Two-Dimensional Nuclear Magnetic Resonance Spectra of Cellulose and Cellulose Triacetate

Keisuke KOWSAKA, Kunihiko OKAJIMA, and Kenji KAMIDE*

*Fundamental Research Laboratory of Fibers and Fiber-Forming Polymers,
Asahi Chemical Industry Co., Ltd.,
11–7 Hacchonawate, Takatsuki, Osaka 569, Japan*

ABSTRACT: An attempt was made to give a full assignment, using only NMR information, to all peaks in ^1H and ^{13}C NMR spectra for systems of cellulose in 2.5 N NaOD/D_2O and of cellulose triacetate (CTA, total degree of substitution 2.92) in deuterated trichloromethane (TCM-d), and in deuterated dimethylsulfoxide (DMSO-d_6). For this purpose two-dimensional (2D) homonuclear ^1H shift correlation spectroscopy (COSY), heteronuclear ^1H–^{13}C shift correlation spectroscopy (C–H COSY), and long-range heteronuclear ^1H–^{13}C shift correlation spectroscopy (long-range C–H COSY) were applied to the above systems. By COSY ^1H peaks of cellulose/aq. alkali solution were assigned, from lower magnetic field, to H_1, H_6, $H_6{}'$, $(H_3 + H_4 + H_5)$, and H_2 protons, respectively. Here, two unequivalent H_6 peaks heavily overlapped in the one-dimensional spectrum were observed very separately in 2D spectrum. By C–H COSY ^{13}C peaks of cellulose were assigned, from lower magnetic field, to C_1, (C_3, C_4, C_5), C_2, and C_6 carbons, respectively. C_3, C_4, and C_5 carbon peaks were unable to be assigned separately, due to mutual and heavy overlapping of H_3, H_4, and H_5 peaks. For cellulose triacetate, through use of COSY and C–H COSY all peaks in the region of glucopyranose backbone in ^1H and ^{13}C NMR wre able to be successfully and completely assigned. Long-range C–H COSY confirmed definitely the existence of the close correlationships between acetyl methyl proton and carbonyl carbon at the different carbon positions of CTA, which showed again the validity of the previous assignment with respect to carbonyl carbons (*i.e.*, C_6, C_3, and C_2 carbons from lower magnetic field).

KEY WORDS   Cellulose / Cellulose Acetate / Cellulose Triacetate / ^{13}C NMR / ^1H NMR / Two-Dimensional NMR / Correlation Spectroscopy / Long-Range Heteronuclear Correlation Spectroscopy /

Recently numerous studies have been published on the high resolution NMR spectra of solutions of cellulose and its derivatives. NMR spectra of cellulose were utilized widely as a method for elucidating the dissolved state of solutes in solvents (*i.e.*, interaction between solutes and solvents) and those of cellulose derivatives were employed for analysis of the average degree of substitution for each three hydroxyl groups $\langle\!\langle f_k \rangle\!\rangle$ ($k = 2, 3, 6$) in the glucopyranose unit: For example, Kamide *et al.*[1] showed, from ^1H NMR spectra of cel-

lulose in dimethylformamide/chloral/pyridine mixture, that cellulose dissolved in the form of cellulose trichlorate (CTC) in the solution. Gagnaire and his coworkers[2] speculated the dissolved state of cellulose in N-methylmorpholine-N-Oxide/dimethylsulfoxide (DMSO), methylamine/DMSO, hydrazine/DMSO, and paraformaldehyde/DMSO by comparing the ^{13}C chemical shifts in these solutions. Kamide and his collaborators[3] showed that a physically treated cellulose, whose intramolecular hydrogen bondings were de-

---

* To whom all correspondence should be addressed.

stroyed to some extent, was completely soluble in aq sodium hydroxide at 0—10°C and measured first ^{13}C NMR spectra of cellulose (prepared thus)/NaOD/D_2O solution.

From systematic analysis on ^1H and ^{13}C NMR spectra of sodium cellulose sulfate,[4] cellulose acetate (CA),[5-7] sodium carboxymethylcellulose,[8] sodium cellulose xanthate (CX),[9] carboxyethylcarbamoylethylcellulose[10] and cyanoethylcellulose,[11] Kamide, Okajima, and their coworkers elucidated $\langle\!\langle f_k \rangle\!\rangle$ ($k=2$, 3, 6), correlation $\langle\!\langle f_k \rangle\!\rangle$ with some physical and physilogical properties. Wu,[12] Clark and Stephenson,[13] and Miyamoto et al.[14] estimated, from NMR spectra, $\langle\!\langle f_k \rangle\!\rangle$ of cellulose nitrate and CA.

