*On the Determination of Fine Structure of Cellulosic Fibers**

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It is well known that the mechanical properties of cellulosic fibers depend on their fine structure. P. H. Herrent and A. Lude suggested double net-work structure, in which the crystalline regions constitute the knots¹⁾. Therefore, it seems significant to clarify the nature of crystalline regions. The mean crystallinity determined by existing methods is insufficient to elucidate the mechanical properties, then it is desirable to estimate the distribution of order and of size. W. A. Sisson and J. A. Howsmon have proposed "lateral order" $\bar{O}$ which was defined by the equation,

$$\bar{O} = (\mathrm{OH})_c/(\mathrm{OH})_t$$

Where $(\mathrm{OH})_c$ is the total number of hydrogen bonds in the region and $(\mathrm{OH})_t$ is the total possible number of hydrogen bonds if all the molecules are perfectly crystallized. This value is dependent on the choice of the volume element. If this volume is too large, the curves as depicted become single sharp peak at $\bar{O}$ corresponding to an average order; if too small, the curves split into two sharp peaks at zero order and perfect order²⁾. To measure the lateral order distribution, Maeda and Yurugi applied fractional solution of hydrolyzed cellulose³⁾ and the methods which determine the moisture regain or levelling-off degree of polymerization after mercerization, were suggested⁴⁾. These methods are based on the thermodynamic properties and do not have direct relation to the fine structure.

Recently, the distribution of crystallite sizes is estimated by means of X-ray diffraction⁵⁾ or electron microscopy⁶⁾.

In the present paper, on the assumption that the length of crystalline residue corresponds to the length of hydrogen-bond train along cellulose molecule chain, we have undertaken to determine its distribution by the molecular weight fractionation of the residue which is freed from the amorphous region by hydrolysis or its modification. Since recrystallization has been found to occur during acid hydrolysis⁷·⁸⁾, the following methods were tried to avoid it.

(1) Ordinary aqueous acid hydrolysis after partial acetylation or partial oxidation with lead tetra-acetate, which may prevent the recrystallization by steric hindrance due to the modification in amorphous region.

(2) Methanolysis, which is carried out in non-aqueous medium to prevent additional forming of hydrogen-bond.

(3) Oxidizing hydrolysis with sulfuric acid containing potassium dichromate. It is effective in removing the amorphous chain ends produced by chain cleavage, before recrystallization takes place. The residues after these treatments were nitrated and fractionated, and the chain length distribution curves were obtained. The availability of these methods and the fine structure of rayon staple were discussed.

Experimental

Materials. Commercial viscose rayon staple (Bright regular 1.5 D) was steeped in water and then the water was replaced with reaction medium.

Methods. *a*) *Apparent total crystallinity.*—It was given as a weight per-cent yield of the residue after the hydrolysis or its modified treatments.

b) *Average degree of polymerization* ($\overline{DP}$).—It was determined from the viscosity of cuprammonium solutions, or that of acetone solution of

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* Presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1957.

1) P. H. Herrent and A. Lude, *Textiel Research J.*, **21**, 137 (1951).

2) Otto-Spurlin "Cellulose and Cellulose Derivatives", Interscience Publishers, New York, Vol. I, (1954) p. 252.

3) H. Maeda, *J. Soc. Textile Cellulose Ind.* (*Japan*), (*Sen-i Gakkaishi*) **12**, 6 (1956); T. Yurugi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kôgyô Kagaku Zassi*) **58**, 27 (1955).

4) L. Jörgensen, *Acta Chem. Scand.*, **3**, 790 (1949); **4**, 185, 658 (1950); O. A. Battista et al. *Ind. Eng. Chem.*, **48**, 333 (1956).

5) K. Kobayashi, presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1957.

6) E. A. Immergut and B. G. Rånby, *Ind. Eng. Chem.*, **48**, 1183 (1956).

7) H. Mark, F. C. Brenner and V. Frilette, *J. Am. Chem. Soc.*, **70**, 877 (1948).

8) P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4**, 315 (1949).

