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Determination of Distribution of *O*-Acetyl Group in Trihydric Alcohol Units of Cellulose Acetate by Carbon-13 Nuclear Magnetic Resonance Analysis

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ABSTRACT: The total degree of substitution, $DS(\equiv\langle\langle F\rangle\rangle)$, the distribution of DS and the distribution of the substituent group in a glucopyranose unit $\langle\langle f_k\rangle\rangle$ (the suffix k means the carbon position in the C1 chain conformation) are accurately defined for cellulose derivatives. $\langle\langle f_k\rangle\rangle$ of cellulose acetate (CA) was evaluated from the ^{1}H nuclear magnetic resonance (NMR) chemical shift of the *O*-acetyl protons and the ^{13}C NMR chemical shift of the *O*-acetyl carbons. ^{1}H NMR method is applicable only to completely substituted cellulose acetate, but the ^{13}C NMR method is proved applicable for the entire range of the DS (0—3). CA (DS=2.92)–trichloromethane, CA (DS=2.46)–acetone, and CA (DS=0.49)–dimethyl sulfoxide systems are employed successfully. $\langle\langle F\rangle\rangle$ values determined by ^{13}C NMR spectrum are in good agreement with those by the chemical analysis. The reactivity of the *O*-acetyl groups during the hydrolysis reaction process using hydrochloric acid as a catalyst decreases in the following order: $C_2 > C_6 > C_3$.

KEY WORDS ^{13}C Nuclear Magnetic Resonance / Cellulose Acetate / *O*-Acetyl Distribution /

Recently, Kamide and his coworkers disclosed the molecular characteristic of cellulose acetate (CA) with various degree of substitution, DS (DS=2.92, 2.46, and 0.49) through a study of their solution properties, using solution viscometry, light scattering, membrane osmometry, gel-permeation chromatography, and ultracentrifuge technique.[1-5] The physical and chemical properties of CA are considered to depend markedly on the total $DS(\langle\langle F\rangle\rangle$ in eq 5) and the distribution of DS averaged for a given polymer ($g\langle F^j\rangle$). The latter of CA as well as cellulose nitrate was successfully evaluated by thin-layer chromatography (TLC).[6-8] As is well known, the glucopyranose unit constituting a cellulose molecule has one primary and two secondary hydroxyl groups at the C_6 and C_2 and C_3 positions. The extent of substitution of these hydroxyl groups with acetyl group may differ with different C positions, to which the hydroxyl group is attached, due to different reactivity. The average degree of substitution for each hydroxyl group ($\langle\langle f_k\rangle\rangle$ in eq 5) is another important parameter for characterizing cellulose derivatives. With the help of three parameters, the molecular properties of CA polymers can be well understood.

Up to now, several attempts have been made to evaluate the *O*-acetyl group distribution in a trihydric alcohol unit by chemical[9,10] and ^{1}H NMR methods.[11] The former is generally based on the difference in reactivity of three unsubstituted hydroxyl groups in tosylation[9] with *p*-toluenesulfonyl chloride, followed by iodination with sodium iodide or tritylation[10] with trityl chloride in the presence of pyridine, being very tedious and time-consuming. In addition, by the chemical method the degree of substitution at C_2 and C_3 positions cannot be principally evaluated. This method is a relative method, which needs the total DS value determined by another method. In contrast to this, the latter is an absolute method, only applicable unfortunately to completely or at least nearly fully-substituted cellulose acetate. Otherwise, the peaks due to the *O*-acetyl proton can not be resolved to the components corresponding to the C_2, C_3, and C_6 positions, since a large number of glucopyranose units with magnetically unequivalent *O*-acetyl groups are possible. To avoid this, Goodlett *et al.*[11] have acetylated incompletely

substituted CA polymer with deuterated acetyl chloride, before ^{1}H NMR measurements. Very recently, Wu analyzed the distribution of substituted glucopyranose unit in cellulose nitrate by ^{1}H and ^{13}C NMR methods.[12]

The samples employed in previous papers[1-5] have sharp molcular-weight distributions, *MWD* (the ratio of the weight- to number-average molecular weight M_w/M_n is 1.4 (DS=2.92), 1.3 (DS=2.46 and 0.49)) and the distributions of $DS(\equiv g\langle F^j\rangle)$ are also reasonably narrow, but their overall distribution of the *O*-acetyl groups in glucopyranose unit ($\langle\langle f_2\rangle\rangle$, $\langle\langle f_3\rangle\rangle$, and $\langle\langle f_6\rangle\rangle$ in eq 4) are not characterized. Note that when the molecular parameters including the unperturbed chain dimensions are to be correlated with the total DS, variation in the extent of acetylation at three different C positions in glucopyranose unit should be simultaneously taken into account.