In the above studies, assignment of NMR peaks was exclusively prerequisite in order to employ the NMR method for $\langle\!\langle f_k \rangle\!\rangle$ determination. It is extremely difficult to get high resolution ^1H NMR spectra for cellulose and its derivatives with high degree of polymerization (DP), enabling us to obtain information on vicinal proton coupling, even if employing selective homonuclear decoupling. Peak assignment of ^{13}C NMR spectrum is generally more difficult than that of ^1H NMR, needing rather considerably complicated, and skillful techniques. For example, by applying the selective heteronuclear spin decoupling technique in measurement of ^{13}C NMR of cellulose oligomer with DP=10 in DMSO, and also by taking into account an isotope effect of deuterated compounds, Gagnaire et al.[2] assigned, from lower magnetic field, the peaks of cellulose oligomer, to C_1, C_4, C_5, C_3, C_2, and C_6 carbons, respectively. Kowsaka and his coworkers,[6] assigned, by applying low-power selective spin decoupling technique, the peaks of carbonyl carbon of acetyl group directly combined with C_2, C_3, and C_6 positions of CA and assigned also,[9] with the help of distortionless enhancement by polarization transfer (DEPT) technique, C_6 peak of CX. In the literature, except for these described here, the peak assignments were not carried out by only

the NMR method, but by an indirect method including a comparison of the peak intensity ratio in NMR spectrum of the sample with $\langle\!\langle f_k \rangle\!\rangle$, determined in advance by non-NMR method or from analogy of the peak assignment of small molecular weight model compounds or of other derivatives.

The assignment given by Gagnaire et al.[2] for cellulose can be considered reasonable in DMSO-d_6; however, mention should be made of the assignment of peaks in other solvents: it could not always be done, by referring to their assignment straightly, because C_5, C_3, and C_2 peaks of cellulose oligomer in DMSO-d_6 were located very close to each other and the order of the peak positions may possibly to change in other solvents. In addition, note that the positions of the ring carbon peaks are significantly influenced by substitution of hydroxyl groups in cellulose derivatives, for which the assignment for cellulose by Gagnaire et al. cannot be straightforwardly applied as it is and the methods proposed hithertofor in analysis of NMR spectra of cellulose derivatives are without exception too elaborate and time-consuming and additionally they are not sufficiently accurate.

Very recent advances in two-dimensional (2D) NMR technique allow us relatively easily to perform an absolute (in other word, by pure NMR method) assignment of ^1H and ^{13}C NMR peaks. Narden and Vincendon[15] attempted, using 2D homonuclear ^1H shift correlation spectrum and 2D heteronuclear ^{13}C–^1H shift correlation spectrum (and for the latter measurement, using 5% ^{13}C enriched cellulose), to assign ^1H and ^{13}C peaks of cellulose in deuterated dimethylacetamide (DMAC-d_9)/lithium chloride mixture, but unfortunately, they failed to distinguish the C_3 peak from C_5 peaks.

This article attempts to privide a much better and more reliable assignment, using 2D NMR alone, of peaks in ^1H and ^{13}C NMR spectra of cellulose in NaOD/D_2O solution and cellulose triacetate (total degree of sub-

stitution $\langle\!\langle F \rangle\!\rangle = 2.92$) in trichloromethane-$d$ (TCM-d) and in DMSO-d_6.

EXPERIMENTAL

Samples

An alkali-soluble, regenerated cellulose with the viscosity-average molecular weight $\bar{M}_v = 1.38 \times 10^4$, as measured by solution viscosity in cadoxen solution at $25°C$ according to Mark–Houwink–Sakurada equation by Brown and Wikström,[16] was prepared by the previously reported method.[1] A 40 wt% NaOD/D_2O solution (99% deuterated; manufactured by Merck, DBR) was diluted with 99.8% deuterated D_2O (Merck, Canada) to prepare at 2.5 N NaOD/D_2O solution, into which a cellulose sample was dissolved carefully at $4°C$ and 2 wt% and 5 wt% solutions of cellulose were prepared for further measurements of ^1H and ^{13}C NMR, respectively.