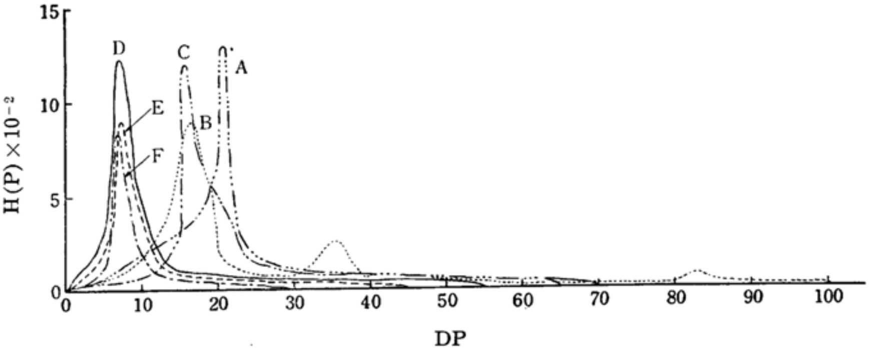

Fig. 1. Chain-length distribution of hydrolyzed cellulose.

A —··· — Maeda's method
B ········ 1 N HCl 1/6 hr.
C —·—·— 1 N HCl 1 hr.
D ——— 4 N HCl 1 hr.
E ------ 4 N HCl 4 hr.
F —·— 4 N HCl 6 hr.

the nitratde products. An Ostwald viscometer was employed and the intrinsic viscosity was calculated by Schulz-Blaschke's Formula.

c) *Chain-length distribution.*—The sample was nitrated with Mitchel's mixed acid[9] and dissolved in acetone and fractionated using water as the precipitant.

d) *Accessibility.* — Iodine sorption method of Hessler and Power[10] was employed. Concentration of sodium sulfate was 200 g./l. and the sorption was carried out at 20±0.1°C for an hour.

e) *Partial acetylation pretreatment.*—The rayon staple swollen with glacial acetic acid was treated at 50°C for twelve hours with the mixture, which consists of 6 volumes pyridine, 8 volumes acetic acid and 60 volumes benzene.

f) *Partial oxidation pretreatment.*—The samples swollen with glacial acetic acid were treated at 50°C for twenty hours with the glacial acetic acid solution which contains 0.077 M lead tetra-acetate. The lead tetra-acetate used was prepared according to Colson's method[11].

g) *Hydrolysis.*—Samples were refluxed at 100°C with hydrolyzing agents. After the pre-determined reaction time, the residue was filtered off with a glass filter and washed with water to neutral. Then its moisture was exchanged with absolute alcohol, and it was dried in vacuo at 50°C for five hours and weighed.

h) *Methanolysis.*—Samples were first refluxed at 68°C with methanol, saturated with dry hydrogen chloride gas, and then the residue was washed to neutral with absolute alcohol and dried in vacuo.

i) *Oxidizing-hydrolysis.*—A similar procedure to hydrolysis was used except that the hydrolyzing mixture, consisted of 1 N sulfuric acid and 0.017 M potassium dichromate.

Results

A) Ordinary Acid Hydrolysis. — The effects of acidity, reaction time and substrate on the yield and the $\overline{DP}$ of the residue are shown in Table I. The levelling-off degree of polymerization (LODP) of these samples was obtained by the treatment with 1 N hydrochloric acid for an hour.

TABLE I

DEGREE OF POLIMERIZATION AND YIELD OF RESIDUE AFTER ORDINARY HYDROLYSIS

Conditions of Hydrolysis			Residue	
Acidity of HCl N (aq.)	Temp. °C	Time hr.	Yield wt. %	$\overline{DP}$ (Nitrate)
1	100	1/6	98.8	26
		1	90.0	22
4	100	1	72.4	22
		2	57.5	22
		4	43.9	22
		6	37.0	22
Maeda's Method*	80	6	98.1	23

* Mixture of 5 parts 3.5 N HCl and 95 parts ethanol.

As shown in Fig. 1, the peak of distribution curve shifts to lower DP regions with the increase of acidity or reaction time, but after the peak has attained a definite DP, only the height of the peak decreases.

TABLE II

DEGREE OF POLIMERIZATION AND YIELD OF HYDROLYZED RESIDUE AFTER PRETREATMENT

(Conditions of Hydrolysis: 1 N HCl, 100°C, 25 hr.)

Pretreatment method	Degree of Substitution (M/C_6 unit)	Residue	
		Yield wt. %	$\overline{DP}$ (Cupram.)
Acetylation	0.331	58.8	17.5
Oxidation	0.157	25.2	
No Treatment	0	65.5	25.4

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[9] R. L. Mitchel, *Ind. Eng. Chem.*, **38**, 843 (1946).

[10] L. E. Hessler and R. E. Power, *Textile Research J.*, **24**, 822 (1954).

[11] A. Colson, *Compt. rend.*, **136**, 1, 676, 892 (1903).