This paper is concerned with a method for determining the relative amounts of acetyl substitution on each of three different hydroxyls, in other words, the distribution of *O*-acetyl groups in trihydric alcohol units of CA samples, employed in previous studies,[1-5] by ^{13}C NMR analysis in comparison with ^{1}H NMR analysis, based on Goodlett *et al.*s' method.[11]

The Distribution of Degree of Substitution in Cellulose Derivatives

At first, arrange all molecules (total number of molecules, N) differing in degree of polymerization p in order of increasing p and define these molecules as the first, second, third, $\cdots$, Nth molecules from the smallest p and write the p of the jth polymer as p_j. Number the glucopyranose units, constituting the jth molecule from 1 to p_j. Then, we define the probability of substitution of hydroxyl group, attached to the C_2, C_3, and C_6 atoms of the ith glucopyranose unit in the jth molecule, with the functional group (in this case, *O*-acetyl group) by $f^j_{2,i}$, $f^j_{3,i}$, and $f^j_{6,i}$, respectively (see Figure 1), and

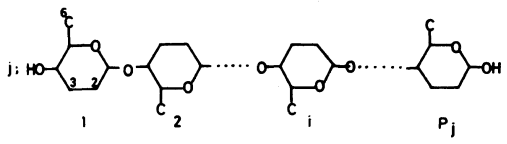

Figure 1. Schematic representation of the jth cellulose molecule having the degree of polymerization, p_j.

designate the total degree of substitution (DS) of the ith ring in the jth molecule by F^j_i. The following relations are readily derived.

$$f^j_{2,i}+f^j_{3,i}+f^j_{6,i}=F^j_i \tag{1}$$

$$\sum_{i=1}^{p_j} F^j_i/p_j=\langle F^j\rangle \tag{2}$$

$$\sum_{j=1}^{N} p_j\langle F^j\rangle \Big/ \sum_{j=1}^{N} p_j=\langle\langle F\rangle\rangle \quad (\equiv DS) \tag{3}$$

$$\sum_{j=1}^{N}\sum_{i=1}^{p_j} f^j_{k,i} \Big/ \sum_{j=1}^{N} p_j=\langle\langle f_k\rangle\rangle, \qquad k=2,\ 3,\ \text{and}\ 6 \tag{4}$$

$$\langle\langle f_2\rangle\rangle+\langle\langle f_3\rangle\rangle+\langle\langle f_6\rangle\rangle=\langle\langle F\rangle\rangle \tag{5}$$

$$\sum_{j=1}^{N} p_j \Big/ N=\bar{P}_n \tag{6}$$

$$\sum_{j=1}^{N} p_j^2 \Big/ \sum_{j=1}^{N} p_j N=\bar{P}_w \tag{7}$$

where $\langle F^j\rangle$ is the average degree of substitution of the jth polymer, $\langle\langle F\rangle\rangle$ is the degree of substitution weight-averaged overall glucopyranose units of all molecules (hereafter, denoted simply as the degree of substitution, DS), and $\langle\langle f_k\rangle\rangle$ is the average probability of substitution of hydroxyl group attached to the C_k position (k=2,3, and 6). $\langle\langle f_k\rangle\rangle$ represents an overall distribution of *O*-acetyl group in trihydric aclcohol unit of CA molecule.

Thin-layer chromatographic method affords us information on the distribution of $\langle F^j\rangle$ ($g(\langle F^j\rangle)$) together with $\langle\langle F\rangle\rangle$. In previous paper,[6-8] we estimated $g(\langle F^j\rangle)$ and $\langle\langle F\rangle\rangle$ on numerous CA and cellulose nitrate samples. By nuclear magnetic resonance (NMR) analysis with or without the chemical analysis, $\langle\langle f_2\rangle\rangle$, $\langle\langle f_3\rangle\rangle$, and $\langle\langle f_6\rangle\rangle$ can be estimated for cellulose derivatives. Evidently, $\langle\langle F\rangle\rangle$ and $\langle\langle f_k\rangle\rangle$ are the doubly-averaged quantities.

