Preparation of Aldehydocelluloses from Completely Allylated Methylcellulose, Allylated Ethylcellulose, and Tri-*O*-Allylcellulose by Ozonization

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Synopsis

In order to prepare aldehydocelluloses which are more stable than periodate-oxidized cellulose, completely allylated methylcellulose, allylated ethylcellulose, and tri-*O*-allylcellulose were subjected to ozonization followed by reduction with dimethylsulfide. The aldehydocelluloses thus prepared without any degradation showed the presence of many free aldehyde groups by IR and ^{13}C-NMR spectrometries, as well as the presence of hydroxyl groups which were produced by deallylation. The degree of substitution (DS) by aldehyde group was 0.6 for the products from both completely allylated methylcellulose and tri-*O*-allylcellulose, and 0.02 for that from allylated ethylcellulose.

INTRODUCTION

Aldehydes react not only with ammonia but also with primary amines to yield imines, which can be converted into secondary amines by reduction. In many cases of coupling of enzymes to cellulose supports having amino groups such as aminoethylcellulose[1-5] and diethylaminoethyl (DEAE) cellulose[6], glutaraldehyde has been used as a crosslinking reagent. Therefore, celluloses having aldehyde groups are expected to couple to enzymes easily without a crosslinking reagent. Nevertheless, few methods have been proposed for introducing aldehyde groups onto cellulose. Dialdehydocellulose prepared by periodate oxidation of cellulose is well known to couple with protein,[7] but is not stable under the acidic conditions.

In a previous paper,[8] the authors reported that completely allylated methylcellulose and tri-*O*-allylcellulose could be prepared almost quantitatively from commercially available methylcellulose (DS 1.6) and cellulose acetate (DS 1.75, 2.24, and 2.39), respectively, by the use of powdered sodium hydroxide and allyl chloride in dimethylsulfoxide (DMSO). Double bonds in allyl groups were also found to be susceptible to air oxidation. Allylation of ethylcellulose (DS 1.9), however, did not occur at all because of its poor solubility in DMSO.

In the present paper, first allylated ethylcellulose was prepared from ethylcellulose (DS 1.9) by the use of acetone instead of DMSO as a solvent. Secondly, completely allylated methylcellulose, tri-*O*-allylcellulose, and allylated ethylcellulose soluble in many organic solvents were converted into

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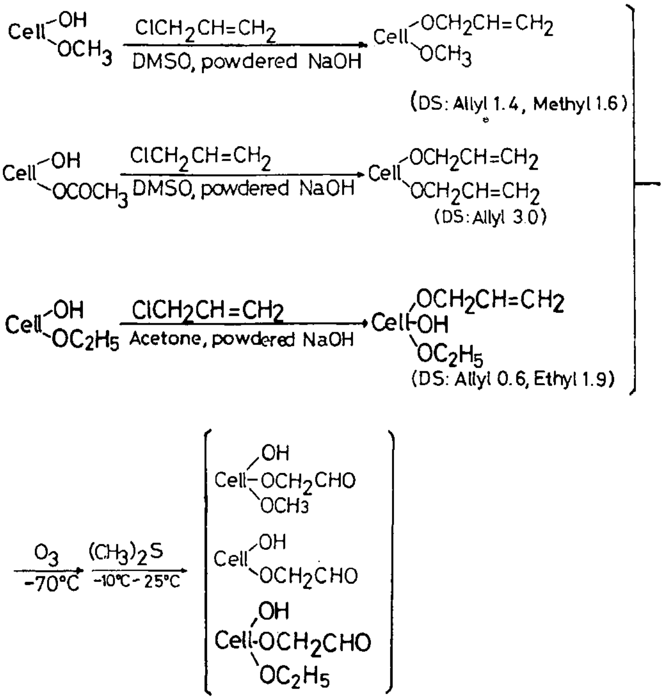


Fig. 1. Scheme of preparation of aldehydocelluloses.

highly reactive aldehydocelluloses without depolymerization by ozonization followed by reduction with dimethylsulfide (Fig. 1). The aldehydocelluloses thus prepared were not soluble in organic solvents and alkali.

EXPERIMENTAL

Samples

Cellulose samples were commercially available methylcellulose (DS 1.6, Wako Chemical Ind. Co., Ltd.), cellulose acetate (DS 1.75, 2.24, and 2.39, Daicel Chemical Ind. Co., Ltd.), and ethylcellulose (DS 1.9, Wako Chemical Ind. Co., Ltd.). These samples were used after being dried at 105°C. DMSO and acetone were dehydrated over molecular sieve 3A. Other solvents and reagents of the special grade were used without any further purification.

