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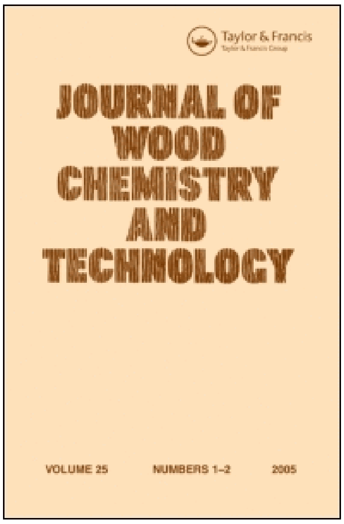

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Miyagi, Yoshifumi , Shiraishi, Nobuo , Yokota, Tokuo , Yamashita, Shigeko and Hayashi, Yoshiyuki(1983) 'Preparation and Thermal Properties of Acetates Derived From Cellulose Dissolved in Dmso-Pf', Journal of Wood Chemistry and Technology, 3: 1, 59 — 78

To link to this Article: DOI: 10.1080/02773818308085151

URL: http://dx.doi.org/10.1080/02773818308085151

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 3(1), 59-78 (1983)

PREPARATION AND THERMAL PROPERTIES OF ACETATES DERIVED FROM CELLULOSE DISSOLVED IN DMSO-PF

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ABSTRACT

Homogeneous acetylation of cellulose dissolved in the dimethyl sulfoxide(DMSO)/paraformaldehyde(PF) system was investigated. Characterization of the acetylated products was performed to evaluate the dissolution mechanism. The dissolution reactions are reasonably divided into three steps: (1)immediately after the dissolution, initial methylolation of cellulose; (2)further methylolation to form oligo-oxymethylene side chains on the cellulose backbone; (3)demethylolation, that is, the break down of the side chain by prolonged heating. The possible methylolation reaction sites are all hydroxyls of the anhydrous glucose unit while the C-6 position is most reactive. Manipulation of the side chain lengths by control of the dissolution conditions makes it possible to prepare acetates with different thermal properties: Tg varied 35°-102.5°C and Tm 65°

0277-3813/83/0301-0059$3.50/0

-122.5°C, depending upon the side chain length. Triethylamine(TEA) was prefered to pyridine, as a promotor of acetylation, in order to understand the dissolution mechanism.

INTRODUCTION

Over the last ten years, there has been increasing interest in the use of organic solvents for dissolving cellulose. For example, cellulose can be dissolved in a dimethylformamide solution of dinitrogen tetroxide, as well as a dimethyl sulfoxide(DMSO) solution of a mixture of sulfur dioxide and amines. More recently, in 1976, Johnson and coworkers[1] reported that cellulose is also soluble in DMSO containing less than 1 % of dissolved paraformaldehyde (PF). The mechanism by which cellulose dissolves in the DMSO/PF mixture was shown to involve the formation of methylol cellulose, which is stabilized through hydrogen-bonding with DMSO in the solution[1]. First the C-6 hydroxyl group of the anhydrous glucose ring of cellulose was thought to be the only methylolation site, but it was later reported that considerable substitution occurs also at the C-2 and C-3 secondary hydroxyl groups depending on the conditions of the dissolution[2,4,5]. It has also been tentatively suggested that cellulose is dissolved as monomethylol cellulose in the solvent[1-3], but it has been proved by more recent studies that cellulose is dissolved as cellulose hydroxy oligo-oxymethylene ether[4-7]. The extent of the substitution at each hydroxyl group and the length of the oligo-oxymethylene chains attached to the cellulose backbone are dependent on the dissolution conditions[4-7].

In order to clarify the substituted positions and the side chain lengths in the methylol cellulose with regard to the dissolution conditions, chemical stabilization of the methylol cellulose through acetalation of its hemiacetal unit is desirable. By converting the methylol cellulose to such stable substances, it became easier to analyze the compounds successfully.

Homogeneous silylation of the methylol cellulose in the DMSO/PF solvent system was investigated in our previous experiment[7].

The silylation reaction was found to proceed at a rate fast enough to prevent altering the hemiacetal structure which had been formed in the methylolation of cellulose. However, the NMR spectra of the products revealed relatively limited information on the substituted positions and the side chain lengths, though they were carefully interpreted[7].

Homogeneous acetylation of the methylol cellulose in the DMSO/PF solvent system proceeds at a slower rate than that of silylation. This is an unfavorable factor, because it is possible that some changes in the chemical structures of the dissolved cellulose would occur. However, the acetylation was effectively utilized in analyzing the chemical structures of cellulosic polymer by ^{1}H-NMR[4,5]. Protons of methylene groups adjacent to the acetyl groups resonate at about 0.42 ppm lower magnetic field than those of the inner methylene groups of the side chain, making it possible to determine the average length of the side chains. Furthermore, ^{13}C-NMR spectral analyses of the acetylated products yield much more information concerning the substituted position of the oligo-oxymethylene side chains[6,7].

The present paper describes the relation between the dissolution conditions of cellulose and the chemical structures of the resulting products. Particularly, the substituted positions and the side chain lengths formed in the polymer are examined with respect to the dissolution conditions. It also reports thermal properties of a series of (cellulose oligo-oxymethylene ether) triacetates having different lengths of the side chains.

