

Some Recent Topics in Cellulose Chemistry*1

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셀룰로오스 化學의 最近研究動向*1

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ABSTRACT

It is well known that polymer chemistry started by the study on cellulose. However, the study on cellulose has not made a significant progress after the 2nd World War, because the interest of researchers has directed to the newly developed synthetic polymer science. Recently the situation has been changing as suggested by the creation of a word "Cellulose Renaissance". This change is due to the recognition that cellulose is a renewable resource and a biodegradable, environmentally friendly material.

In this lecture I'd like to introduce you some recent topics in cellulose chemistry which were reported by Japanese researchers.

1. Complete etherification of cellulose

Researchers in Daicel company found that cellulose triacetate, tribenzoate, tricinnamate and tricarbanilate can separate antipodes of various compounds Table 1.¹⁾ These cellulose derivatives are easily prepared and commercially available.

The preparation of completely etherified derivatives was quite difficult. Generally, cellulose ethers are prepared by the reaction of aqueous alkalicellulose with a etherifying reagent. Namely, this reaction is a heterogeneous reaction carried out in the presence of water. Therefore, hydrophobic etherifying reagents can not penetrate alkalicellulose and furthermore are consumed by the reaction of


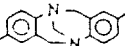
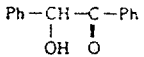

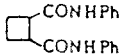
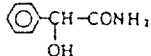
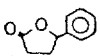
water. As to benzylation, for instance, the highest value in degree of substitution(D.S) was 2.4 even in the presence of a phasetransfer catalyst. German chemists tried the preparation of tri-O-benzyl cellulose under a nonaqueous condition. Namely, they treated cellulose acetate (D.S.=1) twice with benzyl chloride and methylsulfinyl anion (DMSO-NaH) and could obtained the aimed derivative, but the yield was only 30%.

We used a non-aqueous cellulose solvent to prepare completely etherified cellulose derivatives. Cellulose was dissolved in SO₂-diethylamine(DEA)-dimethylsulfoxide (DMSO) and treated with a etherifying reagent and powdered NaOH. Thus we found that among organic chlorides only benzyl chloride²⁾, its nega-

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Table 1. Separation of antipodes by cellulose derivatives

| Substrate | Substituent on cellulose | | | | | |
|-----------------------------------------------------------------------------------|--------------------------|-----------------|------------|-------------------------|--------------|-----------------|
| | COCH ₃ | NO ₂ | CO \odot | CH ₂ \odot | CONH \odot | COCH=CH \odot |
|  | 1.22- | 1.61- | 1.47+ | 1.0 | 1.32+ | 1.15+ |
|  | 1.31+ | 1.33+ | 1.0 - | 1.34+ | 1.32+ | 2.82+ |
|  | 1.05- | 1.0 - | 1.12+ | 1.0 | 1.0 + | 1.08- |
|  | 1.07+ | 1.14+ | 1.47- | 1.0 | 1.14- | 1.26- |
|  | 1.13- | 1.22- | 2.06+ | 1.0 | 1.25+ | 1.52- |
|  | 1.08 | 1.10 | 1.0 | 1.0 | 1.0 | 1.0 |
|  | 1.39+ | | 1.17- | 1.0 | | 1.07- |

* Packing : 20-30% of a cellulose derivative on silicagel

Eluent : hexane-2-propanol (9 : 1)

+, - : optical rotation of a firstly eluted antipode

tively substituted derivatives, allyl chloride and its derivative substituted with a methyl group give tri-O-substituted derivatives²¹. These derivatives give stable cation intermediates. On the other hand, tri-O-alkyl derivatives give stable cation intermediates. On the other hand, tri-O-n-alkyl derivatives (C=1-10) could be obtained by the use of the corresponding alkyl bromides or iodides¹¹. Recently, Kondo and Gray invented a more facile method for the preparation of tri-O-alkyl-cellulose²¹. They treated cellulose acetate with alkyl iodide and NaOH in DMSO containing a small amount of water. Water contributes to saponify acetyl groups. The ability of tri-O-benzyl cellulose to separate antipodes was much lower than those of cellulose esters. Liquid crystalline characteristics were observed for some completely etherified derivatives^{2,61}.

