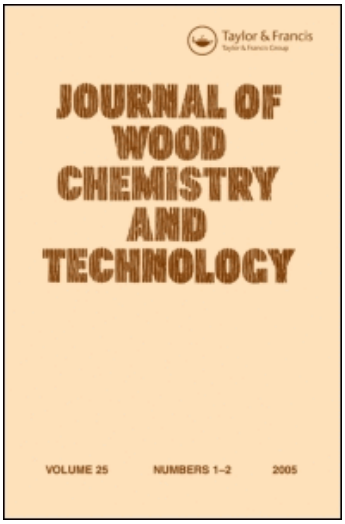

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Homogeneous Tritylation of Cellulose in A Sulfur Dioxide - Diethylamine - Dimethyl Sulfoxide Medium

Ikuo Hagiwara[a]; Nobuo Shiraishi[a]; Tokuo Yokota[a]; Misato Norimoto[b]; Yoshiyuki Hayashi[c]
[a] Department of Wood Science and Technology, Kyoto University, Sakyo-ku, Kyoto, Japan [b] Wood Research Institute, Kyoto University, Kyoto, Japan [c] Department of Dyeing, Kyoto Technical University, Sakyo-ku, Kyoto, Japan

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HOMOGENEOUS TRITYLATION OF CELLULOSE IN A SULFUR DIOXIDE - DIETHYLAMINE - DIMETHYL SULFOXIDE MEDIUM

Ikuo Hagiwara, Nobuo Shiraishi and Tokuo Yokota
Department of Wood Science and Technology, Kyoto University
Sakyo-ku, Kyoto 606, Japan

Misato Norimoto
Wood Research Institute, Kyoto University
Uji 611, Kyoto, Japan

Yoshiyuki Hayashi
Department of Dyeing, Kyoto Technical University
Sakyo-ku, Kyoto 606, Japan

ABSTRACT

The present investigation was undertaken to see if a practical method could be developed for homogeneous tritylation of cellulose in a non-aqueous solvent of cellulose. Our new procedure of tritylation of cellulose can easily be carried out under homogeneous conditions by dissolving cellulose in a sulfur dioxide(SO_2)-diethylamine (DEA)-dimethyl sulfoxide(DMSO) solvent system, one of the non-aqueous cellulose solvents, followed by addition of trityl chloride and pyridine. This new method can avoid the time consuming pretreatment for the decrystallization of cellulose which has been necessary in the traditional procedure and can lower the reaction temperature. IR spectra of the products indicated the formation of trityl cellulose. Measurements of dielectric properties of the products confirmed that trityl groups were selectively introduced at the primary hydroxyl groups in cellulose. This conclusion was also confirmed by a ^{1}H-NMR study in which the tritylated products was first acetylated, detritylated and then trideuterioacetylated and ^{1}H-NMR spectra were taken at each stage and examined comparatively.

INTRODUCTION

It is well known that triphenylmethylation (Tritylation) of cellulose is a useful method for selective protection of the primary hydroxyl groups in cellulose. More detailed studies of tritylation

have been carried out by several workers[1,2] since the first preparation of trityl cellulose by Helferich et al.[3] However, some problems remain to be solved with regard to starting materials and reaction conditions. Native cellulose such as cotton invariably gives insoluble products after tritylation. Thus, decrystallized cellulose has been required for the etherification. For example, decrystallized regenerated cellulose can be obtained when cellulose acetate is deacetylated with 15% aqueous ammonia at room temperature for 2-7 days. For tritylation of decrystallized cellulose, the reaction temperature of 100° C is usually adopted and the product with DS of 1.0 can be obtained after a reaction period of 15 or 4 hr., when 2.5 or 10 moles respectively, of trityl chloride per mole glucose unit are used. In addition, Hearon et al.[1] investigated the temperature dependence of the reaction and observed that it took 50 hr. at 80° C and 113 hr. at 68° C for completion. No reaction was observed at 40° C.

Over the last ten years, a number of non-aqueous cellulose solvents have been found. Their non-aqueous nature has permitted homogeneous reactions of cellulose with organic reagents[4,5].

In this study, we investigated the homogeneous tritylation of cellulose by using a sulfur dioxide(SO_2)-diethylamine(DEA)-dimethyl sulfoxide(DMSO) cellulose solvent as the reaction medium, and tried to establish an easier method for introducing the protective group into cellulose than the conventional one.