EXPERIMENTAL

Materials

The cellulose used was Whatman cellulose powder CF-11. Two kinds of paraformaldehyde for electron microscopy (98 % content): from Nakarai Chemicals (specially prepared reagent, EMS-80) and

Taab Laboratories were used. The former was a powdery substance and the latter has a granulated form. The latter decomposes more readily upon heating than the other. Dimethyl sulfoxide (DMSO) used as solvent, acetic anhydride and pyridine or triethylamine (TEA) used as acetylating agents were all guaranteed grade. Triethylenediamine (DABCO) was used as a catalyst for methylolation of cellulose in DMSO/PF. Methyl alcohol precooled deeply with liquid nitrogen was used as a precipitant.

Preparation of Cellulose Solution

The method for the preparation of the cellulose solution used in this experiment is essentially similar to that reported by Johnson and coworkers[1]. However, in order to obtain information on the process of the dissolution, factors such as temperature-time schedule for the dissolution, the types and the amounts of paraformaldehyde, and others including the use of the catalyst for methylolation were examined according to experimental requirements.

The standard procedure is as follows: dried cellulose (1 g) and PF powder (2 g) were well dispersed in DMSO (25 ml) at room temperature. The mixture was then heated under rapid stirring according to the designed temperature-time schedule. Examples of varied conditions of the dissolution are listed in Table 1. In some experiments less than 2 g of PF was used.

Acetylation

To the cellulose solution prepared and cooled to room temperature just before the acetylation, pyridine (12.5 ml) and acetic anhydride (17.5 ml) were added dropwise through a pressure compensated funnel under continuous stirring. As a part of the experiments triethylamine (TEA) (3 ml) and a mixture of acetic anhydride (6 ml) and TEA (3 ml) were added successively likewise, while the temperature of the resulting mixture was kept under 25 °C with constant stirring. After the addition of the acetylating agents the mixture was allowed to stand at room temperature for 96 hrs in the former acetylating process with pyridine and 24 hrs in the

TABLE 1 Effects of cellulose dissolution and acetylation conditions on the molecular structures (i.e. side chain length) of resulting products.

Sample	PF	Cond. for Dissolution		Acetylation Medium^a	MS	I/E
(CAcOM)		PF/Cell. (g/g)	Temperature Program			
21,(I)	Taab	0.7/1.0	97-106°C/17min.	TEA	2.2	0.1
18,(I)	Taab	0.74/1.0	97-108°C/32min.	Py	3.0	0.6
19,(I)	Taab	1.0/1.0	97-106°C/11min. 106 ± 1°C/13min.	TEA	3.7	0.4
22,(I)	Taab	1.6/1.0	96-105°C/11min.	TEA	3.6	0.5
11,(II)	EMS-80	2.0/1.0	97-115°C/30min. 115-116°C/60min	Py	5.5	1.2
14,(II)	Taab	2.0/1.0	110-114°C/ 3min. 114 ± 1°C/19min.	Py	7.0	1.6
14,(II)	Taab	2.0/1.0	"	TEA	5.1	1.5
26,(II)	EMS-80	2.0/1.0	83-120°C/32min. 120-122°C/14min.	Py	5.3	1.4
4,(II)	EMS-80	2.0/1.0	98-120°C/20min. 123±0.5°C/ 8min.	Py	6.1	1.6
20,(III)	EMS-80	2.0/1.0	99-130°C/28min. 130±0.5°C/20min.	TEA	1.9	0.4
5,(III)	EMS-80	2.0/1.0	86-121°C/30min. 121-130°C/33min. 130±0.5°C/27min.	Py	2.5	0.6
15,(III)	EMS-80	2.0/1.0	83-120°C/23min. 120-130°C/10min. 130±0.5°C/27min.	Py	1.6	0.2
15,(III)	EMS-80	2.0/1.0	"	TEA	1.2	0.0
24,(III)	EMS-80	2.0/1.0	84-122°C/28min. 122-130°C/10min. 130 ± 1°C/73min.	Py	1.3	0.2

a) TEA: triethylamine, Py: pyridine.

Acetylation: 25 °C, 96 hrs(with Py) or 24 hrs(with TEA).

latter case with TEA. The rather long reaction time was employed to ensure peracetylation. The reaction mixture was then poured into an excess amount of methyl alcohol deeply precooled with liquid nitrogen, and the precipitates were filtered or centrifuged at ca. 10,000 rpm. The crude product was purified by repeated dissolution-and-precipitation technique.

Analyses and Characterization

The purity of the acetylated products obtained were examined by gel permeation chromatography using a SHIMADZU GPC 700. Tetrahydrofuran was used as the solvent at 40°-50°C, the flow rate was ca. 1 ml/min, using SG-1 through -6 columns which cover the molecular weight of polymers from 350 through 3×10^6 in permeability. An R-22 HITACHI high resolution NMR spectrometer (90 MHz) and a JEOL JNM-FX 100 Fourier Transform NMR spectrometer (25.05 MHz) were used for ^{1}H-NMR and ^{13}C-NMR respectively. NMR spectra were run using chloroform-d_1 as the solvent containing tetramethylsilane as the internal reference. Three and 10 % solutions of each sample were prepared for ^{1}H-NMR and ^{13}C-NMR measurements respectively. For the ^{13}C-NMR measurements, all protons were decoupled. Chemical shifts are given in δ-values. The ^{1}H-NMR measurements in the presence of a lanthanide shift reagent were undertaken using a 3 % solution of the (cellulose oligo-oxymethylene ether) triacetate containing up to 0.1 M of $Eu(dpm)_3$ in chloroform-d_1. A HITACHI EPI-G3 grating double beam spectrometer was used for IR spectroscopic measurements. The KBr disk technique was employed.

