^1H NMR Study on Substituent Distribution of Cellulose Diacetate

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ABSTRACT: We find nine different types of spin network from the ^1H spectra of cellulose diacetate by the help of the two-dimensional NMR spectroscopy. They are four types of 2,3,6-triacetyl glucose residues flanked by different acetyl glucose units, two different types of 2,3-diacetyl glucose residues, a 2,6-diacetyl glucose residue, a 3,6-diacetyl glucose residue, and a 6-monoacetyl glucose residue. We simulate the ^1H spectra of the cellulose diacetate using these nine different subspectra. From the comparison of the observed spectrum with the simulated one contents of glucose residues different in the distribution of acetyl group are estimated.

KEY WORDS ^1H NMR / Cellulose Acetate / Distribution of Substituent / Degree of Substitution /

Cellulose derivatives in which hydroxyl groups of the glucose residue are replaced with other functional groups are widely used in commercial products.¹ Since the property of cellulose derivatives depends on the degree of substitution (DS), the determination of DS is a very important subject. The total degree of substitution can be determined by the titration method,² the nuclear magnetic resonance (NMR) method,^{3–12} and so on.¹³

In recent years, it has been increasingly recognized that the property of cellulose derivatives depends on not only the total degree of substitution, but also the distribution of substituent on three possible positions of glucose residue, *i.e.*, the 2-, 3-, and 5-positions, as well as the distribution on the whole backbone chain.¹⁴

A great deal of efforts have been made to determine the substituent distribution. Kamide *et al.*^{4,6,8,9} proposed a method for determining the distribution of *O*-acetyl groups in the glucose residue by the ^{13}C NMR spectra

of *O*-acetyl carbonyl carbons. Miyamoto *et al.*⁵ utilized the ^{13}C spectra of the ring carbons and the *O*-acetyl carbonyl carbons to determine the substituent distribution. Imai *et al.*^{7,10,11} reported a method for determining the distribution of substitution of cellulose ethers; their method is based on the combined use of acetylation of unsubstituted hydroxyl groups and ^{13}C NMR. Buchanan *et al.*¹² prepared a series of cellulose acetates labeled at the carbonyl carbons with ^{13}C , and identified 16 carbonyl carbon resonances. They could not assign all resonances to specific monomers, though they made detailed spectral investigations of cellulose triacetate.^{15–18} In this paper, we apply the ^1H NMR to the determination of the distribution of acetyl groups of cellulose diacetate.

Cellulose diacetate is regarded as a copolymer of eight different glucose residues, *i.e.*, the triacetyl glucose residue, three types of diacetyl glucose residues, three types of monoacetyl glucose residues, and the non-substituted

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glucose residue. We deduce the ^1H NMR spectra of various types of acetyl glucose residue from the spectra of cellulose diacetate by the help of the two-dimensional NMR spectroscopy, and determine chemical shift values of each glucose residue. The spectra of various acetyl glucose residues are reconstructed using the chemical shifts and the coupling constants obtained for cellotriose peracetate. By comparing the reconstructed spectra with those of cellotetraose peracetate and cellotriose, we determine the spectra of various types of acetyl glucose residues.

We simulate the spectra of cellulose diacetate using the spectra of these various glucose residues. From the comparison of the observed spectrum with the simulated one we determine the content of various acetyl glucose residues in the cellulose diacetate.

EXPERIMENTAL

The cellulose diacetate with a total degree of substitution (DS) of 2.46 is a gift from Dr. Kenji Kamide of Asahi Chemical Industry Co.,

Ltd. Twenty mg of the sample were dissolved in 0.5 mL of dimethylsulfoxide- d_6 ($\text{DMSO}-d_6$). ^1H NMR spectra were recorded at 80°C on a JEOL JNM-GX500 spectrometer operating at 500 MHz. The chemical shift is referred to the DMSO methyl peak as 2.60 ppm.

The spectral simulation was performed using the COMIC program obtained from JEOL Co., Ltd.

