¹³C NMR Study on the Distribution of Substituent Groups on Trihydric Alcohol Units in Cellulose Xanthate

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ABSTRACT: An attempt was made to investigate ¹³C{¹H} NMR spectra for cellulose xanthate (CX) in sodium hydroxide/D₂O mixture and to assign NMR peaks of CX by applying the DEPT method and by inspecting the change in NMR spectra with ripening time. Based on NMR analysis a direct method is proposed for determining the probability of substitution at hydroxyl groups located at C₂, C₃, and C₆ positions in trihydric glucopyranose unit $\langle f_k \rangle$ ($k=2, 3$, and 6). The difference in $\langle f_k \rangle$ between CXs prepared by the gas-solid (heterogeneous) and liquid-liquid (homogeneous) reactions was also examined. For the latter reactions an alkali-soluble cellulose was employed as starting material. As results, the substitution at C₂ and C₃ positions was greatly enhanced by the gas-solid reaction and the substitution at C₆ was preferential in the liquid-liquid reaction. During ripening, xanthate groups at C₂ and C₃ positions decomposed first and after complete decomposition of these groups xanthate group at C₆ position decomposes very gradually.

KEY WORDS Cellulose Xanthate / Total Degree of Substitution / ¹³C NMR Spectroscopy / Distribution of Degree of Substitution / Viscose / Ripening / Cellulose / Xanthation / Dexanthation /

The alkali solution of cellulose xanthate (hereafter referred to as CX) was first made by Cross and Bevan¹ as early as 1892. Since then, the solution, known commercially as viscose solution, has long been world-widely utilized for production of cellophane, viscose rayon and so on for almost 100 years. CX is one of the most popular cellulose derivatives. CX is prepared by various methods²: Reaction of solid alkali cellulose with gaseous carbon disulfide (CS₂) (Hereafter denoted simply as the gas-solid reaction), reaction of fibrous cellulose in emulsified CS₂/aqueous alkali mixture (emulsion method) and the reaction of CX solution in alkali with CS₂ (after-xanthating method). Note that no homogeneous xanthation of cellulose has been carried out. The total degree of substitution $\langle F \rangle$ of CX lies between 0.4 and 0.6 for commercial

use² although CX having $\langle F \rangle=3$ has been obtained experimentally.² Generally, CX is known to be very unstable in water, rapidly decomposing to cellulose and in alkali $\langle F \rangle$ of CX gradually decreases, accompanying a significant change in viscosity as well as other properties. The latter phenomenon is widely known as ripening. Variations in preparation and ripening conditions have a significant influence on the properties of resultant viscose solution and this has encouraged many investigators to make efforts to establish a method for determining the probability of substitution of xanthate groups to hydroxyl groups located at C₂, C₃, and C₆ positions in trihydric glucopyranose unit ($\langle f_k \rangle$, $k=2, 3$ and 6). Lieser³ first reported in 1926 the method for evaluating $\langle f_k \rangle$ and thereafter many improved methods appeared. The typ-

ical procedures proposed so far are briefly illustrated in Figure 1. These methods are principally based on the quantitative conversion of CX to methylated glucose derivatives, which are chemically and gravimetrically analyzed. As is obvious from Figure 1, these methods are very time-consuming, not reliable in accuracy of $\langle f_k \rangle$ because of inclusion of severe destructive analysis and the possibility of change in $\langle f_k \rangle$ during many steps of analysis and are evidently not the proper way to study $\langle f_k \rangle$ of CX systematically. On the basis of the methods illustrated in Figure 1, many authors reported $\langle f_k \rangle$ of CX: For example, Lieser³ insisted that $\langle f_2 \rangle$ was predominant for CX with $\langle F \rangle = 0.5$. Noguchi⁴ pointed out that CX with $\langle F \rangle = 0.5$ and 0.7, both prepared by the gas-solid reaction, produced only 2-methyl glucose and, 2- and 2,6-methyl glucoses, respectively, when reacted with diazomethane. By using CX prepared in the same manner as Noguchi did, Lauer⁵ obtained only 2- and 2,3-methyl glucoses from CX with $\langle F \rangle = 0.75-0.80$. Chen,⁶ by applying Lauer's method for evaluation of CX,

