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A structural study of fluorinated cellulose: crystallization of fluorinated cellulose by conversion treatments used for cellulose

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A deoxyfluorocellulose derivative, with regioselective substitution mostly at the C-6 carbon atoms, has been studied by an X-ray diffraction method. The results showed that the crystallinity of the fluorinated cellulose is low but can be enhanced by a specific conversion treatment. The hydrothermally treated sample displayed a spectrum similar to that of cellulose IV. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Cellulose has several allomorphs and their structures have been extensively investigated by using X-ray (Gardner & Blackwell, 1974; Sarko & Muggli, 1974; Woodcock & Sarko, 1980) and electron diffraction methods (Sugiyama *et al.*, 1990; Sugiyama *et al.*, 1991), infrared spectroscopy (Marrinan & Mann, 1956), solid-state CP/MAS ^{13}C NMR (VanderHart & Atalla, 1984; Horii *et al.*, 1987; Yamamoto *et al.*, 1989) and conformation analysis (Pizzi & Eaton, 1985; Simon *et al.*, 1988a,). The physical structures of these allomorphs, however, are still not fully understood, especially the details of their intermolecular and intramolecular hydrogen bonding patterns.

A deoxyfluorocellulose in which the hydroxyl groups are partially replaced by fluoro functions would have a crystalline structure similar to that of cellulose and the study of its characteristics may provide information related to the structure and hydrogen bonding of cellulose. Because the fluorine atom, like the hydroxyl oxygen, has a high electronegativity and because the van der Waals' radius of fluorine is similar to that of oxygen, the substituted fluorine atoms might get involved in the hydrogen bonding system. It follows that the fluoro substituent in deoxyfluorocellulose may participate in both intermolecular and intramolecular bonds with the hydroxyl hydrogen (C-F—H-O) mimicking those between hydroxyl groups (O-H—O-H) in the original cellulose.

In this paper we use X-ray characterization to show a structural resemblance between cellulose and its fluorinated analogue, 6-deoxy-6-fluorocellulose.

EXPERIMENT

Reagents

Alfusone, a 25% (w/w) HBr–acetic acid solution and a CH_3ONa/CH_3OH solution were purchased from Wako Pure Chemical Industries, Ltd. An Alfusone reagent solution (50 g/l) was prepared by dissolving the Alfusone in deionized water.

Fluorinated cellulose

The fluorinated cellulose samples used in this study were prepared by the method described in a previous paper (Kasuya *et al.*, 1994). In general, powdered cellulose dissolved in a LiCl-N,N-dimethylacetamide solution system was converted homogeneously to the 6-O-triphenylmethylcellulose and then esterified with acyl chloride (acetyl/benzoyl) in pyridine. The resulting product, containing trityl substituents at C-6 and acetyl (or benzoyl) groups at C-2 and C-3, was detritylated

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*Present address: Faculty of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183, Japan with a 25% (w/w) HBr–acetic acid solution in CH_2Cl_2. The detritylation product was fluorinated with diethylaminosulphur trifluoride using one of four different media: nitrobenzene, chloroform, diethylene glycol dimethylether or 1,4-dioxane. Each of the fluorinated products was dissolved in pyridine and saponified with a CH_3ONa/CH_3OH solution.

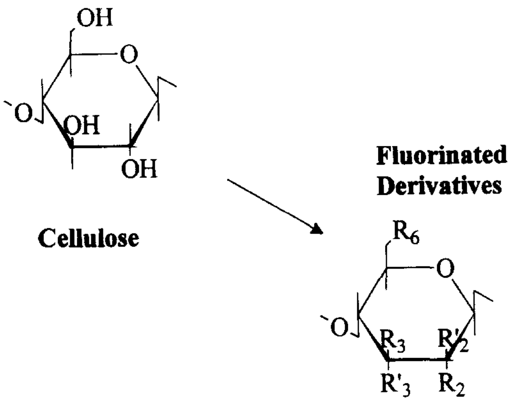
The degree of substitution (DS) and the distribution of fluoro functions were estimated for each of the deoxyfluorocelluloses and the influence of solvents and starting materials on the fluorination pattern of cellulose (Fig. 1) is shown by the listings in Table 1.