EXPERIMENTAL

General

Whatman cellulose powder CF-11 was used as the cellulose source. A HITACHI model EPI-G3 grating double beam spectrometer was used for IR spectrometry. The KBr disk technique was employed to prepare samples for IR spectra.

Dielectric properties of trityl cellulose (dried at 70° C in vacuo for 24 hr.) with various DS were examined on each trityl cellulose (150 mg) disk, 0.4 mm in thickness and 20 mm in diameter, shaped under a pressure of 760 kg/cm^2. An inductive-ratio-arm bridge (Ando Electric Co. Ltd., TR-10C) was employed as the measuring device and for the accurate determination of the dielectric properties a three-electrode arrangement was adopted. Dielectric loss factors

(ε'') were measured as a function of frequency over the range from 50 Hz to 1 MHz at -50° C under anhydrous conditions.

An R-22 HITACHI high resolution NMR spectrometer (90 MHz) was used for ^{1}H-NMR spectrometry. NMR spectra were run using chloroform -d_1 as the solvent and tetramethylsilane as an internal standard. Samples were examined as 10% solutions.

Preparation of Trityl Cellulose (1)

To a clear solution of cellulose (1.0 g) in DMSO (20 ml) containing the SO_2-DEA equimolar complex (4 moles per anhydroglucose unit of cellulose) was added a mixture of trityl chloride and pyridine (and/or dimethylformamide) with stirring at room temperature. In some experiments, the amount of SO_2-DEA complex was varied as described later. The mixture was kept at 50° C for a definite period (2.5 - 16 hr.) under continuous shaking. The tritylation reaction proceeded under homogeneous conditions. After the reaction, the solution was poured into an excess of methanol to precipitate trityl cellulose. The precipitate was filtered and again stirred in fresh methanol. This was repeated three times and the precipitate was filtered, washed with methanol and dried.

2,3-Di-O-acetyl-6-O-trityl Cellulose (2)

Trityl cellulose was acetylated according to the procedure of Hall et al.[7] To a solution of trityl cellulose (1g) in pyridine (12.5 ml) was added acetic anhydride (10 ml) with stirring. The solution was kept at 90° C for 9 hr. with continuous stirring. After cooling to room temperature, the solution was poured into an excess of methanol. The precipitate was filtered, washed with methanol and dried.

2,3-Di-O-acetyl cellulose (3)

Detritylation of compound 2 was accomplished by slight modification of the procedure reported by Horton et al.[8] To a solution of compound 2 (1g) in chloroform (30 ml) was added acetic acid (5 ml). The solution was kept at 20° C. Hydrogen bromide saturated acetic acid solution (1 ml) was added and the mixture was stirred for 5 min. The resulting precipitate was filtered, washed with chloroform, poured

into methanol with constant stirring, filtered, washed with methanol and dried.

2,3-Di-O-acetyl-6-O-trideuterioacetyl Cellulose[8] (4)

After compound 3 (1g) was dissolved in pyridine (10 ml), acetic anhydride-d_6 (2 ml) was added and the solution was mixed well. The solution was held at 90° C for 9 hr., and then poured into water. The precipitate was filtered, washed with water and then methanol, and dried. The samples used for NMR spectra were purified further by repeating the precipitation technique using chloroform and methanol twice

Determination of the Trityl Content

The trityl content of trityl cellulose was determined by the procedure reported by Green[6]. A sample (1.0 g) of trityl cellulose, previously dried in vacuo at 70° C for 24 hr., was dissolved with stirring in concentrated sulfuric acid (10 ml). After complete dissolution gave a clear and dark-tan colored solution, distilled water was carefully added until the solution turned gray. Then, additional water (90 ml) was gradually added to precipitate triphenylmethanol. The precipitate was filtered, washed free of sulfate ion with water, dried and weighed.

$$\% \text{ Trityl} = \frac{\text{wt. of triphenylmethanol} \times 243 \times 100}{\text{sample wt.} \times 260}$$

$$\text{DS} = \frac{1.62 \times (\% \text{ trityl})}{243 - 2.42 \times (\% \text{ trityl})}$$

RESULTS AND DISCUSSION

The cellulose used as starting material for preparation of the trityl ether was known to be of importance. It has been known that decrystallized regenerated cellulose is effective as a sample for tritylation[2]. As a method for preparing regenerated cellulose, deacetylation of cellulose acetate under non-aqueous conditions is often used, though the hydrolysis is also carried out under aqueous conditions as mentioned before. However, the deacetylated cellulose obtained by the above methods has a minimum value of 1% acetyl[6]. Therefore, it is difficult to rule out the possibility that such samples have a slight amount of acetyl group in the C-6 position.

