

## NOTE

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**Studies on the thermal properties and structures of deoxyhalocelluloses**

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**Abstract** The thermal properties and structures of deoxyhalocelluloses were studied using thermogravimetric and differential scanning calorimetric analyses and an X-ray diffraction method. The X-ray diffraction curves of the cellulose derivatives were obtained after subjecting them to a specific treatment that was supposed to render a specific cellulose allomorph from the amorphous state cellulose; all of the cellulose derivatives examined without such treatment exhibited no crystalline features. Only deoxyfluorocellulose was found to give a diffraction pattern similar to that of the corresponding cellulose allomorph, which was cellulose IV in this case. On the basis of the thermal analyses, it was confirmed that chlorodeoxycellulose has a flame-retardant property, whereas deoxyfluorocellulose was found not to be flame-retardant. The difference is supposedly due to the difference in the bonding energy between C–Cl and C–F.

**Key words** Deoxyhalocellulose · Chlorodeoxycellulose · Deoxyfluorocellulose · Thermal · Structure

**Introduction**

Incorporation of a fluoro function into cellulose has long been one of the subjects of inquiry in cellulose chemistry because of its difficulty (due to the low nucleophilicity of a fluoride ion and the vulnerability of glucosidic linkages). Recently, we developed a method to obtain a highly substituted deoxyfluorocellulose<sup>1</sup> and prepared a 6-deoxy-6-fluorocellulose<sup>2</sup> that has a fluoro function at the C-6 position instead of a hydroxyl group. The degree of substitution by

fluorine was estimated to be 0.99. The structural resemblance between hydrothermally treated 6-deoxy-6-fluorocellulose and cellulose with the allomorph of cellulose IV<sup>3</sup> was also reported.

To determine if the structural resemblance to a cellulose allomorph is specific to a fluoro analogue, we prepared chlorodeoxycelluloses and studied their structures using an X-ray diffraction method after subjecting them to a conversion treatment used for cellulose. We also studied the thermal behavior of deoxyhalocelluloses, including deoxyfluorocellulose, which is reported in this paper.

**Experiments****Materials**

Whatman cellulose CF-11 was used as the starting cellulosic material. Chlorodeoxycelluloses were prepared according to the method of Furuhata et al.<sup>4</sup> The degree to which the cellulose was substituted [degree of substitution (DS)] by chloro functions was controlled by changing the reagent ratio, the reaction time, or both. The resultant DSs of the chlorodeoxycelluloses were determined using a Japanese industrial standard<sup>5</sup> and were found to be 0.97, 1.36, and 1.84. Deoxyfluorocellulose was prepared according to a method previously reported.<sup>2</sup> The DS was estimated to be 0.85 by the alizarin-complexon method.<sup>6</sup> Phosphoric acid solutions of the cellulosic materials were prepared according to the method used by Isogai and Usuda.<sup>7</sup> After the solutions were stored for 6 weeks, they were poured into MeOH. The precipitate was washed thoroughly with MeOH and dried under a vacuum. Treatment with gaseous NH<sub>3</sub> and a hydrothermal treatment were undertaken as reported in previous papers.<sup>8,9</sup> Amorphous cellulose was obtained by pouring the cellulose–LiCl–*N,N*-dimethylacetamide solution into MeOH. Amorphous cellulose was used as a control because the deoxyhalocellulose prepared by the method described above showed few crystalline features.

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## X-ray diffraction method

The samples were analyzed using an X-ray powder diffraction method. The diffractograms were obtained using a JEOL JRX-12VA equipped with a Ni filter, operated at 40 kV and 100 mA.

## Thermal analysis

Shimadzu TG-20 and Shimadzu DSC-50 were used for thermogravimetric and differential scanning calorimetric (DSC) analyses, respectively. Each sample used for the research was placed in a platinum pan and measured under a nitrogen stream (20 ml/min). The temperature was raised at a rate of 10°C/min for each run.

## Results and discussion

### Characterization of chlorodeoxycellulose by X-ray diffraction measurements

Because the chlorodeoxycelluloses and the 6-deoxy-6-fluorocellulose,<sup>3</sup> prepared according to the methods described above exhibited few crystalline features, they were subjected to several conversion treatments used for cellulose so the crystallinity might be enhanced. After the treatments, the DSs were determined and are listed in Table 1. Unexpectedly, the decrease in DS after these treatments was found to be significant except for the samples reprecipitated from their aqueous phosphoric acid solution, which maintained a considerable amount of chloro function.