Preparation of Completely Allylated Methylcellulose, Tri-*O*-allylcellulose and Allylated Ethylcellulose

Completely allylated methylcellulose and tri-*O*-allylcellulose were prepared according to the procedure in the previous paper.[8]

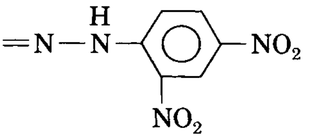
Allylated ethylcellulose was prepared from ethylcellulose by the almost same method as that used for allylation of methylcellulose and cellulose acetate except for the use of acetone instead of DMSO. Namely, 1 g of ethylcellulose was dissolved completely in 60 mL acetone at room temperature with stirring for 1 h. Powdered NaOH of 12.5 mol per hydroxyl group in ethylcellulose was added to this solution at room temperature, and the resultant suspension was stirred for 1 h under a nitrogen atmosphere. After the addition of allyl chloride equivalent to the amount of powdered sodium hydroxide all at once, the temperature was raised to 70°C. The reaction mixture was refluxed with stirring at that temperature for 4 h. The products were isolated, purified immediately after allylation in order not to deteriorate their quality by oxidation, and then stored under a nitrogen atmosphere at the temperature below 0°C. The products were characterized by ^{13}C-NMR and IR spectrometries.

Ozonization and Subsequent Reduction

One gram of each sample was dissolved in 60 mL of dichloromethane-methanol (5 : 1). Oxygen containing ozone was bubbled into the solution with a flow rate of 0.5 L/min at -70°C for about 30 min, until the color of the solution became blue. After ozonization, the remaining ozone was purged off from the solution with nitrogen gas, and 1 mL of dimethylsulfide [$(CH_3)_2S$] was added at -60°C. The reaction mixture was stirred at -10°C and 0°C for 1 h each. Then, the temperature was raised to room temperature and kept for another 2 h. The solution was evaporated under reduced pressure at 40°C to yield film or filmlike residues. The product was washed thoroughly with water in order to remove formaldehyde and paraformaldehyde produced by ozonization, and dried under vacuum at 40°C. Ozonization products before and after $(CH_3)_2S$ treatment were characterized by ^{13}C-NMR and IR spectrometries. The film (0.1 g) was subjected to a treatment with 2,4-dinitrophenylhydrazine/2N HCl (50 mL) at 0°C for more than 2 h, and the contents of aldehyde groups were calculated according to the following formula:

$$\mathrm{N}(\%) = \frac{1 \times A/1000 \times 4 \times 14}{1 + 1 \times A/1000 \times 180} \times 100$$

where N(%) = nitrogen content calculated on the basis of elementary analyses of hydrazone, A = content of aldehyde group (meq/g cellulose), and 180 = Molecular weight of



$1 \times A/1000 \times 4 \times 14$ = weight of nitrogen contained in the hydrazone, and $1 + 1 \times A/1000 \times 180$ = weight of the hydrazone obtained from 1 g of aldehydocelluloses. The content of hydroxyl groups were calculated by the formula in our subsequent paper.[9]

General Analyses

Degrees of substitution (DS) of cellulose ethers were determined based on the elementary analyses, IR spectra, ^{1}H-NMR, and/or the content of double bonds.[8] IR spectra were measured by the KBr disk technique and the deposited film technique from chloroform solutions, using a Shimazu IR-435 spectrophotometer. ^{1}H-NMR spectra were measured by the use of an MH-100 type spectrometer [Japan Electro Optics Laboratory (JEOL)]. ^{13}C-NMR spectra were measured on a JEOL FX-100 type spectrometer, and the measuring conditions were as follows: 8000 points, 6000 Hz, pulse delay 0.8 s, and the Fydac accumulation method. The GPC (gel permeation chromatography) instrument was a Waters ALC/GPC 244 system equipped with five Styragel columns in the porosity ranges: 10^5, 10^4, 10^3, 500 and 10^2. Polystyrene standards were used for preliminary calibration.

RESULTS AND DISCUSSION

Preparation of Allylated Ethylcellulose

Figure 2 shows the relation between the amount of powdered NaOH added as a base and the total DS of allylated ethylcellulose. Allylated ethylcellulose with the DS of 1.9 by ethyl and 0.6 by allyl groups was prepared by the addition of reagents more than 12.5 mol per mol of hydroxyl group in ethylcellulose, but completely allylated ethylcellulose was not obtained. This allylated ethylcellulose described above was soluble in many organic solvents such as chloroform, dichloromethane, benzene, and tetrahydrofuran. Its ^{13}C-NMR spectrum was shown in Figure 3 (spectrum 1). The chemical shifts of C-1, C-6, C-2, (or C-3), C-3 (or C-2) and two allyl carbons involved in a double bond were about 102, 68, 82, 83.2, 131 ($-\underline{C}H{=}CH_2$) and 119($-CH{=}\underline{C}H_2$) ppm, respectively, being almost the same as those of the corresponding signals of completely allylated methylcellulose. Its IR spectrum has an absorption band around 1640 cm^{-1} due to carbon-carbon double bonds in allyl groups (Fig. 4, spectrum 5).