Effect of conversion treatment on crystallization of fluorinated cellulose

Because the fluorinated cellulose obtained has a low crystallinity, it was subjected to several conversion treatments that might enhance crystallinity.

Caustic soda treatment

The caustic soda treatment is known to convert cellulose I to cellulose II. A fluorinated cellulose sample (0.5 g) was immersed in 20 ml of 18% (w/w) NaOH solution for 6 h at room temperature. After 50 ml of MeOH was added, the mixture was stirred for 30 min, filtered, washed again with MeOH and dried under vacuum at 60°C.



(R_2,R'_2) = (OH,H) or (H,F)
(R_3,R'_3) = (OH,H) or (H,F)
R_6 = OH or F

Fig. 1. Structural representations of cellulose and its fluorinated derivatives.

Reprecipitation from formic acid

Formic acid is one of the few solvents that can dissolve deoxyfluorocellulose and we expected that a reprecipitation of the fluorinated cellulose could cause some structural changes. We therefore dissolved fluorinated samples (0.5 g) in 20 ml of formic acid, stored the solutions at room temperature for 24 h, poured each into 100 ml of MeOH and centrifuged the mixture. The precipitate was washed with MeOH three times and then dried under vacuum at 60°C for more than 24 h.

Treatment with NH_3 gas

The NH_3 treatment is known to generate the cellulose III allomorph (Yatsu *et al.*, 1986). A fluorinated sample (0.5 g) placed in a 10 ml autoclave was cooled in a Dewer bottle containing dry ice and acetone. Liquid ammonia (about 5 ml), cooled in the same way, was poured into the autoclave, which was then capped and heated in an oil bath at 140°C for 2 h. After the mixture was cooled, it was poured into 50 ml of MeOH and filtered. After the cellulosic material was washed three times with 50 ml of MeOH, it was dried under vacuum at 60°C for 24 h.

Hydrothermal treatment

The hydrothermal treatment reported by Isogai *et al.* (1991) causes the formation of cellulose IV. A sample (0.5 g) was placed in a 10 ml autoclave with 5 ml of phosphate buffer solution (pH 6.86). The vessel was then sealed and heated in an oil bath at 160°C for 2 h. After the vessel cooled, its content was washed three times with 50 ml of MeOH and dried under vacuum at 60°C for 24 h.

Determining the DS of fluorinated cellulose

The DS values of fluoro substituent in fluorinated cellulose were determined according to the alizarin-complexation method (Hashitani *et al.*, 1967). A

Table 1. Extent of fluorination and the distribution of fluoro substituents in fluorinated celluloses

Fluorinated cellulose	Starting material[a]	Reaction medium	DS C-2	DS C-3	DS C-6	DS Total
A	1	Nitrobenzene	nd[b]	0.04	0.95	0.99
B	2	Chloroform	0.14	nd	0.69	0.83
C	2	Diglyme	nd	0.13	0.70	0.83
D	2	1,4-dioxane	0.12	0.13	0.77	1.02

[a] 1 = Cellulose 2,3-dibenzoate; 2 = cellulose 2,3-diacetate. [b] nd = not detected.

sample (10 mg) was burnt in a combustion flask previously filled with 20 ml of water under an oxygen atmosphere. The resulting solution was quantitatively transferred into a 100 ml volumetric flask and diluted to that volume with deionized water. A 5 ml aliquot of this solution, 6 ml of the Alfusone reagent solution and 20 ml of acetone were added to a 50 ml volumetric flask and diluted to that volume with deionized water. After one hour, the UV absorbance of the solution was measured at 610 nm and the fluorine content was calculated by using a calibration curve made with known concentrations of sodium fluoride solution.

