

Preparation of Completely Allylated and Methallylated Celluloses from Methylcellulose and Cellulose Acetate

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Synopsis

Cellulose ethers having various amounts of carbon—carbon double bonds were prepared by allylation or methallylation of commercial methylcellulose (DS = 1.6). Namely, methylcellulose dissolved in dimethylsulfoxide (DMSO) was treated with allyl chloride or methallyl chloride in the presence of powdered sodium hydroxide as a base. Tri-*O*-allyl and tri-*O*-methallyl celluloses were also prepared easily from commercial cellulose acetate (DS = 1.75) with powdered sodium hydroxide and the corresponding chlorides. Thermal stabilities of these cellulose derivatives and their behaviors to oxygen in the air were studied by the use of TG-DSC and solubility test, respectively.

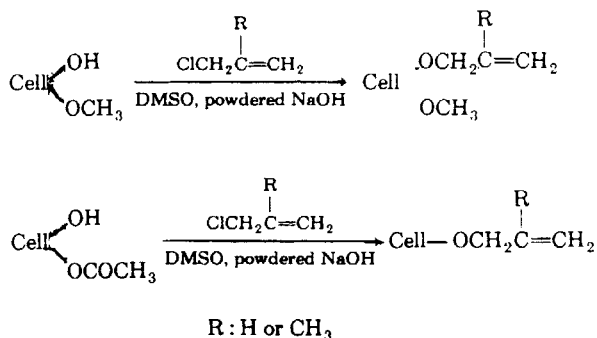
INTRODUCTION

The carbon—carbon double bonds in the organic compounds are generally highly reactive and are, therefore, useful for the modification of those compounds. For this reason the introduction of carbon—carbon double bonds onto cellulose and its derivatives by esterification and etherification has also been studied¹⁻⁸ to open the possibilities of a number of chemical and physical modifications of cellulose. Recently, highly reactive cellulose derivatives have attracted attention in various fields of high technology such as electronics, medical engineering, biochemistry, and others.

The authors have developed a new simple preparation method of tri-*O*-substituted cellulose ethers, which are soluble in many organic solvents and have some chemically reactive groups such as double bonds, aromatic rings, and halogens by the use of the SO₂-diethylamine (DEA)-DMSO mixture, one of nonaqueous cellulose solvents, as a solvent system.⁹

In the present work, first the authors tried to prepare new completely allylated cellulose from DMSO-soluble cellulose derivatives such as partially methylated cellulose and cellulose acetate. However, when cellulose ethers are used as functional polymers such as ion exchangers, enzyme derivatives of cellulose and heavy metal-absorbing celluloses, it is not necessary to introduce two or three functional groups on an anhydroglucose unit of cellulose. Secondly, therefore, it was intended to establish the conditions for introducing the various amounts of allyl or methallyl groups onto cellulose.

Both allylated and methallylated celluloses prepared in the present work were soluble in some organic solvents, and were characterized by infrared (IR) spectroscopy, ¹³C- and ¹H-NMR spectroscopies, and TG-DSC.



Scheme 1. Preparation of completely allylated and methallylated cellulose ethers from methylcellulose and cellulose acetate

EXPERIMENTAL

Samples

Cellulose samples were commercially available methylcellulose (DS = 1.6, 400 cps, Wako Chemical Ind. Co., Ltd.) and cellulose acetate (DS = 1.75, DP = 110, Daicel Chemical Ind. Co., Ltd.) both of which are soluble in DMSO. These samples were used after being dried at 105°C for 3 h in air. The special grade DMSO was used after being dried over molecular sieve 3A. Other solvents and reagents of the special grade were used without any further purifications.

Preparation of Allylated and Methallylated Methylcelluloses

Completely allylated and methallylated methylcelluloses were prepared (Scheme 1) as follows: One gram of methylcellulose was dissolved completely in 60 mL DMSO at 60°C with stirring for 1 h. Powdered sodium hydroxide (10 mol/mol hydroxyl group in methylcellulose) was added to this solution at room temperature and the suspension was stirred for 1–2 h under nitrogen atmosphere. After the addition of allyl chloride or methallyl chloride equivalent to the amount of powdered sodium hydroxide all at once, the temperature was raised to 70°C and kept at this temperature for 4 h. After the reaction mixture was cooled to room temperature, water was added, and then extracted with chloroform.

