of 1.57 g·cm^{-3} and indicates the absence of interstitial or site bound water in the structure. The smaller measured value for the density is a consequence of both defects in the crystals and surface free energy effects.

A structural aspect of particular interest is the constancy of two of the lattice edges, *a* and *c*. Comparison of our and other results for mannan I with published data for guar,[6,8] tara,[6,7] and carob[6,8] gums as well as with lattice constants for more highly substituted galactomannans such as fenugreek and lucerne[29] shows that these two dimensions are conserved irrespective of the galactose to mannose ratio. One rationale explanation of this observation is that the sheetlike structure in the *ac* plane is preserved forming a mannan sheet with an irregular coating of galactosyl units on each of its surfaces.[8]

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Determination of Substituent Distribution in Cellulose Ethers by Means of a ^{13}C NMR Study on Their Acetylated Derivatives. 1. Methylcellulose

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ABSTRACT: The distribution of methyl groups in methylcellulose having various degrees of substitution was determined by means of ^{13}C NMR analysis after the acetylation of the unsubstituted hydroxyl groups of the parent methylcellulose. The acetyl carbonyl carbon signal of the acetylated methylcellulose samples was found to be split into a triplet in DMSO at 100 °C corresponding to the position of the substituent (2, 3, or 6) on the anhydroglucose unit, allowing the determination of the methyl substituent distribution of methylcellulose samples. The ^{13}C NMR assignment of the split methoxy methyl carbon signal of acetylated methylcellulose samples observed in chloroform solution at 30 °C is proposed with the aid of the substituent distribution analysis by the GLC technique. The methoxy methyl carbon signal was found to be sensitive not only to its substitution position but also to the type of the substituent on the other substitution position.

Introduction

Cellulose derivatives, produced through the reaction of hydroxyl groups in the 2-, 3-, and 6-positions of the anhydroglucose ring unit, have been widely used in a variety of applications as indispensable polymeric materials based on a natural resource. Since the substituent distribution in addition to the total degree of substitution (DS) is expected to influence the properties of the resulting cellulose derivatives, it is of great importance to develop an analytical system to give precise information on the substit-

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uent distribution by means of a facile and reliable procedure.

NMR, particularly ^{13}C NMR, has been extensively applied to elucidate the substituent distribution of a variety of cellulose derivatives.[1-13] Nevertheless, a serious limitation of the use of ^{13}C NMR to determine the substituent distribution in cellulose derivatives arises from the fact that the solubility of cellulose derivatives is markedly dependent on their degree of substitution and also on their substituent distribution and also that the chemical shift is quite sensitive to the solvent. Consequently, the precise determination of the substituent distribution of cellulose derivatives over a wide range of degrees of substitution has been scarcely achieved to date, unless the appropriate common solvent is available over a wide range of degrees of substitution, which happens to be the case with DMSO for acetylcellulose.[2-5]

The modification of cellulose derivatives in order to make them soluble in common solvents is another approach to meet this requirement. This technique has been applied to determine the substituent distribution of acetylcellulose by capping the unsubstituted hyroxyl group with the deuteriated acetyl group to facilitate ^1H NMR analysis.[14]

In the present paper, we describe a ^{13}C NMR study of methyl group distribution in methylcellulose by using its acetylated derivatives, which become soluble in common NMR solvents over a wide range of degrees of substitution. Also the recent ^{13}C NMR spectroscopic studies on acetyl group distribution in acetylcellulose[2-5] can be used as a reference to determine the methyl group distribution of the present methylcellulose samples.

It should also be noted that the NMR analysis of cellulose derivatives in their polymeric form is of distinct interest compared to that of their hydrolysate or methanolisate counterparts. Although the latter method by means of GLC[15] or NMR[16] also allows one to determine the substituent distribution of cellulose derivatives, only the former method can provide information on higher order polymer structures such as the interaction between the substituents on the 2-, 3-, and 6-position in the polymeric form and also on the monomer unit distribution along the polymer chain. In addition, it can avoid the complications in the analysis of the hydrolysate due to the anomerization and the sometimes cumbersome hydrolytic procedure to achieve the complete conversion and the complete recovery of the hydrolysate.

