JOURNAL OF APPLIED POLYMER SCIENCE VOL. 13, PP. 785-795 (1969)

Disorder in Cellulosic Fibers*

A. VISWANATHAN and V. VENKATAKRISHNAN,
South India Textile Research Association, Coimbatore, India

Synopsis

Ruland's concept of an isotropic disorder function is applied to estimate the disorder parameter and the degree of crystallinity in a few cellulosic fibers: two cottons, native ramie, and a high-tenacity rayon. The results indicate an increase in disorder without any change in crystallinity on mercerization of native celluloses. On hydrolysis, with or without a pretreatment of mercerization, the samples exhibit a higher crystallinity, disorder remaining the same as for native celluloses. A ball-milled sample of "amorphous" cellulose is still found to be fairly crystalline with the lowest disorder. On being wetted in water and oven-dried, a distorted form of cellulose II with higher crystallinity and disorder was obtained. The polynosic fiber, Tufcel, has low values for the degree of crystallinity, disorder parameter, as well as crystallite dimension. A strong dependence of the degree of crystallinity on the crystallite size, particularly the lateral, is observed.

INTRODUCTION

The degree of crystallinity, i.e., the percentage of crystalline or well-ordered regions in high polymers is an outcome of the two-phase theory of fiber structure now known to be an oversimplification. Diffuse x-ray scatter can arise not only from the noncrystalline portions of a fiber but also from chain-twisting and lattice distortions in the crystalline regions themselves.[1] In an attempt to improve the method of measurement which yielded identical values for both native and mercerised cottons,[2,3] further work was undertaken wherein the lattice distortions were also taken into account following Ruland's concept[4] of an isotropic disorder function. This paper presents the results of applying his technique to the study of cellulosic fibers. As this investigation was in progress, Ruland extended his theory and techniques to include an anisotropic disorder function.[5] Such considerations are, however, unlikely to affect the conclusions drawn in the current study.

THEORY

The degree of crystallinity is given, according to Ruland, by the expression

* This paper was presented at the Institute of Physics and the Physical Society X-Ray Analysis Group Spring Conference held at the University of York, United Kingdom, April, 1968.

$$X_{cr} = K \frac{\int_{S_o}^{S_p} s^2 I_{cr}(s) ds}{\int_{S_o}^{S_p} s^2 I(s) ds} \tag{1}$$

where s is the reciprocal space vector ($= 2 \sin \theta / \lambda$), s_o and s_p being the limits of integration, $I_{cr}(s)$ and $I(s)$, intensities of coherent scattering at s due to the crystalline part and the total, respectively, and K is a "constant" of proportionality to correct the crystallinity for the disorder function. K assumes different values with the varying integration limits and is given by

$$K = \int_{S_o}^{S_p} s^2 \overline{f^2} ds \Big/ \int_{S_o}^{S_p} s^2 \overline{f^2} D ds \tag{2}$$

where $\overline{f^2}$, the mean-square amplitude of atomic scattering, is given by

$$\overline{f^2} = (\sum N_i f_i^2) / \sum N_i \tag{3}$$

N_i being the number of atoms of type i with a scattering factor f_i. The disorder function D is in the first approximation taken to be $\exp \{-ks^2\}$. (For further details on the theoretical aspects Ruland's original work may be consulted.)

In the present work, Ruland's concept of the disorder function is applied to a few cellulosic fibers so chosen as to enable one to detect differences between fibers with the same structure or between fibers with different structures (cellulose I and cellulose II) or between fibers differently treated (mercerized, hydrolyzed or both, ball-milled).

EXPERIMENTAL

Samples and Their Preparation

Raw cottons, Karnak and Punjab Desi, representing a fine and a coarse variety, respectively, were first cleaned to remove dirt and foreign matter; after wax removal by Soxhlet extraction, the samples were washed, boiled in 1% NaOH for 90 min, and finally washed and dried. Raw cottons consist of cellulose I structure just as does ramie, which was studied for comparison after degumming and a mild bleach.

Dewaxed cotton as well as ramie fibers were then mercerized with 25% NaOH solution at 27°C for 5 min. Mercerized cellulose exhibits type II structure. One of the cottons, Karnak, and ramie were also hydrolyzed, both with and without a mercerization pretreatment. A polynosic fiber, Tufcel, of commercial interest provided another comparison.