Thermal Softening and Melting Temperature Measurements

Thermal softening and melting of the acetylated cellulose derivatives were observed as the collapse of column powder under a constant load of 3 Kg/cm^2 in a heated glass capillary tube using a SHINKU RIKO's thermomechanical analyzer TM 1500. The measurements were conducted over the temperature range from 30° to 350°C at a programmed heating rate of 1°C/min.

RESULTS AND DISCUSSION

Purity

Neither GPC curves nor IR spectra for the acetylated products prepared and purified as described in the experimental section showed significant contamination by any low molecular weight substances. In ^{1}H-NMR spectra (Fig. 1, upper half) no signals attributable to the solvents, reagents, or by-products were detected, either. Thus the repeated precipitation technique employed utiliz-

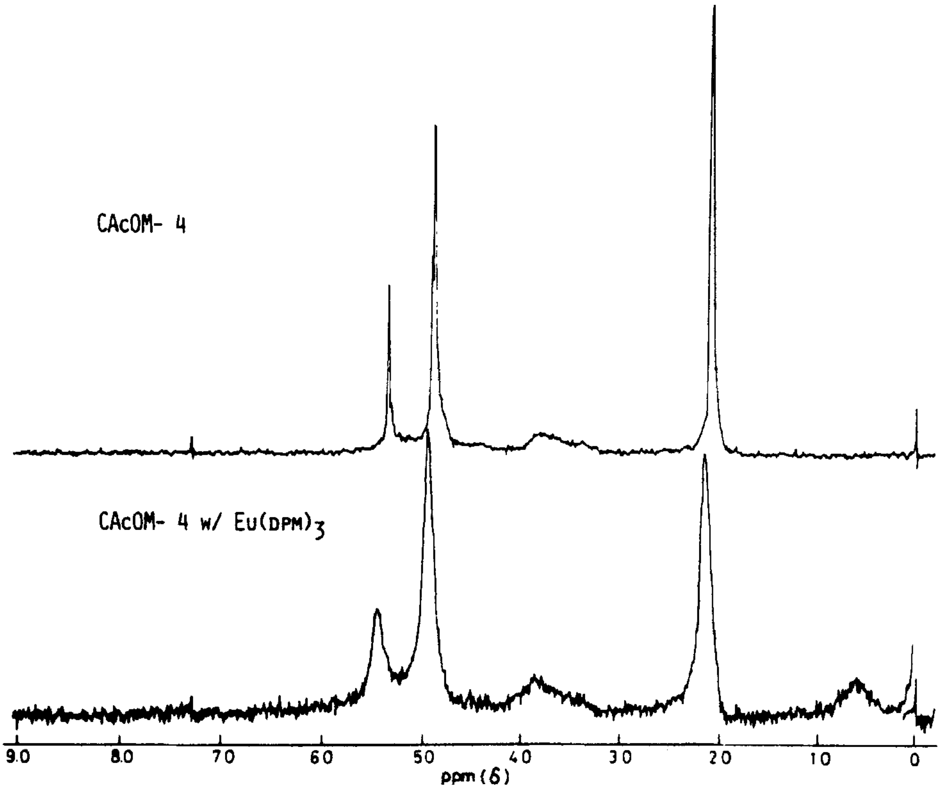

FIGURE 1 Effects of Eu(dpm)$_3$ on two different methylene dioxy proton peaks of (cellulose oligo-oxymethylene ether) triacetate, CAcOM.

ing deeply-cooled methyl alcohol as the precipitant was a suitable method for the separation and purification of (cellulose oligo-oxymethylene ether) triacetate, CAcOM.

The IR spectra have been interpreted previously[2] which reveals that the acetylation has proceeded satisfactorily.

Oxidation of Cellulose by DMSO/Acetic Anhydride

Seymour and Johnson[9] have discussed the possible oxidation of cellulose when acetic anhydride was used as an acylating agent in the DMSO/PF system. It was postulated that, in the acetylation system, dimethyl acetoxysulfonium acetate is formed, and the dimethyl acetoxysulfonium ions are believed to mediate the acetylation and the oxidation of the cellulose to form cellulose acetates, 2,3-diketo-cellulosics, and their corresponding hydrates. Oxidized cellulosics, in line with the discussion above, were shown to contribute toward the color change (dark amber color) in their products obtained in the DMSO/PF system[9].

It is necessary, however, to take into account the roles of pyridine added in the system. Chemical species subject to the attack by acetyl carbonium ion ($\mathrm{CH_3\overset{+}{C}{=}O}$) or acetic anhydride in addition to cellulose, are DMSO and pyridine, if the latter is added to the cellulose solution as in the Seymour and Johnson's[9] and other experiments[2,4-6,8]. In this case, acetylpyridinium intermediate is more easily formed than acetoxydimethylsulfonium ion, because the nucleophilicity and basicity of the lone electron pair of pyridine is stronger than that of DMSO by several orders. Furthermore, it should be pointed out that the rate of acetylation of cellulose with acetylpyridinium salt is substantially higher than that of the reaction between cellulose and the acetoxydimethylsulfonium salt.