EXPERIMENTAL

Polymer Samples and Solvents

Three cellulose acetate (CA) whole polymers, of different combined acetic acid content, prepared and molecularly characterized in the previous papers,[1-5] are used and their molecular characteristics are summarized in Table I. CA (DS=0.49) sample was synthesized by hydrolysis of CA (DS=2.46) sample with hydrochloric acid in acetic

Table I. Molecular characteristics of cellulose acetate samples used

Polymer code	Degree of substitution DS (≡《F》)	Weight-average molecular weight, $M_w \times 10^{-4}$	Number-average molecular weight, $M_n \times 10^{-4}$
TA2	2.92	23.5	5.84
EF3W	2.46	12.0	4.4
MAW-9	0.49	8.0	3.9

acid solution. The total degree of substitution DS(≡《F》) of the samples was determined, according to the procedure of ASTMD-871-61T, by the hydrolysis of the sample with sodium hydroxide, followed by neutralization titration with hydrochloric acid.

Deuterated trichloromethane (TCM)-d_1, acetone-d_6, and diemthyl sulfoxide (DMSO)-d_6, supplied by E. Merck (Dalmstad, DBR) were used as received.

^{13}C and ^1H NMR

^{13}C and ^1H NMR spectra (100 MHz) were obtained from a JOEL FX 100 Pulse-Fourier Transform NMR spectrometer at 37°C. In order to obtain reliable integral curves, the nuclear overhauser effect was eliminated by the addition of ferric chloride (5 ppm) and by the selection of proper operating conditions (see Table II). The chemical shifts for CA in various deuterated solvents were measured with respect to the inernal tetramethylsilane (TMS) as a reference at the concentration of 5—7 g dl^{-1}. ^{13}C NMR spectra were recorded in ^1H-decouple mode. ^1H-off resonance mode for ^{13}C NMR was also carried out for CA (DS=2.46)–acetone system to ascertain that the carbonyl carbon peaks were all singlets. The other operating conditions for ^{13}C NMR are summarized in Table II.

RESULTS AND DISCUSSION

Figures 2a and 2b show the 100 MHz ^1H NMR and ^{13}C NMR spectra of CA (DS=2.92) sample in TCM-d_1. The *O*-acetyl-proton signal of CA (DS=2.92) in TCM-d_1 splits into three distinguishable peaks centered at δ=2.13, 2.02, and 1.98 ppm. These chemical shifts values are nearly equal to those (2.10, 1.99, and 1.94 ppm) reported by

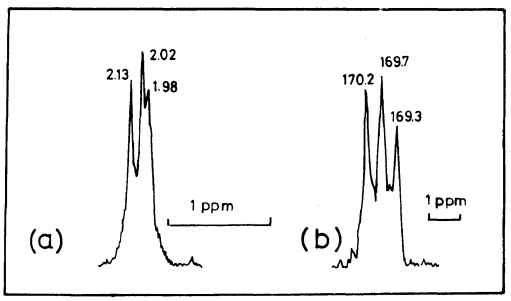

Figure 2. ^1H and ^{13}C NMR spectra of TCM-d_1 solution of CA (DS=2.92) sample in the *O*-acetyl proton region and *O*-acetyl carbonyl carbon region, respectively: (a), ^1H NMR; (b), ^{13}C NMR.

Table II. Operating conditions for ^{13}C NMR experiments

Sample	Off set obsd (irr.)[a]	Width	Single pulse (45°)			Data point
			Repetition	Number	Window	
	kHz	s	s		Hz	
CA (DS=2.92)/ TCM-d_1	47.0 51.45	6	5.0	1500	0.5	4095
CA (DS=2.46)/ acetone-d_6	47.0 51.8	6	10.0	1000	1.0	4095
CA (DS=0.49)/ DMSO-d_6	33.0 54.7	13	2.0	28000	0.5	4095

[a] irr., irradiation.