X-ray diffraction measurement

The X-ray diffraction patterns of pellet samples were recorded using Ni-filtered CuK radiation on a Rigaku Denki RTP 300 diffractometer equipped with a reflection-type goniometer and operating at 100 kV and 50 mA.

Estimating the change of crystallinity

The change of crystallinity due to conversion treatment was estimated roughly by the following procedure. A solid line was drawn between the two points at 2θ of 10 and 31 deg. (Fig. 2). The area surrounded by the curve and the solid line for a control sample was defined as I_0, whereas the corresponding area for a treated sample was defined as I. The ratio I/I_0 was used to evaluate the change of crystallinity.

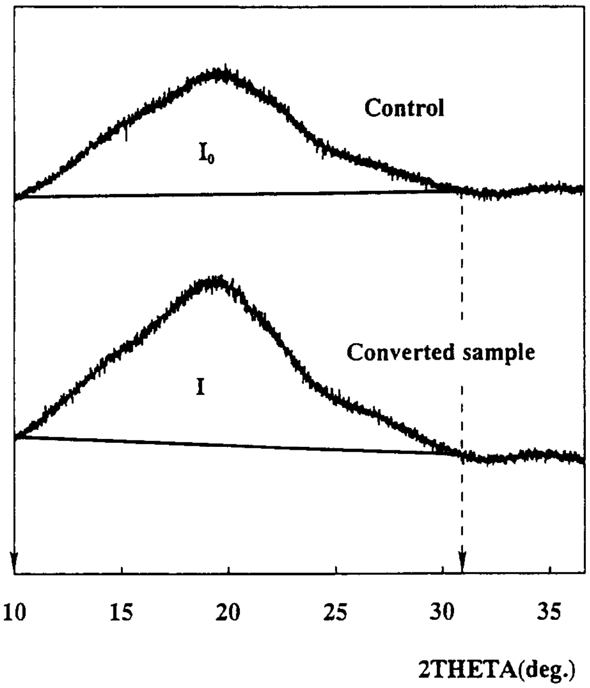


Fig. 2. X-ray diffractograms illustrating the areas I_0 and I used for the assessment of crystallinity changes.

RESULTS AND DISCUSSION

As seen in Fig. 1, the fluoro functions incorporated at C-2 and C-3 were estimated to be in the axial position with regard to the glucopyranose ring as indicated by ^{19}F NMR (Kasuya *et al.*, 1994). The incorporation of fluorine in the axial position was caused by imperfect protection of hydroxyl groups in the preparation and by Walden inversion on fluorination. Although such a fluorinated derivative cannot be termed as deoxyfluorocellulose in a strict sense, the amount of incorporation at the axial position seemed to be negligible.

The influence of the various conversion treatments on the DS can be inferred from the results listed in Table 2. Although the distribution of fluoro substituents was not evaluated for aliquots of the samples after a treatment, it is evident that in all cases the DS of the treated samples are only slightly less than those of corresponding control samples. Thus most of the fluoro substituents probably were preserved.

The results of X-ray measurements are shown in Figs 3–6 and in Table 3. As seen in all diffractograms, the crystallinity of control samples that were not subjected to any conversion treatment was low except for sample C. Why only sample C had a distinctly higher crystalline state is not unclear. A similar tendency was seen after the caustic soda treatment.

For the formic-acid-treated and NH_3-gas-treated samples, we could not identify a specific crystalline property. Their amorphousness is thought to be caused mainly by the incorporation of the fluoro function at C-6, resulting in a reduction in the ability of the cellulosic polymer to form hydrogen bonds.