It was shown, on the other hand, that sterically less hindered hydroxyl groups (equatorial) were not oxidized smoothly with DMSO/acetic anhydride forming actually a small amount of carbonyls, oxidized products, (for example, 13 % in the case of an alkaloid) and a large amount of the corresponding methylthiomethoxy derivatives (56 % in the same case), while the oxidation proceeded slowly but smoothly with high yield at sterically hindered hydroxyl groups (axial)[13]. Cellulose has sterically less hindered equatorial hydroxyl groups. Though the reaction of cellulose with the methylthiomethoxy groups is more probable than its oxidation, elemental analyses of our acetylated products revealed no sulfur content indicating that methylthiomethoxy functions were not incorporated into these products.

From these discussions and the finding, it is concluded that the oxidation of cellulose, that is, the formation of 2,3-diketo cellulose[9], does not take place very readily during the acetylation of cellulose by pyridine and acetic anhydride in the DMSO/PF system.

When triethylamine (TEA) was used instead of pyridine, as will be discussed later, the acetylation was almost completed within 6 hrs at 25 °C and yielded products without the dark amber color. Thus it is a reasonable explanation that the change in color of the products obtained by acetylation in the presence of pyridine is due to contamination of the acetyl pyridinium derivatives in the acetylated products.

Lengths of Side Chain

Experiments on acetylation[4,5,6] and trimethylsilylation[7] revealed that cellulose is dissolved in the DMSO/PF system as methylol cellulose with oxymethylene units formed from formaldehyde which compose side chains of lengths or molar substitution (MS) controllable by dissolution conditions.

Figure 1 shows further evidence for the formation of oligo-oximethylene side chains. The acetyl methyl protons resonate at around 2.1 ppm and the cellulose ring protons are observed as a broad band occurring between about 3.2-5.6 ppm[4,5,7]. The carbonyl of the acetyl group deshields the neighboring protons such that the methylene dioxy protons at the end of the side chain give a peak near 5.3 ppm and the inner methylene dioxy protons not deshielded resonate at about 4.9 ppm[4]. These methylene dioxy proton peaks and some of the cellulose ring proton peaks are overlapping. Intensities of the two types of the methylene proton peaks were utilized to evaluate the MS of the methylol cellulose[4,5]. To obtain the spectrum of the lower part of Fig. 1, a paramagnetic shift reagent, tris(dipivaloylmethanato)europium ($Eu(dpm)_3$), was added to the chloroform $-d_1$ solution of the CAcOM sample. This reagent strongly coordinates with the oxygen of carbonyl group when compared to the ether oxygen. Hence comparatively greater downfield shift, about 19 Hz, is observed for the methylene dioxy protons next to the carbonyl groups (5.3 ppm). And a smaller downfield shift, about 11 Hz, is observed for the inner methylene dioxy protons (4.9 ppm). This clearly indicates that the side chain consists of two different types of protons, one near to and another distant from the carbonyl group.

In order to obtain more confirming information on the ^1H-NMR results, ethyl and isopropyl alcohol were treated under the cellulose dissolution conditions in the DMSO/PF system. Figure 2 shows

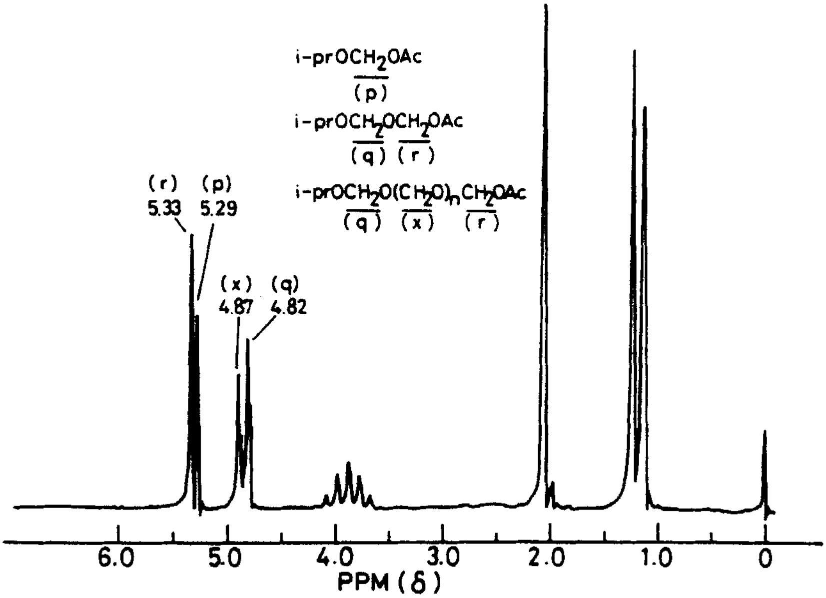

FIGURE 2 ^1H-NMR spectrum of mixture of acetates of (monoisopropyl ethers of oligo-oxymethylene glycols).

the ^{1}H-NMR spectrum of the methylolated isopropyl alcohol followed by acetylation. The sample was found to be a mixture of acetylated products of methylolated isopropyl alcohol with different numbers of oxymethylene unit ranging mainly from one to three. The acetylated product with one oxymethylene unit gives a single peak of methylene dioxy protons at 5.29 ppm (p) as a result of the inductive effect of the carbonyl. With two units, the methylene dioxy protons next to the acetyl function resonate at 5.33 ppm (r) likewise, and the other at 4.82 ppm (q) unaffected by the carbonyl. With three or more, trimeric side chain or longer, the protons at the end of the side chain resonate at 5.33 ppm (r), those in the middle of the chain at 4.87 ppm (x), and those attached to the isopropyl alcohol moiety at 4.82 ppm (q). For ethyl alcohol, similar results were obtained. The assignment of the chemical shifts was based on those of the acetylated monoethyl or monoisopropyl ethers of polyoxymethylene glycol up to the tetramers isolated by fractional distillation[14].

