Preparation of Glycidyl Celluloses from Completely Allylated Methylcellulose and Tri-O-allylcellulose

TETSUO KONDO, ATSUSHI ISHIZU, and JUNZO NAKANO,

Department of Forest Products, Faculty of Agriculture, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Synopsis

Glycidyl celluloses were prepared from completely allylated methylcellulose and tri-O-allylcellulose with m-chloroperbenzoic acid in homogeneous chloroform solutions. The degrees of substitution (DS) by epoxy groups were 0.60 and 1.33 for the products prepared from allylated methylcellulose and tri-O-allylcellulose, respectively. They were soluble in not only many organic solvents, but also methanol–water mixtures [more than 70% (v/v)]. These products were characterized by infrared spectroscopy (IR), ^{13}C-NMR spectroscopy, and gel permeation chromatography (GPC).

INTRODUCTION

Epoxy groups are highly reactive to amines, alcohols, phenols, carboxylic acids, carboxylic anhydrides, Lewis acids, and their complexes. Many glycidyl ethers of synthetic polymers, therefore, have been prepared[1-10] and utilized in combination with suitable curing agents for practical uses.[9-13] On the other hand, only two cellulose derivatives containing glycidyl groups have been prepared.[14,15] Rogovin and his co-workers introduced glycidyl groups into cellulose by alkaline treatment of 3-chloro-2-hydroxypropylcellulose ethers.[14] Iwakura et al. introduced this group onto cellulose fiber by grafting with glycidyl methacrylate from the standpoints of the preparation of the reactive fiber to dyes and of its application as an ion exchange fiber.[15]

The authors succeeded in complete allylation of celluloses[16] with allyl chloride and powdered sodium hydroxide in dimethylsulfoxide (DMSO) solutions, and investigated their chemical modifications[17,18] and their application[19] as supports for immobilized enzymes.

In this article, glycidyl celluloses with high DS by epoxy groups were prepared from completely allylated celluloses with m-chloroperbenzoic acid in their homogeneous chloroform solutions (Scheme 1). These new derivatives are expected to be composite materials by grafting with synthetic polymers.
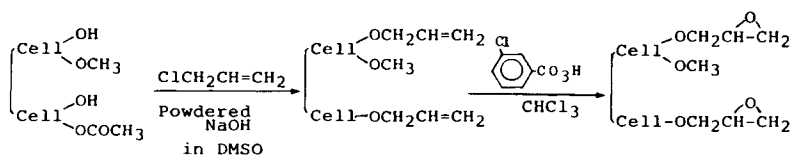
Scheme 1. Preparation of glycidyl cellulose ethers.

EXPERIMENTAL

Samples

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

Completely allylated methylcellulose (AMC; DS by methyl 1.6, by allyl 1.4) and tri-O-allylcellulose (TAC; DS by allyl 3.0) were prepared from these cellulose samples according to the procedure in a previous article.[16]

Preparation of Glycidyl Celluloses

One gram of each sample (AMC and TAC) was dissolved in 30 mL of chloroform at room temperature. After complete dissolution, 35 mL of m-chloroperbenzoic acid–chloroform solution was added dropwise to the cellulose solution. The optimum preparation condition was investigated by changing the amount of the reagent, the reaction time, and the reaction temperature.

After epoxidation, the reaction mixture was poured into 100 mL of 20% aqueous sodium bisulfite, and extracted with chloroform. The chloroform layer was extracted in turn three times with 100 mL portions of 10% aqueous sodium bicarbonate solution and washed with water. The chloroform solution was evaporated under reduced pressure at 40°C to syrup. Then, 50 mL of water was added to the syrup, and the resultant solution was lyophilized. White cottonlike products were obtained and characterized by IR, ^{13}C-NMR, and GPC.

Determination of Glycidyl Groups

The epoxidation product (0.1 g) was suspended in 20 mL of acetic anhydride. An adequate amount of trimethylamine hydrochloride was added to the suspension. After 2 h at room temperature, the liberated amine was titrated with $0.1N$ perchloric acid in acetic acid to a crystal violet end point (violet–yellow–green). The DS's of glycidyl groups, X, were calculated according to the following formula:

$$\frac{\text{sample (g)}}{M} \times X = A$$

where M = molecular weight of an epoxidized allylated anhydroglucose unit, $240.4 + 16X$ for epoxidized AMC and $282 + 16X$ for epoxidized TAC, and A = moles of $HClO_4$ consumed by titration.