concluded that $\langle f_2 \rangle > \langle f_6 \rangle > \langle f_3 \rangle$ was generally obtained for CX prepared by the gas-solid reaction. For ripened CX with $\langle F \rangle = 0.31$, $\langle f_2 \rangle \cong \langle f_6 \rangle > \langle f_3 \rangle$ was reported by Willard and Pacsu⁷ and contrary to this, Phillip and Liu⁸ insisted that only CX substituted at C₆ position existed in ripened viscose solution. Horio *et al.*⁹ studied extensively the difference in $\langle f_k \rangle$ of CX prepared by different methods (the gas-solid reaction and the emulsion methods), and concluded that $\langle f_2 \rangle \gg \langle f_6 \rangle > \langle f_3 \rangle$ held in both cases and the ripening did not bring about the drastic change in the order of the magnitude of $\langle f_k \rangle$ discovered above. These results indicate that $\langle f_2 \rangle$ is the largest in CX, but an apparent disagreement of conclusion on $\langle f_k \rangle$ values, especially of the ripened CX led by many researchers is obviously large, requiring a more rigorous and accurate evaluation method other than the conventional methods used so far, which have the commonly several fatal short points described before. Accordingly, it is still one of the unsolved problems to determine $\langle f_k \rangle$ of CX and their change

Figure 1. Typical procedures for determination of $\langle F \rangle$ and $\langle f_k \rangle$ by chemical analysis.

during ripening despite of 60 year's voluminous studies.

Recently, we successfully determined by NMR analysis $\langle f_k \rangle$ of sodium salt of cellulose sulfate (NaCS)^{10,11} and sodium salt of carboxymethylcellulose (NaCMC)¹² and showed that anticoagulant activity and acute toxicity of NaCS ¹¹ and absorbency of NaCMC ¹² towards various aqueous liquids are governed primarily by their $\langle f_k \rangle$. NMR analysis also has been utilized for evaluating $\langle f_k \rangle$ of various cellulose derivatives.¹³⁻¹⁵ There has been no study on $\langle f_k \rangle$ of CX in viscose solution by NMR analysis, probably due to an inevitable decomposition of xanthate group (*i.e.*, gradual decrease in $\langle F \rangle$ and $\langle f_k \rangle$) when stored and during NMR measurement. ^1H NMR spectrum can be recorded in a very short time (3–100 s), compared with chemical analysis, but the resolution of NMR peaks is not sufficiently high and also peaks overlap heavily with large water proton signals. In contrast to this, ^{13}C NMR is a very convenient tool for analyzing the change in $\langle f_k \rangle$ of CX in viscose solution as a function of ripening time.

In this paper, we first intend to select the optimum operating conditions of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for CX in aq. alkali, and to assign NMR peaks of CX by applying DEPT method and by inspecting the change in NMR spectra obtained as a function of ripening time. In addition, we also intend to clarify the difference in $\langle f_k \rangle$ between CXs prepared by the gas-solid (heterogeneous) and the liquid-liquid (homogeneous) reactions. For the latter case, we employed an alkali-soluble cellulose, reported by Kamide *et al.*^{16,17}

EXPERIMENTAL

Samples

A cellulose having the viscosity-average molecular weight $\bar{M}_v = 3 \times 10^4$ (evaluated by Mark-Houwink-Sakurada equation established by Brown and Wikström¹⁸ in cadoxen at

25°C) and having the low degree of intramolecular hydrogen bond¹⁷ (crystal form: cellulose I) was used as a starting material for the preparation of CX in the liquid-liquid reaction. The liquid-liquid reaction was carried out as follows: A 0.5 g of the cellulose was immersed into 5 g of 2.5 *N* sodium hydroxide (NaOH)/deuterium oxide (D_2O) solution at 0°C, stirred vigorously. Into the resultant cellulose solution 0.3 g of carbon disulfide (CS_2) was added and the reaction was carried out for 48 hr at 0°C. The resultant xanthate solution was subjected to the apparent ripening at 20°C and after given ripening times, the solutions were subjected to the NMR measurement.

A hydrolyzed wood pulp ($\bar{M}_v = 6 \times 10^4$, cellulose I) was also used as a starting material of the gas-solid reaction. Alkali cellulose was prepared from the cellulose sample as described in the previous paper.¹⁶ A 1.4 g of the alkali cellulose (0.5 g of cellulose, 0.9 g of 17.5 wt% aq NaOH in D_2O) and 0.5 g of CS_2 were reacted in a sealed tube for 2 h at 30°C, and the reaction mixture was diluted with $\text{NaOH}/\text{D}_2\text{O}$ solution at 20°C for 2 h to produce viscose solution with 10 wt% cellulose content and *ca.* 2.5 *N* NaOH concentration. The resultant xanthate solution was subjected to the ripening at 20°C for given times and subjected to the NMR measurement.

