under the same DS, the distribution of the substituent of CMC produced in the benzene-ethanol medium at the C<sub>6</sub> position is higher than that in ethanol only.
- DS of CMC can be determined by <sup>1</sup>H-NMR spectrum, which approximate that determined by the ashing method.

## REFERENCES

- E. Jansen, Ger. Patent, 322, 2031 (1918).
- W. Raehse, N. Kuehne, W. Wuest, K. Engelskirchen, Ger. Offen., 3, 303, 153 (1984).
- M. D. Nicholson et al., *Cellulose Chem. Tech.*, **11**, 349 (1977).
- J. Zhang et al., *Tianjin Chem. Ind.*, **4**, 53 (1989).
- M. Y. Loelovich and G. H. Veveris, *Khim. Drevesiny*, **2**, 10 (1983).
- D. Gagnaice, *J. Appl. Polym. Sci. Polym. Symp.*, **37**, 261 (1983).
- K. H. Gardner et al., *Biopolymers*, **13**, 1975 (1974).
- A. Doikhman, *Zh. Prikl. Khim.*, **8**, 909 (1985).
- F. F-L. Ho et al., *J. Am. Chem. Soc.*, **74**, 2677 (1952).
- R. G. H. Siu et al., *Tex. Res. J.*, **19**, 484 (1949).
- S. P. Rowland and N. R. Bertoniere, *Cellulose Chemistry and its Applications*, T. P. Nevell, Ed., Wiley, New York, 1985, p. 112.
- S. P. Rowland, *Tex. Res. J.*, **39**, 749 (1969).
- U. R. Karimova, PhD Diss., Kand. Khim. Nauk. Tashchkent, NIIK HTTS, 1988, p. 157.

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