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^{13}C NMR Structural Study on Methylhydroxypropylcellulose Obtained by Different Procedures†

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ABSTRACT: A series of methylhydroxypropylcellulose (MHPC) samples were prepared by different procedures and the distribution of methyl and hydroxypropyl substituents was determined by means of a ^{13}C NMR analysis after the acetylation of both the unsubstituted hydroxyl groups on the anhydroglucose unit and those at the end of hydroxypropyl substituents. The methoxy methyl and the acetyl carbonyl signal analysis of acetylated MHPC samples allowed one to provide the detailed distribution pattern of two substituents and to correlate with the preparation procedure of the starting MHPC samples.

KEY WORDS Methylhydroxypropylcellulose / ^{13}C NMR / Substituent Distribution / Cellulose Derivatives /

Cellulosic materials have recently gained a renewed interest due to the development of application possibilities both in "high-tech" and "bio-tech" fields.[1] Since cellulose derivatives are produced through the reaction of the hydroxyl group either at 2, 3, or 6 position on an anhydroglucose unit, the precise determination and control of substituent distribution are particularly important for the elucidation of the structure–property relationship and for the eventual molecular design of products.

We have recently proposed a new analytical technique applicable for diverse cellulose ethers, in which their acetylated derivatives are subjected to a ^{13}C NMR measurement.[2-7] The following advantages are noted for this method:

1) The acetylation of cellulose ethers is an easy and simple pretreatment to provide acetylated derivatives readily soluble in common NMR solvents over a wide range of degree of substitution, facilitating the comparison with model polymers. This may be regarded as a significant progress since the practical use of NMR techniques has been so far limited because the solubility of cellulose derivatives is pronouncedly dependent not only on their total degree of substitution but also on the distribution of substituents and the NMR chemical shift is quite sensitive to the measurement solvent.

2) The carbonyl carbon signal of the acetyl groups is remarkably sensitive to its location at the anhydroglucose ring unit to allow one to determine directly the distribution of substituents.[8]

3) The acetylation of the hydroxyl groups can eliminate spectral complications caused by intra- and intermolecular hydrogen bonds.

4) This procedure can provide a convenient and reliable analytical method for cellulose

† Part 5 of ^{13}C NMR Structural Study on Cellulose Ethers by Means of Their Acetylated Derivatives. For Part 4, see ref 5.

derivatives in retaining the polymer form and thus can avoid sometimes troublesome hydrolysis or alcoholysis pretreatment inevitable for chromatographic techniques.

We have so far demonstrated the potential of this technique in the structural analysis of such cellulose ethers as methyl,[2] hydroxyethyl,[4] and hydroxypropylcellulose,[3] as well as methylhydroxyalkylcelluloses possessing two different ether substitutents.[5]

As the extension of the preceding studies, we describe in the present paper on the structural analysis of a series of methylhydroxypropylcellulose (MHPC)s obtained through different procedures. MHPC is known to undergo a thermoreversible gellation in aqueous solution.[9] Thus the structural details, in particular the distribution of substituents, were compared among different MHPC samples, and were correlated with their preparation procedures.

EXPERIMENTAL

Samples

Methylhydroxypropylcellulose (MHPC) samples were synthesized by three different procedures shown in Scheme 1. Acetylation of these cellulose ethers was carried out by refluxing in an acetic anhydride/pyridine mixture and the complete acetylation was confirmed by IR analysis as detailed before.[5] The molecular weight of MHPC samples[10] was approximated by GPC measurements on their acetylated derivatives and was around 2×10^4 through the calibration with polystyrene standard samples.