However, the situation is apparently different for sample D, which was treated hydrothermally in an

Table 2. Degree of substitution in deoxyfluorocellulose after the conversion treatment

Fluorinated cellulose[a]	Control sample	Caustic soda treatment	Formic acid treatment	NH_3 gas treatment	Hydrothermal treatment
A	0.99	0.86	0.95	0.87	0.85
B	0.83	0.83	0.80	0.83	0.82
C	0.83	0.80	0.80	0.83	0.75
D	1.02	0.98	0.93	0.93	0.92

[a] see Table 1.

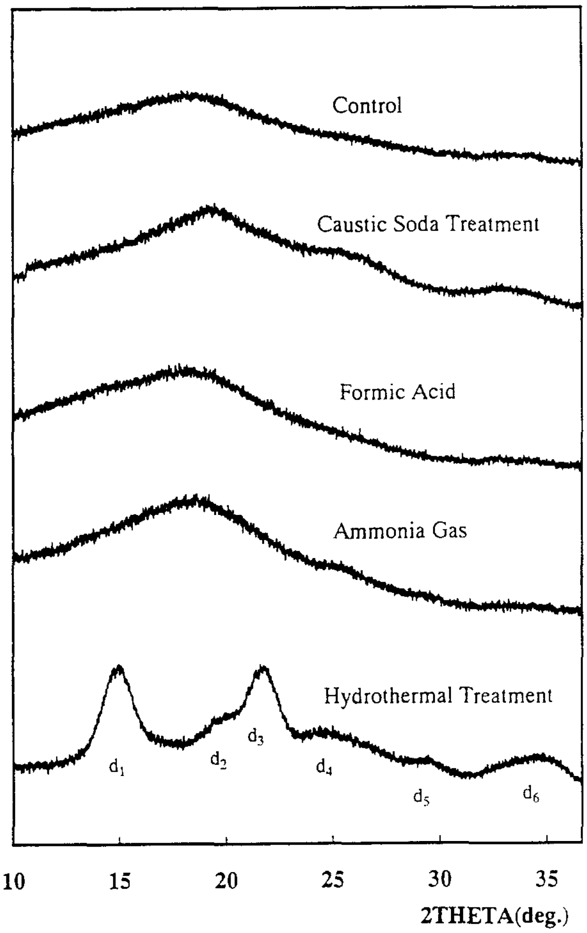


Fig. 3. X-ray diffractograms of fluorinated cellulose (A).

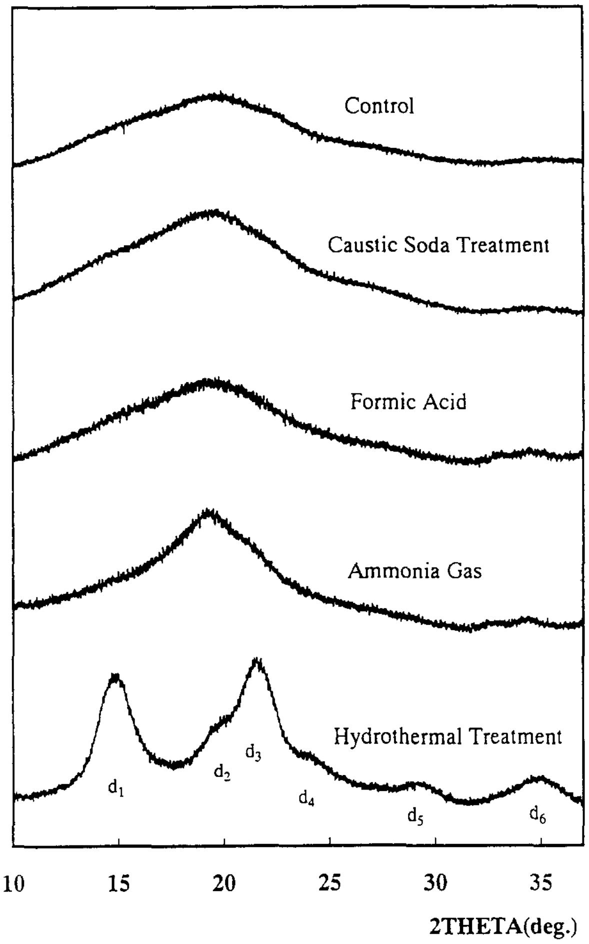


Fig. 4. X-ray diffractograms of fluorinated cellulose (B).