Experimental Part

(1) Samples. Methylcellulose samples with a series of degrees of substitution were supplied by Shin-Etsu Chemical Co., Ltd.; they were produced by the reaction of alkali cellulose with methyl chloride, except for the methylcellulose sample of degree of substitution 2.89, which was prepared by the method described by Isogai et al.[17] Acetylation of methylcellulose samples was carried out by refluxing methylcellulose in an acetic anhydride/pyridine mixture; 20 g of methyl cellulose, 100 mL of pyridine, and 50 mL of acetic anhydride were placed in a 500-mL three-neck flask and heated to reflux for 3 h. The product was isolated by precipitation into 1.2 L of water and washed repeatedly with water; then finally it was purified by reprecipitation from acetone/water. Triacetylcellulose was prepared from cellulose by this same procedure.

(2) Measurements. ^{13}C NMR analyses were carried out at 67.8 MHz by means of a JEOL JNM-GX270 spectrometer equipped with a 5-mm i.d. C–H dual probe at 100 °C in DMSO-d_6, at 30 °C in $CDCl_3$, at 30 °C in $CDCl_3$, and at 30 °C in D_2O. Chemical shift values were referenced from solvent signals, i.e., 43.5 (DMSO-d_6), 77.0 ($CDCl_3$), and 128.0 ppm (C_6D_6), or from the C_1 carbon signal at 103.0 ppm in D_2O. The sample solution of ca. 5% w/v was used with the bilevel complete decoupling mode by using a flip angle of 45° and a pulse repetition time of 2.0 s with 20000–30000 transients. Spectrum width was 20000 Hz with 32K data points.

GLC analysis of the substituent distribution of the methylcellulose samples was carried out according to a slight modification of the method described by Albersheim et al.[18] Fifty milligrams of methylcellulose was hydrolyzed with 3.5 mL of 1.0% sulfuric acid at 140 °C for 2 h. After neutralization with calcium carbonate, the solvent was removed by heating at 80 °C for 6–7 h. The sample was redissolved in 5.0 mL of 80% aqueous methanol and filtrated with a 0.45-μm filter. The sample solution was then condensed to 1.0 mL. Thereupon, 100 μL of sodium borohydride solution, prepared with 1.5 g of sodium borohydride in 10 mL of 0.2 N sodium hydroxide, was added and stirred for 1 h. Acetic acid, 100 μL, was then added and the solution was dried up by heating followed by washing and evacuating twice with 3.0 mL of methanol. Finally, 1.0 mL of acetic anhydride and 1.0 mL of pyridine were added and the mixture was heated at 120 °C for 3 h. The reaction solution was directly analyzed by injecting 1 μL of the sample solution into the Shimadzu GC-7A gas chromatograph apparatus equipped with a cross-linked 5% phenylmethylsilicone capillary column of 0.2-mm i.d. × 25 m (Hewlett-Packard) with a column temperature of 150–220 °C and with a heating rate of 2 °C/min. The GLC peak assignment was performed with reference to the mass spectroscopic analysis reported by Lindberg.[19]

The TLC analysis[20] was carried out after the hydrolysis treatment of the methylcellulose sample described above and an aliquot of 2 μL was spotted on Merck Kiesel Gel 70 (20 cm × 20 cm) and developed by a chloroform/acetic acid/water (60/70/10 ml) mixture for 2.5 h and then stained with 10% sulfuric acid at 150 °C for 7 min. The spot was traced with Shimadzu Chromatoscanner CS-930 at 410 nm.

Chemical analysis of methyl and acetyl content of methylcellulose derivatives was performed by the GLC[21] method for the former and by the GLC[22] or the titration[23] method for the latter.

Results and Discussion

(1) Determination of the Methyl Group Distribution in Acetylated Methylcellulose. Cellulose ethers such as methylcellulose, ethylcellulose, (hydroxyethyl)cellulose, and (hydroxypropyl)cellulose are common cellulose derivatives and have been used for a wide variety of commercial applications. ^{13}C NMR spectroscopic studies on cellulose ethers like methylcellulose,[6,7] (hydroxyethyl)cellulose,[6,8] (hydroxypropyl)cellulose,[9,10] and (carboxymethyl)cellulose[6] have been carried out to characterize the structural details of these cellulose derivatives. Nevertheless, the substituent distribution has not yet been fully elucidated, particularly over a wide range of degrees of substitution.

