Fine Structure of Carbamoylethylated and Carboxyethylated Cotton Cellulosic Fibers

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Synopsis

The fine structure of cotton cellulosic fibers carbamoylethylated and carboxyethylated at 30 and 20°C in the presence of 3% and 20% sodium hydroxide was investigated by measuring moisture regain, water imbibition, x-ray photograph, degree of crystallinity, spacing, and crystallite size under dry and wet conditions. As carbamoylethyl and carboxyethyl substituents are introduced in amorphous regions of the samples reacted with acrylamide in 3% sodium hydroxide, the fine structure of the crystalline regions is not affected by the reaction. On the other hand, in the samples reacted in 20% sodium hydroxide, the substituents are introduced not only in amorphous regions but also in crystalline regions to make them disordered. Although spacing between (10$\bar{1}$) planes does not change, spacing between (101) planes increases by the reaction in 20% sodium hydroxide. Comparing crystallite sizes normal to (hkl) planes under dry conditions with those under wet conditions, it is supposed that cohesive forces between (101) planes are different from those between (10$\bar{1}$) planes, and the former is hydrogen bonds and the latter resemble Van Der Waals forces. As a result, carbamoylethyl and carboxyethyl groups are introduced selectively between (101) planes.

INTRODUCTION

It has been found that cellulose is carbamoylethylated and carboxyethylated by acrylamide in the presence of alkali.[1,2] It has also been reported that by adjusting reaction conditions, the amount and ratio of the substituents can be controlled, and the mechanism of the reaction has also been proposed.[3] But the fine structure of cotton fibers carbamoylethylated and carboxyethylated has hardly been investigated.[4]

On the other hand, the fine structure of cotton cellulose has been extensively studied. Ray,[5,6] Creely and Tripp,[7] and Heyn[8] studied the effect of relative humidity of air on the degree of crystallinity of some cellulose samples. But the results are not the same, because the way of calculating the degree of crystallinity is different. Warwicker et al., studying the swelling of cotton cellulose by sodium hydroxide, said that the true fundamental unit in the reaction is a sheet of chains held together chiefly by Van Der Waals forces.[9,10]

In this paper, the fine structure of carbamoylethylated and carboxyethylated cotton cellulosic fibers is discussed by measuring moisture regain, water imbibition, x-ray photograph, degree of crystallinity, spacing, and crystallite size under dry and wet conditions. Emphasis is put on these characteristics under wet conditions.

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EXPERIMENTAL

Materials

Scoured cotton cellulosic fibers of the Acala variety supplied by Kanebo Co. Ltd. were purified by extracting with hot benzene–ethanol mixture (1:1 volume ratio) for 24 hr. Then the cotton fibers were washed with methanol and distilled water and air dried.

Acrylamide was purified by recrystallization from benzene for several times. Other chemicals used were reagent grade and were used without further purification.

Alkali Treatment

The purified cotton fibers were treated in 3% sodium hydroxide aqueous solution for 5 hr at 30°C or in 20% sodium hydroxide aqueous solution for 5 hr at 20°C. Then the samples were washed with distilled water, immersed in 0.1% acetic acid, washed with distilled water until acetic acid was thoroughly removed, and then air dried.

Carbamoylethylation and Carboxyethylation

The purified cotton cellulosic fibers were treated with aqueous solutions containing 7% acrylamide and 3% sodium hydroxide at 30°C or 7% acrylamide and 20% sodium hydroxide at 20°C. Then the samples were washed with distilled water, 0.1% acetic acid, and distilled water and air dried.

Degree of Substitution

Degree of carbamoylethylation and carboxyethylation per anhydroglucose residue of the samples was determined by the micro Kjeldahl method and back-titration technique, respectively. Total degree of substitution was shown as the sum of degree of carbamoylethylation and carboxyethylation.

Moisture Regain

The samples were conditioned for 7 days at 65% R.H. and 20°C and weighed. The samples were then dried under reduced pressure and weighed. Weight increase by moisture was determined as moisture regain.

Water Imbibition

After the weighed samples were immersed in distilled water for 24 hr at room temperature, they were centrifuged for 4 min. The same procedure was carried out several times to plot the weight increase by water against time of centrifuging. Finally, weight increase at time 0 was obtained by extrapolation, and the value was shown as water imbibition.