An whole cellulose triacetate (CTA) with the weight-average molecular weight $\bar{M}_w = 2.32 \times 10^5$ (by light scattering in DMAC) and $\langle\!\langle F \rangle\!\rangle = 2.92$ was dissolved in 99.8% deuterated TCM-d at $40°C$ and in 99.9% deuterated DMSO-d_6 (Merck, Canada) at $80°C$ to give 8 wt% solutions, used for NMR measurements.

NMR Measurement

A JEOL FT-NMR spectrometer JNM-FX-200 (C/H, 10 mmϕ probe) was used. ^1H and ^{13}C resonance frequencies were 199.5 and 50.18 MHz, respectively.

Homonuclear ^1H shift correlation spectroscopy (COSY)[17] experiments were carried out using the pulse sequence as shown in Figure 1(a). The trapezoidal window was employed for Fourier-transform. The detailed measuring conditions for each sample are collected in Table I. For cellulose/NaOD/D_2O system, homogate decoupling was simultaneously employed in order to reduce signals originating from remained protons in the solvent mixture.

The heteronuclear ^{13}C–^1H shift correlation spectrum (C–H COSY)[17] was recorded using the pulse sequences shown in Figure 1(b). The mixing time Δ was set up to be 2.0 ms ($= 1/(4J_{C-H})$), where J_{C-H} is the coupling constant between C and H nuclei. For CTA long-range C–H COSY was concurrently employed to determine correlations between carbonyl carbon and acetyl methyl protons. In this case, Δ was first taken as 166 ms ($= 1/(4J_{C-C-H})$,
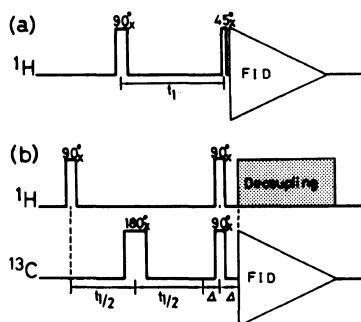

Figure 1. Pulse sequences used for 2D NMR measurements: a, proton COSY; b, C–H COSY.

Table I. Experimental conditions employed for COSY measurements

Polymer/solvent	Temp °C	90° pulse width μs	Spectral width Hz	Data matrix[a]	Accumulation times
Cellulose/NaOD[b]	40	27.0	625	512 × 177 (1024 × 256)	128
CTA/TCM-d	40	14.0	1666	1024 × 512	16
CTA/DMSO-d_6	90	14.4	1000	1024 × 256	128

[a] Number in parenthesis indicates expanded matrix by zero-filling.
[b] Homogate decoupled.

K. Kowsaka, K. Okajima, and K. Kamide

Table II. Experimental conditions for C–H COSY measurements

| Polymer/solvent	Temp °C	¹H 90° pulse width µs	¹³C 90° pulse width µs	¹H spectral width Hz	¹³C spectral width Hz	Δ ms	Data matrix[a] ¹³C × ¹H	Accumulation
Cellulose/NaOD	20	27.0	23.0	625	4000	2.0	1024 × 99 (2048 × 128)	2048
CTA/TMC-*d*	40	14.0	13.0	1666	6002	2.0	2048 × 94 (2048 × 128)	2048
CTA/TCM-*d*	40	14.0	13.0	250	250	20.0	512 × 128 (1024 × 256)	512
CTA/DMSO-d_6	90	14.0	13.0	1250	6002	2.0	2048 × 96 (2048 × 128)	512
CTA/DMSO-d_6	90	14.0	13.0	1000	500	30.0	512 × 188 (1024 × 256)	128

[a] Number in parenthesis indicates expanded matrix by zero-filling.

J_{C-C-H} is the long-range C–H coupling constant), but the signal was extremely weak to obtain a sufficiently large signal noise (S/N) ratio due to the remarkably short (< 50 ms) spin–spin relaxation time T_2 and then we chose the adequate value of Δ, determined by trial-and-error method under the conditions of $\Delta < 50$ ms. The exponential and trapezoidal windows were employed for t_2(^{13}C) and t_1(^{1}H), respectively. The detailed measuring conditions are summerized for each polymer-solvent system in Table II.

2D spectra were demonstrated by a stacked plot and plane figures were constructed by taking into the consideration the one-dimensional spectra of cross sections. ^{13}C and ^{1}H chemical shifts for cellulose and CTA were determined from one-dimensional spectra, independently measured, by an internal reference of sodium trimethylsilylpropionate-d_4 (TSP ($=0$ ppm)) and tetramethylsilane (TMS ($=0$ ppm)), respectively.