aqueous medium. The diffractograms for samples A and B are similar, and they also resemble that of the hydrothermally treated cellulose in showing the presence of an allomorph of cellulose IV (Ellefsen & Norman, 1962; Hayashi *et al.*, 1973; Gardiner & Sarko, 1985; Isogai *et al.*, 1991). The diffractograms for samples C and D also show some crystalline features, but they differ from each other. In addition, they are both different from any other diffractograms of cellulose allomorphs.

Table 3 shows the d-spacings obtained from the diffractograms. The changes of crystallinity caused by the conversion treatment were assessed as defined in the experimental section (see Fig. 2). As can be seen in Table 4, the I/I_0 values for sample A and

Table 3. d-spacings (Å) of the deoxyfluorocelluloses treated hydrothermally at 160°C for 2 h

	d_1	d_2	d_3	d_4	d_5	d_6
A	5.72	4.38	4.01	3.53	2.99	2.55
B	5.72	4.35	4.01	3.62	3.00	2.52
C	6.81	5.87	5.31	4.46	3.90	3.43
D	7.03	6.03	4.44	3.92	—	—

Table 4. Values of I/I_0[a] for deoxyfluorocelluloses after conversion treatment

	Sample A	Sample B	Sample C	Sample D
Caustic soda	1.7	1.5	0.6	0.8
Formic acid	1.3	1.1	0.6	0.9
NH_3 gas	1.6	1.2	0.5	0.7
Hydrothermal treatment	1.8	1.4	1.0	1.0

[a] See experiment section in text and Fig. 2.

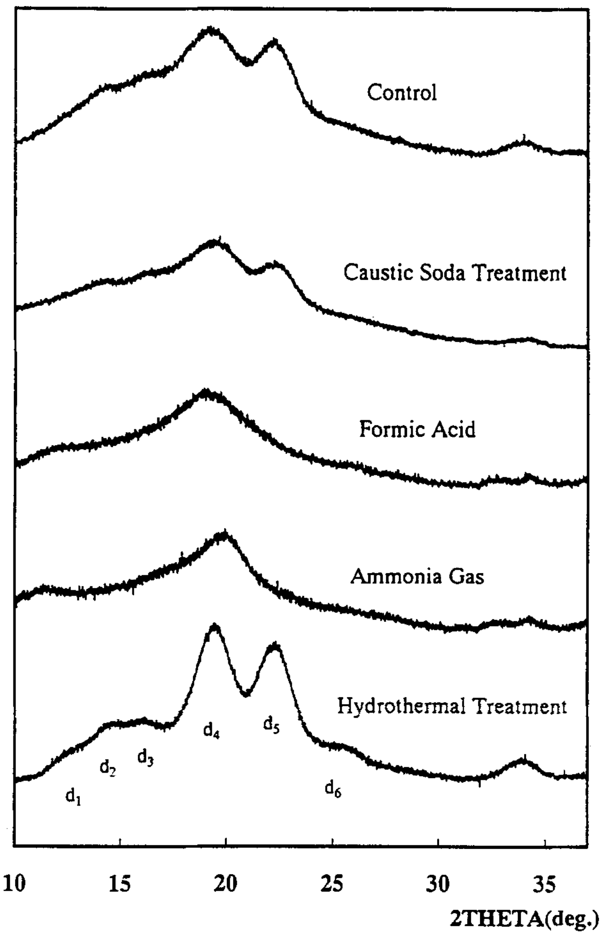


Fig. 5. X-ray diffractograms of fluorinated cellulose (C).

sample B are larger than those of samples C and D. These variations may be related to the manner of the incorporation of the fluoro function at the C-3 position.