Goodlett *et al.*,[11] who have assigned these three peaks at 2.10, 1.99, and 1.94 ppm to the *O*-acetyl-protons attached to the positions C_6, C_2, and C_3, respectively, by comparing the reaction rate of *p*-toluenesulfonyl chloride with three hydroxyl groups at C_6, C_2, and C_3 positions. Recently, Shiraishi *et al.*[13] confirmed the validity of Goodlett *et al.*s' assignment, by the correlation between the order of acidicity of *O*-acetyl methyl attached to C_6, C_2, and C_3 and the electron-deshielding effect and a comparison of the shift of the *O*-acetyl-proton peaks of CA ($DS=2.92$) in TCM-d_1 to lower the magnetic field by the addition of trifluoroacetic acid (TFA). According to Goodlett *et al.*s' assignment,[11] from the ratio between peak heights or the area under the peaks and the total DS, $\langle\langle F\rangle\rangle=2.92$ by chemical analysis, we obtain $\langle\langle f_6\rangle\rangle=0.98$, or 0.99, $\langle\langle f_2\rangle\rangle=1.09$ or 1.01 and $\langle\langle f_3\rangle\rangle=0.85$ or 0.92, respectively for CA ($DS=2.92$) sample. When peak areas are used, the accuracy for evaluating $\langle\langle f_k\rangle\rangle$ is ± 4—8%. The $\langle\langle f_k\rangle\rangle$ value exceeding unity is rather unrealistic because theoretically, the upper limit of $\langle\langle f_k\rangle\rangle$ is 1.00 and may be due to the experimental uncertainty.

On the other hand, the corresponding ^{13}C NMR spectra of CA ($DS=2.92$) in TCM-d_1 show three major features of the carbonyl carbon covering 170—169 ppm, whose peak height ratios and area ratios are found to be 1.00 : 1.04 : 0.84, and 1.00 : 1.02 : 0.89 being in good agreement with the values estimated by ^1H NMR for C_6, C_2, and C_3 positions, respectively. Therefore, from ^{13}C NMR spectra and $\langle\langle F\rangle\rangle$ value (2.92) obtained by chemical analysis, we can assign the chemical shifts at 170.2, 169.7, and 169.3 ppm to the *O*-acetyl carbonyl carbons in C_6, C_2, and C_3 positions, and finally it is found that $\langle\langle f_6\rangle\rangle=1.00$, $\langle\langle f_2\rangle\rangle=1.02$, and $\langle\langle f_3\rangle\rangle=0.89$ when calculated from peak area ratios. It is clear that the hydroxyl group in the C_3 position is less reactive than the those in the C_6 and C_2 positions.

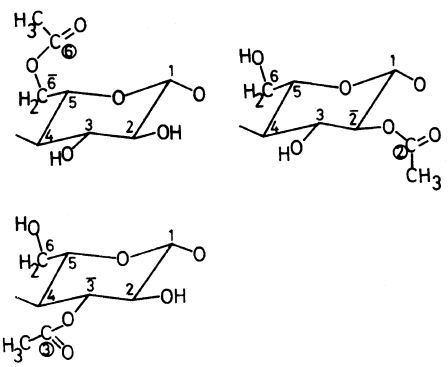

Figure 3. Possible conformations of glucopyranose units in CA ($DS=0.49$). Numbers denote the position of carbon atoms, to which nonsubstituted hydroxyl group is attached, constituting glucopyranose units. Numbers in circle denote the position of carbonyl carbon atoms. Numbers with bar denote the position of carbon atoms, to which *O*-acetyl group is attached.

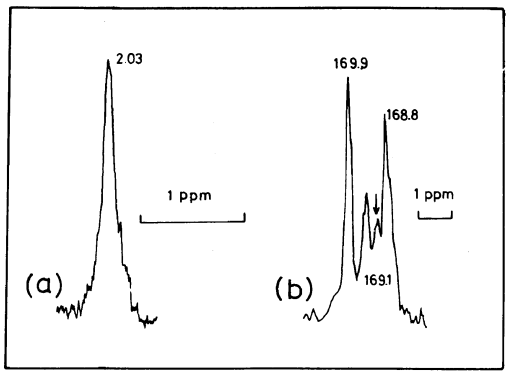

Figure 4. ^1H and ^{13}C NMR spectra of DMSO-d_6 solution of CA ($DS=0.49$) sample in the *O*-acetyl proton region and the *O*-acetyl carbonyl carbon region, respectively: (a), ^1H NMR; (b), ^{13}C NMR.