Moreover, as previously stated, the preparation of the regenerated cellulose is obviously a time-consuming procedure. These problems which occur in the traditional tritylation method for cellulose can be avoided if the tritylation is performed in a homogeneous solution utilizing a non-aqueous cellulose solvent.

Initially, we tried to determine the optimum conditions for tritylation of cellulose using a SO_2-DEA-DMSO cellulose solvent as the reaction medium. Figure 1 shows the effect of the amount of pyridine on cellulose tritylation in the cellulose solvent. The other conditions were held constant, that is, the reaction temperature was 50° C and the amount of trityl chloride was 5 moles per mole glucose unit of cellulose. Trityl chloride was mixed with pyridine ranging in quantities from 10 to 40 ml, and each mixture was added to the cellulose solution prepared in advance as shown in the experimental section. In Fig. 1, the calculated concentrations of the pyridine based on the total quantity of solvents are 67, 50 and 25%. From this figure, it is clear that the degree of substitution

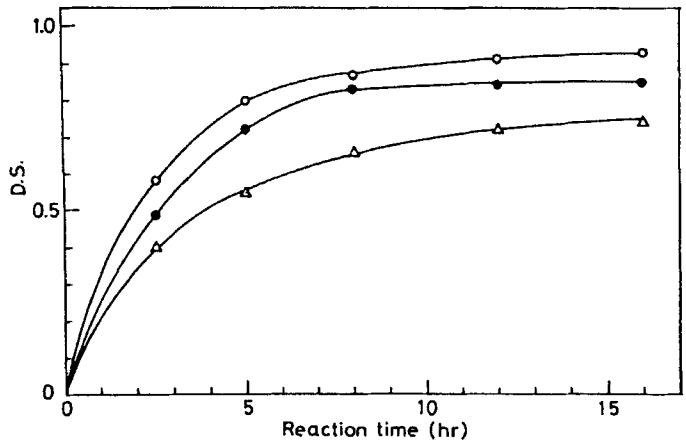


FIGURE 1. Effect of the amount of pyridine on the tritylation of cellulose.
Cellulose (1.0 g) was dissolved in DMSO (20 ml) with SO_2-DEA equimolar complex (4 moles per mole glucose unit). To the solution, trityl chloride (5 moles per mole glucose unit) and pyridine or pyridine-DMSO mixture were added. Reaction temperature: 50° C.
△ : pyridine 40 ml, ● : pyridine 20 ml, ○ : pyridine 10 ml-DMSO 10 ml.

with trityl groups increases with a decrease in the quantity of pyridine. However, under these conditions, trityl cellulose having a DS of 1.0 could not be effected within 16 hr. reaction. It would be expected from the results of Fig. 1 that an additional decrease in pyridine concentration might cause an increase in the trityl substitution.

Therefore, in order to obtain trityl cellulose with a DS of 1.0, we tried to tritylate cellulose utilizing reaction systems having smaller quantities of pyridine than those used in Fig. 1. However, pyridine is a good solvent for trityl chloride and a decrease in pyridine ratio in the solvent resulted in a significant decrease in the solubility of trityl chloride in the reaction solution and at the extreme, the homogeneous solution could no longer be realized. Thus, dimethylformamide (DMF) was partially used as a component of the solvents, because trityl chloride is more soluble in DMF than in DMSO. When the amount of pyridine was decreased to 4 ml and 16 ml of DMF was added to compensate for the decrease in the quantity of pyridine, trityl cellulose having a DS of 1.0 could be obtained as shown in Fig. 2. In this reaction, the other conditions such as the amount of trityl chloride, the amount and the composition of the cellulose solution, the reaction temperature and period, are the same as those in the experiments shown in Fig. 1. Thus, the corresponding concentration of pyridine in the solution is calculated to be 10%.