Ozonization of Allylated Cellulose and Allylated Cellulose Alkyl Ethers

The mechanism of ozonization and subsequent reduction with dimethylsulfide[10] of allylated celluloses was shown in Figure 5. Ozone is generally used

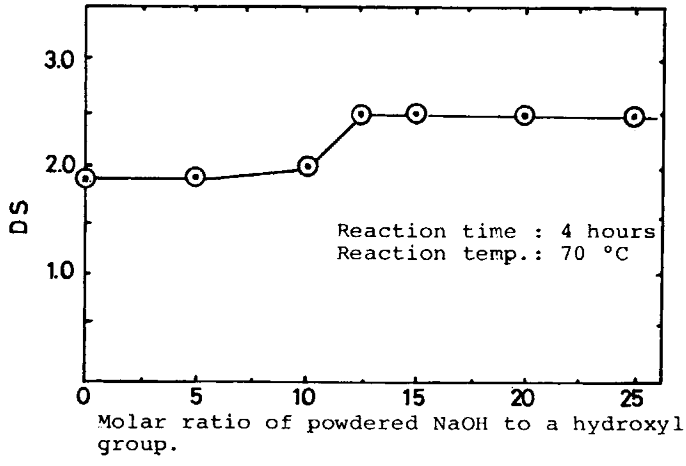


Fig. 2. DS of allylated ethylcellulose vs. the amount of powdered NaOH. Note: Allyl chloride equimolar to NaOH was added. DS by ethyl in ethylcellulose is 1.9.

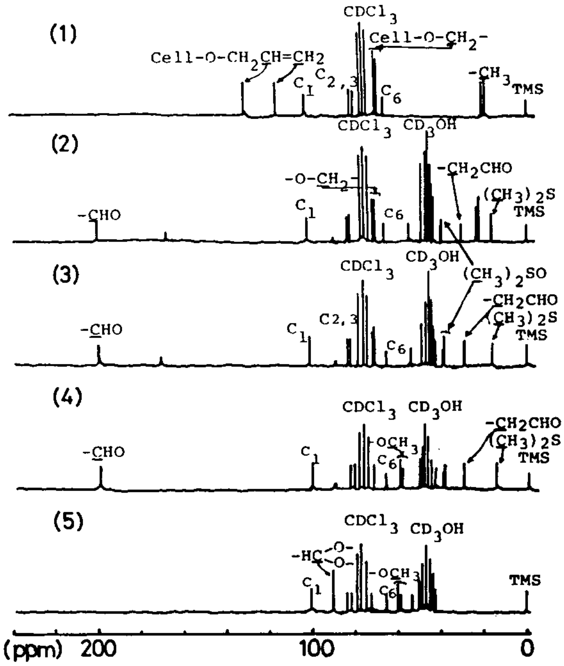


Fig. 3. ^{13}C-NMR spectra of aldehydocelluloses and their preceding derivatives: (1) allylated ethylcellulose (DS of 1.9 by ethyl and of 0.6 by allyl); (2) aldehydocellulose from allylated ethylcellulose; (3) aldehydocellulose from tri-*O*-allylcellulose; (4) aldehydocellulose from completely allylated methylcellulose; (5) ozonization product from completely allylated methylcellulose before $(CH_3)_2S$ treatment. Allylated celluloses were ozonized in the mixture of $CDCl_3$ and CD_3OH (5 : 1).