For CA ($DS=0.49$) sample, there are three differently-substituted glucopyranose units, in which all carbonyl carbons are magnetically different with each other, as shown, in Figure 3. Note that the sample of CA ($DS=0.49$) was prepared from the CA ($DS=2.46$) sample by the hydrolysis reaction and accordingly, acetyl groups can be evenly hydrolyzed with respect to different glucopyranose units. Therefore, the hydrolysis reaction seems to reflect accurately the reactivity of acetyl groups attached to the C_6, C_2, and C_3 positions and the chemical shifts of carbonyl carbons in CA ($DS=0.49$) sample are expected to split exactly into three peaks.

Figures 4a and 4b demonstrate the ^1H and ^{13}C NMR spectra of CA ($DS=0.49$) sample in DMSO-d_6. The ^{13}C NMR spectrum exhibits 4 resonance peaks, covering the range of about 168.8—170 ppm from TMS : $\delta=169.9$, 169.4, 169.1, and 168.8 ppm. Among these, the peak at $\delta=169.4$ ppm originates from contaminated acetic acid in the CA sample. With reference to the assignment of the chemical shifts of the carbonyl carbons in CA ($DS=2.92$)

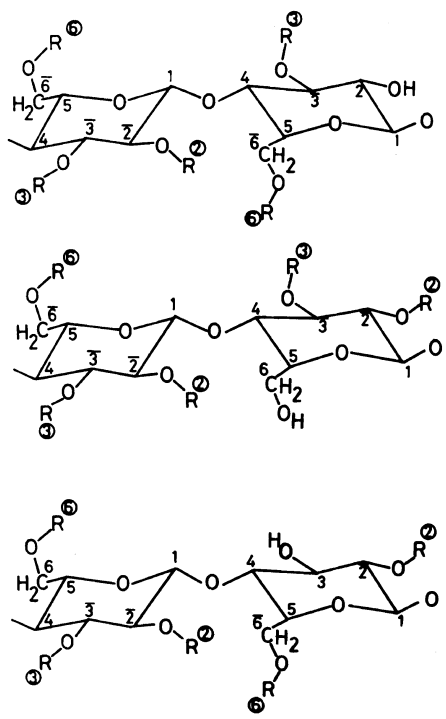

Figure 5. Possible conformations of glucopyranose units in CA ($DS=2.46$). Numbers and symbols are the same as described in Figure 3.

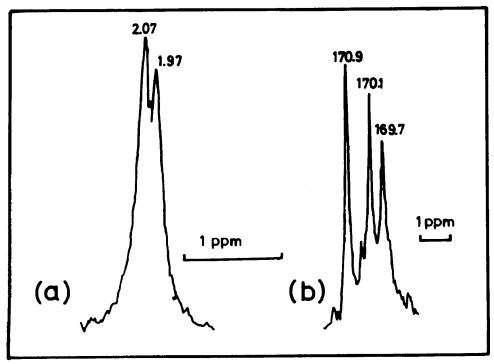

Figure 6. ^{1}H and ^{13}C NMR spectra of acetone-d_6 solution of CA ($Ds=2.46$) sample in the *O*-acetyl proton region and the *O*-acetyl carbonyl carbon region, respectively: (a), ^{1}H NMR; (b), ^{13}C NMR.

sample in TCM-d_1, we can assign three peaks at 169.9, 169.1, and 168.8 ppm to the carbonyl carbons at C_6, C_2, and C_3 positions, respectively. $\langle\langle f_k \rangle\rangle$ of this sample was thus estimated: $\langle\langle f_6 \rangle\rangle = 0.19$, $\langle\langle f_2 \rangle\rangle = 0.10$, and $\langle\langle f_3 \rangle\rangle = 0.20$; $\langle\langle F \rangle\rangle = 0.49$. In the ^{1}H NMR spectrum of CA ($DS=0.49$), the sample single broad peak was observed at 2.03 ppm, and corresponds to the *O*-acetyl-proton and the $\langle\langle f_k \rangle\rangle$ value can not be determined.