The source of the amorphous cellulose was Karnak cotton. It was dewaxed, dried at 110°C for 3 hr, and sealed into the ball-milling chamber. It was then ball-milled for a few hours, taken out, and allowed to come in contact with normal ambient air.

The hydrolyzed and ball-milled samples were already in powder form

and therefore quite suitable for Debye-Scherrer powder work, but the other samples were cut into tiny fragments (of the order of 0.2 mm) before x-ray examination by the transmission technique.

Specimen Absorption and Preferred Orientation

The transmission factor for this geometry is given by

$$A_c = t \sec \theta e^{-\mu t \sec \theta} \tag{4}$$

For this to be a maximum its first derivative should vanish and hence $t_{max} = 1/(\mu \sec \theta)$. Also the second derivative should be negative, which is true only when $\mu t \sec \theta$ is less than 2. If μt is approximately equal to 1, the transmission factor remains reasonably constant over the angular range covered, viz., $2\theta = 3$–$102°$. This value of μt was obtained by compressing about 700 mg of the sample into a compact flat cake approximately 1 mm. thick. The fragments were quite cohesive and required no special adhesive.

For checking preferred orientation, a complete azimuthal scanning of one equatorial and one meridional plane of the substance was recorded. For this purpose, the Philips Texture Goniometer PW 1078 was adapted as reported elsewhere.[6] Reflections (002) and (040) for cellulose I and reflections $(10\bar{1})$ and (040) for cellulose II displayed a fairly even distribution of intensity along the arcs, thus indicating an absence of preferred orientation in the samples. The 5 mm integrating motion helped in reducing considerably any persistent preferred orientation.

Scanning the Reflections

By using transmission geometry, scattered radiation was measured by a point-to-point technique which ensured a good accuracy in intensity estimation and an easy conversion of the diffractogram obtained in arbitrary intensity units versus Bragg angle into a chart of absolute intensity versus reciprocal space vector. The incident beam was Ni-filtered copper $K\alpha$ radiation from a stabilized generator (Philips PW 1010) operated at 40 kV and 20 mA. A Philips wide-angle Goniometer PW 1050 and diffractometer PW 1051 were employed to analyze the scattered radiation. The ambient temperature was about 20°C and relative humidity 50%. Fixed count method was used for intensity corresponding to more than 10 counts per second and fixed time was adopted for lower rates of counting. This procedure ensured good speed and accuracy in measurement. Each observed intensity value (higher than 100 cps) was corrected for nonlinearity arising from the Geiger counter dead time (150 μsec).

Corrections for Specimen Absorption, Air Scatter, and Incoherent Scattering

It is customary to correct the observed intensities for absorption in the specimen by the use of an exponential expression involving mass absorption coefficients. However, Ruck and Krässig[7] pointed out that absorption in

high polymers is also a function of the colloidal particle size. Therefore an entirely different principle was suggested by them for making corrections for absorption. This consists of taking two diffractograms under identical conditions by placing the specimen first between the collimator and the counter tube and next between the collimator and the x-ray port. The difference between the two readings at any given position on the arc of movement of the counter automatically eliminates the errors due to absorption by the sample and also due to air scatter. This procedure was followed in the present work.

Incoherent scattering for carbon, oxygen and hydrogen was read directly from the International Tables for x-ray crystallography (Vol. III), and the average scatter per atom was next calculated, on the basis of the chemical composition of cellulose, viz., glucose residue $C_6H_{10}O_5$. Compton scattering thus worked out for different values of s was then corrected also for the Breit-Dirac recoil factor which is given by $R = B^{-3}$, where $B = 1 + (2h\lambda/mc)(\sin\theta/\lambda)^2$. The symbols have their usual meaning of atomic constants. For copper $K\alpha$ radiation, the value of B reduces to $1 + 0.0744\ (\sin\theta/\lambda)^2$. Though this is not significantly different from unity, the corrections have been applied in order to make the method as nearly perfect as possible.