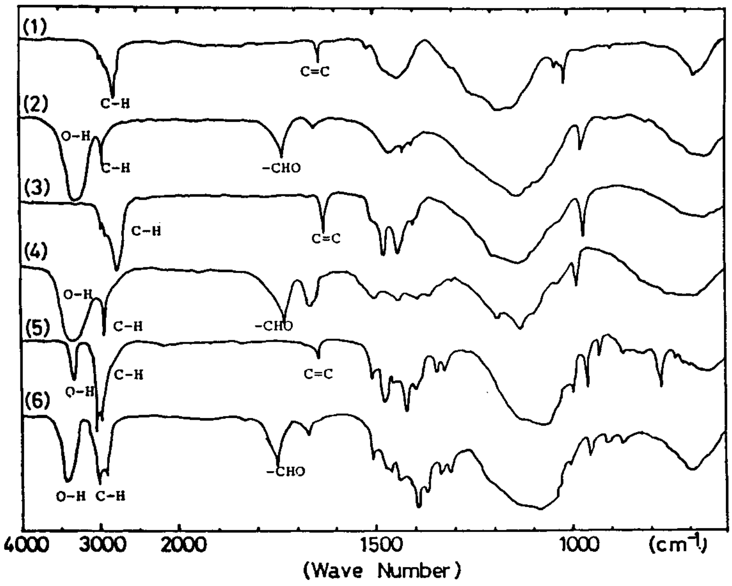


Fig. 4. IR spectra of allylated celluloses and aldehydocelluloses. (1) completely allylated methylcellulose (DS by allyl: 1.4); (2) aldehydocellulose from completely allylated methylcellulose; (3) tri-*O*-allylcellulose; (4) aldehydocellulose from tri-*O*-allylcellulose; (5) allylated ethylcellulose (DS by allyl: 0.6; by ethyl: 1.9); (6) aldehydocellulose from allylated ethylcellulose.

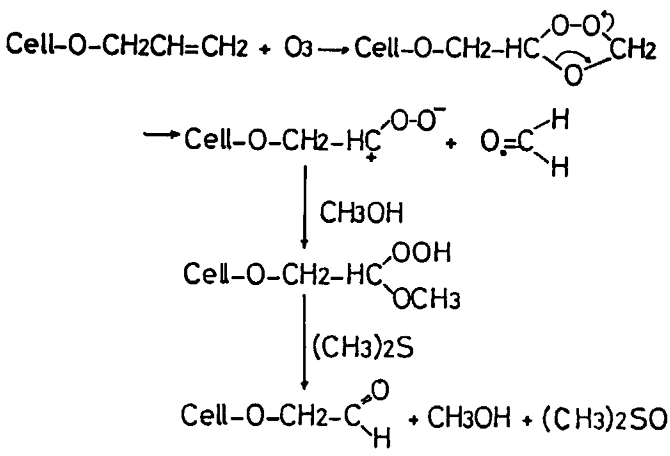


Fig. 5. Mechanism of ozonization and subsequent reduction of allylated celluloses.

to cleave C=C double bonds selectively. The use of ozone in pulp bleaching, however, caused the decrease of pulp viscosity;[11] this indicates that glycosidic linkages are cleaved during ozonization. Therefore, number average molecular weights ($\overline{M}_n$) of allylated methylcellulose before and after ozonization were determined by GPC in order to ascertain whether or not depolymerization occurs during ozone treatment under the condition adopted in the present work. Table I shows $\overline{M}_n$ does not change essentially before and after ozonization. Namely, ozone did not attack the glycosidic linkages. Ozone was found, however, to cleave allyl ether bonds to liberate free hydroxyl groups as shown from the increase of the absorption of 3400 cm^{-1} in IR spectrum (Fig. 4). The free hydroxyl groups after ozonization were 0.5, 1.0, and 0.7 for completely allylated methylcellulose, tri-*O*-allylcellulose, and allylated ethylcellulose, respectively.[9]

Comparison of ^{13}C-NMR spectra of ozonization products before and after $(CH_3)_2S$ treatments (spectra 5 and 4 in Fig. 3) revealed that, after $(CH_3)_2S$ treatment, a signal around 90 ppm was hardly detected, and instead a signal due to an aldehyde carbon appeared around 200 ppm. This indicates that $(CH_3)_2S$ reduces a peroxide generated by ozonization (—O—CH—O—) to yield aldehydocelluloses. The signal of the aldehyde carbon in formaldehyde

TABLE I

Number Average Molecular Weight before and after Ozonization and Subsequent $(CH_3)_2S$ Treatment of Completely Allylated Methylcellulose[a] of Various Temperatures

Sample	$\overline{M}_n$
Before ozonization	4.4 × 10^4
After ozonization	
for 30 min	
At −5°C	4.3 × 10^4
At −30°C	4.3 × 10^4
At −70°C	4.6 × 10^4

[a] DS of allyl: 1.4; DS of methyl: 1.6.

TABLE II
Contents of Aldehyde Groups in Aldehydocellulose Prepared from Completely Allylated Methylcellulose[a] vs. Ozonization Temperature

Sample	meq/g cellulose	DS (—CHO)
Ozonized at −5°C	1.57	0.36
Ozonized at −30°C	2.55	0.57
Ozonized at −70°C	2.74	0.62

[a] DS for allyl: 1.4.