General Analyses

DS's of cellulose ethers were determined on the basis of the elementary analyses, IR spectra, and/or the content of double bonds.[15] IR spectra were measured by the deposited film technique from chloroform solutions, using a Shimazu IR-435 spectrophotometer. ^{13}C-NMR spectra were measured on a

JEOL (Japan Electro Optics Laboratory) FX-100 type spectrometer, and the measuring conditions were as follows: 8000 points, 6000 Hz, pulse delay 0.3 s, and the Fydac accumulation method. The GPC 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 Glycidyl Celluloses

Figure 1 shows IR spectra of TAC oxidized with m-chloroperbenzoic acid under various conditions. All products have absorption bands around 990, 800, and 710 cm^{-1} due to symmetrical and asymmetrical stretchings of epoxy rings. On the other hand, absorption bands around 1640 cm^{-1} due to C$=$C double bonds were not detected. Instead, absorption bands around 3400 and 1730 cm^{-1} due to hydroxyl and carbonyl groups, respectively, appeared. This indicates that epoxy rings were cleaved to yield hydroxyl groups, and a part of these groups were oxidized to carbonyl groups. The relationship between DS
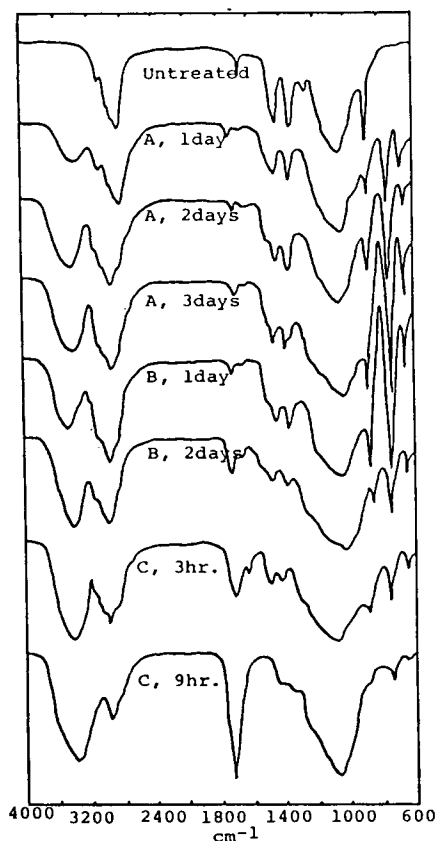

Fig. 1. IR spectra of epoxidized tri-O-allylcellulose; (A) reagent/ C$=$C = 1.5, 25°C; (B) reagent/ C$=$C = 3.0, 25°C; (C) reagent/ C$=$C = 1.5, 50°C.
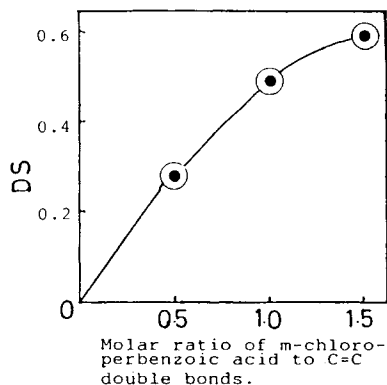
Fig. 2. Relationship between DS by glycidyl groups and the amount of m-chloroperbenzoic acid in the epoxidation of completely allylated methylcellulose: Temp, room temp (25°C); time, 3 days; solvent, $CHCl_3$.

and reaction conditions was investigated by changing reaction time, reaction temperature, and the amounts of reagents. Figures 2 and 3 show that the DS by glycidyl groups was controlled by changing the amounts of m-chloroperbenzoic acid under the used condition. It was also confirmed that an excessive addition (more than 2.0 mol/mol carbon—carbon double bonds) caused further oxidation of produced hydroxyl groups. Judging from Figures 1–4, the optimum reaction condition for preparing highly substituted glycidyl celluloses is as follows: reaction time, 3 days; reaction temperature, room temperature (25°C); the amounts of m-chloroperbenzoic acid, 1.5 mol per mol of carbon—carbon double bonds. Under the above conditions adopted here, DS's by glycidyl groups in epoxidized AMC and TAC were 0.60 and 1.33, respectively.
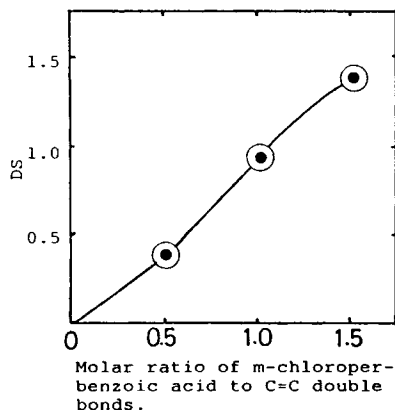

Fig. 3. Relationship between DS by glycidyl groups and the amount of m-chloroperbenzoic acid in the epoxidation of tri-O-allylcellulose: temp, room temp (25°C); time, 3 days; solvent, $CHCl_3$.
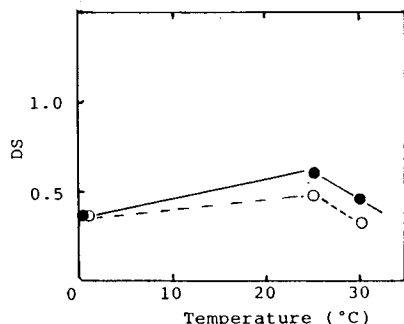
Fig. 4. Effect of temperature on epoxidation of completely allylated methylcellulose: reagent/ C=C = 1.5; solvent, CHCl$_3$. Time: (●) 3 days; (○) 4 days.