Conversion of Intensities from Arbitrary into Absolute Units

The observed intensities (in arbitrary units) which had been already corrected for specimen absorption, air scatter, and nonlinearity, were now multiplied by $(1/P)$ to correct for the polarization effect, where $P = (1 + \cos^2 2\theta)/2$. These intensities were then normalized to average scattering per atom by the Fourier transform method described by Norman.[8] This procedure is preferred to the one based on the assumption of identity between the observed intensity at large scattering angles on the one hand and the sum of the squares of the atomic form factors and incoherent scattering on the other. The reasons for this are two-fold as pointed out by Krogh-Moe:[9] (1) the difficulties in the measurement, to the required accuracy, of the necessarily low intensities observed in the high-angle region; (2) the ambiguity in curve-fitting arising from appreciable undulations in observed intensity at high angles.

Having determined the normalization constant and consequently the absolute intensity at all angles in electron units, compton scattering calculated as per atom on an average, is now subtracted from the intensity at each angle, the residual intensity being the coherent part of the scattered radiation $I(s)$.

RESULTS

Disorder Function and Degree of Crystallinity

The values for K in expression (2) were first worked out for different values of k appearing in the disorder function $\exp\{-ks^2\}$. Simple integral

values of $k = 0,1,2,3,\ldots$, were assumed, and where the application of expression (1) to estimate the degree of crystallinity justified it, an intermediate value between simple integers was assumed. The constancy of the degree of crystallinity was checked by its coefficient of variation within the angular range. The values of K for different values of k are shown in Figure 1 as a function of s_p, the lower limit s_o being taken to be 0.10 as was done by Ruland. Table I gives typical results for the degree of crystallinity in a mercerized and subsequently hydrolyzed ramie sample estimated from the curve $s^2I(s)$ versus s for the same sample in Figure 2.

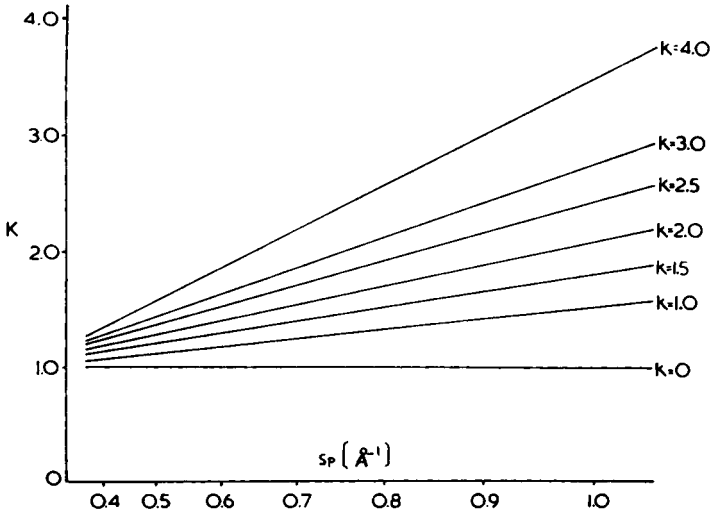

Fig. 1. Proportionality factor K as function of s_p for different values of k.

TABLE I
Crystallinity as Function of k and Integration Interval for Mercerized nd Hydrolyzed Ramie

Sample	$s_o - s_p$	Degree of crystallinity				
		$k = 0$	$k = 1.0$	$k = 1.5$	$k = 2.0$	$k = 3.0$
I	0.10–0.36	0.512	0.543	0.568	0.589	0.620
	0.10–0.70	0.396	0.499	0.554	0.614	0.741
	0.10–1.00	0.324	0.492	0.590	0.684	0.901
	Coefficient of variation, %	23.1	5.5	3.2	7.8	18.7
	Mean x_{cr}	—	—	0.571	—	—
II	0.10–0.36	0.514	0.545	0.571	0.591	0.622
	0.10–0.70	0.381	0.480	0.533	0.591	0.712
	0.10–1.00	0.307	0.467	0.559	0.648	0.853
	Coefficient of variation, %	26.2	8.5	3.4	5.4	15.6
	Mean x_{cr}	—	—	0.554	—	—