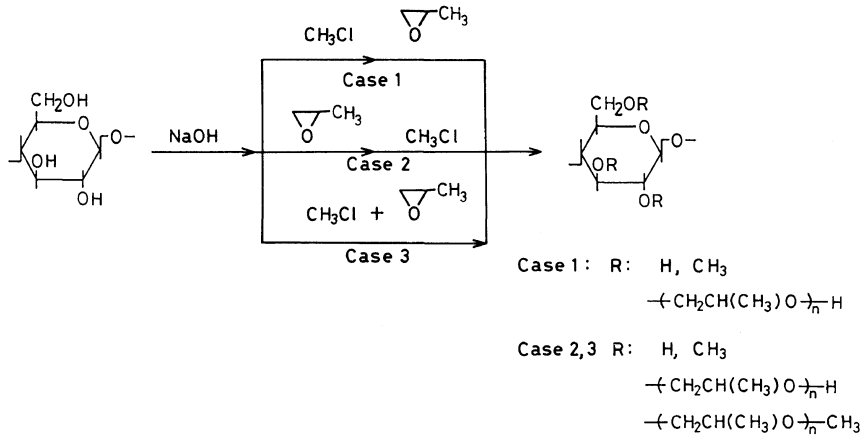
Measurements

^{13}C NMR measurements were carried out at 67.8 MHz by means of a JEOL JNM-GX 270 spectrometer equipped with a 5 mm or 10 mmϕ C–H dual probe in dimethyl sulfoxide-d_6 (DMSO-d_6) solution at 100 °C. Chemical shift values were referenced from the solvent signal of DMSO-d_6 (43.5 ppm). Quantitative ^{13}C NMR measurements were carried out using a 10 mmϕ C–H dual probe by means of a non-NOE mode gated-decoupling technique with a pulse repetition time of 100 sec to avoid the error from T_1 variation of signals. Approximately 2000 transients were accumulated to afford a spectrum of sufficient S/N ratio for the integration, where C_1 signal area was used as a base unit for the calibration. IR measurements were performed with a JASCO model IR-816 spectrophotometer. GPC measurements were carried out by TOHSO High Speed Liquid Chromatograph equipped with a G4000HXL as a column and tetrahydrofuran (THF) as an eluent with a flow rate of 1.0 ml min^{-1}. Chemical analysis of methyl and hydroxypropyl contents of MHPC samples were performed by the method detailed before.[5]

RESULTS AND DISCUSSION

Methylhydroxypropylcellulose (MHPC) samples were synthesized by three different procedures shown in Scheme 1. Those were either by the stepwise reaction first with methyl chloride and then with propylene oxide (Case 1), by a similar stepwise reaction but in the opposite order of addition of the reagents (Case 2), or by a simultaneous reaction with the mixture of two reagents (Case 3). Thus the two types of substituents, namely methoxy groups and hydroxypropyl groups having hydroxyl end groups, are expected in Case 1. In Cases 2 and 3, on the other hand, an additional type of substituent, namely hydroxypropyl groups with methoxy end groups may be formed.

MHPC samples having similar contents of both methyl (1.47—1.90) and hydroxypropyl (0.25) groups were obtained after several attempts and used in the present study. Although hydroxypropyl substituents of MHPC samples are, in principle, comprised of a mixture of oligo(propylene oxide) groups having different degrees of polymerization, the substituents in the present MHPC samples having low hydroxypropyl contents are thought to contain



Scheme 1.

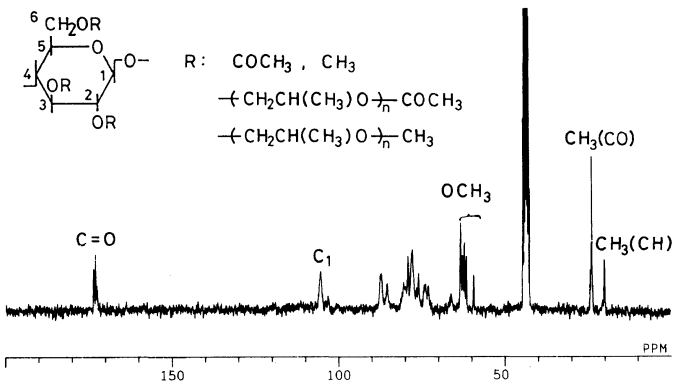


Figure 1. ^{13}C NMR full range spectrum of an acetylated methylhydroxypropylcellulose in DMSO-d_6 at 100°C. (Sample: Case 3 in Scheme 1.)