X-Ray Photography

X-Ray photographs from the samples were obtained by using a Rigaku Denki D-9C x-ray generator and a Laue camera operated at 35 kV and 18 mA with Cu $K\alpha$ radiation. The bundle of the fibers was set with the fiber axes perpendicular to the x-ray beam. The distance between the sample and the camera was 5.9 cm.

Degree of Crystallinity

X-Ray diffraction traces from the samples under dry conditions were obtained under the same conditions described above. While the bundle of the fibers in which the fiber axes were mutually parallel was rotated in the plane vertical to the x-ray beam (80 rpm), the diffraction intensity was measured at $2\theta = 6°–50°$ (θ is the diffraction angle). Also diffraction traces were taken in the same angular range at the various azimuth angles. The positions of the lowest intensities at each 2θ angle were then connected on the diffractograms to determine the amount of amorphous parts.[11–13] Then the corrections to the diffraction traces were made for air scattering, incoherent scattering, sample absorption, polarization and Lorentz factors. The degree of crystallinity of the samples was determined by the integral method as follows:

$$\text{degree of crystallinity (\%)} = [(I_t - I_a)/I_t] \times 100 \qquad (1)$$

where I_t and I_a are the integral scattering intensities corresponding to the amount of the total and amorphous parts, respectively.

For measurement under wet conditions, the bundled samples were immersed in distilled water for 24 hr at room temperature and pressed out so that pickup was 50% and were set in a sample container with a PMMA film window. The other measuring conditions were the same as those under dry conditions. To correct the diffraction traces for wet samples, the x-ray diffraction trace from water in the sample container with PMMA film window was also obtained. Water contribution was also subtracted from the diffraction traces under wet conditions in addition to the same corrections as those under dry conditions. The degree of crystallinity for the wet samples was then decided in the same way as that for dry samples, eq. (1).
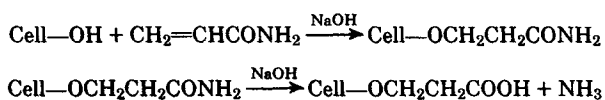
Crystallite Size and Spacing

For crystallite size and spacing measurements, equatorial x-ray diffraction traces were recorded and corrected in the same way as mentioned above. The corrected data were then resolved into diffraction peaks as a combination of Gaussian and Cauchy functions, and a background[14,15] using a HITAC 8800/8700 (OS-7) at the Tokyo University Computer Center. The resolution program gave peak widths and peak positions. Crystallite size normal to the diffraction plane (hkl) was determined by the Sherrer equation,[15] and spacing $d(hkl)$ was determined by the Bragg equation.

RESULTS AND DISCUSSION

Degree of Substitution

Degree of carbamoylethylation and carboxyethylation per anhydroglucose residue is shown in Figure 1. In the reaction system containing 3% sodium hydroxide, the degree of carbamoylethylation and carboxyethylation increased as reaction time proceeded.

However, in the reaction system with 20% sodium hydroxide, there was a maximum point on degree of carbamoylethylation. That is, the number of carbamoylethyl groups increased at the initial period of reaction and decreased at the latter stage of reaction. On the contrary, the degree of carboxyethylation increased rapidly as that of carbamoylethylation decreased. However, the total degree of substitution increased as reaction time proceeded, and to a larger extent than in the presence of 3% sodium hydroxide. These phenomena are elucidated as follows[3]:

$$\text{Cell—OH} + \text{CH}_2\text{=CHCONH}_2 \xrightarrow{\text{NaOH}} \text{Cell—OCH}_2\text{CH}_2\text{CONH}_2$$

$$\text{Cell—OCH}_2\text{CH}_2\text{CONH}_2 \xrightarrow{\text{NaOH}} \text{Cell—OCH}_2\text{CH}_2\text{COOH} + \text{NH}_3$$

In both reactions sodium hydroxide acts as catalyst.

Moisture Regain and Water Imbibition

Moisture regain and water imbibition of the samples are shown in Figures 2 and 3, respectively. Although the moisture regain of the fibers treated in the presence of 20% sodium hydroxide was larger than that of fibers treated in 3%
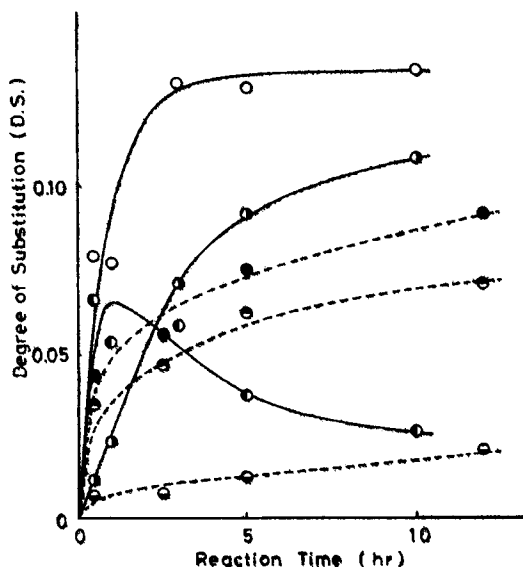