RESULTS AND DISCUSSION

Figure 2(a) and (b) show ^{1}H (homogate decoupled) and ^{13}C 1D NMR spectra of cellulose/NaOD/D$_2$O systems. Figure 3 shows
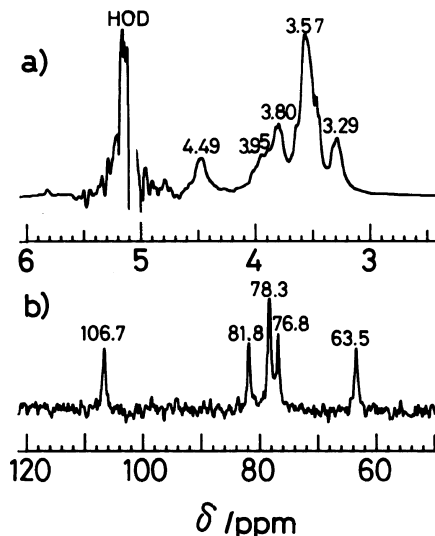
Figure 2. 1D NMR spectra of cellulose/NaOH/D$_2$O system: a, ^{1}H NMR (homogate decoupled); b, ^{13}C NMR (gated decoupled).

COSY (stacked plot, cellulose region) of the same system. Evidently, a peak at 3.57 ppm is relatively higher in intensity than the other peaks, and suggesting plural proton peaks. Despite homogate decoupling, a large peak due to residual proton in the solvent was observed. A rapid exchange in proton of the hydroxyl group in glucopyranose ring with
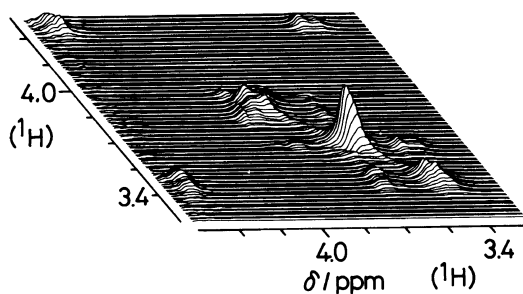
1094

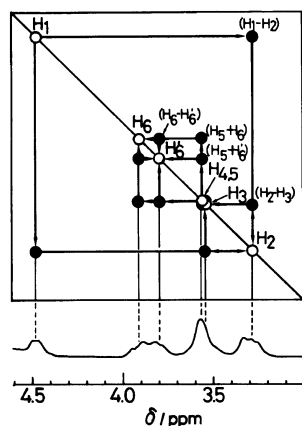**Figure 3.** Stacked plot for COSY spectrum of cellulose/NaOD/D_2O (cellulose region).

Figure 4. Schematic COSY spectrum of cellulose/ NaOD/D_2O: Filled and unfilled marks denote cross-peaks and dia-peaks, respectively. In the figure, correlations between protons are shown in parenthesis.

Figure 5. Cross-sections of C–H COSY spectrum of cellulose/NaOD/D_2O.

residual proton in the solvent does not enable us to distinguish, in ^1H NMR spectra, the hydroxyl proton peak from the residual proton peak. Over the 3.8—4.0 ppm region of the 1D-spectrum, a broad peak is observed. The existence of cross-peak in COSY indicates more explicitly that this is a triplet, consisting of closely overlapping two peaks (3.80 and 3.95 ppm), both combined with a single 3.57 ppm peak.