Figure 1 shows the diffractograms of the chlorodeoxycelluloses obtained by reprecipitation from their phosphoric acid solution along with that of the treated cellulose. The crystalline features could be seen to some extent in the diffractograms, especially for those of DS 0.97. However, they are too small to be used for elucidating informative data. (The diffractograms for the other treatments were omitted because almost all the chloro functions were cleaved from the cellulosic polymers.) Thus, the structural resemblance between cellulose and chlorodeoxycellulose was not seen in this study, although that between cellulose and deoxyfluorocellulose was reported in a previous paper.<sup>3</sup> Crystallization under milder conditions might be pursued to

**Table 1.** DS of chlorodeoxycelluloses before and after conversion treatments

Initial DS	DS after conversion treatments		
	Phosphoric acid	Liquid NH <sub>3</sub>	Hydrothermal
0.97	0.69	0.10	0.24
1.36	1.03	0.04	0.09
1.84	1.37	0.05	1.23

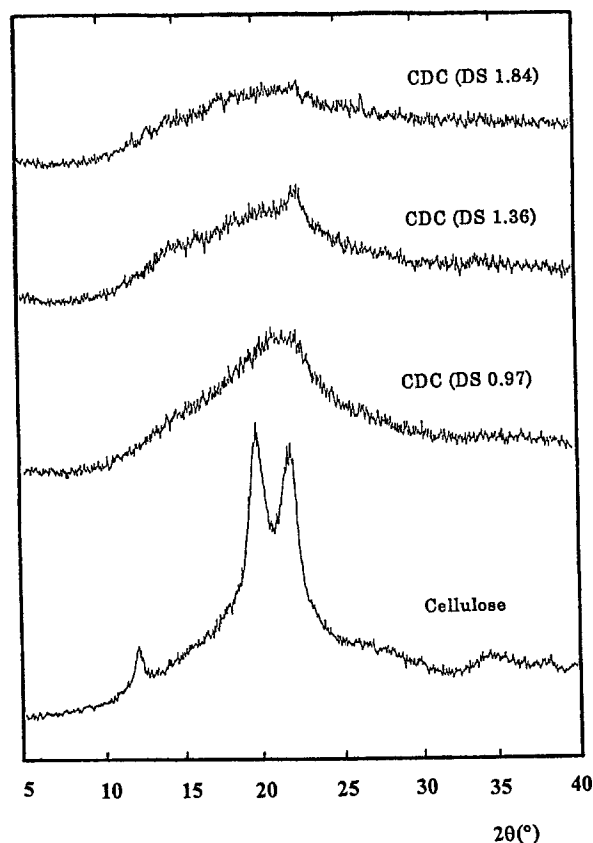
DS, degree of substitution.

ensure that these modified celluloses truly do not have a space arrangement similar to that of the original cellulose.

### Thermal behavior of chlorodeoxycellulose and deoxyfluorocellulose

Thermogravimetric (TG) and DSC curves for the chlorinated celluloses (DS 0.97, 1.36, and 1.84) were obtained together with those for a deoxyfluorocellulose having a DS of 0.85.

The TG curves show that amorphous cellulose has the best heat resistance, followed by fluorinated cellulose (DS 0.85), and then chlorodeoxycellulose (DS 0.97) (Fig. 2). The chlorodeoxycellulose with DS 0.97 (Figs. 2, 3) seems to act similarly to amorphous cellulose and deoxyfluorocellulose. On the other hand, the other two samples (DS 1.36 and 1.84) exhibit significantly different features (Fig. 3). They start to decompose at fairly lower temperatures (150°C), and their total mass loss even after the temperature reached 600°C is estimated to be approximately 70%, although the mass loss of the chlorodeoxycellulose with DS 0.97 is evaluated to be 90%. These features might be caused by the cleavage of the C–Cl bond at the axial position. It is thought that the C–Cl bond at C-3 begins to be cleaved at 150°C, bearing hydrogen chloride, and that the gaseous hydrogen chloride created during heating covers the surface of the



**Fig. 1.** X-ray diffractograms for chlorodeoxycelluloses (CDC) and cellulose obtained by treatment with phosphoric acid