We decided to develop a facile and reliable method to determine the substituent distribution of cellulose ethers by means of NMR. As the first and basic result of this series of studies, we will describe here the determination of methyl group distribution of methylcellulose after converting the unsubstituted hydroxyl group of methylcellulose to an acetyl group. This modification allows, first, these cellulose derivatives to become soluble in common NMR solvents over a wide range of degrees of substitution and, second, the acetyl carbonyl carbon signal remains sensitive to its substitution position, leading to the subsequent determination of methyl group distribution.

The importance of a common solvent will be demonstrated by the following example, where methylcellulose of degree of substitution 1.74, which is soluble in water, and of degree of substitution 2.89, soluble in benzene, were analyzed and compared as shown in Figure 1. The methoxy methyl carbon was found to be sensitive to the substitution position, namely, the 2-, 3-, or 6-position, as is clearly seen in the methylcellulose sample of degree of substitution 2.89. On the other hand, the methylcellulose

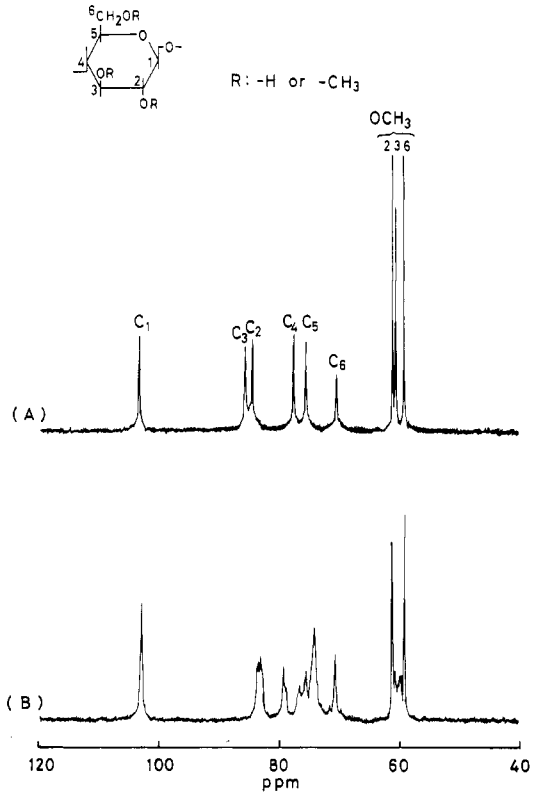

Figure 1. ^{13}C NMR spectra of methylcellulose of (A) DS = 2.89 in C_6D_6 at 30 °C (sample 8 in Table I) and of (B) DS = 1.74 in D_2O at 30 °C (sample 5 in Table I).

Table I
Preparation and Solubility of Acetylated Methylcellulose Samples[a]

sample	DS of methyl-cellulose, OCH_3	DS of acetylated methylcellulose		solubility[b]		
		OCH_3	$OCOCH_3$	$CHCl_3$	DMSO	C_6H_6
1	0.45	0.46	2.49	O	O	X
2	0.95	0.93	2.05	O	O	X
3	1.20	1.20	1.72	O	O	O
4	1.48	1.50	1.48	O	O	O
5	1.74	1.63	1.28	O	O	O
6	2.02	1.98	0.94	O	O	O
7	2.35	2.31	0.64	O	Δ	O
8	2.89			O	X	O

[a] DS values from chemical analysis. [b] O, soluble; Δ, partly insoluble; X, insoluble.

sample of degree of substitution 1.74 gives two principal signals for the methoxy methyl carbon region in water. These signals did not exactly correspond to any methoxy methyl signals of methylcellulose of degree of substitution 2.89, measured in benzene, thus preventing precise and unambiguous assignment of the individual signals.

A series of methylcellulose samples with various degrees of substitution were then treated with acetic anhydride/pyridine to convert the unsubstituted hydroxyl groups of methylcellulose to acetyl groups. The results are summarized in Table I. The acetylation reaction proceeded quantitatively without affecting the methoxy group of methylcellulose; this was confirmed by the agreement of the methoxy content before and after the acetylation treatment as well as the sum of the methoxy content and the acetyl content being nearly 3.0.