The SO₂-DEA-DMSO solvent can dissolve unbleached KP containing 4.7% of Klason lig-

nin⁷¹. Thus, this pulp was completely methylated in this solvent with methyl iodide and powdered NaOH⁸¹. The completely methylated product was fractionated into three portions by gel permeation chromatography. Since no molecular association can be expected for these completely methylated products, these fractions are sure to be separated on the basis of their molecular weight. As seen in Table 2, the highest molecular weight fraction also contains both lignin and sugars derived from hemicellulose⁹¹. Molecular weights of these components in KP can not be expected to be comparable to that of cellulose. Therefore, these two components should combine chemically to cellulose in either way shown in Fig. 1. The same experiment on holocelluloses of spruce and beech gave the same conclusion¹⁰¹. This means that it is almost impossible to produce completely pure cellulose from wood cellulose. Actually, commercial cellulose powder "Avicel" prepared by acid hydrolysis

Table 2. Composition of methylated sugars of fractions separated from methylated UKP

| Sample | Yield (%) | Lignin (%) | Sugar composition(%) ^a | | | | | |
|--------|-----------|------------------|-----------------------------------|------|------|------|------|------|
| | | | Rha. | U.a. | Xyl. | Man. | Gal. | Glc. |
| Me-UKP | | 4.2 ^b | | 0.8 | 5.6 | 6.6 | 0.3 | 86.7 |
| Fr.1 | 54.0 | 3.5 ^c | | 0.3 | 3.4 | 3.4 | 0.1 | 90.8 |
| Fr.2 | 23.9 | 4.2 ^c | | 0.3 | 5.8 | 6.0 | 0 | 87.9 |
| Fr.3 | 22.1 | 7.3 ^c | 0.8 | 0.6 | 7.4 | 6.1 | 0.3 | 84.9 |
| Fr.1~3 | 100.0 | 4.5 | 0.2 | 0.4 | 4.9 | 5.7 | 0.1 | 88.7 |

^aa : total adjusted to 100%.

^bb : calculated according to the formula (2).

^cc : calculated by using ¹³C290 and ¹³C290.

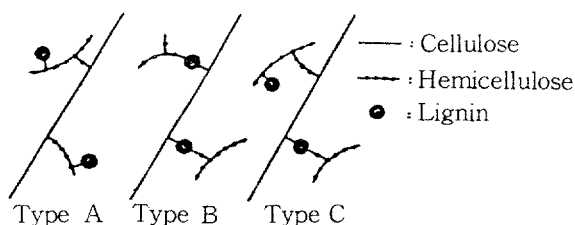


Figure 1. Possible models of chemical linkages between cellulose, the residual hemicellulose, and the residual lignin.

of wood cellulose contains about 1% of xylose residue.

2. Regio-selective substitution

In the abovedescribed complete etherification, one of nonaqueous solvents, namely SO_2 -DEA-DMSO system was used, but this reaction is not homogeneous reaction, because cellulose precipitates owing to the neutrali-

zation of one of component of the solvent system, SO_2 , with NaOH which was added as a reagent. This precipitation of cellulose as an amorphous state contributes to the complete etherification.

On the other hand, the reactions shown in Table 3, in which non-aqueous solvents are used, are true homogeneous reactions. In the 1st example a product with the D.S. of ca. 1 by chlorine was prepared very easily, whereas in the 2nd example a product with the D.S. of 1.8 was prepared. Regioselectivity in the 3rd example was observed until the D.S. attained 1. Interestingly cellulose acetate (D.S. : ca.1) prepared in the 4th example has much less water-solubility than that which was prepared by saponification of commercial tri-O-acetate. The distribution of substituents in the latter is more even than that in the former.

Table 3. Examples of reactions in nonaqueous solvent

| Solvents | Reagents | Reacting positions | Ref. |
|------------------------|---------------------------------------------|--------------------|------|
| Chloral-DMF | Methanesulfonyl chloride | C-6 | 11 |
| LiCl-DMA ^{*1} | Sulfuryl chloride | C-6 > C-3 | 12 |
| LiCl-DMA | Cinnamoyl chloride + a weak organic base | C-6 | 13 |
| LiCl-DMA | AC ₂ O + pyridine | C-6 > C-3 > C-3 | 14 |

^{*1} DMA : dimethylacetamide

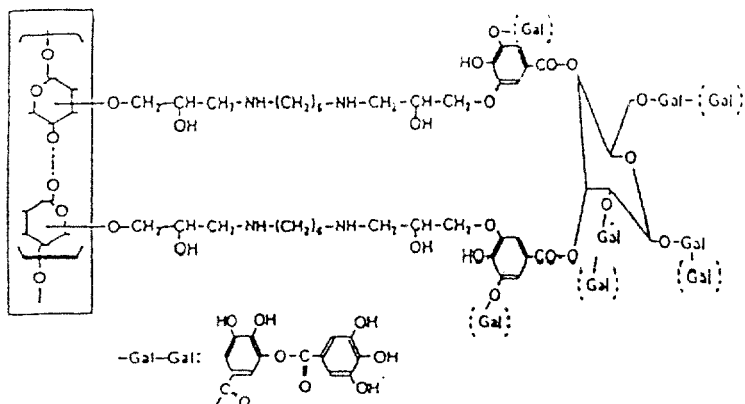


Figure 2. Chemical structure suggested for tannin-immobilizing cellulose.