In Fig. 2 the result of examination whether the tritylation of cellulose is affected by use of DMF as a partial substitute for DMSO is also shown. This comparison was done using the pyridine concentration of 25%. Namely, 10 ml of pyridine was mixed with either 10 ml of DMF or DMSO, followed by addition of the trityl chloride, and each mixture was added to the cellulose solution. Both of these solution systems allowed homogeneous tritylation of cellulose at 50° C, because of the presence of sufficient pyridine. The reaction rates for the two reactions were essentially the same as shown in Fig. 2. Thus, the tritylation reaction is not affected by the partial replacement of the DMSO with DMF.

The effect of the amount of trityl chloride on the reaction was also investigated. A constant pyridine concentration of 10% was used in these experiments. The other reaction conditions were

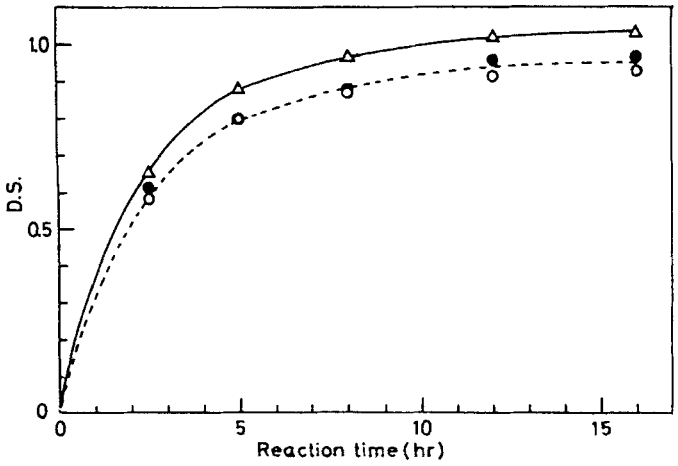


FIGURE 2. Effect of the amount of pyridine on the tritylation of cellulose.
Reaction conditions were identical to those described in Fig. 1 except the amounts and the composition of the pyridine solution added.
○ : pyridine 10 ml-DMSO 10 ml, ● : pyridine 10 ml-DMF 10 ml, △ : pyridine 4 ml-DMF 16 ml.

identical to those used in the previous experiment. The results are shown in Fig. 3.

When the amount of trityl chloride was 2.5 moles per mole glucose unit of cellulose, the tritylation did proceed satisfactorily, resulting in trityl cellulose with a DS of 0.5. Trityl cellulose with a DS of 1.0 could only be obtained by using more than 5 moles of trityl chloride per mole repeating unit of cellulose.

On the other hand, it has been reported that for a conventional tritylation procedure[2], use of 2.5 mole of trityl chloride per mole glucose unit of cellulose resulted in trityl cellulose having a DS of 1.0. Thus, our method requires a larger amount of trityl chloride than that used in the conventional procedure. This can be attributed to the reaction of trityl chloride with diethylamine, DMSO and water in the reaction system, as discussed later.

Triphenylmethyl chloride, on dissolution in polar aprotic solvents such as DMSO, nitromethane etc., immediately exhibits spectra of the triphenyl carbonium ion, showing ionization of the reagent in

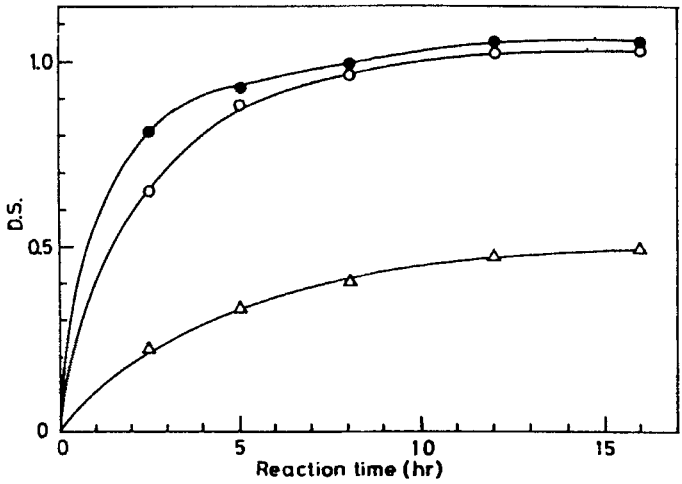


FIGURE 3. Effect of the amount of trityl chloride on the tritylation of cellulose.
Reaction conditions were identical to those described in Fig. 1 except that the concentration of pyridine was kept constant at 10% and that the concentration of trityl chloride was changed.
Trityl chloride : 7.5 (●), 5.0 (○), 2.5 (△) moles per mole glucose unit.