The solubility in some NMR solvents of acetylated methylcellulose samples having a range of degree of substitution are also listed in Table I. It is found that chloroform is a common solvent to dissolve acetylated methylcellulose over a range of degrees of substitution from 0 to 3. DMSO was also found to dissolve acetylated methylcellulose over a wide range of degrees of substitution except for samples of very high methoxy content.

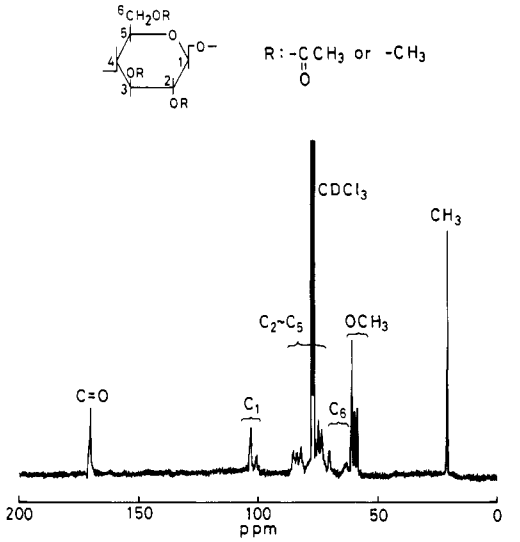

Figure 2. ^{13}C NMR spectrum of acetylated methylcellulose in $CDCl_3$ at 30 °C (sample 5 in Table I).

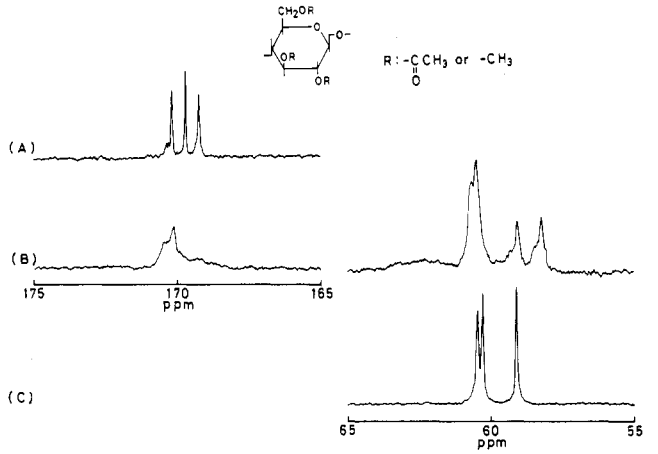

Figure 3. ^{13}C NMR spectra of methoxy methyl and carbonyl region of acetylated methylcellulose (B) together with triacetylcellulose (A) and trimethylcellulose (C) (acetylated methylcellulose; sample 5 in Table I, in $CDCl_3$ at 30 °C).

Based on the solubility behavior of acetylated methyl cellulose samples, a ^{13}C NMR study was first carried out in $CDCl_3$ solution at 30 °C. Figure 2 shows the full spectrum of acetylated methylcellulose having a degree of substitution 1.74. Figure 3 also shows the expanded spectrum of the methoxy and carbonyl region of this acetylated methylcellulose sample. Although this sample is readily soluble in $CDCl_3$, the acetyl carbonyl region signal was found to collapse and did not give a resolved spectrum like that of the triacetylcellulose model compound, which gives the clearly resolved carbonyl signal as shown in Figure 3. In addition, careful comparison of the methoxy carbon region of acetylated methylcellulose with that of trimethylcellulose indicates that, although the methoxy carbon signal is split into a triplet in both cases, the chemical shifts of the individual signals do not precisely correspond to those of the model trimethylcellulose. The assignment of the methoxy triplet signal observed in $CDCl_3$ will be discussed in more details in a later section of this paper.

When DMSO was used as the solvent at 100 °C, acetylated methylcellulose was found to give a better resolved spectrum than in $CDCl_3$. The full spectrum of acetylated

Table II
Distribution of Methyl Groups on the Anhydroglucose Unit of Methylcellulose Samples[a]

sample[b]	2, 3, 6	2, 3	2, 6	3, 6	2	3	6	none
1	0.9	2.4	4.1	0.4	16.3	1.2	13.1	61.6
2	6.1	5.4	10.1	1.6	18.5	1.5	18.1	38.7
3	9.4	8.6	13.9	3.1	18.6	2.6	16.1	27.7
4	15.0	9.7	20.8	4.1	20.5	2.4	13.1	14.4
5	21.4	12.1	24.4	3.7	20.2	1.7	9.0	7.5
6	29.8	8.2	25.5	5.6	12.4	1.5	11.7	5.3
7	49.2	8.4	20.8	6.4	5.3	1.5	5.1	3.3
8	88.5	6.6	2.5	2.4	nd[c]	nd	nd	nd

[a] Substitution position in parenthesis, fractions in percent. [b] See also Table I. [c] Not detected.