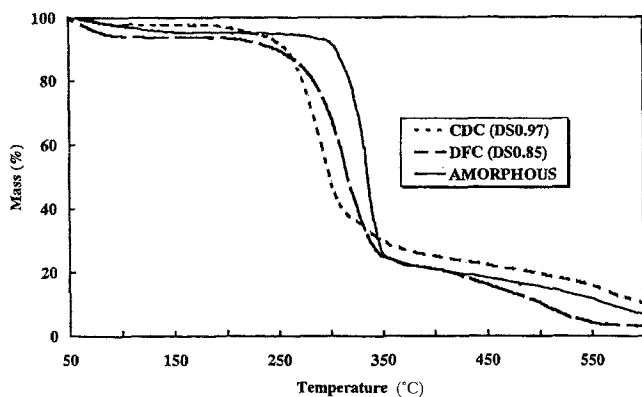


Fig. 2. Thermogravimetric (TG) curves for cellulosic polymers

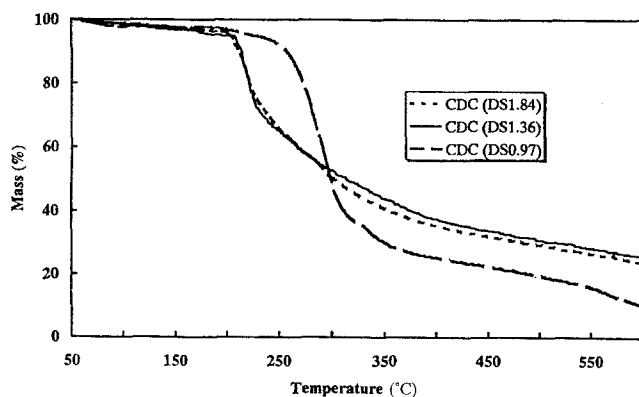


Fig. 3. TG curves for chlorodeoxycelluloses

materials so it prevents oxygen from coming in through the surface, which eventually leads to flame retardancy. As expected, deoxyfluorocellulose, which is thought to have a stronger bond (C-F) than the C-OH/C-Cl bond, was found not to be flame-retardant.

The DSC curves for these samples exhibit a similar tendency (Fig. 4). The large, broad endothermic peak at around 200°C in the curve for chlorodeoxycellulose (DS 1.84) is thought to be attributable to the cleavage of hydrogen chloride and decomposition of the pyranose ring that follows. The peaks at around 260°C might be attributable to decomposition of the pyranose ring without chlorine functions.<sup>10,11</sup>

Large endothermic peaks are seen for the chlorodeoxycellulose with DS values of 1.36 and 0.97, and their temperatures increase as the amount of chloride being incorporated into them decreases. Corresponding peaks cannot be found in the curves for deoxyfluorocellulose and amorphous cellulose.

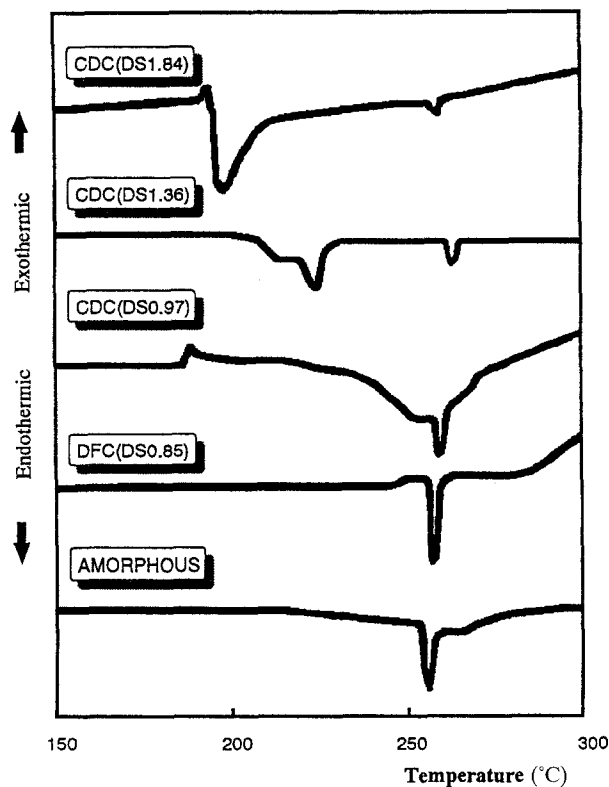


Fig. 4. Differential scanning calorimetric (DSC) curves for chlorodeoxycellulose (CDC), deoxyfluorocellulose (DFC), and amorphous cellulose

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