We were then interested in preparing CAcOM samples with different side chain lengths. Acetylated methylol cellulose, dissolution type I (designated as CAcOM-sample number, (I)) was prepared by acetylation of the methylol cellulose obtained immediately after the dissolution of the cellulose (PF/cellulose: 0.7-1.6/1 by weight). In this case, PF with a granulated form (Taab) was used so as to make it possible to ascertain the completion of dissolution immediately after it was accomplished. The dissolution of cellulose was completed by heating up to 108 °C. Acetylated methylol cellulose, dissolution type II (CAcOM-sample number, (II)) was prepared through acetylation of the methylol cellulose solution obtained by further heating of the dissolved cellulose up to the temperature of 123 °C, in the presence of excess paraformaldehyde (PF/cellulose: 2/1 by weight at the start of the reaction), and acetylated methylol cellulose, dissolution type III (CAcOM-sample number, (III)) was obtained by acetylation of the methylol cellulose solution which has been submitted to prolonged heating at 130 °C or higher temperature. In these two cases, PF of both the powdery and the granulated forms could be used.

Typical ^{1}H-NMR spectra of these three types are shown in Fig. 3. The integral of the spectra allowed calculation of the length of the polyoxymethylene side chain[4,5]. The portion of the integral due to the O-acetyl substituent was set equal to nine protons[4,5]. The seven ring protons of the anhydroglucose unit were then subtracted from the remaining integral which left the number of protons per anhydroglucose unit contributed by the methylol substituents[5]. The MS is equal to one-half the value of the methylol protons per anhydroglucose unit[5]. Furthermore, if it can be assumed that the signal at δ5.3 ppm is due only to protons of methylene dioxy at the end of the side chain, the number of protons of the end methylene dioxy groups (E) and that of other inner methylene protons (I) of the polyoxymethylene chain are separately obtainable. The I/E values, together with the MS values, are shown in Table 1, related with dissolution and acetylation conditions. These values are good indications of the degree of substitution and the length of the side chain.

From the table and Fig. 3, it was learned: that three types of CAcOM (I through III) different in the length of the side chain can be prepared by control of the cellulose dissolution conditions; that CAcOM-I and -III have shorter side chains or lower MS compared with CAcOM-II; that the cellulose solutions are stable during the acetylation reaction following the dissolution; and that pyridine can be replaced by TEA.

For the last point above further comments can be made. The use of TEA was found to be more favorable over pyridine. A CAcOM-III sample of a low I/E value was chosen to compare the effects of these two basic promotors on the acetylation. The ^{1}H-NMR spectra of the two differently acetylated products are shown in Fig. 4. The acetylation time of 96 hrs was employed for the pyridine/acetic anhydride combination and 24 hrs for the TEA/acetic anhydride combination. Two points to be noted on the acetylation are: (I) shorter reaction