The chloroform layer was washed three times with water and evaporated under reduced pressure at 40°C to a syrup. Allylated and methallylated methylcelluloses were precipitated from the syrup by the addition of 95% methanol. The precipitate was filtered off and dried under vacuum at 40°C. Yields of these products were 90–95% of theoretical one. They were stored under a nitrogen atmosphere at the temperature below 0°C in order to avoid oxidation. These products were characterized by ¹³C-NMR, ¹H-NMR, and IR spectrometries.

Partially allylated and methallylated methylcelluloses prepared by changing the amounts of reagents, the reaction time, and the reaction temperature were characterized as described above.

Preparation of Allylated and Methallylated Celluloses from Cellulose Acetate

Tri-*O*-allyl and tri-*O*-methallyl celluloses were prepared from cellulose acetate by the almost same method as that used for allylation and methallylation of methylcellulose (Scheme 1). Namely, 1 g of cellulose acetate was dissolved completely in 60 mL DMSO at 60°C with stirring for 1 h. Powdered NaOH of 30 mol per anhydroglucose unit 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 or methallyl chloride equivalent to the amount of powdered sodium hydroxide all at once, the temperature was raised to 70°C and kept at this temperature for 4 h. The reaction products were isolated and purified immediately after etherification in order not to deteriorate their quality by oxidation. This is the same procedure as used for the preparation of completely allylated and methallylated methylcelluloses. Products were stored under a nitrogen atmosphere at the temperature below 0°C in order to avoid oxidation.

Partially allylated and methallylated products were also prepared with the reduced amounts of reagents.

General Analysis

Degrees of substitution (DS) of cellulose ethers were determined based on elementary analyses,* IR spectra, ¹H-NMR and/or the content of double bonds. Contents of double bonds were determined by the Wijs method.¹⁰ IR spectra were measured by the KBr disk technique and the deposited film technique from chloroform solutions, using a Shimadzu IR-435 spectrophotometer. ¹H-NMR spectra were measured by the use of MH-100 type spectrometer (Japan Electro Optics Laboratory; JEOL). ¹³C-NMR spectra were measured on JEOL FX-100 type spectrometer and the measuring conditions were as follows: 8000 points, 6000 Hz, pulse delay 0.3 s and Fydac accumulation method. TG and DSC curves were measured from room temperature to 500°C at the rate of 5°C/min in He and air atmospheres by the use of Rigaku-denki Standard Type TG-DSC equipment.

RESULTS AND DISCUSSION

Preparation of Allylated and Methallylated Methylcelluloses

Figure 1 shows the relation between the amount of powdered NaOH as a base and DS of allylated methylcellulose. DS was calculated on the basis of elementary analyses. A completely allylated methylcellulose was prepared by the addition of reagents more than 10 mol/mol hydroxyl group in methylcellulose. Figures 2 and 3 show DS of allylated and methallylated methylcelluloses vs. reaction time at 50, 70, and 90°C, respectively. In the case of

*DS of allyl groups in allylated methylcellulose, X , was calculated using the relationship $C(\%) = (91.2 + 36X)/(184.4 + 40X) \times 100$, where 184.4 = molecular weight of an anhydro-methylglucose unit (DS = 1.6), 184.4 + 40 X = molecular weight of an allylated anhydro-methylglucose unit, and 91.2 + 36 X = the amount of C in an allylated anhydro-methylglucose unit.