Fig. 1. Effects of alkali concentration and reaction time on degree of substitution per anhydroglucose residue: (◐,◑) carbamoylethyl substituents; (◕,◔) carboxyethyl substituents; (○,●) total substituents; (——) reacted with acrylamide at 20°C in 20% sodium hydroxide; (- - -) reacted with acrylamide at 30°C in 3% sodium hydroxide.
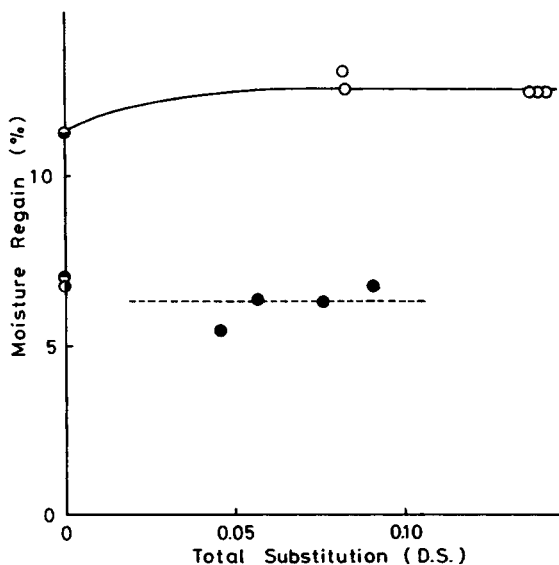
Fig. 2. Effects of total degree of substitution per anhydroglucose residue on moisture regain: (—○—) reacted with acrylamide at 20°C in 20% sodium hydroxide; (- - -●- - -) reacted with acrylamide at 30°C in 3% sodium hydroxide; (◑) untreated; (◒) mercerized; (◓) treated at 30°C in 3% sodium hydroxide.
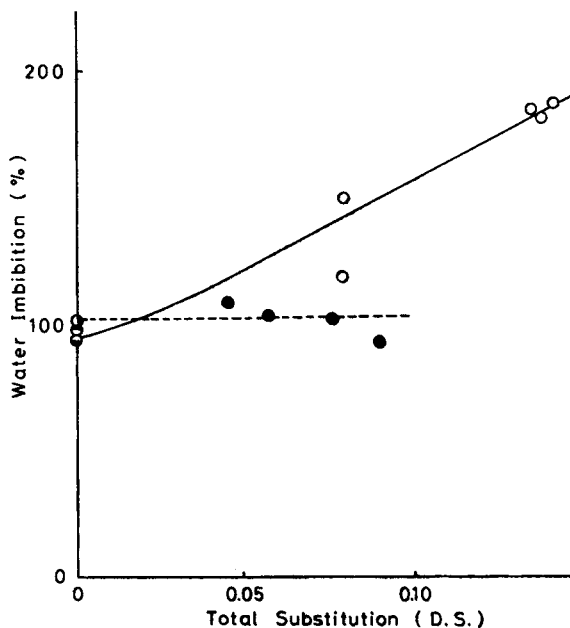

Fig. 3. Effects of total degee of substitution per anhydroglucose residue on water imbibition: (—○—) reacted with acrylamide at 20°C in 20% sodium hydroxide; (- - -●- - -) reacted with acrylamide at 30°C in 3% sodium hydroxide; (◑) untreated; (◒) mercerized; (◓) treated at 30°C in 3% sodium hydroxide.

sodium hydroxide, there was almost no moisture regain change with increase in total degree of substitution in both reaction systems.

However, as shown in Figure 3, water imbibition increased with increase in

total degree of substitution by treatment in the reaction system containing 20% sodium hydroxide. Therefore, it is assumed that structural changes occur in the samples reacted in 20% sodium hydroxide.

X-Ray Photography

X-Ray photographs of the samples are shown in Figure 4. The photographs of the samples treated in the reaction system containing 3% sodium hydroxide are almost the same as those of untreated cotton fibers. It is therefore assumed that carbamoylethylation and carboxyethylation in 3% sodium hydroxide generate no changes in the crystalline structure of the fibers.