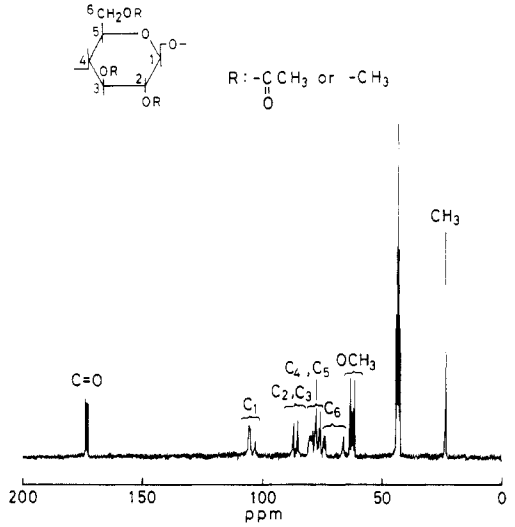

Figure 4. ^{13}C NMR spectrum of acetylated methylcellulose in DMSO-d_6 at 100 °C (sample 5 in Table I).

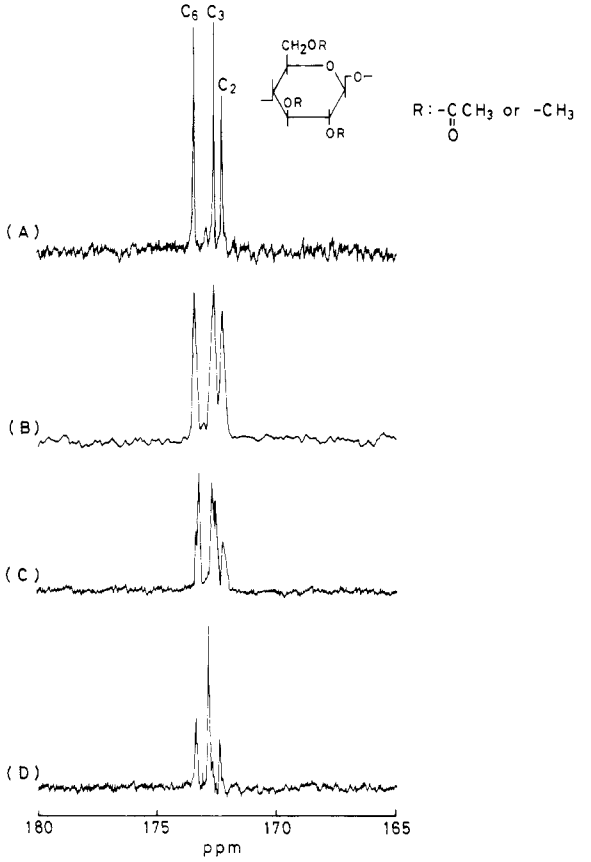

Figure 5. ^{13}C NMR carbonyl region spectra of acetylated methylcellulose samples in DMSO-d_6 at 100 °C (DS of methyl substituent: (A) 0; (B) 0.95; (C) 1.74; (D) 2.35).

methylcellulose of degree of substitution 1.74 and the carbonyl spectra of a series of varied degree of substitution samples are shown in Figures 4 and 5, respectively. The acetyl methyl carbon signal was observed as a doublet at 23.5 and 23.8 ppm, respectively. The C_6 methylene carbon signal was found to be sensitive to the type of substituent, i.e., methyl at 74–75 ppm and by acetyl at 65.9 ppm. The C_1 acetal carbon signal also split into a doublet according to the nature of the substituent on C_2, i.e., methyl at 105.4 ppm while acetyl at 102.9 ppm. The methoxy methyl carbon signal was found to split into a quadruplet.