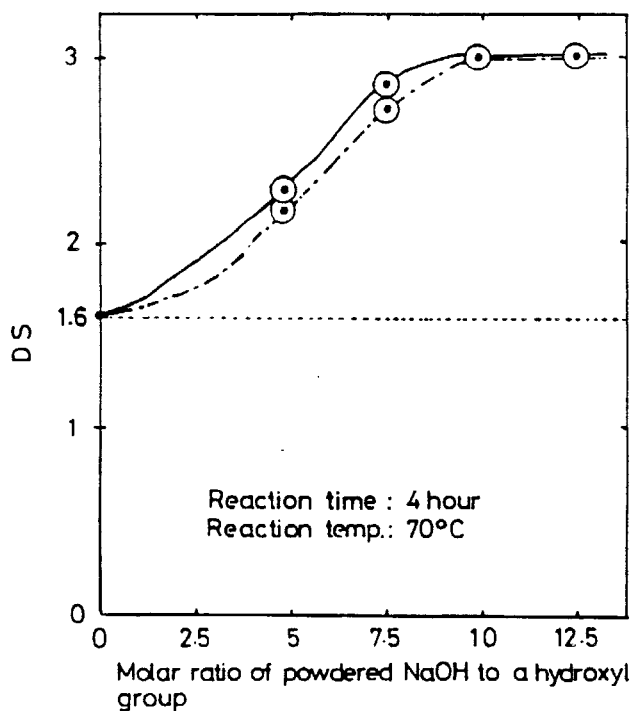


Fig. 1. DS of allylated (—) and methallylated (---) methylcellulose (DS by methyl, 1.6) vs. the amount of powdered NaOH. Allyl or methallyl chloride equimolar to NaOH was added:

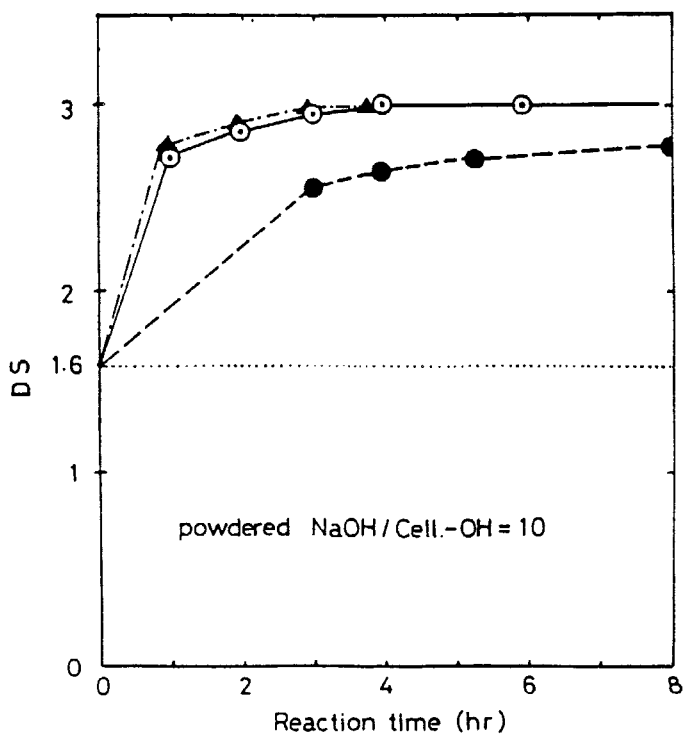


Fig. 2. DS of allylated methylcellulose vs. reaction time: (---▲---) 90°C; (—○—) 70°C; (---●---) 50°C.