On the other hand, x-ray photographs of carbamoylethylated and carboxyethylated cotton fibers in 20% sodium hydroxide are almost similar to the diagram

(a)   (b)

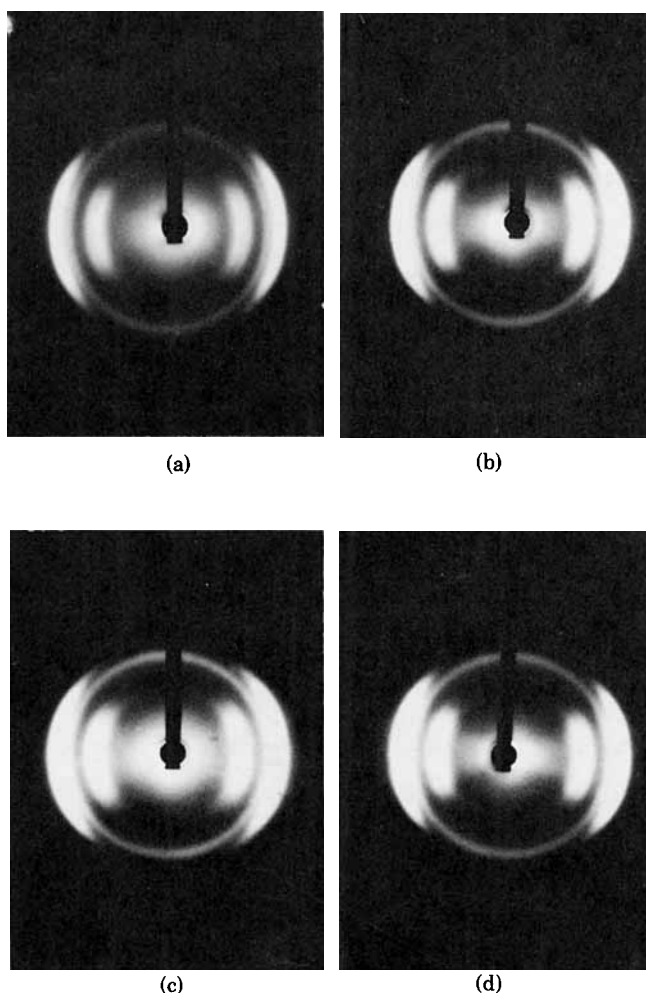(c)   (d)

Fig. 4. X-Ray photographs: (a) untreated; (b) treated at 30°C in 3% sodium hydroxide; (c) reacted with acrylamide at 30°C in 3% sodium hydroxide for 1 hr; (d) reacted with acrylamide at 30°C in 3% sodium hydroxide for 24 hr; (e) mercerized; (f) reacted with acrylamide at 20°C in 20% sodium hydroxide for 1 hr; (g) reacted with acrylamide at 20°C in 20% sodium hydroxide for 10 hr.
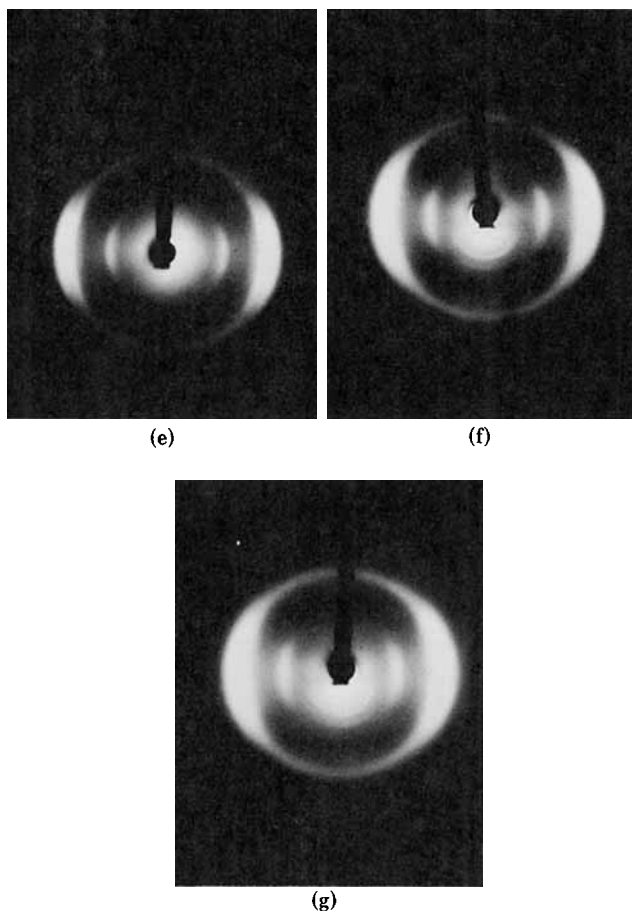
(e)   (f)