Finally, the carbonyl carbon signal was observed to split into a triplet at 172.2, 172.6, and 173.4 ppm, representing the substitution position (2, 3 and 6, respectively) on the anhydroglucose ring unit.[3,5] As shown in Figure 5, the carbonyl carbon signal was resolved into a triplet regardless of the degree of substitution of the sample. This allows one to determine the substituent distribution of acetyl groups in acetylated methylcellulose samples with reference to that of the model triacetylcellulose. In addition, the absolute degree of substitution at the C_2 position can be obtained from the peak area ratio of the corresponding C_1 carbon signal, which is sensitive to the type of substituent at the C_2 position. Thus the methoxy group distribution of the parent methyl cellulose sample can be determined by subtracting the acetyl group distribution of the acetylated methylcellulose sample. The total degree of substitution obtained by summing up the values of the individual carbons was compared to that obtained by chemical analysis and showed good agreement, as shown in Table III. A slightly lower calculated degree of substitution was observed in the high methoxy content samples as measured by NMR compared to that obtained by chemical analysis. This is ascribed to the poor solubility in DMSO of the acetylated methylcellulose sample with high methoxy content, excluding the contribution of this particular portion of the sample in the NMR measurement.

The relationship between the total degree of substitution and the individual degree of substitution of the substitution position for the methylcellulose sample of various degrees of substitution is listed in Figure 6. The reactivity series of the hydroxyl groups on an anhydroglucose ring unit, namely, $C_2 > C_6 > C_3$,[14] is found to hold also in the present case.

(2) ^{13}C NMR Assignment of Methoxy Signals Based on GLC Analysis. Although the methyl group distribution of methylcellulose of varying degree of substitution can be determined by analysis of the ^{13}C carbonyl region of the acetylated methylcellulose in DMSO at 100 °C, this technique cannot be applied to methylcellulose samples with relatively high (more than 2.0) methoxy content because of their low solubility in DMSO. On the other hand, acetylated methylcellulose is soluble in chloroform over the whole range of degrees of substitution and the methoxy methyl signal was found to be split into a triplet (58.3, 59.1, and 60.5 ppm) as mentioned before. However, the split signals were not directly assignable by comparison with

Table III
Distribution of Methyl Groups in Methylcellulose Samples

	total DS				indiv posit, GLC (NMR)			anhydroglucose unit,[c] GLC (TLC)			
sample[a]	CA[b]	GLC	NMR	TLC	2	3	6	tri	di	mono	none
1	0.45	0.48	0.48	0.64	0.24	0.05	0.19	0.9	6.9	30.6	61.6
					(0.25)	(0.05)	(0.18)	(0.7)	(11.9)	(37.6)	(49.8)
2	0.95	0.91	1.04	1.06	0.40	0.15	0.36	6.1	17.1	38.1	38.7
					(0.40)	(0.24)	(0.40)	(8.7)	(21.2)	(37.6)	(32.5)
3	1.20	1.18	1.17	1.10	0.51	0.24	0.43	9.4	25.6	37.3	27.7
					(0.54)	(0.23)	(0.40)	(8.0)	(23.8)	(38.3)	(29.9)
4	1.48	1.50	1.45	1.36	0.66	0.31	0.53	15.0	34.6	36.0	14.4
					(0.65)	(0.25)	(0.55)	(11.8)	(30.9)	(39.2)	(18.1)
5	1.74	1.76	1.65	1.75	0.78	0.39	0.59	21.4	40.2	30.9	7.5
					(0.75)	(0.35)	(0.55)	(25.1)	(35.7)	(28.2)	(11.0)
6	2.02	1.94	1.88	1.97	0.76	0.45	0.73	29.8	39.3	25.6	5.3
					(0.82)	(0.38)	(0.68)	(34.5)	(34.3)	(24.6)	(6.6)
7	2.35	2.32	2.12	2.25	0.84	0.66	0.82	49.2	35.6	11.9	3.3
					(0.87)	(0.50)	(0.75)	(43.3)	(38.7)	(18.0)	(nd)
8	2.89	2.89		2.86	0.98	0.98	0.93	88.5	11.5	nd[d]	nd
					(—)	(—)	(—)	(85.6)	(14.4)	(nd)	(nd)

[a] See also Table I. [b] Chemical analysis. [c] Fractions in percent. [d] Not detected.