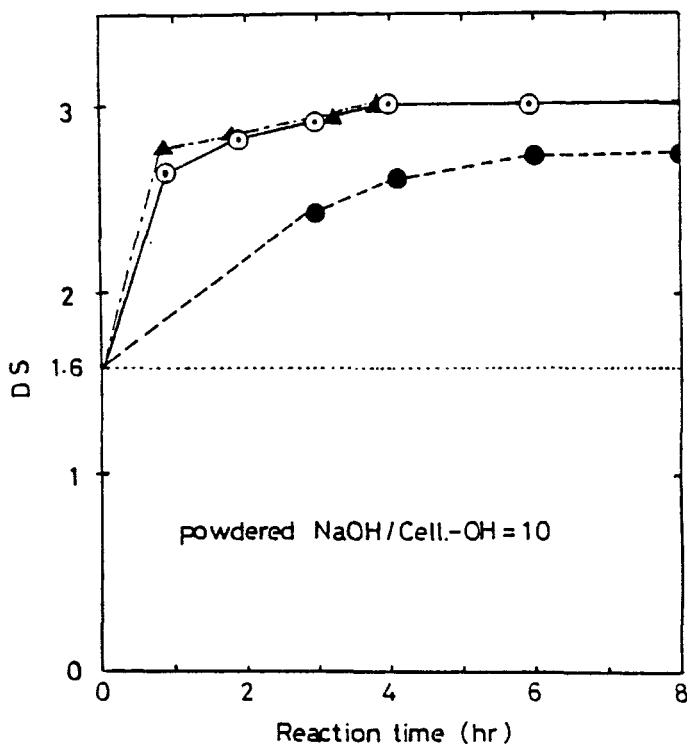
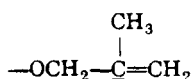


Fig. 3. DS of methallylated methylcellulose vs. reaction time: (---▲---) 90°C; (---○---) 70°C; (---●---) 50°C.

methallylated methylcellulose, DS was calculated not only on the basis of elementary analyses but also on the integration of methyl protons (around 1.8 ppm) of methallyl groups to that of total protons in a $^1\text{H-NMR}$ spectrum. The results shown in both figures indicate that 4 h treatment at 70°C is necessary to prepare the two kinds of completely substituted products. As was shown in Figure 4, IR spectra of these new cellulose derivatives have no absorption band around 3400 cm^{-1} due to the hydroxyl group, but have the absorption bands around 1640 or 1650 cm^{-1} due to $\text{C}=\text{C}$ stretching vibrations. $^{13}\text{C-NMR}$ spectra of four kinds of derivatives are shown in Figure 5. The chemical shift of C-1, C-6, C-2 (or C-3), and C-3 (or C-2) of both allylated and methallylated anhydroglucose units are found to locate around 102, 68, 82, and 83.2 ppm, respectively. Two peaks around 60 ppm are due to methyl groups in methylcellulose. In the case of methallylated derivatives, the chemical shift of methyl groups in methallyl groups are found to be 20 ppm. The chemical shifts of two allyl carbons involved in a double bond are found to locate around 135 ($-\text{CH}=\text{CH}_2$) ppm and 115 ($-\text{CH}=\text{CH}_2$) ppm. The chemical shift of each carbon in a substituent varies slightly depending on the positions to which the substituent is linked. The chemical shift of two methallyl carbons involved in a double bond are found to be around 143 ppm,