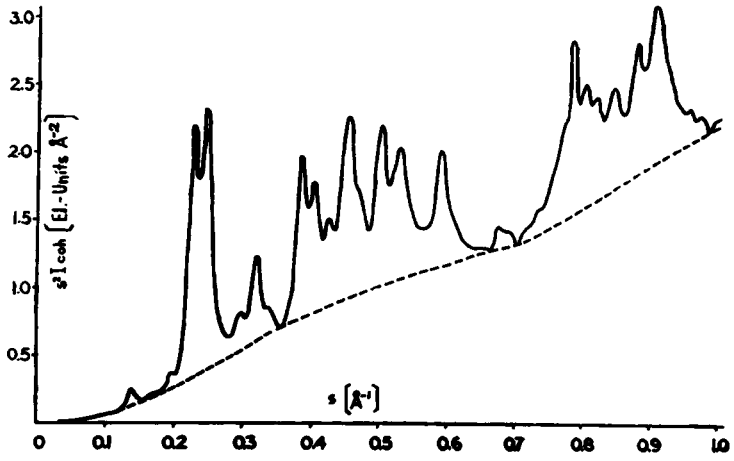

Fig. 2. The curve $s^2I(s)$ vs. s for a mercerized and subsequently hydrolysed sample of ramie.

Before the degree of crystallinity could be estimated from Figure 2 according to expression (1), the question of how to distinguish between the crystalline and the noncrystalline part arose. The same procedure as was applied by Ruland in the case of his polypropylene samples was followed here, i.e., the separation lines between the crystalline peaks and continuous scattering were established by drawing smooth curves from tail to tail following the general slope of the continuous scattering. The smooth background connecting the valleys at $s = 0.36$ and $s = 0.70$ was an additional guiding factor. Table II gives a summary of the results for all the samples investigated. The values for the disorder parameter in Table II are those values of k which ensure the constancy of X_{cr} as shown in the example of Table I.

Crystallite Sizes

The crystallite sizes were estimated after making corrections for instrumental line broadening from the x-ray interferences due to a compact flat cake of hexamethylenetetramine. This serves as an excellent standard and also gives by transmission technique intensities comparable to those obtained in cellulosic fibers in the angular range of interest under identical conditions of operation. The doublet broadening correction was applied to the instrumental profile.

While making the corrections for instrumental line broadening, the shape of the line profile assumes a great importance, the Gaussian function giving a much larger resultant line breadth than the Cauchy form. Since neither of the expressions could be adopted without ambiguity in the present study, the sizes were estimated by using the geometric mean of the breadths result-

TABLE II
Degree of Crystallinity, Disorder Parameter, and Crystallite Sizes of the Cellulosic Samples

Sample description	Treatment	Degree of crystallinity	Disorder parameter	D_{101}, Å	D_{002}, Å	D_{040}, Å
Punjab Desi cotton	—	0.446	1.5	—	69	110
"	Mercerized	0.422	2.0	54	—	83
Karnak cotton	—	0.472	1.5	—	72	110
"	Mercerized	0.424	2.0	51	—	91
"	Hydrolyzed	0.513	1.5	—	86	134
"	Mercerized and hydrolyzed	0.534	1.5	89	—	85
Ramie	—	0.444	1.5	—	61	167
"	Mercerized	0.454	2.0	56	—	79
"	Hydrolyzed	0.557	1.5	—	83	130
"	Mercerized and hydrolyzed	0.562	1.5	85	—	85
Tufcel	—	0.356	1.0	43	—	—
Amorphous cellulose[a]	—	0.280	1.0	—	—	—
"	Water-wet and oven-dried	0.367	1.5	59	—	—

[a] This sample has a broad peak near $2\theta = 20°$. The peak breadth corresponds to a crystallite size of 11 Å.

ing from the two forms as given in the International Tables for x-ray crystallography (Vol. III).

The background for estimation of the crystallite sizes was determined for each value of s from the quotient of $s^2I_b(s)$ by s^2, i.e. $s^2I_b(s)$ from the curve in Figure 2 divided by s^2. This background $I_b(s)$ is shown distinctly as a dotted line in Figure 3, representing the coherent intensity distribution $I(s)$ as a function of s. The crystallite dimensions D_{002} and D_{040} for cellulose I and D_{101} and D_{040} for cellulose II were calculated from the line profiles above the background. The inset in Figure 3 illustrates the procedure for (040) reflection. The values so obtained are included in Table II. However, the crystallite length could not be determined in a few cases owing to a great overlapping of the adjacent reflections.