(g)

Fig. 4. (*Continued from previous page.*)

of mercerized sample, but the former photographs are obscure as compared with the latter. Such results are probably attributable to the fact that carbamoylethylation and carboxyethylation in 20% sodium hydroxide were generated not only in amorphous regions but also in crystalline regions of the cotton fibers.

X-Ray Diffraction Traces

It is of interest to check whether degree of crystallinity of cellulose in dry and wet conditions is equal or not.[5-8] As the methods of calculating the degree of crystallinity were different in the reports, the results can not be compared with each other. As seen from the x-ray photographs in Figure 4, the degree of orientation may be changed by carbamoylethylation and carboxyethylation. Therefore, to diminish the effect of orientation of the samples on the degree of crystallinity, the diffraction traces under dry and wet conditions were measured while the samples were rotated in the plane vertical to the x-ray beam in this report.

In Figure 5, the corrected diffractograms of mercerized cellulose and carba-
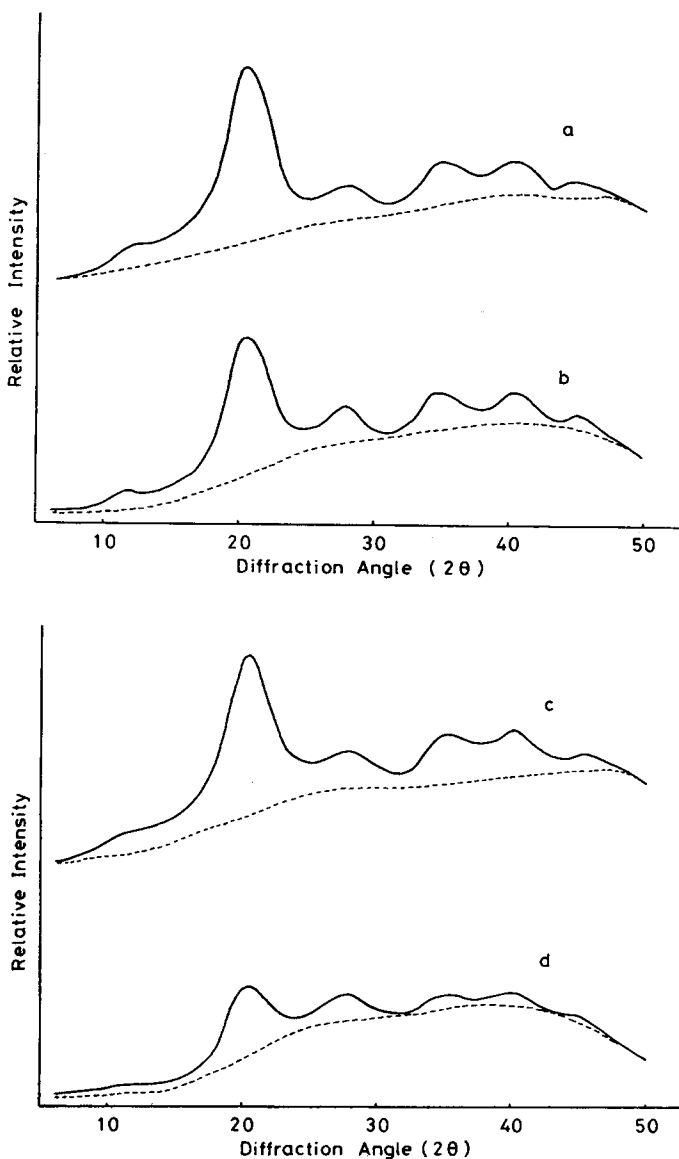
Fig. 5. X-Ray diffraction traces: (a) mercerized cellulose under dry conditions; (b) mercerized cellulose under wet conditions; (c) cellulose carbamoylethylated and carboxyethylated in 20% sodium hydroxide for 10 hr, under dry conditions; (d) cellulose carbamoylethylated and carboxyethylated in 20% sodium hydroxide for 10 hr, under wet conditions.

moylethylated and carboxyethylated cellulose in 20% sodium hydroxide for 10 hr are shown. Comparing the intensities under dry conditions, they were reduced when the samples contained water. The other samples containing water also gave diffractograms with reduced intensities. The tendency was especially distinct in the substituted samples in 20% sodium hydroxide. Therefore, it is considered that some part of the samples was disordered by immersion in water.