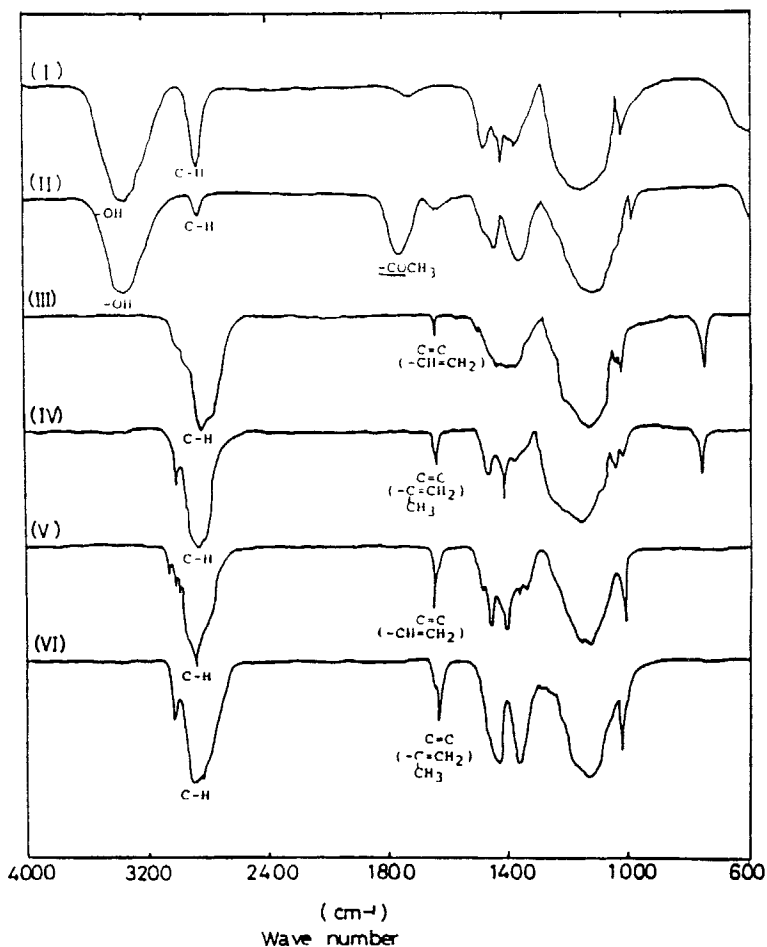


Fig. 4. IR spectra of allylated and methylated products: (I) methylcellulose (DS = 1.6); (II) cellulose acetate (DS = 1.75); (III) completely allylated methylcellulose; (IV) completely methylated methylcellulose; (V) tri-*O*-allyl cellulose; (VI) tri-*O*-methyl cellulose.

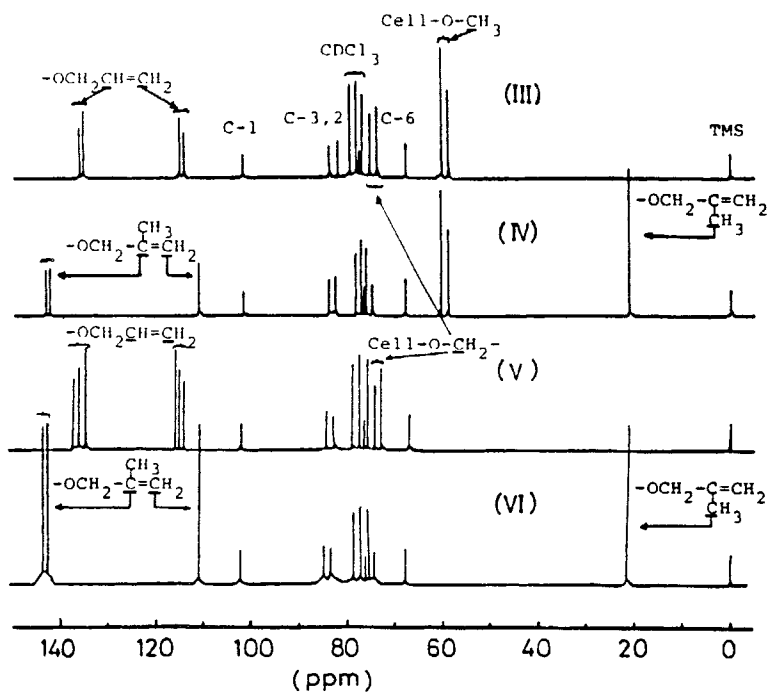


Fig. 5. ^{13}C -NMR spectra of allylated and methylated products: (III, IV, V, and VI) the same as those shown in Figure 4.