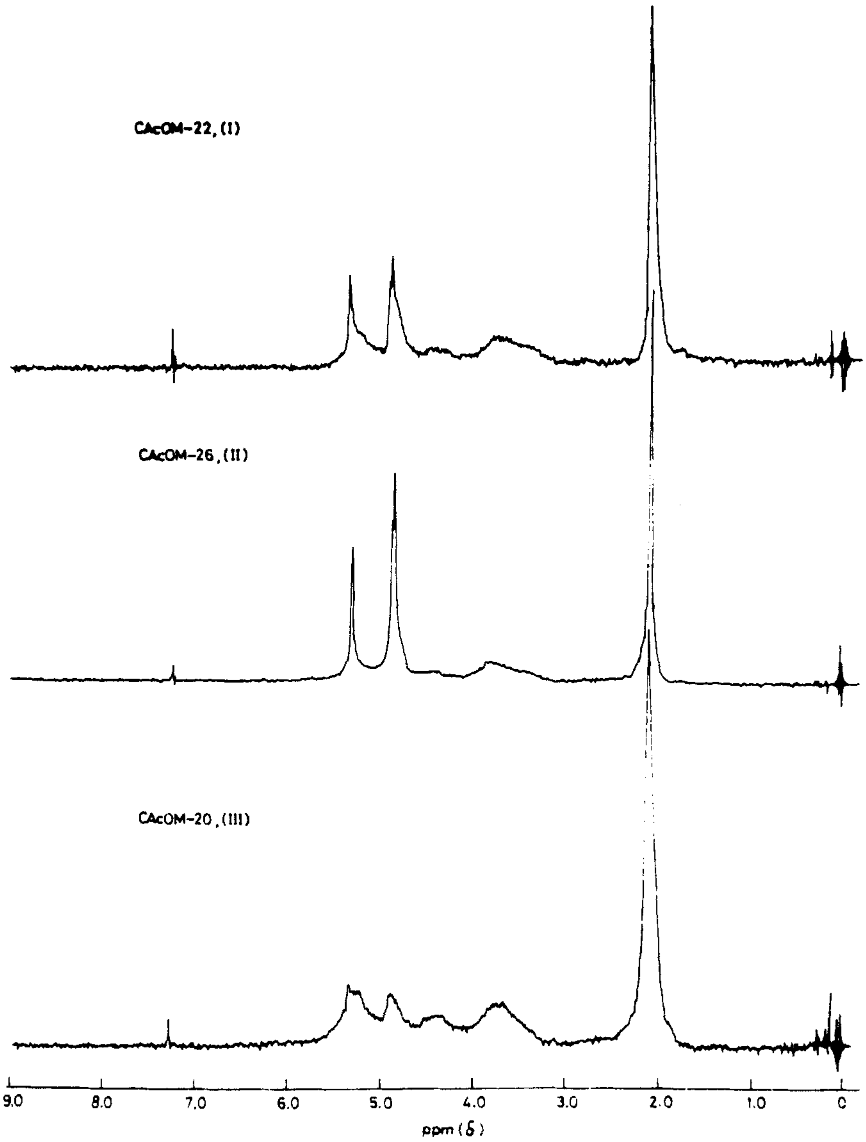

FIGURE 3 ^{1}H-NMR spectra of three types of (cellulose oligo-oxymethylene ether) triacetate, CAcOM-(I), -(II), and -(III).

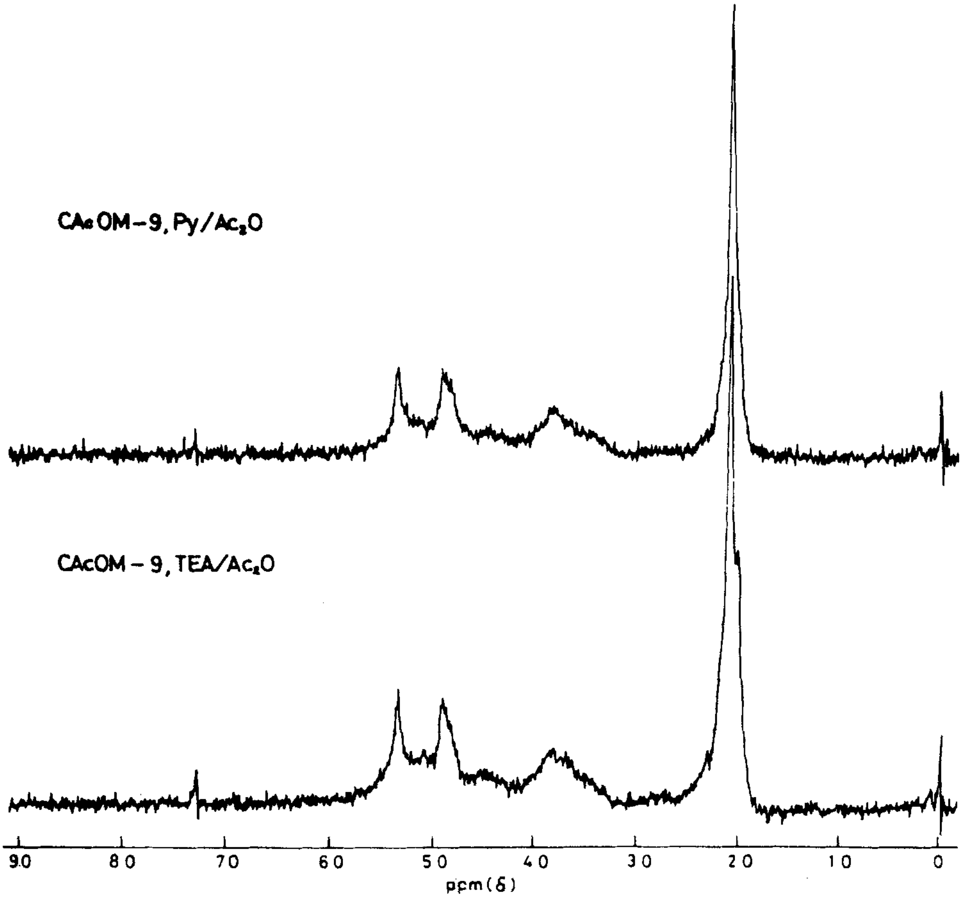

FIGURE 4 Comparison of ^{1}H-NMR spectra of (cellulose oligo-oxymethylene ether) triacetates, CAcOM, acetylated by pyridine/acetic anhydride and triethylamine/acetic anhydride.

times can be employed to obtain highly acetylated products with TEA; and (2) the products obtained with TEA do not undergo any color change. The shape of the acetyl methyl proton peaks suggests that the original oxymethylene unit distribution along the cellulose back bone, obtained just after dissolution, can be preserved for shorter reaction duration, that is, when TEA is used in the acetylation system.