Degree of Crystallinity

The degree of crystallinity of the samples under dry and wet conditions calculated from the diffractograms as shown in Figure 5 and the wet/dry ratio are shown in Table I. The wet/dry ratio is thought to suggest the degree of disorder in the crystalline or semicrystalline regions.

The degree of crystallinity of cellulosic fibers treated with acrylamide in 3% sodium hydroxide was almost unchanged as compared with the sample treated in the same concentration of sodium hydroxide without acrylamide and untreated cellulose under dry and wet conditions, respectively. However, the degree of crystallinity of cellulosic fibers carbamoylethylated and carboxyethylated in the presence of 20% sodium hydroxide decreased greatly under wet conditions as the degree of substitution increased, regardless of the fact that the degree of crystallinity under dry conditions was almost independent on carbamoylethylation and carboxyethylation.

The wet/dry ratio of the samples is less than unity. Therefore, it is considered that some part of the crystalline regions under dry conditions is disordered and counted as amorphous regions under wet conditions.

The wet/dry ratio of the samples reacted in 3% sodium hydroxide is almost the same as the ratio with untreated cellulose. From such a result it is assumed that carbamoylethylation and carboxyethylation occur only in amorphous regions in the reaction system containing 3% sodium hydroxide. On the other hand, the wet/dry ratio of the samples reacted in 20% sodium hydroxide decreased as the degree of substitution increased. Therefore, it is inferred that carbamoylethylation and carboxyethylation in the reaction system containing 20% sodium hydroxide proceed simultaneously with mercerization and consequently make the crystalline regions disordered because the pendent groups are introduced not only in the amorphous regions but also in the crystalline regions.

Spacing Parameters

Equatorial x-ray diffraction traces of the samples were corrected and resolved by computer into (101), (10$\bar{1}$), and (002) diffraction peaks and a background. From each peak position, spacing parameters were evaluated by the Bragg

TABLE I
Degree of Crystallinity

Sample	DS[a]			Degree of Crystallinity, %		
	CONH$_2$	COOH	Total	Dry	Wet	Wet/dry
Untreated	—	—	—	43.2	32.9	0.76
3% NaOH	—	—	—	43.9	34.8	0.79
3% NaOH 1 hr 7% AM	0.036	0.009	0.045	40.9	30.9	0.76
3% NaOH 24 hr 7% AM	0.069	0.021	0.090	43.0	30.9	0.72
20% NaOH	—	—	—	36.6	30.0	0.82
20% NaOH 1 hr 7% AM	0.056	0.025	0.081	33.6	22.4	0.67
20% NaOH 10 hr 7% AM	0.027	0.115	0.142	34.4	16.7	0.49

[a] Degree of substitution (DS) per anhydroglucose residue.

equation.   Spacing parameters measured under dry and wet conditions are shown in Table II.

The spacing parameters of the samples carbamoylethylated and carboxyethylated in the presence of 3% sodium hydroxide were the same as those of cellulose treated in 3% sodium hydroxide without acrylamide and untreated cellulose under both dry and wet conditions.   The values under dry conditions were equal to those under wet conditions.

On the other hand, spacing parameters $d(101)$ under dry conditions increased a little by carbamoylethylation and carboxyethylation in 20% sodium hydroxide, but $d(10\bar{1})$ under dry conditions was not affected by the substitution reaction. The values $d(101)$ under wet conditions were greater than those under dry conditions in the samples mercerized and reacted in 20% sodium hydroxide.   The tendency became more pronounced in the samples with a larger degree of substitution, but $d(10\bar{1})$ under wet conditions was the same as that under dry conditions.

As mentioned above, the substitution reaction did not change $d(hkl)$ under dry conditions in the samples treated in 3% sodium hydroxide.   By carbamoylethylation and carboxyethylation in 20% sodium hydroxide, $d(10\bar{1})$ did not change, but $d(101)$ increased a little under dry conditions.   Therefore, it is considered that carbamoylethyl and carboxyethyl groups are introduced mainly in amorphous regions in the samples reacted in 3% sodium hydroxide, and are introduced not only in the amorphous regions but also in the crystalline regions in the samples reacted in 20% sodium hydroxide.   It is also inferred that carbamoylethyl and carboxyethyl groups are introduced between (101) planes and make the $d(101)$ large.