The cellulose solution obtained in the preparation process for CX in the liquid-liquid reaction was employed as reference solution for NMR measurement in order to aid the peak assignment of CX.

$^{13}\text{C}\{^1\text{H}\}$ NMR

NMR spectra were recorded on a 200 MHz JEOL FT-NMR spectrometer JNM-FX-200. Measuring conditions are as follows: Frequency 50.15 MHz, irradiation 199.5 MHz (^1H), gated decoupling mode (NNE), pulse width 10 μs (*ca.* 40°), data point 16384, sampling data points 8192 (followed by 8192 points zero-filling), temperature 20°C.

These conditions were carefully selected so as to minimize the temperature rise induced by the ^1H irradiation in alkaline solution. Accumulation was more than 3600 times.

Distorsionless enhancement by polarization transfer (DEPT)¹⁹ method was applied to assign the peaks. In this NMR technique the flip angle was set at 135° . Chemical shifts were determined using methylene carbon peak (67.4 ppm) of dioxane as an internal reference, after confirming the peak for dioxane experimentally. Peak intensity was estimated from integral curve and when peaks are overlapped, the integral curve was visually separated.

RESULTS AND DISCUSSION

Peak Assignment in $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of Cellulose Xanthate

Figure 2 shows typical $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of whole region (a) and magnified spectra of substituent peak region (b) and of

glucose ring carbon region (c) of the 5 hour's ripened xanthate solution obtained by the liquid-liquid reaction. Twenty peaks, numbered as 1—20 from lower magnetic field, are detected in the range 270—60 ppm. Chemical shifts of these peaks are summarized in Table I. Peak No. 19 will be proved later as originated from methylene carbon of dioxane. Peaks No. 1 and 4 may be attributable to impurities produced by reaction of CS_2 with alkali, because of their narrow peak width, and were discarded in further analyses.

Figure 3 shows $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of cellulose/aq NaOD (a), ripened CX solution for 5 h (b) and ripened CX for 120 h (c) and DEPT spectrum for ripened CX for 75 h (d). Peak assignment for cellulose/NaOH/ D_2O system is indicated on the spectrum, according to Gagnaire *et al.*²⁰: 104.4 ppm; C_1 carbon, 79.7 ppm; C_4 carbon, 76.0 ppm; C_3 and C_5 carbons, 74.4 ppm; C_2 carbon and 61.5 ppm; C_6 carbon. These peaks appeared in the NMR

Table I. Chemical shift (δ), species of atomic group and assignment of carbon peaks in ^{13}C NMR spectrum of CX obtained from liquid-liquid reaction and ripened at 4°C 48 h and 20°C 0—10 h

Code	δ/ppm^a	Species ^b	Assignment
1	269.9	q	NaCS_3 (byproduct from CS_2 and NaOH)
2	233.2	q	$-\text{CS}_2\text{Na}$ (substituent group at C_2 , C_3)
3	232.5	q	$-\text{CS}_2\text{Na}$ (substituent group at C_6)
4	169.1	q	NaCO_3 (byproduct from CS_2 and NaOH)
5	104.4	t	C_1 in unsubstituted glucose unit
6	103.5	t	C_1 in substituted glucose unit
7	102.9	t	C_1 in substituted glucose unit
8	83.2	t	C_3 in 3-substituted glucose unit
9	82.0	t	C_2 in 2-substituted glucose unit
10	79.7	t	C_4 in unsubstituted glucose unit
11	77.3	t	? (ring carbon in substituted unit)
12	76.0	t	C_3 & C_5 in unsubstituted glucose unit
13	75.5	t	? (ring carbon in substituted unit)
14	74.4	t	C_2 in unsubstituted glucose unit
15	73.5	t	? (ring carbon in substituted unit)
16	72.7	s	C_6 in 6-substituted glucose unit
17	71.6	t?	? (ring carbon in substituted unit)
18	70.0	t?	? (ring carbon in substituted unit)
19	67.4	s	Dioxane (reference)
20	61.5	s	C_6 in 6-unsubstituted glucose unit

^a 67.4 ppm for dioxane.