these solvents. Tritylation of alcohols involves a slow bimolecular reaction of the alcohol with the resultant carbonium ion. The tritylation can be run to completion if pyridine is added to neutralize the hydrogen chloride which forms. Pyridine also forms a complex with the carbonium ion, presumably a pyridinium ion in which the positive charge is delocalized over the nitrogen atom and the aralkyl group. In the presence of excess pyridine, trityl chloride is considered to exist completely as the pyridine-trityl complex which is reactive toward nucleophiles. Pyridine also acts as a base in the reaction system, accelerating other base-catalyzed side reactions, for example the reactions of trityl chloride with DEA, DMSO and water. This latter fact helps to explain the large consumption of trityl chloride during tritylation of cellulose in the presence of the cellulose solvent, and the observed effect of the amount of pyridine on the trityl substitution of cellulose.

In Fig. 4 are shown the results of reactions using quantities of SO_2-DEA equimolar complex up to 10 moles per glucose unit. A

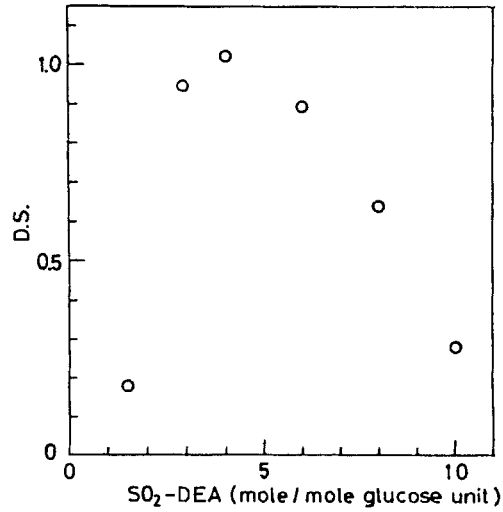


FIGURE 4. Effect of the amount of SO_2-DEA complex on the tritylation of cellulose.
Reaction conditions were identical to those described in Fig. 1 except that the pyridine concentration and the reaction period were kept constant at 10% and 12 hr., respectively, and that the concentration of SO_2-DEA complex was changed.

maximum value of trityl substitution was obtained when 4 moles of SO_2-DEA complex per glucose unit was used. It is known that total dissolution of cellulose in this cellulose solvent can be achieved by utilizing more than 3 moles of SO_2-DEA complex per mole glucose unit. This explains the low substitution of trityl groups attained with the samples prepared by using less than 3 moles of SO_2-DEA per glucose unit. Although better cellulose dissolution can be thought to occur, the presence of SO_2-DEA complex in quantities greater than 4 moles per mole glucose unit depresses the tritylation of cellulose. Thus, further investigation was carried out to clarify the influence of SO_2-DEA complex on the reaction. The effects of the quantity of SO_2 and that of DEA on the reaction were examined separately, while the other reaction conditions were the same as described previously.

In Table 1 the results of reactions using a fixed quantity of SO_2 (4 moles per glucose unit) and quantities of DEA ranging from 4 to 12 moles per mole glucose unit of cellulose are reported. The

amount of trityl substitution decreased markedly with an increase in the quantity of DEA. On the other hand, when the quantity of SO_2 was increased, while that of DEA was held constant, little change was found in the amount of trityl substitution (Table 1). These results reveal that the decrease in the amount of trityl substitution with an increase in the quantity of SO_2-DEA complex in the range above 4 moles per glucose unit shown previously in Fig. 4 is ascribable to the effect of DEA. These results also support the assumption, which was mentioned in connection with Fig. 4, that DEA as an active nucleophile will react with trityl chloride.

From results thus far it is obvious that homogeneous tritylation of cellulose can yield a product which contains about one trityl group for each glucose unit. Some characterization of the products were made. In Fig. 5, infrared (IR) spectra of trityl celluloses prepared by the present procedure (A and B) are compared with that of trityl cellulose with DS of 1.30 prepared by the conventional method (C). The DS values for the samples with spectra A and B were 0.65 and 1.02, respectively. A comparison of spectra A and B reveals that the intensities of bands at 3000 - 3100, 1600, 1500, 1450 and 700 - 800 cm^{-1}, all of which are attributable to the trityl group, increase with an increase in the degree of trityl substitution. When spectrum B is compared with C,