Comparing $d(hkl)$ under dry conditions with that under wet conditions, it is found that $d(101)$ increased a little by immersion in water in the samples carbamoylethylated and carboxyethylated in 20% sodium hydroxide, but $d(101)$ in samples reacted in 3% sodium hydroxide and $d(10\bar{1})$ in all samples were not changed by water.   Therefore, it is considered that water can penetrate between the (101) planes in the samples carbamoylethylated and carboxyethylated in 20% sodium hydroxide because such samples have open structures and contain water as spacer more easily than mercerized samples.

TABLE II
Spacing Parameter

| Sample | Total DS | Spacing parameter, Å | | | |
| | | $d(101)$ | | $d(10\bar{1})$ | |
		Dry	Wet	Dry	Wet
Untreated	—	6.1	6.1	5.5	5.5
3% NaOH	—	6.1	6.1	5.5	5.5
3% NaOH 1 hr 7% AM	0.045	6.1	6.1	5.5	5.5
3% NaOH 24 hr 7% AM	0.090	6.1	6.1	5.5	5.5
20% NaOH	—	7.5	7.6	4.5	4.5
20% NaOH 1 hr 7% AM	0.081	7.7	8.0	4.5	4.5
20% NaOH 10 hr 7% AM	0.142	7.6	8.0	4.5	4.5

Crystallite Size

By computational analysis, equatorial X-ray diffraction traces were resolved into three peaks and a background. From each peak width, weight average crystallite sizes $L(hkl)$ normal to diffraction planes (hkl) were estimated by the usual Sherrer equation:

$$L(hkl) = K/[\cos \theta d(2\theta)] \tag{2}$$

where $K = 1$ and $d(2\theta)$ is the integral width. The relationship between crystallite size $L(hkl)$ and the crystalline network of cellulose is shown in Figure 6. Values of crystallite size measured under dry and wet conditions are shown in Table III.

Carbamoylethylation and carboxyethylation in 3% sodium hydroxide did not change crystallite sizes $L(101)$ and $L(10\bar{1})$ under both dry and wet conditions as compared with those of the samples treated in 3% sodium hydroxide without acrylamide and untreated cellulose. The values $L(101)$ under dry conditions were greater than those under wet conditions, but the values $L(10\bar{1})$ under dry
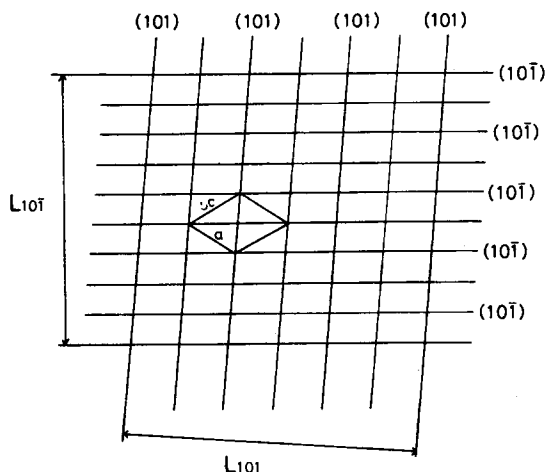

Fig. 6. Relationship between crystallite size $L(hkl)$ and crystalline network of cellulose.

TABLE III
Crystallite Size

| Sample | Total DS | Crystallite size parameter, Å | | | |
| | | $L(101)$ | | $L(10\bar{1})$ | |
		Dry	Wet	Dry	Wet
Untreated	—	39	26	51	53
3% NaOH	—	42	29	38	61
3% NaOH 1 hr 7% AM	0.045	42	27	39	53
3% NaOH 24 hr 7% AM	0.090	39	30	35	53
20% NaOH	—	56	21	33	48
20% NaOH 1 hr 7% AM	0.081	26	18	26	33
20% NaOH 10 hr 7% AM	0.142	29	21	27	37

conditions were less than those under wet conditions in the samples treated in 3% sodium hydroxide and untreated cellulose.

On the other hand, the substitution reaction in 20% sodium hydroxide greatly decreased $L(101)$ under dry conditions as compared with that of mercerized samples, but $L(10\bar{1})$ values under dry conditions were almost unchanged by the reaction. $L(101)$ values under dry conditions were greater than those under wet conditions, but $L(10\bar{1})$ values under dry conditions were less than those under wet conditions.