^b s, secondary (methylene) carbon; t, tertiary (methyne) carbon; q, quaternary carbon.

Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of CX obtained by the liquid-liquid reaction and ripened for 5 h: (a), entire spectrum; (b), substituent region; (c), ring carbon region.

Figure 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of cellulose and CXs (obtained by the liquid-liquid reaction): (a), cellulose in 9.1 wt% aq NaOH soln.; (b), CX ripened for 5 h; (c), CX ripened for 120 h; (d), DEPT spectrum of CX ripened at 75 h.

spectrum of CX and can be assigned to unsubstituted ring carbons of glucopyranose unit. Other peaks in the region 110–60 ppm

are derived from ring carbons magnetically influenced by derivatization of cellulose and standard peak (dioxane). From the DEPT spectrum shown in Figure 3d, together with a well-known experimental fact that phase of DEPT spectrum is positive for methyl and methine carbons and negative for methylene carbon, and non-observable for quaternary carbon, we can easily assign the peaks based on carbon species (number of coupling protons). The results are listed in the third column of Table I. Here, note that methyl carbon does not exist in the system and any positive carbon peaks must be attributed to methine carbons. The number of coupling protons for carbons corresponding to peaks No. 17 and No. 18 could not be evaluated due to their very weak intensities and a heavy overlapping with a neighbouring strong negative peak located at lower magnetic field. Of methylene carbon peaks, (No. 16, 19, and 20), No. 19 peak is assignable to that for dioxane because of its narrow peak width and strong intensity and this peak was defined as 67.4 ppm. Peak No. 20 appeared at the same position as that for C_6 carbon of cellulose and therefore is assigned as unsubstituted C_6 carbon. Methylene carbon is available only for C_6 carbon and peak No. 16 can be attributed to substituted C_6 carbon. Peaks No. 1 and No. 4 are derived from carbons having no proton of inorganic impurities produced by the side reaction of CS_2 and alkali. Peaks No. 2 and 3 at 233.2 and 232.5 ppm respectively, were also proved to be quaternary carbons and their intensities decreased after ripening as shown in Figure 3b and 3c. Then, these peaks are attributable to carbons for xanthate substituent and in fact these chemical shifts are reasonable by taking into consideration that the chemical shift of CS_2 carbon is about 200 ppm. The existence of two xanthate carbon peaks may reflect the different OH positions substituted and will be discussed later. Figure 3b and 3c can aid to assign roughly ring carbons by considering that intensity of the peak which newly

appeared by xanthation, compared with those for cellulose, should decrease after dexanthation occurred during ripening. Thus, No. 8 (83.2 ppm) and No. 9 (82.0 ppm) are assigned to substituted C_3 and C_2 carbons, respectively. These chemical shifts are always found for other cellulose ethers.¹² Since α -substitution of C_2 and C_3 may induce the same order of deshielding effect, the lower field peak (C_3) for cellulose might appear at the lower magnetic field even for xanthate. Peaks No. 6 (103.5 ppm) and No. 7 (102.9 ppm) proved to decrease in their intensities by ripening and contrary to this, peak No. 5 (104.4 ppm) increased by ripening. Increased peaks by dexanthation should be regarded as those for unsubstituted ring carbons. Then, peaks at 104.4 ppm are attributable to unsubstituted C_1 carbon. As reported by Kamide *et al.*¹² and others,²¹ ether type substituents such as carboxymethyl and methyl groups give rise to (a) higher magnetic field shifts of 0.5–1.8 ppm for the β and γ carbons. Then, two peaks at 103.5 and 102.9 are responsible for C_1 carbons influences by xanthate substitution at either C_2 , C_3 , or C_6 . As mentioned before, peaks No. 10 (79.7 ppm), No. 12 (76.0 ppm), No. 14 (74.4 ppm) are attributed to unsubstituted C_4 , C_3+C_5 , and C_2 carbons, respectively. Other peaks (No. 11, 13, 15, 17, and 18) unassignable are responsible for either C_2 , C_3 , C_5 , and C_6 carbons influenced by xanthation. Peak assignment is given in Table I.