For CA ($DS=2.46$) polymer, one unsubstituted

Table III. Evaluation of $\langle\langle f_k \rangle\rangle$ for CA molecules by ^{1}H NMR and ^{13}C NMR

Solvent	$\langle\langle F \rangle\rangle$ by chemical analysis	Substituted position	By ^{1}H NMR		By ^{13}C NMR	
			O-acetyl proton peak	$\langle\langle f_k \rangle\rangle$	Carbonyl carbon peak	$\langle\langle f_k \rangle\rangle$
			ppm		ppm	
Trichloro-methane-d_1	2.92	C_6	2.13	$k=6$, 0.99[a] (0.98[b])	170.2	$k=6$, 1.00[c] (1.00[d])
		C_2	2.02	$k=2$, 1.01[a] (1.09[b])	169.7	$k=2$, 1.02[c] (1.05[d])
		C_3	1.98	$k=3$, 0.92[a] (0.85[b])	169.3	$k=3$, 0.89[c] (0.86[d])
Acetone-d_6	2.46	C_6	2.07		170.9	$k=6$, 0.82[c]
		C_2	1.97		170.1	$k=2$, 0.75[c]
		C_3			169.7	$k=3$, 0.89[c]
Dimethyl sulfoxide-d_6	0.49	C_6	2.03		169.9	$k=6$, 0.19[c]
		C_2			169.1	$k=2$, 0.10[c]
		C_3			168.8	$k=3$, 0.20[c]

[a] Estimated from the peak area ratios when calculated as a triangle approximation.
[b] Estimated from peak height ratios.
[c] Estimated from integrated peak intensity ratios.
[d] Estimated from peak height ratios.

Table IV. Comparison of ⟪F⟫ and ⟪f_k⟫ ($k=2$, 3, and 6) values of CA by ^{13}C NMR method with those obtained by ^{13}C NMR/chemical analysis method

Polymer sample code	^{13}C NMR method				^{13}C NMR/chemical analysis method			
	⟪F⟫	⟪f_2⟫	⟪f_3⟫	⟪f_6⟫	⟪F⟫[a]	⟪f_2⟫	⟪f_3⟫	⟪f_6⟫
EF 3W	6 I_2/I_1 : 2.44 6 I_3/I_1 : 2.44	0.74	0.88	0.81	2.46	0.75	0.89	0.82
MAW-7	6 I_2/I_1 : 0.44 6 I_3/I_1 : 0.46	0.09	0.18	0.17	0.49	0.10	0.20	0.19

[a] By chemical analysis.

hydroxyl remains for each cellobiose unit. Therefore, there are as many as 15 magnetically unequivalent *O*-acetyl groups as illustrated in Figure 5. Figures 6a and 6b depict the ^1H and ^{13}C NMR spectra of CA ($DS=2.46$) sample in acetone-d_6. Three carbonyl carbon peaks are definitely observed at 170.9, 170.1, and 169.7 ppm. The relative peak fields of these peaks are in good agreement with those of CA ($DS=0.49$) in dimethyl sulfoxide (DMSO)-d_6, and can be clearly resolved. A small peak at 170.4 ppm is probably a reflection of contaminated acetic acid in the polymer. Thus, we may assign the above three peaks from the lower magnetic field) to the C_6, C_2, and C_3 positions, as in the case of those for the CA ($DS=2.92$ and 0.49) polymers. From the peak area data from the ^{13}C NMR spectrum and the chemical analysis data on ⟪F⟫ ($\equiv 2.46$), we can estimate ⟪f_k⟫ for this polymer; ⟪f_6⟫$=0.82$, ⟪f_2⟫$=0.75$, and ⟪f_3⟫$=0.89$. In contrast to ^{13}C NMR spectrum, the corresponding ^1H NMR spectrum shows two *O*-acetyl-proton peaks, from which ⟪f_k⟫ can not be determined.

Table III collects the observed proton- and carbon-resonance peak positions, evaluated by NMR method. It should be noted that the absolute magnitude of ⟪f_k⟫ values are determined with the aid of ⟪F⟫ value by chemical analysis and hereafter this is referred to simply as the ^{13}C NMR/chemical analysis method.