As mentioned above, crystallite sizes $L(101)$ and $L(10\bar{1})$ under dry conditions were not changed by the substitution reaction in 3% sodium hydroxide. By carbamoylethylation and carboxyethylation in 20% sodium hydroxide, $L(10\bar{1})$ did not change but $L(101)$ decreased under dry conditions. Therefore, it is considered that carbamoylethyl and carboxyethyl groups are introduced between (101) planes and (101) planes are exfoliated by the reaction in 20% sodium hydroxide.

It was also found that $L(101)$ under dry conditions was greater than that under wet conditions, and $L(10\bar{1})$ under dry conditions was less than that under wet conditions in the samples obtained in both reaction systems. Therefore, it is inferred that water plays different roles in (101) and (10$\bar{1}$) planes, and different kinds of cohesive forces act in (101) and (10$\bar{1}$) planes.

Fine Structure of Carbamoylethylated and Carboxyethylated Cotton Fibers

As mentioned before, in spite of rather high degrees of substitution, the moisture regain, water imbibition, x-ray photograph, and degree of crystallinity under dry and wet conditions of the samples carbamoylethylated and carboxy-ethylated in 3% sodium hydroxide are almost the same as those of the sample treated in 3% sodium hydroxide without acrylamide and untreated cellulose. Therefore, it is inferred that carbamoylethylation and carboxyethylation in 3% sodium hydroxide occur mainly in the amorphous regions of the samples. On the other hand, in carbamoylethylated and carboxyethylated samples in 20% sodium hydroxide, moisture regain, x-ray photographs, and degree of crystallinity under dry conditions were almost the same as those of mercerized samples, but water imbibition and degree of crystallinity under wet conditions were greatly changed as compared with those of mercerized samples. It is thus considered that the crystalline regions of the samples are disordered by the reaction in 20% sodium hydroxide, because carbamoylethyl and carboxyethyl groups are intro-duced not only in amorphous regions but also in crystalline regions.

The $L(hkl)/d(hkl)$ values, which indicate the number of diffraction planes constructing the crystallite, are shown in Table IV. $L(101)/d(101)$ and $L(10\bar{1})/d(10\bar{1})$ under dry and wet conditions were not affected by carbamoyl-ethylation and carboxyethylation in 3% sodium hydroxide, but $L(101/d(101)$ under dry conditions became small by the substitution reactions in 20% sodium hydroxide. This means that (101) planes are easily exfoliated by carbamoyl-ethylation and carboxyethylation. $L(10\bar{1})/d(10\bar{1})$ under dry conditions was affected little by the substitution reaction. Therefore, it is assumed that car-bamoylethyl and carboxyethyl groups are introduced mainly between (101) planes. $L(101)/d(101)$ under wet conditions was less than that under dry con-

TABLE IV
Number of Diffraction Planes Constructing Crystallite

| Sample | Total DS | Number of diffraction planes | | | |
| | | $L(101)/d(101)$ | | $L(10\bar{1})/d(10\bar{1})$ | |
		Dry	Wet	Dry	Wet
Untreated	—	6.4	4.3	9.3	9.6
3% NaOH	—	6.9	4.8	6.9	11.1
3% NaOH 1 hr 7% AM	0.045	6.9	4.4	7.1	9.6
3% NaOH 24 hr 7% AM	0.090	6.4	4.9	6.4	9.6
20% NaOH	—	7.5	2.8	7.3	10.7
20% NaOH 1 hr 7% AM	0.081	3.4	2.3	5.8	7.3
20% NaOH 10 hr 7% AM	0.142	3.8	2.6	6.0	8.2

ditions in the samples reacted in both reaction systems. Accordingly, it is considered that (101) planes in all samples including untreated cellulose might be exfoliated by penetration of water. But $L(10\bar{1})/d(10\bar{1})$ under wet conditions was greater than that under dry conditions in all samples. Such a result can probably be attributed to the fact that water might join $(10\bar{1})$ planes. As Van Der Waals forces are not affected and weakened by aqueous solution of sodium hydroxide, the forces between $(10\bar{1})$ planes are considered to be somewhat like Van Der Waals forces. The forces between (101) planes are assumed to be hydrogen bonds. By the difference of cohesive forces between (101) and $(10\bar{1})$ planes, carbamoylethyl and carboxyethyl substituents are introduced selectively between (101) planes.

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