Determination of $\langle F \rangle$ and $\langle f_k \rangle$

Based on the peak assignment shown in Table I, $\langle F \rangle$ and $\langle f_k \rangle$ can be principally estimated:

$$\langle F \rangle = \frac{I_2 + I_3}{I_5 + I_6 + I_7} \quad (1)$$

$$\langle f_6 \rangle = 1 - \frac{I_{20}}{I_5 + I_6 + I_7} \quad (2)$$

$$\langle f_2 \rangle = \frac{I_9}{I_5 + I_6 + I_7} = 1 - \frac{I_{14}}{I_5 + I_6 + I_7} \quad (3)$$

$$\langle f_3 \rangle = \frac{I_8}{I_5 + I_6 + I_7} = 2 - \frac{I_{12}}{I_5 + I_6 + I_7} \quad (4)$$

$$\langle f_6 \rangle = \frac{I_{16}}{I_5 + I_6 + I_7} \quad (5)$$

It should be noted that under the NMR measuring conditions employed here, neither NOE nor progressive saturation exists because we adopted the gated decoupling mode and used pulse interval (10s) sufficiently larger than the anticipated spin-lattice relaxation time T_1 value (0.1–2s) for xanthate. I_k in eq 1–5 denotes the peak intensity for the corresponding peak No. k. Equations 3–5 cannot be practically used for estimation of $\langle f_2 \rangle$, $\langle f_3 \rangle$, and $\langle f_6 \rangle$ due to experimental uncertainty in I_8 , I_9 , I_{12} , I_{14} , and I_{16} . The former two are too small to determine accurately and the peaks for others heavily overlap. The most reasonable value for $\langle f_2 \rangle + \langle f_3 \rangle$ can be obtained using the following equation:

$$\langle f_2 \rangle + \langle f_3 \rangle = \langle F \rangle - \langle f_6 \rangle \quad (6)$$

Here, $\langle F \rangle$ and $\langle f_6 \rangle$ are determined from eq 1 and 2, respectively. The values estimated from eq 1, 2, and 6 have an uncertainty of ± 0.03 .

$\langle f_k \rangle$ of CXs Prepared under Different Conditions

Figure 4 shows $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of a 7 hour ripened CX solution obtained by the gas-solid reaction (a, entire spectrum; b, substituent group region; c, glucopyranose ring region). Compared with the spectra of CX solution obtained by the liquid-liquid reaction, shown in Figure 2, the spectra in Figure 4 are broader and less resolved, except for the peaks responsible for impurities (low molecular weight substance), because of the higher molecular weight and the higher viscosity of the CX sample in the latter case. But, in Figure 4, peaks No. 8 and No. 9 responsible for substituted C_2 and C_3 carbons are much more intense than those in Figure 2, and also peak

Figure 4. ¹³C{¹H} NMR spectra of CX obtained by the gas-solid reaction and ripened for 7 h: (a), entire spectrum; (b), substituent region; (c), ring carbon region.

No. 2 which appeared as a shoulder peak in Figure 2 is distinctively observable. This strongly suggests that No. 2 peak is correlated to Nos. 8 and 9 peaks and that $\langle f_2 \rangle + \langle f_3 \rangle$ is higher in the CX prepared by the gas-solid reaction than in the CX by the liquid-liquid reaction. The experimental fact mentioned above points to that the peak No. 2 is attributable to the substituent groups attached to C₂ and C₃ positions, and consequently we can also assign peak No. 3 to the substituent groups at C₆ position.

Change in $\langle F \rangle$ and $\langle f_k \rangle$ of CXs during Ripening

Variation of $\langle F \rangle$ and $\langle f_k \rangle$ of CX, prepared by the liquid-liquid reaction is shown as a function of ripening time in Figure 5. Here, NMR measurement usually required a 10 hour pulse accumulation at 20°C; thus, ripening of CX during NMR measurement could not be avoided. The apparent ripening time is often defined as the time between the end of the reaction and the initiation of the NMR measurement, but in strict sense, the reasonable ripening time, shown on the horizontal axis in Figure 5, is the value in which 5 h (average of

Figure 5. Change in $\langle F \rangle$ (○), $\langle f_2 \rangle + \langle f_3 \rangle$ (△), and $\langle f_6 \rangle$ (□) of CX (obtained by the liquid-liquid reaction) as a function of ripening time.

Figure 6. Change in $\langle F \rangle$ (○), $\langle f_2 \rangle + \langle f_3 \rangle$ (△), and $\langle f_6 \rangle$ (□) of CX (obtained by the gas-solid reaction) as a function of ripening time.