RESULTS AND DISCUSSION

The methine and methylene proton region of the NMR spectrum of cellulose diacetate with $\text{DS}=2.46$ in $\text{DMSO}-d_6$ at 80°C is shown in Figure 1(a). All resonances except for the methyl resonance of acetyl group appear in a region from 3.0 to 5.5 ppm. The resonances of various types of glucose residues different in substitution of acetyl group overlap in this small region.

The phase-sensitive COSY spectrum is shown in Figure 1(b). A number of cross peaks are clearly distinguishable. Each acetyl glucose unit forms an independent spin network. We

Figure 1. (a) Ring proton region of ^1H spectra of cellulose diacetate ($\text{DS}=2.46$) in $\text{DMSO}-d_6$ at 80°C , (b) phase-sensitive COSY spectra of cellulose diacetate, and (c) relayed COSY spectra.

try to extract spin networks.

It is found that a resonance at 4.43 ppm has only one cross-peak with a resonance at 3.19 ppm. The latter resonance has another cross-peak with a resonance at 4.92 ppm, which is further connected to a resonance at 3.63 ppm. More extended connectivity is, however, not easy to be identified in Figure 1(b).

Figure 1(c) shows the relayed COSY spectrum in the same region as Figure 1(b). We assign the resonance at 4.43 ppm to the H1-proton, because this has only one cross peak with the H2-proton in COSY spectra. We can hence assign sequentially the resonances at 3.19, 4.92, 3.63, 3.75, 4.09, and 4.28 ppm, respectively, to the H2-, H3-, H4-, H5-, H6-,

and H6'-protons of a glucose residue.

We identified nine different types of spin network which correspond to nine different types of glucose residues by careful inspection of a number of enlarged spectra of phase-sensitive COSY and related COSY. Table I lists chemical shift values of these nine residues. The line broadening and signal overlapping cause an error of ± 0.02 ppm. The chemical shift values of No. 1 are in agreement with those reported by Buchanan *et al.* for cellulose triacetate except for the difference in the reference value of chemical shift (we take DMSO as 2.60 ppm, while they take it as 2.49 ppm).¹⁵

We reconstruct the ¹H spectrum of each of the nine glucose residues using chemical shift values listed in Table I and the coupling constants obtained for cellotetraose peracetate ($J_{1,2}=8$, $J_{2,3}=9$, $J_{3,4}=9$, $J_{4,5}=9$, $J_{5,6}=5$, $J_{5,6'}=2$, and $J_{6,6'}=12$ Hz).¹⁹ We adopt a value of 20 Hz as full line-width for a good agreement with the observed spectrum of

Table I. Ring proton chemical shifts of individual glucose residues in cellulose acetate (DS = 2.46) at 80°C in DMSO-*d*₆^a

No.	1	2	3	4	5	6	6'
1	4.77	4.67	5.15	3.80	3.90	4.14	4.38
2	4.83	4.67	5.15	3.80	3.90	4.14	4.38
3	4.94	4.78	5.18	3.94	3.77	4.21	4.32
4	4.86	4.76	5.12	3.82	3.97	4.16	4.48
5	4.78	4.63	5.07	4.83	3.55	3.69	3.79
6	4.78	4.63	5.03	3.88	4.42	3.88	3.99
7	4.67	4.59	3.68	3.60	3.75	4.14	4.38
8	4.43	3.19	4.92	3.63	3.75	4.09	4.28
9	4.29	3.05	3.46	3.46	3.46	4.34	4.47

^a Error is ± 0.02 ppm.

Figure 2. Simulated spectra for six different glucose residues. Top, the spectrum of the internal residue of cellotriose; bottom, the spectrum of the internal residue of cellotetraose peracetate nearest to the non-reducing unit.

cellulose diacetate.

