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SYNTHESIS OF AMINO-DEOXY CELLULOSE

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Amino-deoxy cellulose of up to 3 % nitrogen content was synthesized by a new method in which cellulose pyridinium sulfate was treated with ammonia in ethanol under mild conditions.

Amino-cotton[1], a chemically modified cotton in which amino groups are introduced into the cellulose molecule, is known to have a excellent affinity for wool-type acid dyes, good ion-exchange capacity[2], and a high degree of reactivity. The introduced amino groups are utilized for further chemical modification such as the attachment of flame proofing agents[3]. A common procedure for the amino-deoxy cellulose involves the conversion of hydroxyl group into good leaving groups, such as sulfonic[4] and nitric esters[5] or tosyl groups[6], followed by displacement reactions with nitrogen containing nucleophiles, such as ammonia, hydrazine, and so forth.

The breaking strength of amino-cellulose fiber prepared so far, becomes very weak because of its severe preparing conditions, and the nitrogen content is also less than 1.5 % generally[7]. But the amino-cellulose prepared by our new method has almost the same strength with that of raw cellulose fiber.

In this letter we describe some preliminary results which demonstrate that a new route for amino-deoxy cellulose under mild conditions is developed. The amino-deoxy cellulose was prepared according to the following scheme:

$$\underset{\text{I}}{\text{Cell-OH}} + \text{ClSO}_3\text{H}\cdot\text{Pyridine} \xrightarrow[\text{Pyridine}]{-\text{HCl}} \underset{\text{II}}{\text{Cell-O-SO}_3\text{H}\cdot\text{Pyridine}} + \text{HCl}\cdot\text{Pyridine}$$

$$\text{II} + \text{NH}_3 \xrightarrow[\text{Ethanol}]{-\text{H}_2\text{SO}_4} \underset{\text{III}}{\text{Cell-NH}_2} + (\text{NH}_4)_2\text{SO}_4 + \text{Pyridine}$$

Although cellulose pyridinium sulfate was synthesized by Trauve and coworkers[8], it has never been treated with ammonia. In our research the cellulose pyridinium salt (II) was prepared by treating bleached cotton cellulose (I) with chlorosulfonic acid in pyridine solution at 60°C, followed by washing completly with pyridine and ethanol. The amino-deoxy cellulose (III) was synthesized by the reaction of II with ammonia in ethanol at 100°C, for 24 hours. The experimental results are summarized in Table 1.

Table 1. Nitrogen contents of aminated cellulose

sample no.	sulfonation[a] $ClSO_3H$ (% V/V)	sulfonation[a] liquor ratio	sulfonation[a] reaction time(hr)	amination[b] liquor ratio	amination[b] reaction time(hr)	nitrogen cont.(%)
1	1	1 : 50	24	1 : 100	24	2.17
2	2	1 : 50	24	1 : 100	24	2.52
3	3	1 : 50	24	1 : 100	24	2.92
4	4	1 : 50	24	1 : 100	24	3.06
5	10	1 : 100	40	1 : 100	24	3.08

a, reaction temp. : 60°C

b, reaction temp. : 100°C

ethanol is saturated with ammonia at 0°C

The IR spectra of bleached cotton cellulose before and after treatment with chlorosulfonic acid and after amination reaction are shown in Fig. 1. The bands of II at 1640 and 810 cm^{-1} are assigned to N-H deformation, at 1540, 1490 and 1620 cm^{-1} are due to C=N stretching and breathing of pyridinium ring, respectively. There appears also a band of sulfate ester at 1190 cm^{-1}. This spectrum is identified with that of cellulose pyridinium sulfate shown by Zhbankov[9].

After the amination reaction these characteristic bands disappear, and sharp bands appear at 1630 and 810 cm^{-1}, and 1250 cm^{-1}, which are assigned to N-H deformation and C-N stretching[10], respectively. As another ancillary conviction, by-product which precipitated from the amination solution, which was identified as ammoniumsulfate by IR spectroscopy.

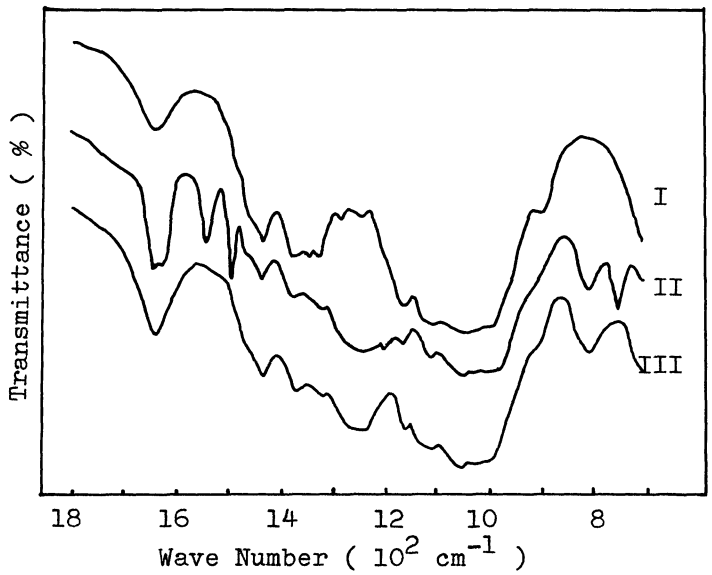

Fig. 1 IR spectra of cotton cellulose (I), cellulose pyridinium sulfate (II), and amino-deoxy cellulose (III)

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