TABLE III
Contents of Aldehyde Groups in Aldehydocelluloses[a]

Sample (DS by allyl)	meq/g	DS (—CHO)	DS (—OH)[a]
From allylated methylcellulose (1.4)	2.74	0.6	0.5
From tri-*O*-allylcellulose (3.0)	2.33	0.6	1.0
From allylated ethylcellulose (0.6)	0.10	0.02	0.7

[a] Ozonized at −70°C.

produced by ozonization was not detected. It is known that formaldehyde cannot be present as it is in nonaqueous solvents and is removed as gas or paraformaldehyde from these solvents.[12] As shown in Figure 3, all aldehydocelluloses have signals due to $—O—\underline{C}H_2—CHO$ and aldehyde groups around 30 and 200 ppm, respectively. The signals around 47 ppm are due to DMSO converted from $(CH_3)_2S$.

Periodate-oxidized cellulose (dialdehydocellulose) is known to show no absorption band around 1730 cm^{-1} in its IR spectrum, because of the formation of the hemiacetal crosslinking.[13] However, the new derivatives have an absorption band around 1730 cm^{-1} due to free aldehyde groups (spectra 2, 4, and 6 in Fig. 4). This bond was hardly detected after the treatment of aldehydocelluloses with 2,4-dinitrophenylhydrazine, supporting the absorption at 1730 cm^{-1} is surely due to free aldehyde groups.

The contents of aldehyde groups in the aldehydocelluloses and the dependence of these values on an ozonization temperature were shown in Tables III and II, respectively. The content of aldehyde groups increases with decreasing the ozonization temperature (Table II). This may be due to the restraint of side reactions such as deallylation during ozonization at higher temperature. DS by allyl groups in completely allylated methylcellulose is about a half of that in tri-*O*-allylcellulose. Nevertheless, as shown in Table III, DS by aldehyde group in aldehydocelluloses derived from both celluloses is almost the same. In other words, the efficiency in the conversion of allyl groups into aldehyde groups is lower for tri-*O*-allylcellulose than for completely allylated methylcellulose. The following factors may contribute to these results:

(1) the difference in the extent of deallylation by ozonization yielding free hydroxyl groups,

(2) the difference in the extent of formation of hemiacetal crosslinking which could not be determined as aldehydes,
(3) the difference in the extent of further oxidation of aldehyde groups to carboxyl groups.

As the DS by hydroxyl group was 0.5 and 1.0 for ozonization products of completely allylated methylcellulose and tri-*O*-allylcellulose, the factor (1) clearly contributed to the conversion efficiency. Although the signal around 170 ppm in Figure 3 may be assigned to carboxyl groups, the formation of those does not seem to be essential. Allyl groups were completely removed after the ozonization as seen in Figure 3. Nevertheless, the total DS by aldehyde and hydroxyl groups are less than 3 especially for aldehydocellulose from tri-*O*-allylcellulose. This suggests that the condition used for the determination of aldehyde groups may be incomplete for samples in the form of film. The more severe conditions, however, could not be adopted, because aldehyde groups may be produced secondarily by hydrolysis of glucosidic linkages.

Aldehydocelluloses from three kinds of cellulose derivatives were not soluble in organic solvents and alkali after recovery from their dichloromethane–methanol solutions by evaporation. This is probably due to the formation of hemiacetal linkages. On the other hand, the products by ozonization without subsequent $(CH_3)_2S$ treatment dissolved alkali, because peroxide in ozonized allylcelluloses was converted into carboxyl groups by alkali treatment.[9]

CONCLUSION

1. Allylated ethylcellulose with DS of 0.6 by allyl and of 1.9 by ethyl groups was prepared by the use of acetone, allyl chloride, and powdered sodium hydroxide.
2. Completely allylated methylcellulose, tri-*O*-allylcellulose, and allylated ethylcellulose were converted into aldehydocelluloses (DS by —CHO; 0.6, 0.6, and 0.02) by ozonization followed by reduction with dimethylsulfide.
3. There occurred no depolymerization during the preparation of aldehydocelluloses.
4. Aldehyde groups in the aldehydocelluloses were detected by ^{13}C-NMR and IR, differing from those in periodate-oxidized cellulose.
5. The content of aldehyde groups in a aldehydocelluloses increases by decreasing ozonization temperature.
6. The aldehydocelluloses were recovered as film or filmlike residue after evaporation of their dichloromethane–methanol solutions and were not soluble in organic solvents and alkali.

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