Figure 4 shows a schematic 2D spectrum of the cellulose/NaOD/D_2O system, constructed from Figure 3 and its cross section. In the figure, the projection of spectra in Figure 3 on the two axis is also illustrated. Diapeaks (open circle) in 2D spectrum correspond to each
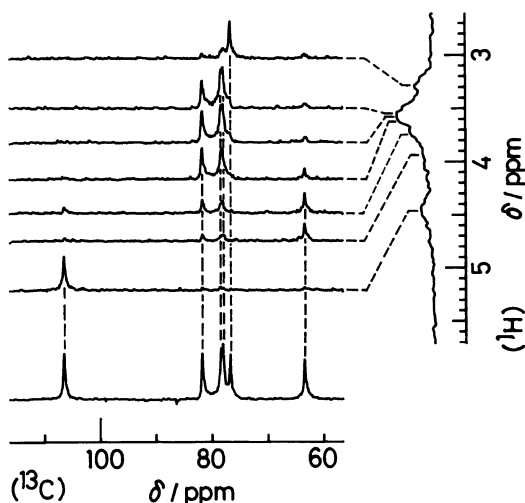
peak in the 1D spectrum and cross-peaks (filled circle) reveal the existence of coupling between neighbouring protons. For a doublet peak at 4.5 ppm in 1D-spectrum only single cross-peak is observed in 2D-spectrum. This means clearly that the peak has only a single vicinal coupling proton: The proton is obviously a proton at C_1 position (H_1). Accordingly, a triplet proton peak reveals vicinal coupling with the H_1 peak at 3.29 ppm and is assigned to H_2. In a similar manner, a peak at 3.57 ppm, coupled with H_2 peak is assigned to H_3, but, as described previously, this peak is heavily overlapped by other peaks and is not separable. Peaks at 3.80 and 3.95 ppm couple to each other and also both couple with a 3.57 ppm peak, strongly suggesting that the two former are non-equivalent H_6 proton peaks and the latter peak is assigned to H_5 proton. Then, it can be considered that a not-yet assigned H_4 peak overlaps with a H_5 peak (3.57 ppm).

Figure 5 shows the projection of C–H COSY of cellulose/NaOD/D_2O system on each axis, and its cross section spectra at ^1H peak position. A schematic 2D spectrum was drawn from the figure and is shown in Figure
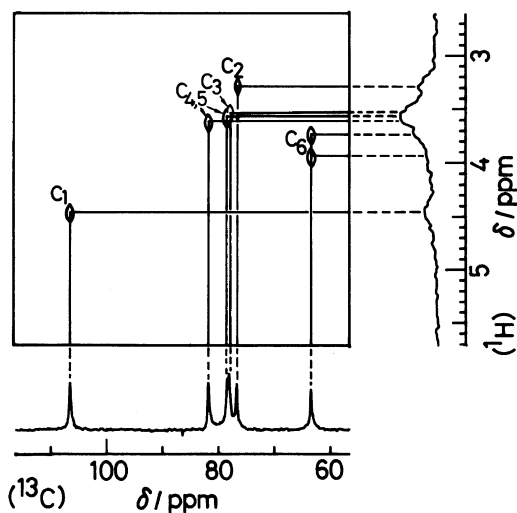
Figure 6. Schematic C–H COSY spectrum of cellulose/NaOD/D$_2$O.

6. Horizontal and longitudinal axes are ^{13}C and ^{1}H chemical shifts, respectively and projections on each axis are also shown. Peaks on 2D-spectrum clearly show C–H scalar-coupling, indicating the correlation between ^{13}C–^{1}H peaks. Then, based on the assignment on proton peaks, determined in Figure 4, three peaks at 106.7, 76.8 and 63.5 ppm in ^{13}C NMR spectrum are exactly assigned to the C$_1$, C$_2$, and C$_6$ carbon peaks, respectively. A peak at 81.8 ppm and a doublet peak at 78.3 ppm (in total three carbon peaks) cannot be assigned .explicitly due to the heavy overlapping of the proton peaks at 3.57 ppm which are directly correlated with the above three carbon peaks. The above assignment carried out here for ^{13}C peak is, as far as C$_1$, C$_2$, and C$_6$ carbon peaks are concerned, in good coincidence with those by Gagnaire *et al.*[2] for cellulose oligomer/DMSO-d_6 system and by Nardin and Vincendon[15] for cellulose/DMAC/LiCl system.

Figure 7(a) shows the ^{1}H 1D-NMR spectrum of CTA/TCM-d system. In the spectrum, proton peaks due to the glucopyranose skeleton are observed in 3.5—5.2 ppm, and three acetyl methyl proton peaks are observed at 2.11, 1.99, and 1.95 ppm. Figure 7(b), (c), and (d)
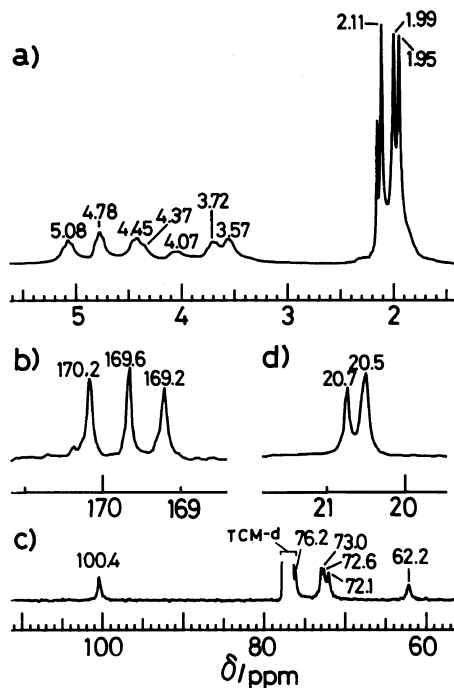