It appears that the replacement of hydroxyl groups at C-6 by fluorine atoms had little effect on the spatial structure of a fluorinated sample that had been treated hydrothermally. When the replacement of hydroxyl groups occurred at the C-2 or C-3 position, however, the incorporation of fluorine atoms at the axial position changed the cellulose structure significantly. Furthermore, the inhibition of the hydrogen bonds between the 3-OH and 5′-O positions of successive glucose residues, which is caused by the substitutions of fluoro functions for the hydroxyl groups, seems to be unable to produce a rod-like structure in the cellulose chain.

There are two possible explanations for the fact that the diffractogram of thermally treated 6-deoxy-6-fluorocellulose resembles that of cellulose IV. One is that the fluoro functions at C-6 in fluorinated samples and the hydroxyl groups at C-6 in cellulose IV samples might have little effect on the formation of crystal. Thus, the hydrogen bonds they might form with other hydroxyl groups would have no effect on the spatial structure of the hydrothermally treated samples. The second possibility is that the fluoro functions at C-6 could form intermolecular or intramolecular hydrogen bonds with hydroxyls in the fluorinated samples, mimicking the C-6 hydroxyl groups in cellulose IV. The likelihood of these possibilities needs to be further evaluated.

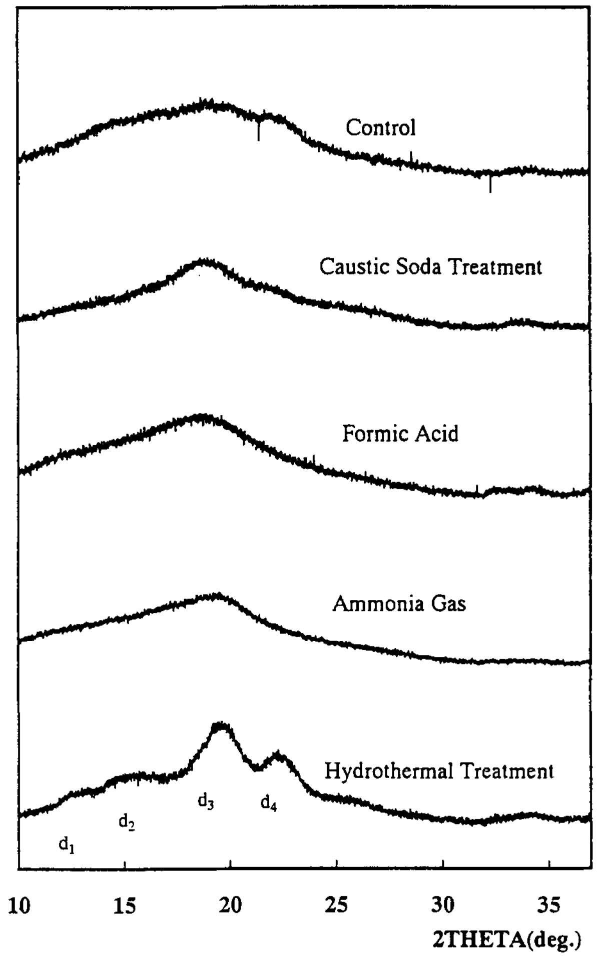


Fig. 6. X-ray diffractograms of fluorinated cellulose (D).

Because crystalline samples were obtained only after the hydrothermal treatment, we have continued to study how the crystalline nature of the hydrothermally treated samples may be affected by another treatment, such as caustic soda or ammonia gas.

CONCLUSIONS

The deoxyfluorocellulose derivative generally has a low crystallinity and a hydrothermal treatment resulted in an increase in crystallinity. The X-ray diffractogram of the hydrothermally treated 6-deoxy-6-fluorocellulose indicates that the crystal structure of this material resembles that of an allomorph of cellulose IV.

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