It is well-known that autoxidation or Cannizzaro reaction of formaldehyde gives formic acid. DMSO, when heated in air, gives a trace amount of strong acid, probably CH_3SO_3H. The demethylolation leading to the CAcOM-III is, however, not mainly due to acids formed in situ but probably due to thermal reaction, since it was observed even with a basic catalyst, triethylene diamine (DABCO) in DMSO/PF system. DABCO is thought to assist base-catalysed nucleophilic addition of cellulose to formaldehyde. Hence, when DABCO was used as a catalyst, the dissolution of cellulose can be achieved within a short period at about 110 °C, substantially lower than without the catalyst.

Methylolation Sites

^{13}C-NMR spectra of CAcOM-I through -III and cellulose triacetate are shown in Fig. 5. By comparison of the CAcOMs with the cellulose triacetate, peaks in the area of 80.8–98.9 ppm are attributed to the oligo-oxymethylene side chain carbons. This was confirmed by ^{13}C-NMR analyses of acetylated products of methylolated ethyl and isopropyl alcohol[14]. That is, in the case of acetate of (monoethyl ether of polyoxymethylene glycols), the acetylated product with one oxymethylene unit gives a single peak of methylene dioxy carbon at 89.8 ppm. With two units, the methylene dioxy carbon next to the acetyl group resonates at 85.6 ppm, and the other at 94.1 ppm unaffected by the carbonyl. With three or more, trimeric side chain or longer, the carbon at the end of the side chain resonates at 85.8 ppm, that in the middle of the chain at 90.5 ppm, and that attached to the ethyl alcohol moiety at 92.4 ppm[14].

On the other hand, at 62.1 ppm the carbons of the C-6 position which are not methylolated resonate, and C-2 and C-3 carbons at around 72.5 ppm. The C-1 carbon resonates at around 100 ppm. All three CAcOM samples exhibit new peaks due to downfield shifts of about 5 ppm for the C-6 (the new peak at 67.0 ppm) and C-3 and -2 (74.4 ppm) carbons compared with the triacetate. The downfield shift clearly demonstrates that the methylolation takes place at these positions, as the new lower magnetic field peaks are of the carbons

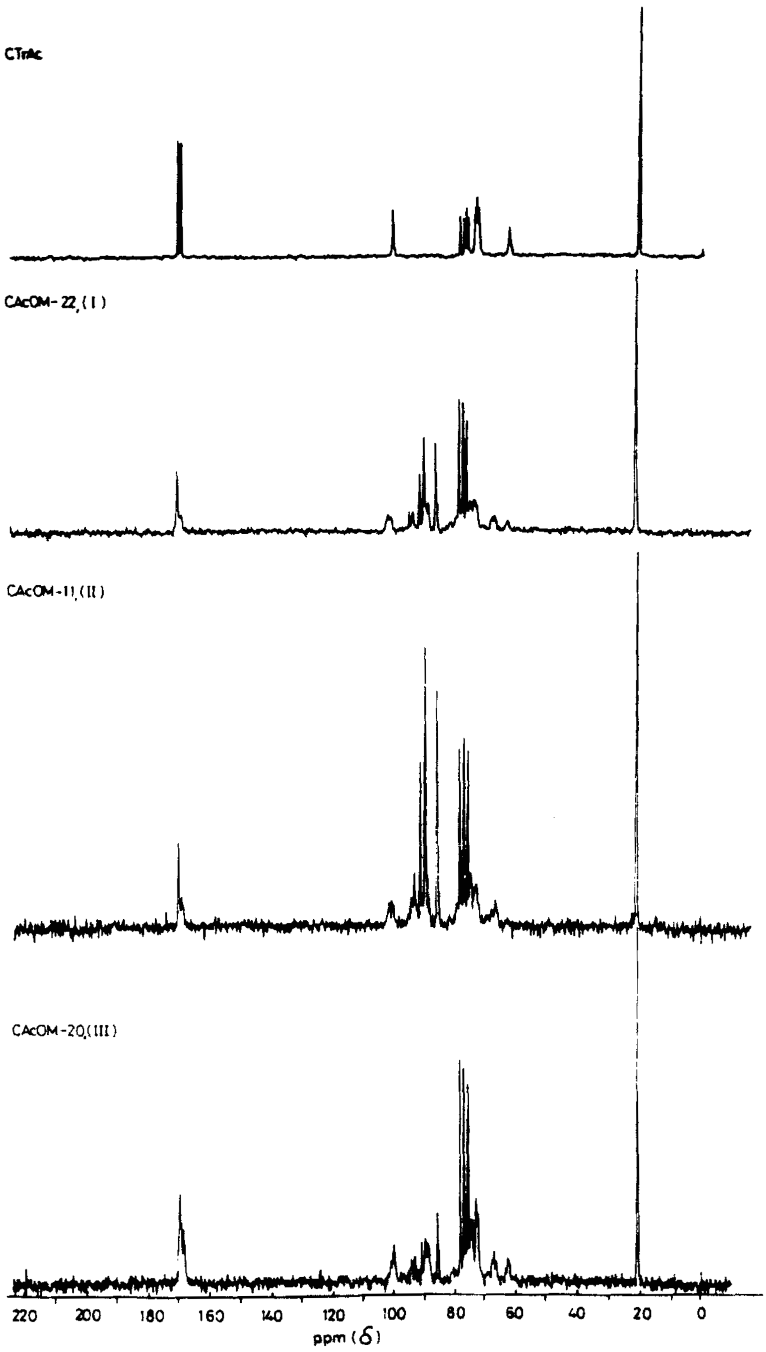

FIGURE 5 ^{13}C-NMR spectra of cellulose triacetate, CTrAc, and three different (cellulose oligo-oxymethylene ether) triacetates, CAcOM-(I), -(II), and -(III).

which form ether bonding with the acetoxy oligo-oxymethylene side chain. The shift from the original carbon peaks are in a good agreement with calculations based on the additivity rule. Further examinations reveal that only one peak at 67.0 ppm, a new peak, is observed for the C-6 carbon in the CAcOM-II sample, while both new peaks at around 74.4 ppm and the original at around 72.5 ppm are observed for the C-2 and -3 carbons. As for the CAcOM-III the situation is similar to that with the CAcOM-I which has the original and new peaks for all the C-6, -2, and -3 carbons.