Figure 7. 1D NMR spectra of CTA/TCM-d system: a, ^{1}H NMR; b,c,d, ^{1}H noise decoupled ^{13}C NMR; b, carbonyl carbon region; c, glucopyranose carbon region; d, acetyl methyl carbon region.
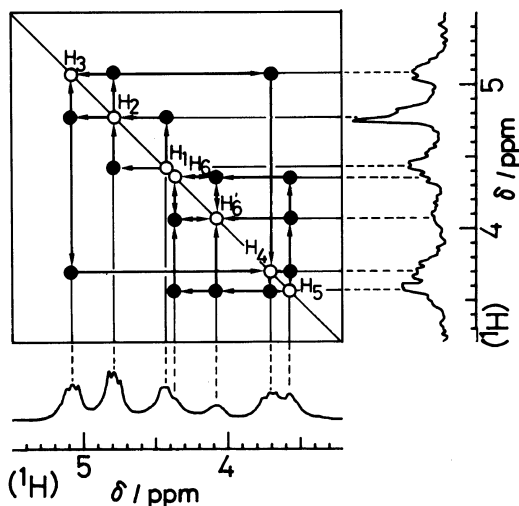

Figure 8. Schematic COSY spectrum of CTA/TCM-d (glucopyranose region): Filled and unfilled marks denote cross-peaks and dia-peaks, respectively.
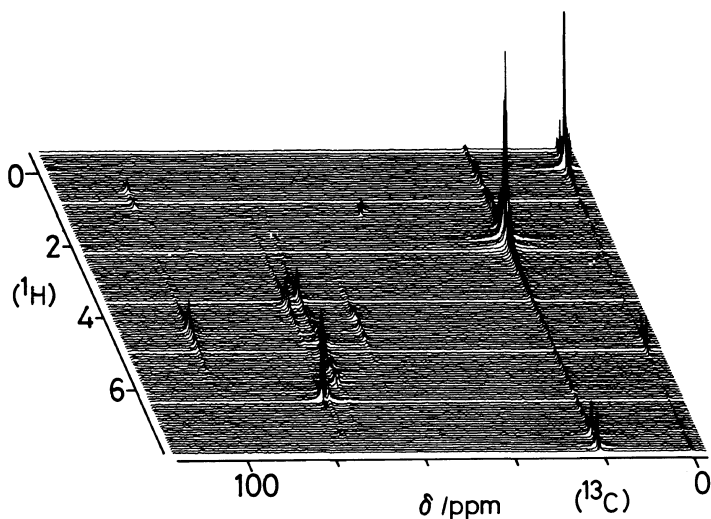
Figure 9. Stacked plot for C–H COSY spectrum of CTA/TCM-*d*.

show acetyl, glucopyranose and acetyl methyl regions of ^{13}C 1D-NMR spectrum of the CTA/TCM-*d* system.

Figure 8 shows a schematic COSY 2D-spectrum of the glucopyranose skeleton region of the CTA/TCM-*d* system, constructed from a stacked plot and cross sections of COSY spectrum, as well as its projection. A peak at 4.45 ppm reveals vicinal coupling with a peak at 4.78 ppm alone, being assigned to H_1. In the same way as in the case of the cellulose/NaOD/D_2O system, we can assign H_2 and H_3. In addition, in the case of CTA H_3, H_4, and H_5 peaks are observed separately and then each peak is able to be assigned completely. As result, all peaks are assigned, from lower magnetic field, to H_3, H_2, H_1, H_6, H_6', H_4, and H_5, respectively (here H_6' is the other half of unsymmetric H_6 peaks). This assignment is denoted on dia-peaks (open circle) in Figure 8. Note that in 1D-spectrum (Figure 7(a)) a H_6' peak heavily overlaps a H_1 peak so that peak separation is impossible, but such a separation becomes very easy with the help of a cross-peak in the 2D-spectrum.