exclusively one hydroxypropyl unit.[3]

The structural details of a series of MHPC samples were studied by means of a ^{13}C NMR analysis with using their acetylated derivatives.[5] A full-range spectrum of the acetylated MHPC sample from the Case 3 procedure is shown in Figure 1. The methoxy methyl and the acetyl carbonyl carbon signals were, among others, present as resolved peaks to reflect the structural details of the parent MHPC sample. The integration of whole methoxy methyl signals visible at 59—64 ppm allowed one to estimate the total content of methoxy groups by comparing with the intensity of the C_1 signal, which was resolved by the type of the substituent on C_2 position, *i.e.*, with methyl or hydroxypropyl groups at around 105 ppm and with an acetyl group at 102.9 ppm.[5] In a similar manner, the total content of hydroxypropyl groups was estimated from the integration of the hydroxypropyl methyl signal at around 20 ppm. And these values were found to agree with those obtained from the chemical analysis as listed in Table I.

In Figure 2, the expanded methoxy methyl region spectra of a series of acetylated MHPC samples were compared. The signal of the methoxy methyl groups at the end of hydroxypropyl substituent appears at 59.4 ppm, separated from the signals of those attached

Table I. Structural parameters of methylhydroxypropylcellulose prepared by different methods

Sample	Method[a]	CH_3			$CH_2CH(CH_3)O$–X			D.S.[b]			
		glu[c]	sub[d]	Total	H	CH_3	M.S.[e]	2	3	6	Total
1	Case 1	1.58	—	1.58	0.32	—	0.31	0.68	0.32	0.64	1.64
				1.47[f]			0.25[f]	0.70[g]			
2	Case 2	1.73	0.13	1.86	0.13	0.13	0.25	0.82	0.53	0.71	2.06
				1.90[f]			0.25[f]	0.83[g]			
3	Case 3	1.81	0.06	1.87	0.17	0.06	0.26	0.82	0.57	0.80	2.19
				1.90[f]			0.25[f]	0.83[g]			

[a] See also Scheme 1.
[b] Sum of methyl and hydroxypropyl groups.
[c] On the anhydroglucose unit.
[d] On the hydroxypropyl unit-end.
[e] Total content of hydroxypropyl units.
[f] From chemical analyses.
[g] From C_1 signal analysis.[5]

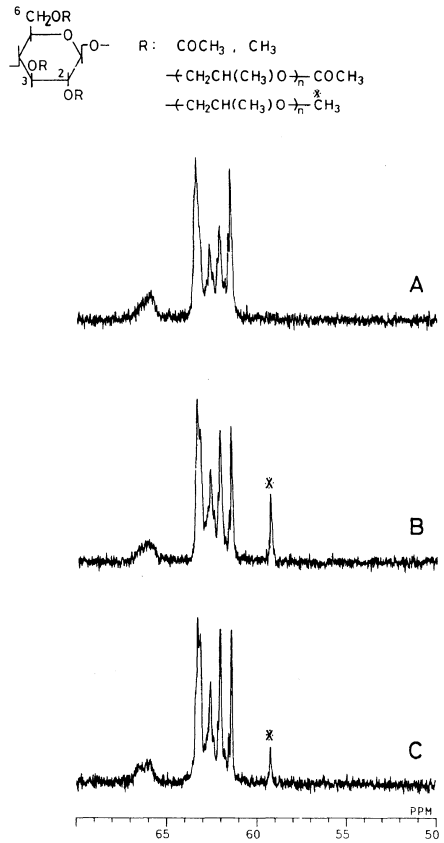


Figure 2. ^{13}C NMR methoxy methyl region spectra of acetylated methylhydroxypropylcelluloses in DMSO-d_6 at 100°C. (Samples: [A], Case 1; [B], Case 2; [C], Case 3 in Scheme 1.)