10 hour pulse accumulation) is added to the apparent ripening time. From the figure the following relations for CX, prepared by the liquid-liquid reaction, are observed.

$$\langle f_6 \rangle > \langle f_2 \rangle + \langle f_3 \rangle$$

(CX in initial stage of ripening)

$$\langle f_6 \rangle \gg \langle f_2 \rangle + \langle f_3 \rangle = 0$$

(CX ripened for more than 50 h)

$\langle F \rangle$ and $\langle f_k \rangle$ of the CX at zero ripening time was estimated from extrapolating dexanthation curve in Figure 5 as follows:

$$\langle F \rangle = 0.67, \langle f_6 \rangle = 0.53$$

and

$$\langle f_2 \rangle + \langle f_3 \rangle = 0.14$$

Figure 6 shows similar results for CX, prepared by the gas-solid reaction, as in Figure 5. From the figure, the following relations are obtained:

$$\langle f_6 \rangle > \langle f_2 \rangle + \langle f_3 \rangle$$

(CX at the initial stage of ripening)

$$\langle f_6 \rangle \gg \langle f_2 \rangle + \langle f_3 \rangle = 0$$

(CX ripened for more than 50 h)

$\langle F \rangle$ and $\langle f_k \rangle$ values of the CX extrapolated to zero ripening time is:

$$\langle F \rangle = 1.24, \quad \langle f_6 \rangle = 0.68,$$

$$\langle f_2 \rangle + \langle f_3 \rangle = 0.56$$

Inspection of Figure 5 and 6 clearly shows that at the initial stage of ripening the xanthate groups substituted at C_2 and C_3 decompose much faster than those substituted

at C_6 , independent of the preparation methods of CX. In other words, at the initial stage the xanthate groups substituted at C_6 is relatively stable, although the xanthate groups at C_2 and C_3 decompose rapidly. The xanthate group at only C_6 position was proved to exist after a long ripening time. The results obtained in this study, especially for CX prepared by the gas-solid reaction can be compared with those reported so far, listed in Table II. The CXs having $\langle F \rangle = 0.7$ – 0.8 obtained by the gas-solid reaction in Table II revealed that $\langle f_2 \rangle$ was the highest among $\langle f_k \rangle$. From Figure 6 it is obvious that xanthate group exists almost only at C_6 position in the CX having $\langle F \rangle = 0.7$ – 0.8 prepared by the gas-solid reaction in this study, being quite contrast to the literature data. However, note that the CXs described in the literatures were prepared according to the commercial process and the amount of CS_2 reacted to alkali cellulose was around 30–40% against original cellulose

Table II. Results for distribution of xanthate groups

Researchers	Year	Technique ^a	Sample ^b	$\langle F \rangle$	Result	Ref.
Lieser	1929	Ch(MC)	G-S, Un	—	At least C_2	3
Noguchi	1950	Ch(MC, TC)	G-S, Un	0.7	2-Monosub. and 2,6-disub. only	4
Lauer	1950	Ch(MC, VD)	G-S, Un	0.75	2-Monosub. and 2,3-disub. only	5
Chen <i>et al.</i>	1951	Ch(MC, VD)	G-S, Un	0.72	$\langle f_2 \rangle = 0.27$, $\langle f_3 \rangle = 0.21$, $\langle f_6 \rangle = 0.24$	6
Swan and Purves	1957	Ch(SMX)	G-S, Un	—	6-Sub. (53.5%) and 3-sub. (46.5%)	23
			G-S, Ri	—	81% 6-Sub.	23
Philipp and Liu	1959	Ch	GS, Un	—	41% 6-Sub.	8
			G-S, Ri	—	100% 6-Sub.	8
Willard and Pacsu	1960	Ch(MC', PC)	G-S, Ri	0.31	$\langle f_2 \rangle = 0.13$, $\langle f_3 \rangle = 0.06$, $\langle f_6 \rangle = 0.11$	7
Horio <i>et al.</i>	1963	Ch(MC, PC)	G-S, Un	0.62	$\langle f_2 \rangle = 0.37$, $\langle f_3 \rangle = 0.09$, $\langle f_6 \rangle = 0.13$	9
			G-S, Ri	0.50	$\langle f_2 \rangle = 0.32$, $\langle f_3 \rangle = 0.08$, $\langle f_6 \rangle = 0.10$	9
			L-S, Un	0.78	$\langle f_2 \rangle = 0.47$, $\langle f_3 \rangle = 0.13$, $\langle f_6 \rangle = 0.18$	9
Kamide <i>et al.</i>	1986	NMR	G-S, Un	1.24	$\langle f_2 \rangle + \langle f_3 \rangle = 0.56$, $\langle f_6 \rangle = 0.68$	This work
			G-S, Ri	0.30	$\langle f_2 \rangle + \langle f_3 \rangle = 0.0$, $\langle f_6 \rangle = 0.30$	This work
			L-L, Un	0.67	$\langle f_2 \rangle + \langle f_3 \rangle = 0.14$, $\langle f_6 \rangle = 0.53$	This work
			L-L, Ri	0.22	$\langle f_2 \rangle + \langle f_3 \rangle = 0.0$, $\langle f_6 \rangle = 0.22$	This work