3. Immobilization of tannin

Enzymes, antibiotics and heavy-metal adsorbing groups have been immobilized onto cellulose by various chemical methods. Immobilization of tannin onto cellulose is introduced here as an example which got a practical success.

In breweries manufacturing Japanese wine, sake in Japanese, they have to use water free from heavy metal ions and proteins. Tannins is known to precipitate heavy metals and proteins. Thus, researchers in a Japanese pharmaceutical company prepared tannin-immobilizing cellulose shown in Fig. 2¹⁷⁾.

4. Anticoagulant cellulose

Blood coagulates when it contacts with artificial materials. Therefore, heparin, a neutral polysaccharide, is necessary as an anticoagulant for the use of artificial organs such as kidney, vein and so on.

Prof. Miyamoto and his co-workers in Kyoto Univ. that polyelectrolyte complexes formed between a cationized cellulose and an anionic cellulose such as cellulose sulfate and CMC.¹⁸⁾

¹⁷⁾ Thus, they prepared a film for blood dialysis by etherification of cellulose film with glycidyltrimethylammonium and a subsequent treatment of the product with an anionic cellulose¹⁸⁾. This material is still in the experimental stage.

5. Pharmaceuticals for AIDS

AIDS (Acquired Immunodeficiency Syndrome) is now world-wide prevailing disease and how to cure this disease is a keen subject to be solved as soon as possible. Prof. Uryu and his co-workers found that dextran sulfate is effective for preventing Human Immunodeficiency Virus (HIV) from the increase in blood. They also prepared sulfates of branched cellulose derivatives shown in Fig.3. and reported that sulfated product with high D.S. values showed high anti-HIV activity¹⁹⁾.

6. Synthesis of cellulose

One of the sensational works in cellulose chemistry is the *in vitro* synthesis of cellulose via a nonbiosynthetic path utilizing cellulose as a catalyst. Prof. Kobayashi and his group

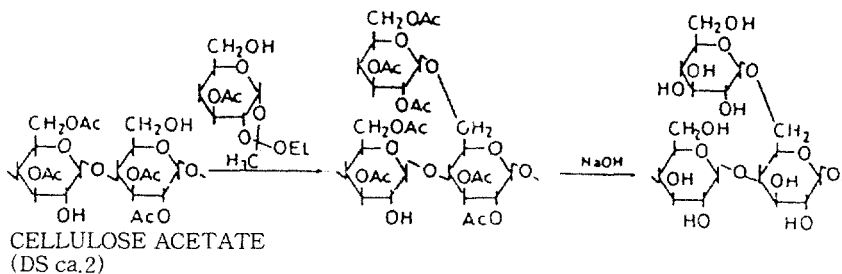


Figure 3. Branched polysaccharides derived from cellulose.

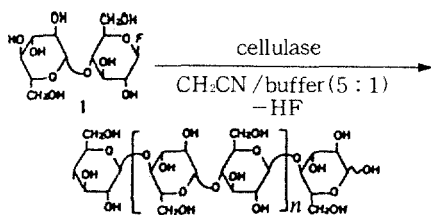


Figure 4. Scheme of cellulose synthesis.

achieved this work by using β -D-cellobiosyl fluoride as a substrate in the mixed solvent of acetonitrile and acetate buffer (pH 5, 5 : 1)²⁰⁾ (Fig.4). The cellulose thus obtained has the D. P. higher than 22 and the crystal structure of cellulose II with high crystallinity(Fig.5).

I have introduced you some recent topics on cellulose research : some are practically important and some are academically interesting. Although I could not have time to explain here, cellulose films made cellulose and its acetate are widely used as membranes for filtration of blood, for preparation of pure water from salt water and so on. It is sure that such utilizations with a high added value will increase more and more in future.

In Japan, they are going to organize the society for cellulose research this autumn. Therefore, I expect that research and development on cellulose will be accelerated and you will be able to hear a more interesting lecture at the next chance.

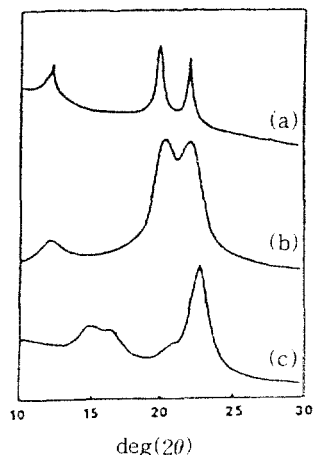


Figure 5. X-ray diffractograms of (a) the water-insoluble part of the product (type II), (b) mercerized cellulose, and (c) natural cellulose (type I).

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