Figure 2 shows six typical reconstructed spectra for different glucose residues. At the bottom of Figure 2, we show the spectrum of the internal residue of cellotriose, which can be regarded as the spectrum non-acetylated glucose unit. The top of Figure 2 shows the spectrum of the internal residue of cellotetraose peracetate nearest to the non-reducing unit; this can be regarded as the 2,3,6-triacetyl glucose residue. The comparison of spectra of triacetyl glucose residue with the non-acetylated one indicates that the substitution with acetyl group shifts down-field the resonance of the ring proton at the substituted position. The shift is more remarkable for the 2- and 3-positions than for the 6-position.

The chemical shift values of spectra No. 1 to No. 4 (spectra No. 2 and No. 4 are not shown) are close to those of the triacetyl glucose residue. These spectra are, therefore, assignable to 2,3,6-triacetyl glucose residues. The small dispersion of chemical shift is caused by the variety of adjacent glucose residues. Since a 2,3,6-triacetyl glucose residue is flanked by eight different residues, 64 different species are possible. It is suggested that the most populated species appear as the four spectra.

Spectra No. 5 and No. 6 (not shown) are assigned to the 2,3-diacetyl glucose residues, because the chemical shifts of the H2- and H3-protons are close to those of the triacetyl glucose residue and because those of the H6- and H6'-protons are close to those of the non-acetylated glucose residue. The most populated species appear as the two spectra. Spectrum No. 7 is assigned to the 2,6-diacetyl glucose residue. This is because the chemical shifts of the H2- and H6-protons are close to those of triacetyl, while the other resonances are close to those of the non-acetylated one. The resonance of the H2-proton of spectrum No. 8 is close to the resonance of cellotriose, while the other resonances are close to the resonance of cellotriose peracetate. Spectrum No. 8 is, therefore, assigned to the 3,6-diacetyl

glucose residue. For spectrum No. 9, all resonances except for 6,6'-protons are close to cellotriose. Spectrum No. 9 is assignable to the 6-monoacetyl glucose residue. The results of assignment are shown in Figure 2.

We simulate the observed spectrum of the cellulose diacetate using the nine spectra obtained above. We adjust contents of the nine residues to obtain a good agreement between the observed spectrum (Figure 3(a)) and the simulated one (Figure 3(b)). The factor of discrepancy between the two, which is analogous to the R factor in the x-ray crystal

Figure 3. (a) Ring proton region of ^1H NMR spectrum of cellulose acetate (DS=2.46) and (b) simulated spectrum using the spectra shown in Fig. 2. The acetylation causes the resonances of ring protons downfield-shift.

Table II. The contents of the glucose residues of cellulose acetate (DS=2.46)

No.	Residues	Content/%
1	2-Ac, 3-Ac, 6-Ac	30
2	2-Ac, 3-Ac, 6-Ac	13
3	2-Ac, 3-Ac, 6-Ac	10
4	2-Ac, 3-Ac, 6-Ac	3
Sub-total		56
5	2-Ac, 3-Ac, 6-OH	9
6	2-Ac, 3-Ac, 6-OH	4
Sub-total		13
7	2-Ac, 3-OH, 6-Ac	17
8	2-OH, 3-Ac, 6-Ac	9
9	2-OH, 3-OH, 6-Ac	5

Table III. The degree of substitution of cellulose diacetate (DS = 2.46)

Position	NMR	Titration
2	0.86 ± 0.09	
3	0.78 ± 0.08	
6	0.87 ± 0.09	
Total	2.51 ± 0.3	2.46

structure analysis, is estimated by the ratio of the absolute value of difference area of the two spectra and the total area of the observed spectrum. It is 0.18, suggesting a good agreement. The difference between the observed and simulated spectra is largely attributed to minor species that are not assigned.

The contents are shown in Table II. Table III lists the degree of substitution at the three positions. The total degree of substitution of 2.51 is close to the value of 2.46 obtained by the titration method.² The error involved in the values listed Tables II and III can not be estimated correctly, but probably not more than ±9%. It is of interest to note that the order of degree of substitution is 6 > 2 > 3.

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