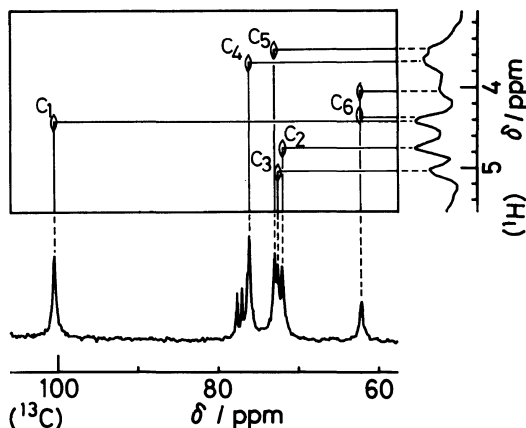Figure 9 shows the glucopyranose region and acetyl region of C–H COSY (stacked plot)

Figure 10. Schematic C–H COSY spectrum of CTA/TCM-*d* (glucopyranose region).

for the CTA/TCM-*d* system. In the 1D–^{13}C spectrum (Figure 7(c)) a solvent (TCM-*d*) peak at 77 ppm is extraordinarily large and overlaps some of the CTA peaks, making further analysis on CTA spectrum impossible. In contrast to this, in the 2D-spectrum, no peak of TCM-*d*, in which C–H coupling does not exist, is observed.

Figure 10 shows a schematic C–H COSY 2D-spectrum constructed from Figure 9 and
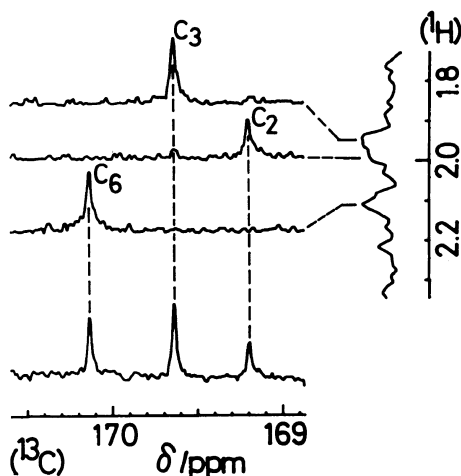
Figure 11. Cross-sections of long-range C–H COSY spectrum of CTA/TCM-*d* (acetyl carbonyl carbon region).

its cross section for the CTA/TCM-*d* system. In the figure, the projection of spectrum on the ^{13}C (horizontal) axis and the ^{1}H (longitudinal) axis are also shown. Carbon peaks can be assigned based on assignment of proton peaks, using the C–H correlations shown in Figure 10, from lower magnetic field, to C_1, C_4, C_3, C_5, C_2, and C_6. However, here C_3 and C_5 overlap and are unseparable.

Figure 11 shows cross section spectra of long-range C–H COSY spectrum between the acetyl methyl proton and the acetyl carbonyl carbon in CTA/TCM-*d*. Three correlation peaks in these figures are peaks, originating from long-range scalar coupling of the carbonyl carbon of acetyl group and acetyl methyl proton. If we denote carbonyl carbon peaks, from lower magnetic field, as a, b, and c, then the acetyl methyl proton peaks are assigned, using these correlation peaks, to a, c, and b. These relations are in an excellent agreement with the correlation, obtained by long-range selective spin decoupling method by Kowsaka *et al.*[6] Using these results, together with the assignment of the acetyl methyl proton peak chemically speculated by Goodlett *et al.*,[18] carbonyl carbon peaks can

be assigned, from lower magnetic field, to C_6, C_3, and C_2, respectively. It is also expected that if long-range scalar coupling between the glucopyranose skeleton proton and carbonyl carbon could be observed, carbonyl carbon peaks at C_2, C_3, and C_6 positions could be ultimately. However, actually a possible long-range coupling constant between the proton attached to glucopyranose carbon and carbonyl carbon (*i.e.*, H_6 proton and carbonyl carbon at C_6 position) is too small indeed to detect and in addition, in long-range C–H COSY measurements, the S/N ratio is significantly low due to the rapid transverse relaxation of magnetization of nuclei in CTA molecules. For this reason, we could not observe this kind of coupling for this polymer system. Similarly, we measured long-range COSY of protons in order to determine the correlation between the ring proton and the acetyl methyl proton, but failed due to the low S/N ratio.