These findings indicate: (1) that, for the dissolution type I, cellulose dissolves in the DMSO/PF system as partial methylolation takes place at all of C-6, -2, and -3 positions, while the C-6 is most reactive; (2) that, with the dissolution type II, unreacted hydroxyl groups are further reacted and especially the hydroxyl groups at almost all C-6 position are methylolated (as the side chain becomes longer as indicated by the ^{1}H-NMR spectra); and (3) that, with the dissolution type III, demethylolation proceeds to expose free hydroxyl groups at all of C-6, -2, and -3 positions, especially at C-6 position (as the side chain becomes shorter).

Thermal Properties

Acetylated products with I/E values (an indication of the side chain length) of 1.2 (CAcOM-II, (II)), 0.6 (CAcOM-5, (III)), and 0.0 (CAcOM-20, (III)) were chosen for thermal property analyses. Apparent melting points (Tm) and glass transition temperatures (Tg) were obtained and the thermomechanical curves are shown in Fig. 6. These temperatures were found to decrease tremendously by the introduction of the oligo-oxymethylene chain between the pyranose ring and the acetyl group. These temperatures become lower with an increase in the length of the side chain.

The relation between physical and thermal properties and the side chain length or introduced functional groups at the end of the side chain should be studied in detail. Some of them are under way and will be reported elsewhere.

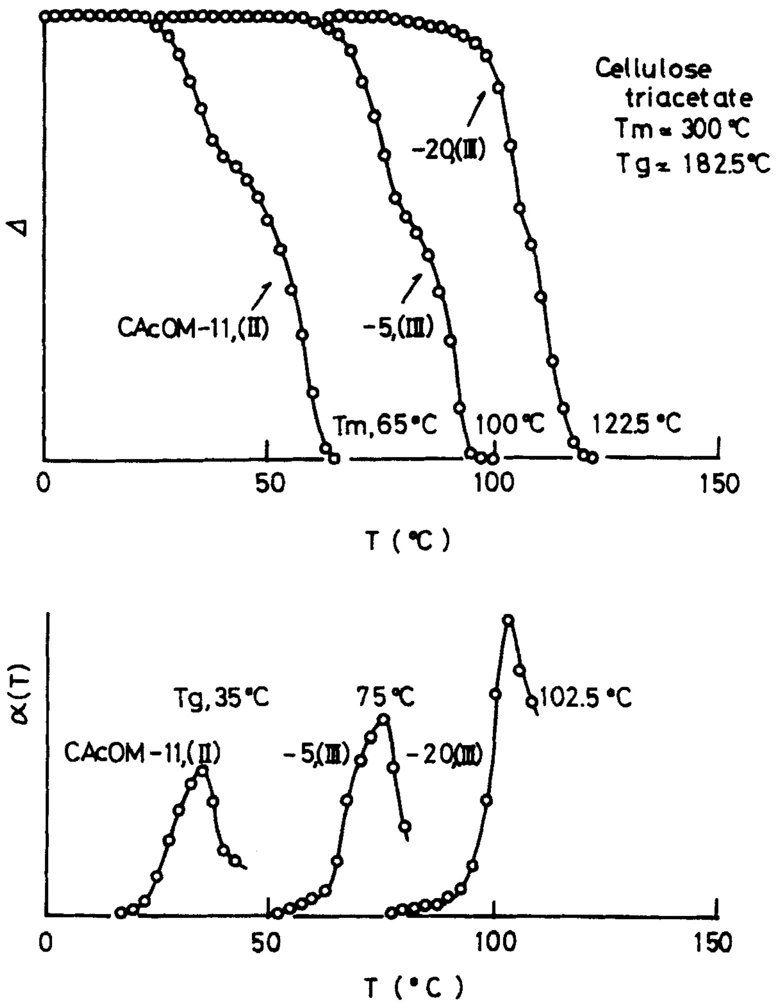

FIGURE 6 Thermomechanical behavior of (cellulose oligo-oxymethylene ether) triacetates with different I/E values of 1.2 (CAcOM -11, (II)), 0.6 (CAcOM-5,(II)), and 0.0 (CAcOM-20,(III)). Δ : deformation; $\alpha(T)$: rate of deformation at temperature T

ACKNOWLEDGEMENTS

The authors wish to thank Dr. T. Aoki, Kobe University and Miss F. Higuchi, Kyoto University for the thermal property and the ^{13}C -NMR measurements, respectively. Also, we thank Dr. D. C. Johnson, Weyerhaeuser Company for the critical reading of the manuscript. We are grateful to the Ministry of Education, Science, and Culture, Japan for Grant-in -Aid for Scientific Research.

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