B) Effect of Pretreatment. — The weight loss and $\overline{DP}$ of the hydrolyzed residue after pretreatment are shown in Table II. Generally speaking, pretreatments caused severe degradation. The chain length distributions of the above residues are shown in Fig. 2.

C) Methanolysis.—The effects of acidity in methanolysis are shown in Table III. The reaction is accelerated by the increase of acidity and the yield of residue decreases. However, little decrease in LODP and accessibility was observed.

The reaction rate of methanolysis is retarded by the addition of water, and the yield and the $\overline{DP}$ of the residue decreases with the increase in water content. Hydrochloric acid in the reagent is consumed very rapidly in the absence of water, but little at 100% aqueous medium, as shown in Fig. 3. The methanolysis gives higher ultimate yields of residue than the hydrolysis, although methanolysis proceeds initially at higher rates.

The results of fractional solution in which caustic soda solutions up to 8% are used as solvents and by which the residual amorphous portions may be dissolved owing to the probable imperfect removal, are shown in Fig. 4. Fig. 5 gives the chain-length distribution of methanolyzed

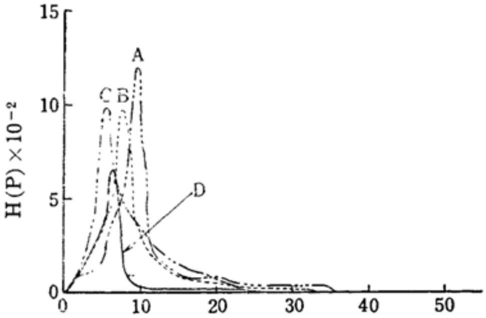

Fig. 2. Chain-length distribution of hydrolyzed cellulose after pretreatment.

Pretreatment		Hydrolysis	
		Acidity of HCl	Time hr.
A	None	1 N	25
B	None	4 N	2
C	Acetylation	1 N	25
D	Oxidation	1 N	25

TABLE III

DEGREE OF POLYMERIZATION, ACCESSIBILITY AND YIELD OF RESIDUE AFTER METHANOLYSIS

(Temp. of Methanolysis, 67±1°C)

Condition		Residue		
Acidity	Time	Yield	$\overline{DP}$ (Cupram.)	Accessibility
N	hr.	wt. %		%
2.5	0	100.0	293.5	
	1/3	93.0		
	1	90.0		33.9
	3	87.0	30.0	
	8	83.5	27.9	25.8
	24	78.9	27.0	24.3
4	2	75.6	30.6	28.2
	6	74.7	28.4	25.3
	12	73.0	26.2	24.8
6	2	71.7	29.0	23.6
	6	67.7	27.4	24.3
	12	64.6	26.2	22.9
8	12	58.3	26.2	19.5

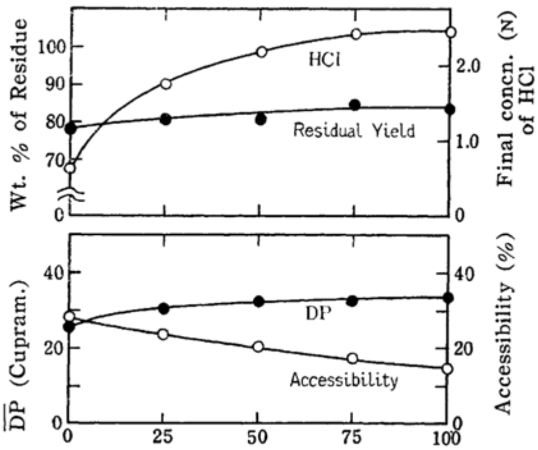

Fig. 3. Effects of water in methanolysis reagent. Methanolysis, 2.5 N HCl, at 68°C, 24 hr.

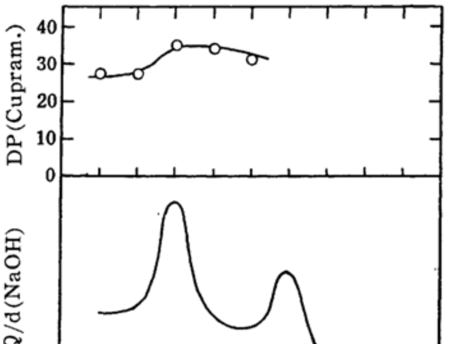

Fig. 4. Alkali extraction of methanolyzed cellulose. Methanolysis 1 N HCl, 68°C, 24 hrs. alkali extraction 20°C, 1 hr.
Q: weight loss of alkali extraction.