⟪F⟫ value can also be evaluated to a certain extend from only the ^{13}C NMR spectra of carbons 1—6 and *O*-acetyl carbonyl carbon or *O*-acetyl methyl carbon by the equation:

$$\langle\!\langle F \rangle\!\rangle = 6I_2/I_1 = 6I_3/I_1 \qquad (8)$$

where I_1 is the integrated peak intensity of carbons at C_1—C_6 positions at 60—104 ppm; I_2, the integrated peak intensity of the *O*-acetyl carbonyl carbon at 167—171 ppm; I_3, the integrated peak intensity of the *O*-acetyl methyl carbon (about 20 ppm). In Figures 7a and 7b are illustrated the ^{13}C NMR spectra of the CA ($DS=2.46$) sample in acetone-d_6 and CA ($DS=0.49$) the sample in DMSO-d_6 over a wide range of magnetic field. A combination of the ratio of peak areas of the *O*-acetyl carbons at three different positions (C_2, C_3, and C_6) and ⟪F⟫ enables us to evaluate ⟪f_k⟫. The results are tabulated for CA ($DS=2.46$) and CA ($DS=0.49$) samples in Table IV, and a comparison is made with those evaluated by ^{13}C NMR/chemical analysis method. For CA ($DS=2.46$), ⟪F⟫ value evaluated from the ratio I_2/I_1 by ^{13}C NMR spectrum is found to fit exactly with that from the ratio I_3/I_1 and agrees fairly well with that determined by the titration method. The agreement between the corresponding values for CA ($DS=0.49$) is not so really good, probably due to experimental uncertainty inherent to both methods in determining the low ⟪F⟫. Generally, if the acetic acid is contained in the sample as an impurity, the chemical analysis tends to overestimate the ⟪F⟫ values.

In this manner, ⟪f_k⟫ for CA can be determined by the ^{13}C NMR method, without the measurements of ⟪F⟫ by chemical analysis.

Figure 7 shows the variation in ⟪f_k⟫/⟪F⟫ ($k=2$, 3, and 6) of CA during the hydrolysis reaction of CA. Note that CA ($DS=2.92$) and CA ($DS=2.46$) have no one-to-one correspondence, since the latter polymer is not synthesized from an exactly the same polymer as CA ($DS=2.92$) sample. The ratio of primary to total hydroxyl ⟪f_6⟫/⟪F⟫ and a similar

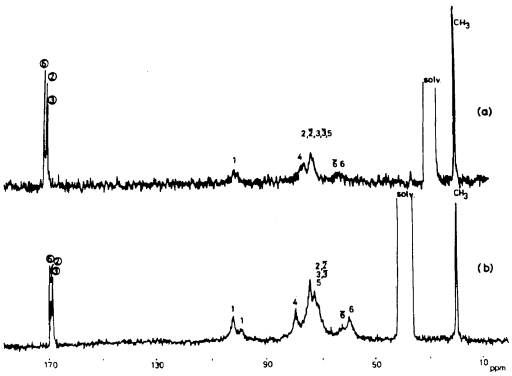

Figure 7. ^{13}C NMR spectra of CA ($DS=2.46$) in acetone-d_6 (a) and CA ($DS=0.49$) in DMSO-d_6 (b). Numbers and symbols are the same as described in Figure 3.

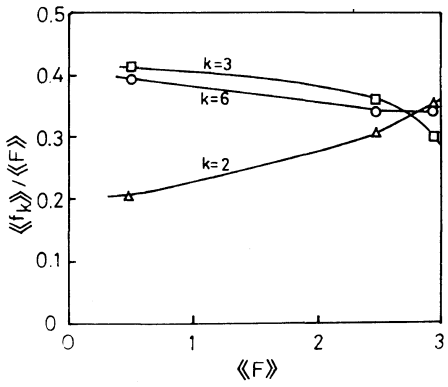

Figure 8. Plot of the ratio $\langle\langle f_k \rangle\rangle / \langle\langle F \rangle\rangle$ ($k=2$, 3, and 6) against $\langle\langle F \rangle\rangle$ for cellulose acetate.

ratio $\langle\langle f_3 \rangle\rangle / \langle\langle F \rangle\rangle$ increased, but $\langle\langle f_2 \rangle\rangle / \langle\langle F \rangle\rangle$ decreases with decreasing $\langle\langle F \rangle\rangle$ (*i.e.*, as the hydrolysis proceeds), indicating the preferential removal of the acetyl group from the C_2 position. The reactivity of *O*-acetyl groups toward hydrochloric acid decreases in the order: $C_2 > C_6 > C_3$. By using the ^{13}C NMR technique, a more detailed discussion on the reactivity of the hydroxyl groups belonging to three different positions will be clarified.

In summary, the ^{13}C NMR technique has proved quite applicable for determining $\langle\langle f_k \rangle\rangle$ in the case of cellulose acetate, irrespective of its overall degree of substitution $\langle\langle F \rangle\rangle$.

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