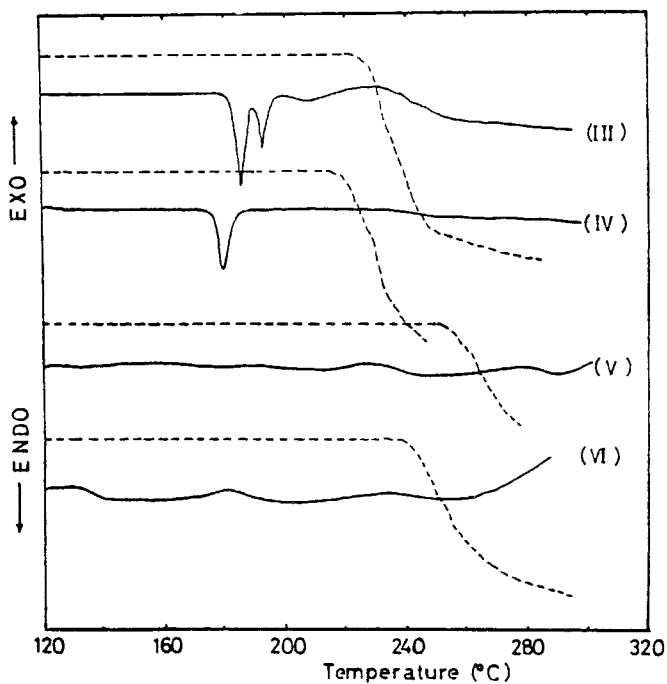


Fig. 6. TG-DSC curves of allylated and methallylated products (in He): (III, IV, V, and VI) the same as those shown in Figure 4; (---) TG, (—) DSC.

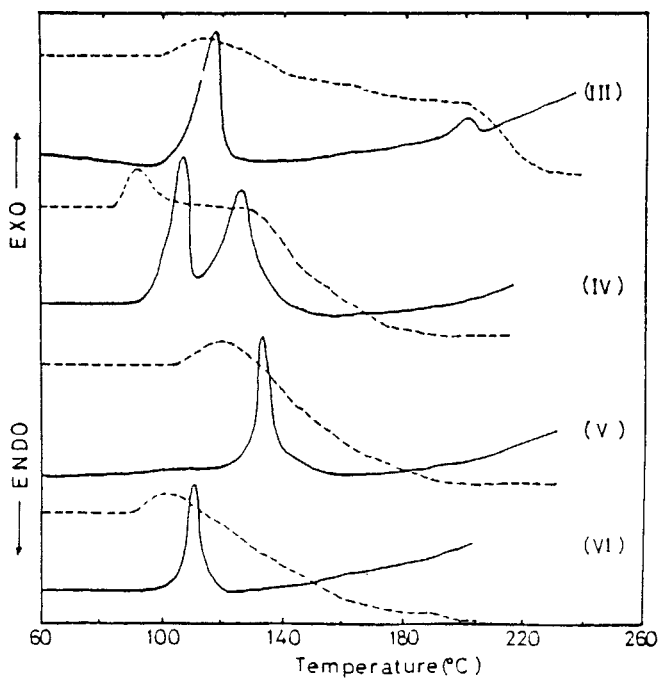


Fig. 7. TG-DSC curves of allylated and methallylated products (in the air): (III, IV, V, and VI) the same as those shown in Figure 4; (---) TG; (—) DSC.

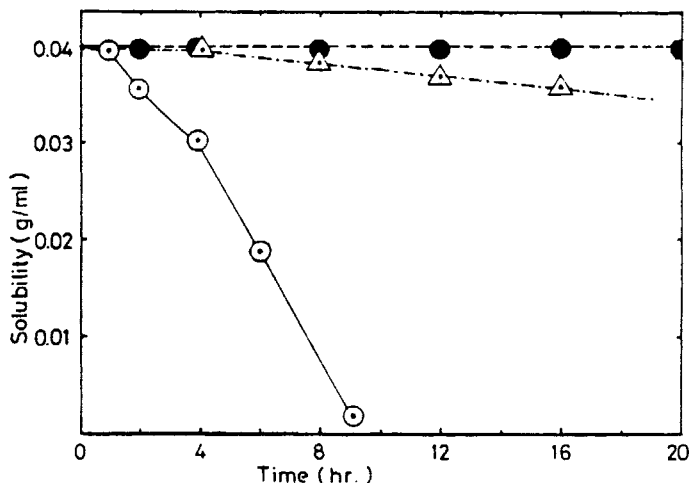
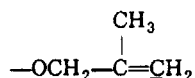