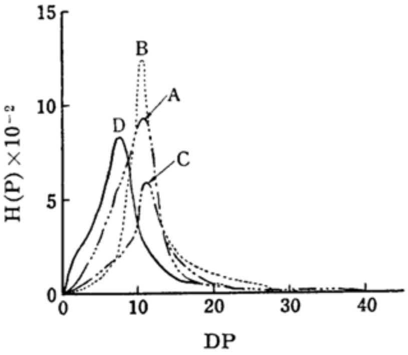

Fig. 5. Chain-length distribution of methanolyzed, and its alkali-extracted cellulose.

A —···— 2.5 N HCl in MeOH 24 hr.
B ········· 2% alkali-extracted residue of A.
C —·-·— 4% alkali-extracted residue of A.
D ——— 8 N HCl in MeOH 12 hr.

TABLE IV

DEGREE OF POLYMERIZATION, ACCESSIBILITY AND YIELD OF RESIDUE AFTER OXIDIZING-HYDROLYSIS

(Conditions of solvolysis: 100°C, 0.017 M $K_2Cr_2O_7$, 1 N H_2SO_4)

Reaction Time hr.	Residue Yield wt. %	Residue $\overline{DP}$ (Cupram.)	Residue Accessibility %
0	100.0	293.5	51.8
1	73.1	27.7	11.8
3	65.7	26.5	11.6
5	61.5	24.6	11.5
8	59.0	24.4	11.4
12	57.0	23.9	11.4

residue and its alkali-extracted residue.

D) Oxidizing - Hydrolysis. — Samples were oxidized and simultaneously hydrolyzed with the mixture of potassium dichromate and sulfuric acid, and the effect of the reaction time on the yield, DP and the accessibility of the residue are shown in Table IV.

It is very characteristic that the accessibility of the residue obtained from the oxidizing hydrolysis, levels off rapidly and exhibits relatively lower values than those of the other degradation residues.

The residue from the oxidizing hydrolysis is wholly dispersed in 2% caustic soda solution. Fig. 6 gives the chain-length distribution of this residue at various reaction times.

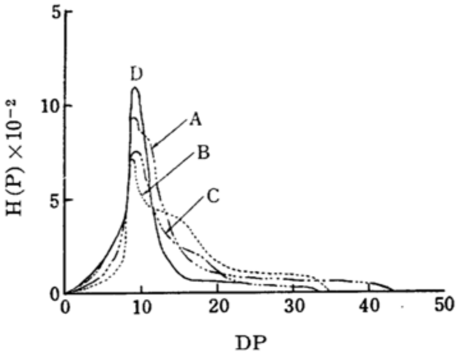

Fig. 6. Chain-length distribution of oxidizing-hydrolyzed cellulose.

A —···— 0.017 M $K_2Cr_2O_7$+1 N H_2SO_4 3 hrs.
B ········· 〃 〃 5 hrs.
C —·-·— 〃 〃 8 hrs.
D ——— 〃 〃 12 hrs.

Discussion

Ordinary Hydrolysis Process. — The results that the peak of chain-length distribution curves of hydrolyzed residue moves initially to lower DP as the hydrolysis proceeds and then after it has attained a definite limit, only the height of the peak decreases, is in agreement with the observation by electronmicroscope that during the hydrolysis process the distribution of crystalline length remains almost constant and the distribution of crystalline width shifts to a more narrow side⁶⁾.

TABLE V

COMPARISON OF VARIOUS METHODS

Method	Conditions Concn.	Conditions Time hr.	Residue Yield wt. %	Residue Accessibility %	Residue $\overline{DP}$	Residue Mode of DP
Ordinary hydrolysis	4 N	2	52.9	12.6	29	7
Hydrolysis after acetylation	1 N	25	58.5			6
Hydrolysis after oxidation	1 N	25	25.2			7
Oxidizing-hydrolysis	0.017 M 1 N	8	61.8	11.4	24	9.5
Methanolysis	8 N	12	58.3	19.5	26	7.5
Alkali extraction after methanolysis	4% 2.5 N	24	31.3	14.0	31	12

Comparison of Various Methods for Removal of the Amorphous Region.—The results of various methods are summarized in Table. V.