TABLE 1

Effect of Concentration of SO_2-DEA Complex and Its Components on the Tritylation of Cellulose[a]

SO_2-DEA (mole/g.u.)	DS	DEA[b] (mole/g.u.)	DS	SO_2[c] (mole/g.u.)	DS
4	1.02	4	1.02	4	1.02
6	0.89	6	0.90	6	0.94
8	0.64	8	0.57	8	0.95
10	0.28	10	0.17	10	0.95
12	--	12	0.10	12	0.96

a Reaction conditions were identical to those described in Fig. 4 except that the concentration of individual components of SO_2-DEA complex was changed.
b SO_2 concentration of 4 mole/glucose unit
c DEA concentration of 4 mole/glucose unit

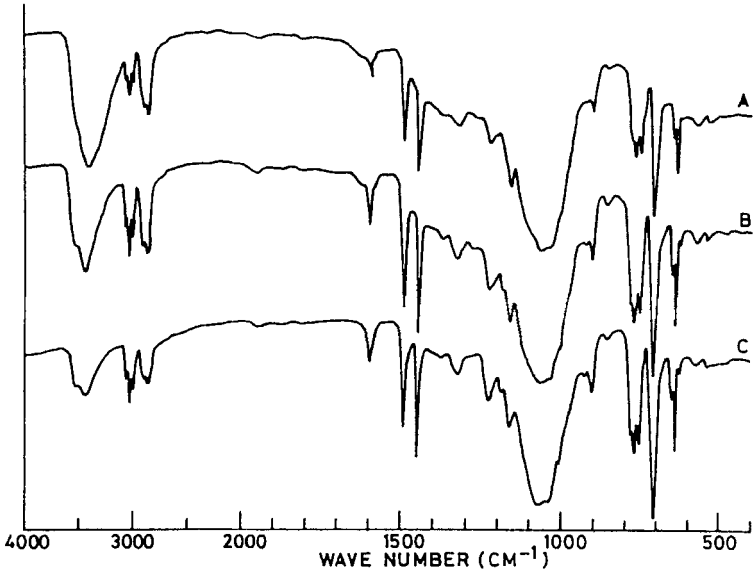


FIGURE 5. IR spectra of trityl cellulose with DS of 0.65 (A), 1.02 (B) and 1.30 (C).
Samples for spectra A and B were prepared by the present method and that for spectrum C was prepared by the conventional method.

the characteristics of both spectra seem to be essentially the same. This result indicates that, in spite of the fact that the present tritylation procedure uses a more complicated reaction system than the conventional method, no side reactions of cellulose take place.

Whether tritylation occurred preferentially at the primary hydroxyls was examined by the following two techniques.

In the first technique, the dielectric absorption properties of trityl cellulose with various DS were measured and then the frequency dependence of dielectric loss factor ε" was studied (Fig. 6). It is known that cellulose has a dielectric dispersion in the frequency range of 30 Hz to 1 MHz at -60° C under anhydrous conditions. Mikkailov et al.[10] reported that this dispersion was due to the orientational polarization of methylol groups in cellulose. Norimoto et al.[11] also reported that the dispersion was associated with the primary hydroxyl groups in the amorphous region of cellulose. In Fig. 6, when dielectric absorption curves for trityl cellulose

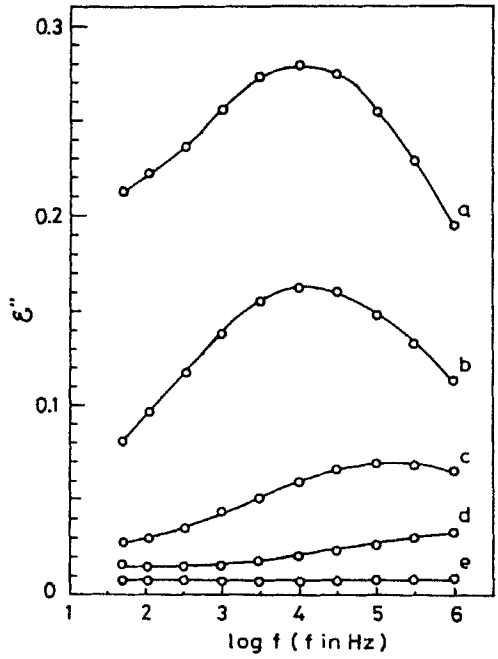


FIGURE 6. Frequency dependence of ε" at -50° C for decrystallized cellulose and trityl cellulose with various DS.
a) : Regenerated cellulose prepared by dissolving in a SO_2-DEA-DMSO solvent and precipitating with an excess of methanol.
b) : Deacetylated cellulose ground in a vibratory ball mill for 6 hr.
c), d) e) : Trityl cellulose with DS of 0.22, 0.65 and 1.02, respectively.