Characterization of Glycidyl Celluloses

Solubility

The glycidyl celluloses thus produced were soluble not only in chloroform but also in other organic solvents. Interestingly, they dissolved in methanol–water mixtures [more than 70% (v/v)].

Characterization by ^{13}C-NMR

Figure 5 shows the ^{13}C-NMR spectra of the cellulose derivatives before and after m-chloroperbenzoic acid oxidation. Both AMC and TAC [spectra (1) and (2)] have chemical shifts around 115 and 135 ppm due to allyl groups. On the other hand, the oxidized products [spectra (3) and (4)] do not have such chemical shifts. This indicates that double bonds in allylated celluloses are completely oxidized by m-chloroperbenzoic acid. In addition, both the products have the chemical shifts around 51–53 ppm due to epoxy rings. Furthermore, they have two kinds of new signals at both the range of methylene carbons [I in spectra (3) and (4)] and of olefin carbons [II in spectra (3) and (4)]. These signals were reported for partly epoxidized cis-1,4-polybutadiene.[20, 21] Therefore, it is clear that the glycidyl celluloses have been prepared from AMC and TAC with m-chloroperbenzoic acid.

Characterization by GPC

m-Chlorobenzoic acid is produced from m-chloroperbenzoic acid as a result of epoxidation of allylated celluloses. This organic acid may cleave the glycosidic linkages of the produced glycidyl celluloses. In order to evaluate the extent of acid hydrolysis of the products, number average molecular weight before and after epoxidation was calculated on the basis of GPC measurement. As shown in Table I, glycosidic linkages of the products are stable during the epoxidation at 25°C.

The glycidyl celluloses are expected to be very reactive to many functional groups and to be grafted with synthetic polymers to give high value-added new cellulose derivatives.
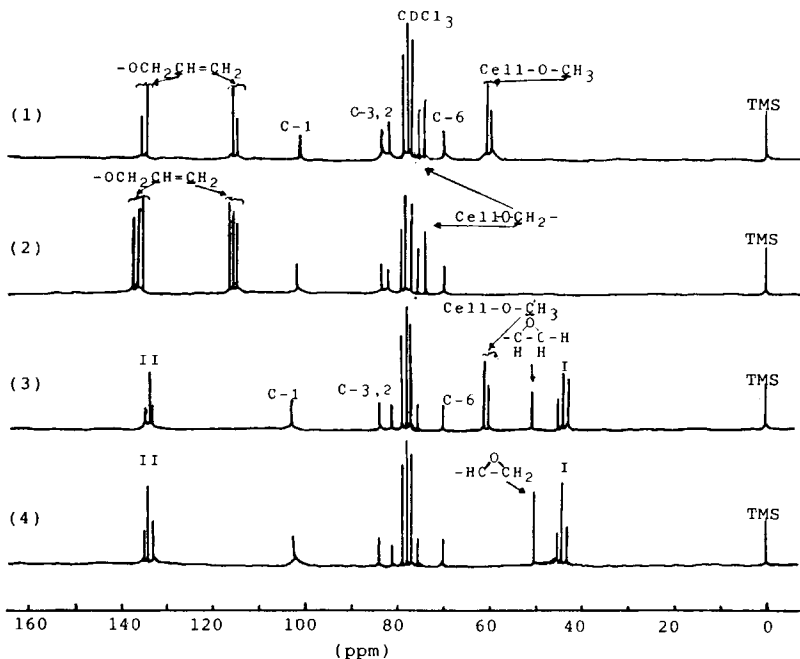
Fig. 5. ^{13}C-NMR spectra of completely allylated methylcellulose, tri-O-allylcellulose, and their glycidyl ethers: (1) completely allylated methylcellulose; (2) tri-O-allylcellulose; (3) epoxidized, completely allylated methylcellulose; (4) epoxidized tri-O-allylcellulose. TMS = tetramethyl silane (internal standard); solvent, CDCl$_3$.

TABLE I
Number Average Molecular Weight before and after Epoxidation

Sample		$\overline{M_n}$
Before treatment (completely allylated methylcellulose[a]		4.4×10^4
After treatment for 3 days	at 0°C	4.4×10^4
	at 25°C	4.3×10^4
	at 30°C	3.5×10^4

[a] DS by methyl, 1.6; by allyl, 1.4.

CONCLUSION

Glycidyl celluloses have been prepared from AMC and TAC with m-chloroperbenzoic acid in chloroform. The epoxy rings in the products are confirmed by IR and ^{13}C-NMR. The products are soluble in many organic solvents such as chloroform, acetone, methanol, and others. Comparing the relationship between DS by glycidyl groups and reaction conditions, it was shown that the DS is controlled by changing the amounts of the reagent, and that the optimum reaction condition for preparing highly substituted derivatives was as follows: reaction time, 3 days; reaction temp, 25°C; the amounts of the reagent, 1.5 mol/mol of C=C in allylated celluloses. The maximum DS's by glycidyl groups after epoxidation of AMC and TAC are 0.60 and 1.33,

respectively. During the oxidation at 25°C, the cleavage of glycosidic linkages did not occur.

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