directly to the anhydroglucose unit present at 61—64 ppm as four major peaks, which are resolved not only by its own substitution position but also by the interaction with the substituents at other substitution positions on the anhydroglucose unit.[2] The signal at 59.4 ppm was not detected for the acetylated MHPC sample obtained by the Case 1 procedure, in which the methylation preceded the reaction with propylene oxide. The methyl group distribution either on the anhydroglucose unit or at the end of the hydroxypropyl groups was quantitatively estimated by comparing those signal areas and listed in Table I.

In Figure 3, the expanded acetyl carbonyl region spectra of a series of acetylated MHPC samples were compared. The acetyl carbonyl carbon signal was found to split into a quadruplet at 172.2, 172.6, 172.9, and 173.4 ppm, and they were assigned to that on the 2 (172.2), 3 (172.6), and 6 (173.4) position on the anhydroglucose unit, respectively, and to that at the end of the hydroxypropyl substituent (172.9).[5] Since the distribution of acetyl groups in acetylated MHPC samples directly corresponds to that of hydroxyl groups in the original MHPC samples, the integration of the individual signals allowed one to provide the relative abundance of the hydroxyl groups at

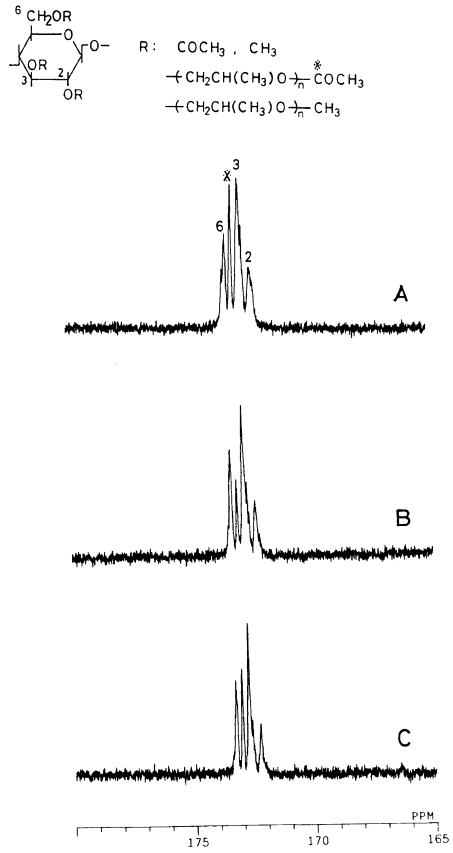


Figure 3. ^{13}C NMR carbonyl region spectra of acetylated methylhydroxypropylcelluloses in DMSO-d_6 at 100°C. (Samples: [A], Case 1; [B], Case 2; [C], Case 3 in Scheme 1.)

each substitution position. The absolute degree of substitution of the mixture of methyl and hydroxypropyl groups in the parent MHPC samples was subsequently determined by subtracting the hydroxyl group distribution.

The structural parameters of MHPC samples, including the methyl group distribution either on the anhydroglucose unit or at the end of hydroxypropyl groups and the distribution of the mixture of two ether substituents on the anhydroglucose unit, were collected in Table I. The ratio between methyl and hydroxyl groups at the end of hydroxypropyl substituent depends significantly on the nature of preparation procedure, *i.e.*, none in the Case 1 while as high as 50% in the Case 2. The notable variation of viscosity in a non-aqueous solution of these MHPC samples may be correlated with this structural difference.[11]

In conclusion, the present ^{13}C-NMR technique allowed one to monitor the structural details of cellulose ethers having diverse substituents prepared by different procedures. Hence, this method will provide a powerful mean to elucidate the structure–property relationship of cellulosic materials and to achieve a strict quality control in the production process.

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