In the future, it may become possible to make a long-range measurement by (1) ^{13}C enrichment, (2) decrease in internal viscosity by lowering the polymer molecular weight, (3) 2D-NMR by high magnetic field NMR apparatus, and (4) using other advanced 2D-NMR techniques such as correlation spectroscopy *via* long-range coupling (COLOC).[17]

From COSY and C–H COSY for the CTA/DMSO-d_6 system, the almost comparable peak assignment, was obtained for the CTA/DMSO-d_6 system in the same line of the discussion carried out for CTA/TCM-*d*. Figure 12 shows a stacked plot of long-range C–H COSY (carbonyl carbon peak region) for CTA/DMSO-d_6 system. From the figure, the correlation between carbonyl carbons and acetyl methyl protons, obtained by long-range selective spin decoupling method by Kowsaka *et al.*,[6] was again confirmed.

Summarizing, the reliability of peak assignment, hithetofor proposed, of ^{1}H and ^{13}C NMR spectra for cellulose and its triacetate was undoubtedly strengthened by use of 2D-
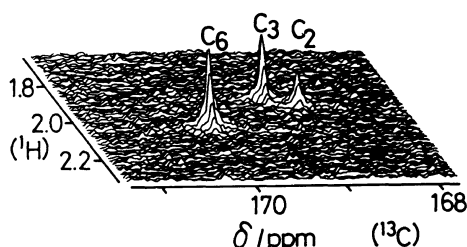
Figure 12. Stacked plot for long-range C–H COSY spectrum of CTA/DMSO-d_6 (acetyl carbonyl carbon region).

NMR. It was demonstrated that overlapping peaks in 1D-NMR whose existence could only be speculated from their intensity, were experimentally verified often from the splitting of peaks on 2D-spectrum.

Now there seems to be the possibility of much further advance in reliable and complete assignment by using 2D-NMR, of almost all peaks in NMR spectra of not-fully substituted cellulose derivatives with 《F》 ranging 0.5—2.5, for which peak assignment was unfortunately impossible by 1D-spectrum alone due to coexistence of various kinds of glucopyranose units (that is, unsubstituted, mono-, di-, and trisubstituted units).

REFERENCES

1. K. Kamide, K. Okajima, T. Matsui, and S. Manabe, *Polym. J.*, **12**, 521 (1980).
2. D. Gagnaire, D. Mancier, and M. Vincendon, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 13 (1980).
3. K. Kamide, K. Okajima, T. Matsui, and K. Kowsaka, *Polym. J.*, **16**, 857 (1984).
4. K. Kamide, K. Okajima, T. Matsui, M. Ohnishi, and H. Kobayashi, *Polym. J.*, **15**, 309 (1983).
5. K. Kamide and K. Okajima, *Polym. J.*, **13**, 127 (1981).
6. K. Kowsaka, K. Okajima, and K. Kamide, *Polym. J.*, **18**, 843 (1986).
7. K. Kamide, K. Okajima, K. Kowsaka, and T. Matsui, *Polym. J.*, **19**, 1405 (1987).
8. K. Kamide, K. Okajima, K. Kowsaka, T. Matsui, S. Nomura, and K. Hikichi, *Polym. J.*, **17**, 909 (1985).
9. K. Kamide, K. Kowsaka, and K. Okajima, *Polym. J.*, **19**, 231 (1987).
10. K. Kamide, K. Okajima, and T. Matsui, *Polym. J.*, **19**, 347 (1987).
11. K. Kamide, K. Okajima, and K. Yasuda, unpublished results.
12. T-K. Wu, *Macromolecules*, **13**, 74 (1980).
13. D. Clark and P. Stephenson, *Polymer*, **22**, 1112 (1981).
14. T. Miyamoto, Y. Sato, T. Shibata, H. Inagaki, and M. Tanahashi, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2363 (1984).
15. R. Narden and M. Vincendon, *Macromolecules*, **19**, 2452 (1986).
16. W. Brown and R. Wikström, *Eur. Polym. J.*, **1**, 1 (1966).
17. For example, E. Breitmeier and W. Voelter, "^{13}C NMR Spectroscopy," 3rd Ed, Verlag Chemie, Weinheim, New York, 1986.
18. V. Goodlett, J. Dougherty, and H. Patton, *J. Polym. Sci., A-1*, **9**, 155 (1977).