Fig. 8. Solubility of completely allylated methylcellulose in CHCl_3 after keeping at various temperatures in the air: (---●---) 0°C ; (---▲---) 20°C ; (---○---) 80°C .

and 111 ppm,



These results deny the possibility of a rearrangement of a double bond from the allyl type to the 1-propenyl type during etherification even under strong basic conditions.⁹

TG and DSC curves of four kinds of samples in He and in the air were shown in Figures 6 and 7, respectively. As shown in Figure 6, all allylated derivatives were stable to heating up to 200°C in He. On the other hand, clear exothermic peaks were detected after TG curves passed their maximum in the air (Fig. 7). The weight increase (15–20%) in the TG curves measured in the presence of the air proved that oxidation occurred in allylated and methallylated celluloses. This oxidation probably occurs at the α -position of double bonds to produce hydroperoxide groups. Then these products decomposed thermally through radical reactions.¹¹ These allylated and methallylated products did not show melting points.

Figure 8 shows that the completely allylated methylcellulose decreases its solubility in chloroform, when it is exposed to air at 20 and 80°C but it is stable at 0°C . The completely methallylated methylcellulose showed similar behavior. Therefore, it is necessary to store them under nitrogen atmosphere at the temperature below 0°C in order to avoid oxidation.

Preparation of Allylated and Methallylated Celluloses from Cellulose Acetate

These two kinds of tri-*O*-substituted cellulose ethers were prepared from cellulose acetate (DS = 1.75) in DMSO solutions. This preparation method seems to be more convenient than that in the SO_2 -DEA-DMSO system. DS of allyl groups was able to be controlled by the amount of powdered NaOH as

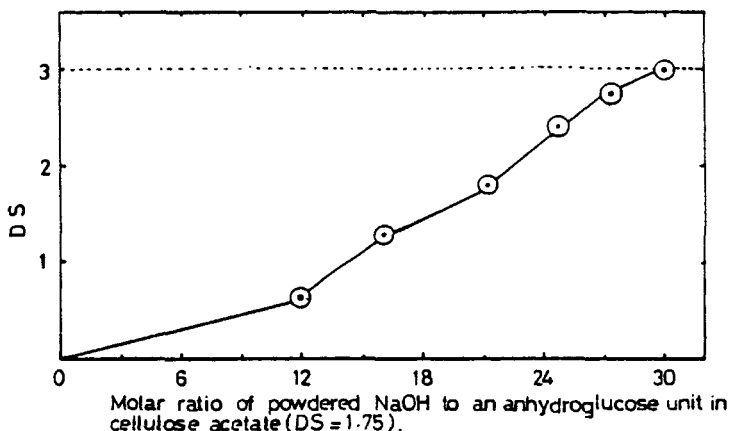


Fig. 9. DS of allyl cellulose prepared from cellulose acetate (DS = 1.75) by addition of various amounts of powdered NaOH. Allyl chloride equimolar to powdered NaOH was added.

a base (Fig. 9). By the addition of 30 mol of powdered NaOH per anhydroglucose unit, tri-*O*-allylated cellulose was prepared successfully, which was confirmed by IR spectra. As shown in Figure 4, the absorption band for hydroxyl groups around 3400 cm^{-1} was not detected, but a new absorption band appeared at around 1650 cm^{-1} , which is due to a C=C stretching vibration. The signals in ^{13}C -NMR spectrum of this compound were reasonably assigned as shown in Figure 5. Tri-*O*-methallylcellulose was also prepared and characterized by ^{13}C -NMR and IR spectrometries (Figs. 4 and 5). Both tri-*O*-allyl and tri-*O*-methallyl celluloses are soluble in chloroform, dichloromethane, benzene, tetrahydrofuran, and so on.⁹

CONCLUSION

Highly reactive cellulose ethers having allyl or methallyl groups were prepared from commercial methylcellulose (DS = 1.6) and cellulose acetate (DS = 1.75), which are soluble in DMSO, by the use of powdered NaOH as a base and DMSO as a solvent. These products were stable under 0°C in the air and stable to the heating up to 200°C in He.

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