In the case of the methanolysis with 8 N hydrochloric acid, the peak of chain-length distribution is located at a somewhat lower DP. However, its residue which is controlled to give similar yield to other methods, exhibits high levelling-off accessibility, high partial solubility in 4% caustic soda solution and somewhat higher DP. These results suggest that the methanolyzed cellulose contains considerable amorphous regions. In our experiment with methanol-water systems, the yield of residue and its DP increase, and its accessibility decreases with the increase in water content. From these results, it may be concluded that water increases the probability of recrystallization and methanol has the reverse effect. However, Nelson et al. have described recently that the methanolysis prevented the reversion of cellulose III to cellulose I but appeared not to avoid the recrystallization[12]. Therefore, methanolysis or hydrolysis is not suitable for our object.

The chain-length distribution of hydrolyzed residue seems to shift its peak to lower DP regions on oxidation pretreatments. Therefore, the pretreatment may hinder the growth of the crystallites, but the low yield may be derived from the destruction of the crystallite, especially by the severe action of lead tetra-acetate. The chain-length distribution of the hydrolyzed residue from acetylation pretreatment has a similar width of DP range, but its peak exists at a slightly lower DP, compared with ordinary hydrolysis. The degree and the distribution of degradation may be influenced by the heterogeneity of the acetylation pretreatment. From the above reason and the troublesome operation which requires a long time, pretreatment methods are not so desirable.

In order to remove the amorphous region which remains around the end of the crystallites during hydrolysis, the oxidizing-hydrolysis method was carried out with dichromic acid whch is considered not likely to penetrate into the crystalline region. The results that the peak of chain-length distribution shifts to slightly higher DP, but the shoulder on the higher DP side disappears and the DP decrease, seem to disprove the recrystallization. Since oxidizing-hydrolysis gives lower levelling-off accessibility than ordinary hydrolysis, the residue of oxidizing-hydrolysis may show probably the original crystalline state. However, since its residue is easily soluble in dilute alkaline solution, the carboxyl groups formed by the oxidation may be responsible for its solubility in alkaline solution and for the poorer iodine sorption which results apparently in lower accessibility.

Although further study by means of X-ray diffraction, infrared absorption analysis etc. is necessary, oxidizing-hydrolysis may be the most hopeful.

Fine Structure of Rayon Staple.—From the above results, it is estimated that the length of crystalline region distributes within the range up to approximately the DP of 40 (ca. 200 Å) and its distribution has one peak between 6 and 10.

Relation between the Lateral Order and the Chain-Length Distribution of Solvolyzed Residue. — Maeda determined " lateral order ", based on the solubility of hydrolyzed residue in alkaline solution, C, which is given by the following equation,

$$C=A\exp(-PE/RT)$$

where P is the degree of polymerization, E transition energy of solution per glucose unit, R gas constant, T absolute temperature, because E can be substituted for " lateral order "[13]. However, even an intensively degraded sample has so wide a chain-length distribution that the solubility in alkaline solution would depend not only on E, but also on P, as the lower DP region of methanolyzed residue is more soluble in alkaline solution.

If the chain-length of suitably degraded residue coincides with the length of the crystallite formed by hydrogen bond without gap, this length may indicate the fine structure of cellulosic fiber more clearly than the so-called " lateral order ", which depends theoretically on the volume in consideration. But the solubility of the methanolyzed residue or the residue from the oxidizing hydrolysis in alkaline solution suggests the possibility of cracks in hydrogen-bonded crystallite.

Summary

In order to clarify the fine structure of

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[12] M. L. Nelson, L. Segal, T. Mares and J J. Creely, *J. Polymer Sci.*, **20**, 29 (1956).

[13] H. Maeda, *J. Soc. Textile Cellulose Ind. Japan*, (*Sen-i Gakkaishi*) **12**, 6 (1956).

rayon staple, it may be necessary to estimate not only the total crystallinity but also the distribution of crystalline size and quality. For this purpose, various methods which seemed to remove the amorphous region without recrystallization, were studied.

Methanolysis is affected by water content in the mixture and its residue may still contain an amorphous region because of its high accessibility. The recrystallization may be possible during not only hydrolysis but also methanolysis.

The hydrolysis after pretreatment is not very effective to prevent recrystallization and may destroy crystalline region. Moreover, its procedure is troublesome.

The oxidizing-hydrolysis, which shifts the crystalline length distribution toward slightly higher DP region diminishing the shoulder on higher DP side and gives the lowest levelling-off accessibility, holds out considerable promise for the elucidation of the original crystalline structure. But its high solubility in alkaline solution may be derived from a carboxyl group formed during oxidation or from the cracks in a hydrogen-bond train of crystallites. Therefore, problems to study still remain.

The crystalline region of viscose rayon staple seems to have the chain-length distribution, which extends to a DP of ca. 40 and shows one maximum between the DP of 6 and 10.

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