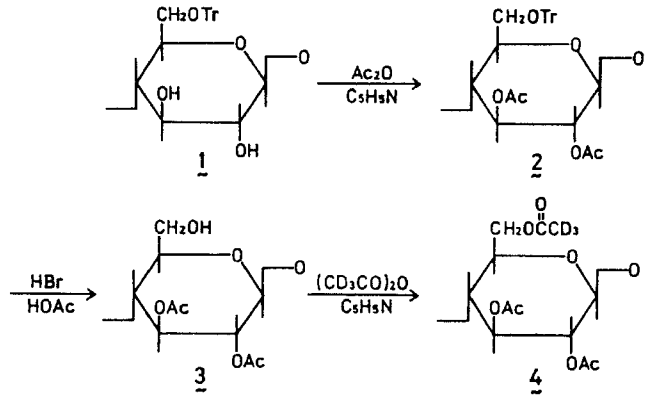
(c - e) are compared, it can be seen that the absorption due to the hindered rotation of methylol groups in cellulose decreases with an increase in the content of the trityl group and it disappears completely when the value of DS for trityl cellulose becomes 1.02. This is consistent with tritylation of cellulose by the present procedure proceeding preferentially at the primary hydroxyl groups, yielding 6-monotrityl cellulose.

On the other hand, when dielectric absorption curves for two kinds of decrystallized cellulose, a and b in Fig. 6, are compared, it is apparent that the sample a has a significantly larger absorption than that of b. The decrystallized cellulose samples a and b

were prepared by a regeneration procedure and a ball-milling procedure, respectively. In the regeneration procedure, cellulose was dissolved in a non-aqueous cellulose solvent and the solution was poured into large excess of methanol, giving regenerated cellulose as a precipitate, which was digested with benzene and then ethyl ether, successively, and dried. For the second decrystallized sample, cellulose acetate was deacetylated and the resultant cellulose was ground in a vibratory ball mill. It is known that the magnitude of dielectric absorption is proportional to the number of methylol groups in the amorphous region per unit volume of cellulose[12]. Thus, the results show that the regeneration procedure is considerably more effective for the decrystallization of cellulose than the ball-milling technique. This finding is of interest because the latter technique has been commonly employed as a decrystallization method.

Furthermore, Fig. 6 shows that the dielectric absorption shifts to a higher frequency range with an increase in the degree of trityl substitution. This phenomenon has not been observed for trityl cellulose prepared by the conventional method[12]. This discrepancy can be rationalized on the basis that the current homogeneous reaction causes a uniform substitution of trityl groups on the methylol groups in cellulose. The intra- and inter-hydrogen bondings in cellulose can effectively be reduced by the uniform introduction of bulky trityl groups along the cellulose chain. This causes an extremely loosened structure of cellulose, which permits the remaining methylol groups to rotate with an accelerated level of freedom.

NMR and IR spectrometry were also used to evaluate the extent to which the trityl group is introduced specifically at the C-6 position. Hearon *et al.*[1] assessed whether trityl groups were selectively introduced at the primary hydroxyl position of cellulose by carbanilation of the trityl cellulose, followed by detritylation, tosylation and iodination, and found that, of the original 1.03 trityl groups introduced per glucose unit, at least 0.90 trityl groups were in the C-6 position. The series of reactions used in this investigation are shown in Scheme 1. The reaction scheme is based on the tentative assumption that the trityl groups are introduced at the C-6 position of cellulose.



SCHEME 1. Preparation of 2,3-di-O-acetyl-6-O-(trideuterioacetyl) cellulose.