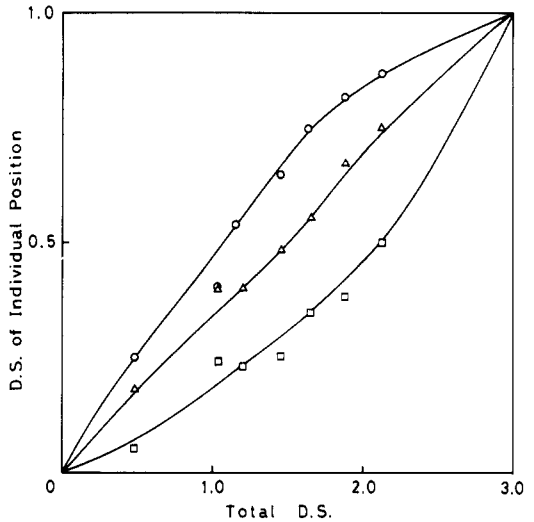

Figure 6. Degree of substitution of (○) C_2, (□) C_3, and (△) C_6 positions in the anhydroglucose unit of a series of methylcellulose samples.

the model trimethylcellulose, where methoxy methyl signal are present at 59.1, 60.3, and 60.5 ppm, respectively.

Nevertheless, as shown in Figure 7, the intensity of each peak of the triplet methoxy methyl signals of acetylated methylcellulose samples changed with the methoxy content of the sample; i.e., an increase of the signal at 58.3 ppm along with a decrease of that at 59.1 ppm was visible with a decrease of the methoxy content. Thus it is believed that the chemical shifts of these three peaks are not only a function of substitution position but also are influenced by the type of the substituent at another substitution position.

The assignment of methoxy methyl triplet signals observed in $CDCl_3$ at 30 °C was then attempted with the help of GLC analysis, where methylcellulose samples were hydrolyzed quantitiatively to the monomeric glucose unit and analyzed, in order to provide the substituent distribution on the individual anhydroglucose unit.[15] The results thus obtained for a series of methylcellulose samples are summarized in Table II. The total degrees of substitution calculated from the GLC data listed in Table II are collected in Table III together with those obtained by chemical analysis, TLC analysis, and NMR analysis, respectively. The total degree of substitution and the degree of substitution of the individual 2-, 3-, and 6-positions were found to agree well with each other as determined by a

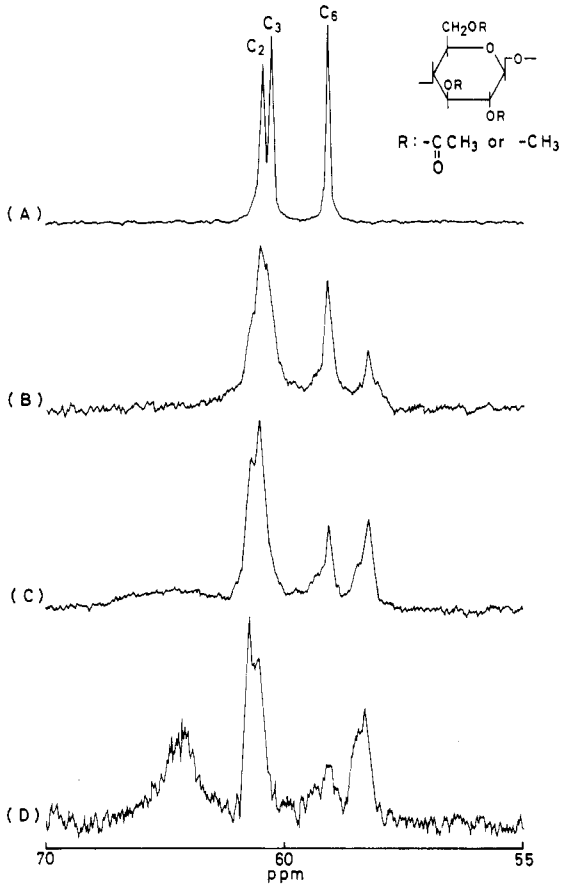

Figure 7. ^{13}C NMR methoxy methyl region spectra of acetylated methylcellulose samples in $CDCl_3$ at 30 °C (DS of methyl substituent: (A) 2.89; (B) 2.35; (C) 1.74; (D) 0.95).

number of analytical techniques.