^a Ch, chemical; MC, conversion to methylcellulose; MC', multi-step conversion to methylcellulose; SMX, conversion to cellulose *S*-methylxanthate; TC, conversion to tritylcellulose; VD, vacuum distillation; PC, paper chromatography.

^b G-S, the gas-solid reaction; L-S, the liquid-solid (emulsion) reaction; L-L, the liquid-liquid reaction; Un, unripened; Ri, ripened.

used, being far lower than that (60%) employed in this study. It is anticipated also from Figure 6 that substitution at C_2 and C_3 is much larger than that at C_6 and $\langle f_2 \rangle$ may become highest among $\langle f_k \rangle$ for CX immediately after the start of reaction. For the ripened CX obtained by the gas-solid reaction shown in Table II the order of the magnitude of $\langle f_k \rangle$ is quite different among researchers. Philip and Liu⁸ suggested the substitution only at C_6 position in the ripened CX by the combination of chemical and paper chromatographic analyses although $\langle F \rangle$ of the ripened CX is not clear. Our results showed that the ripened CXs having $\langle F \rangle$ less than 0.6 remained as xanthate groups only at C_6 position, as seen from Figure 6. Unfortunately, literature data for the CX prepared by the liquid-liquid reaction are not available. Our results show that the preparation method influences significantly $\langle F \rangle$ as well as $\langle f_k \rangle$ of CX: The liquid-liquid reaction exhibits the preferential substitution of xanthate group at C_6 and in contrast to this, substitution at C_2 and C_3 are greatly enhanced by the gas-solid reaction, as described before. The enhanced substitution at C_2 in the gas-solid reaction can be reasonably explained by an experimental fact that in solid alkali cellulose, NaOH preferentially coordinates to the hydroxyl group at C_2 position.²² Contrarily, no preferential coordination of NaOH to any hydroxyl groups for cellulose dissolved in 9.1 wt% aqueous NaOH solution, confirmed in our previous work,¹⁶ leads to the conclusion that the most acidic hydroxyl group (OH at C_6 position in this case) is most reactive. Note that even if the gas-solid reaction started when alkali cellulose contacted with gaseous CS_2 , the nature of the xanthation changes as the reaction proceeds. In other words, the xanthate formed on the skin of cellulose microfibrils is soluble in alkali and then, the further reaction becomes similar to the liquid-liquid reaction. Lower $\langle F \rangle$ of

CX attained by the liquid-liquid reaction, compared with that obtained by the gas-liquid reaction is mainly due to lower amount of CS_2 used. The amounts of CS_2 used for the liquid-liquid and the gas-solid reactions were 60% and 100% against original cellulose, respectively. $\langle F \rangle$ values attained at zero ripening time for both reactions were found to be proportional to the amount of CS_2 employed.

Summarizing, we established a method for determining $\langle F \rangle$ and $\langle f_k \rangle$ by ^{13}C NMR analysis, based on the peak assignment of the NMR spectra. The difference in $\langle F \rangle$ and $\langle f_k \rangle$ between cellulose xanthates obtained under different preparation conditions (the liquid-liquid and the gas-solid reactions) was clarified. It was proved that 1) substitution at C_2 and C_3 positions was greatly enhanced by the gas-solid reaction, 2) the substitution at C_6 was preferential for the liquid-liquid reaction and 3) in both preparation methods, after long ripening time, the xanthate group remained at only C_6 position.

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