Acetylation of 6-O-trityl cellulose (1) gives 2,3-di-O-acetyl-6-O-trityl cellulose (2). Detritylation of 2 gives 2,3-di-O-acetyl cellulose (3). Trideuterioacetylation of 3 gives 2,3-di-O-acetyl-6-O-(trideuterioacetyl) cellulose (4). The IR spectra of these products are shown in Fig. 7. Spectrum A is for trityl cellulose with DS of 1.02. In the spectrum B of 2, the band due to the hydroxyl group around 3400 cm^{-1} disappears and that due to the carbonyl group at 1750 cm^{-1} appears. No change in the bands due to the trityl group at 3000 - 3100, 1600, 1500, 1450 and 700 - 800 cm^{-1} is seen. These facts therefore suggest that virtually complete acetylation and no detritylation occur. Comparison of the spectrum C of 3 with the spectrum B suggests that complete detritylation occurs, since in the spectrum C, the bands due to the trityl group disappear entirely. It has been shown that no acetyl migration from C-2 or C-3 to C-6 position takes place, when detritylation is carried out under the conditions described in the experimental section[13,14]. In spectrum D of 4 the band around 3400 cm^{-1} due to hydroxyl groups is absent suggesting that complete trideuterioacetylation occurred. Horton et al.[14] reported that no exchange of protioacetate by deuterioacetate took place during trideuterioacetylation analogous to that described in the experimental section.

^{1}H-NMR spectra were obtained for acetyl-trideuterioacetyl celluloses derived from trityl celluloses with various degrees of

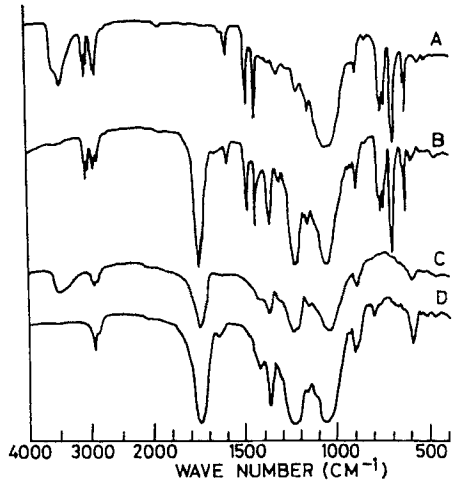


FIGURE 7. IR spectra of trityl cellulose with DS of 1.02 (A), 2,3-di-O-acetyl-6-O-trityl cellulose (B), 2,3-di-O-acetyl cellulose (C) and 2,3-di-O-acetyl-6-O-(trideuterioacetyl) cellulose (D).

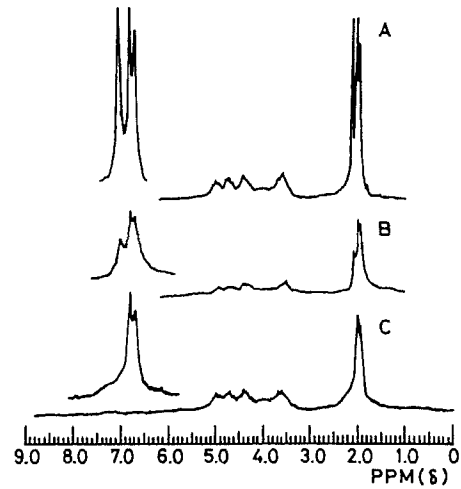


FIGURE 8. ^{1}H-NMR spectra of cellulose triacetate (A) and products prepared from trityl cellulose having DS 0.61 and 1.02 by successive acetylation, detritylation and trideuterioacetylation (B, C).

trityl substitution (Fig. 8). Goodlett et al.[15] observed three signals for acetate-methyl protons of cellulose triacetate at δ 2.09, 1.99 and 1.94 and assigned the signals to acetyl groups at C-6, the C-2 and the C-3, respectively. The fact that the trideuterioacetyl group is not detectable by ^{1}H-NMR spectrometry makes analysis of the original trityl cellulose possible. Conventional cellulose triacetate gives spectrum A in Fig. 8. Spectra B and C are from products obtained after treatment of trityl celluloses having DS of 0.61 and 1.02, respectively. It is readily apparent that the intensity of the signal due to a protioacetyl group at C-6 position (δ 2.09) decreases with an increase in the degree of trityl substitution, being absent in spectrum C. These results also substantiate that the trityl groups in trityl cellulose are predominantly at the primary hydroxyl position.

In conclusion this study has shown that the homogeneous tritylation readily provides products with approximately 1.0 trityl group for each glucose unit of cellulose if the proper reaction conditions are chosen. In addition, it has been demonstrated that trityl substitution occurs preferentially at the primary hydroxyl groups.

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