By taking into account the GLC results and the NMR results on the model trimethylcellulose sample, we have arrived at the assignments shown in Figure 8, where, for example, $C_{2(3)}$ represents the signal of the methoxy methyl signal in the C_2 position with the methoxy group as the substituent in the C_3 position and with the acetoxy group in the C_6 position. This assignment is based on the assumption that the substituents in the 3- and 6-positions influence each other to cause the change of the chemical shift of methoxy methyl signal, while that at the 2-position does little. Thus, the methoxy methyl signals at 3- and 6-positions were considered to shift toward higher magnetic

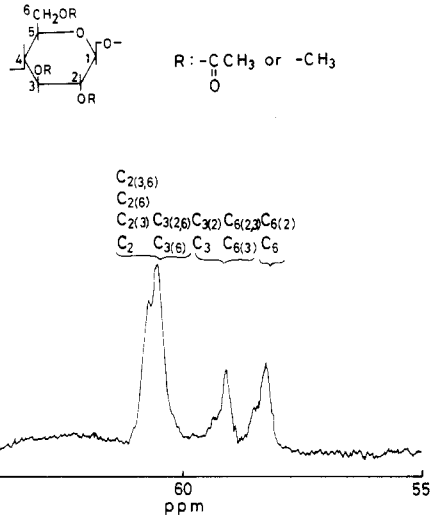

Figure 8. Proposed methoxy methyl peak assignment of acetylated methylcellulose in $CDCl_3$ at 30 °C (sample 5 in Table I, methoxy substitution position in parentheses).

Table IV
Observed and Calculated Peak Area Ratios of Methoxy Methyl Signals of Acetylated Methylcellulose Samples[a]

	obsd ratios			calcd ratios		
sample[b]	I	II	III	I	II	III
1	35	10	55	37	10	53
2	27	17	56	31	16	53
3	25	17	58	26	20	54
4	27	19	58	23	20	57
5	20	20	60	19	22	59
6	19	23	58	20	23	57
7	13	28	59	12	28	60

[a] I, II, and III correspond to signals at 58.3, 59.1, and 60.5 ppm, respectively. Fractions in percent. See also Figure 8. [b] See also Table I.

field by the change of the substituent on 6- and 3-position, respectively, from methoxy to acetyl. The proposed assignment was examined by comparing the calculated peak area ratios based on the substituent distribution results by GLC to those experimentally observed by NMR. The calculated and observed peak area ratios were found to agree satisfactorily, as shown in Table IV, strongly supporting the present assignment.

In conclusion, the present NMR technique using acetylated derivatives of cellulose ethers has proved to be a convenient and reliable method to determine the substituent distribution of cellulose derivatives. The further applications of the present technique to a series of other cellulose derivatives are now under way in our laboratory.

Registry No. Methylcellulose, 9004-67-5; methyl celluloseacetate, 51065-95-3.

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Analysis of ^{13}C NMR of Polybutadiene by Means of Low Molecular Weight Model Compounds

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ABSTRACT: The aliphatic carbon signals of polybutadiene are assigned in terms of diad or triad sequences of cis-1,4, trans-1,4, and 1,2 units, by using model compounds corresponding to monad and diad sequences of each isomeric structure. Carbon atoms between a 1,2–1,2 linkage and a 1,4 unit showed split signals, which were assigned to the tacticity of the 1,2 diad. The sequence distributions of cis-1,4, trans-1,4, and 1,2 units were determined by using relative intensities of methylene carbon signals. Random distribution of these isomeric units was observed in polybutadienes prepared with *n*-BuLi, *n*-BuLi/Et_2O, $CoBr_2$·[$P(Ph)_3$]/Al(*i*-Bu)$_3$·H_2O, and radical catalysts.

Introduction

Butadiene is polymerized to yield three isomeric units; cis-1,4, trans-1,4, and 1,2 units. It is well-known that the physical properties of polybutadiene are governed by the amount and the sequence distribution of these isomeric units. The amounts of the isomeric units can be determined by infrared and ^1H NMR spectroscopies. The sequence distribution of cis-1,4 and trans-1,4 units can be determined by olefinic and aliphatic proton[1-4] or ^{13}C NMR measurement of the olefinic region for 1,4-polybutadiene.[5-7]

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