DISCUSSION

Before discussing the results, it must be emphasized that the degree of crystallinity as measured in this study is still probably a minimum value only, because of the manner in which the background is drawn. Thus, if

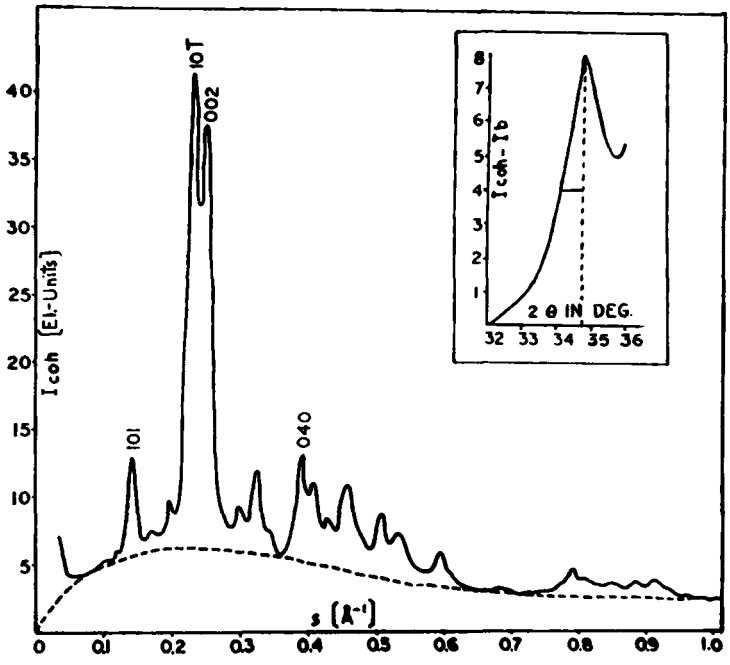

Fig. 3. Coherent intensity $I(s)$ distribution as function of s for the same sample as shown in Figure 2.

the background in Figure 2 were to be redrawn touching more "valleys" in the curve, it is quite likely that the degree of crystallinity could be considerably higher. From Table II, it is observed that the degree of crystallinity is similar for both the native and the mercerized forms of cellulose, whereas Hermans[10] reported 70% and 50%, respectively, for the two forms. This decrease in the degree of crystallinity on mercerization was attributed to a decrease in the degree of order, which was considered to be synonymous with the degree of crystallinity itself at a time when there existed no information whatsoever on the degree of crystallinity of cellulose and most other polymers.[11] Following Ruland, the present study, however, differentiates order from crystallinity and reveals an increase in disorder on mercerization without much change in the degree of crystallinity.

Similarly a regenerated cellulosic fiber such as Tufcel, which would have shown 40% degree of crystallinity according to Hermans and Weidinger, still exhibits a low value for crystallinity in the present study, but this is accompanied by a greater order than was observed for all other cellulosic samples investigated except the amorphous sample. Tufcel is a polynosic fiber, manufactured by Toyo Spinning Co., Osaka, Japan. In the manufacture of polynosic fibers, two spinning baths are generally employed: (1) acid bath, e.g., H_2SO_4 at room temperature, and (2) hot water bath at about 80°C. Both processes are capable of reducing the crystallite sizes

and breaking up the peripheral layers of crystallites. The spun polynosic filaments are next withdrawn under tension at a speed of a few meters per minute through a nozzle containing about 200 holes, each with a diameter of the order of 0.05 mm. All these conditions are apparently most favorable to the formation of only small but fairly perfect, well-oriented crystallites. Similarly, the low disorder parameter for the amorphous cellulose could be due to the small but perfect crystallites resulting from the removal of the distorted peripheral layers of the crystallites by prolonged ballmilling. In view of its surprisingly high crystallinity and low disorder, plots similar to Figures 2 and 3 are drawn for the ball-milled amorphous cellulose (Fig. 4).

It is also noteworthy that samples of cellulose (Karnak cotton and ramie) show an increase in the degree of crystallinity on hydrolysis, with or without a mercerization pretreatment, the disorder parameter for all the hydrolyzed samples remaining the same[1,5] as for native cellulose. It may be that the lattice distortions introduced by the mercerization process are removed by hydrolysis which at the same time leads to a hornification of the adjacent fibrils as pointed out by Ruck.[12] This hornification consists of an enlargement of the crystallites, particularly in the lateral direction, and is perhaps responsible for the higher values of the degree of crystallinity of the hydrolyzed samples and also the water-wetted and oven dried amorphous cellulose. Such a dependence of the degree of crystallinity on the crystal-

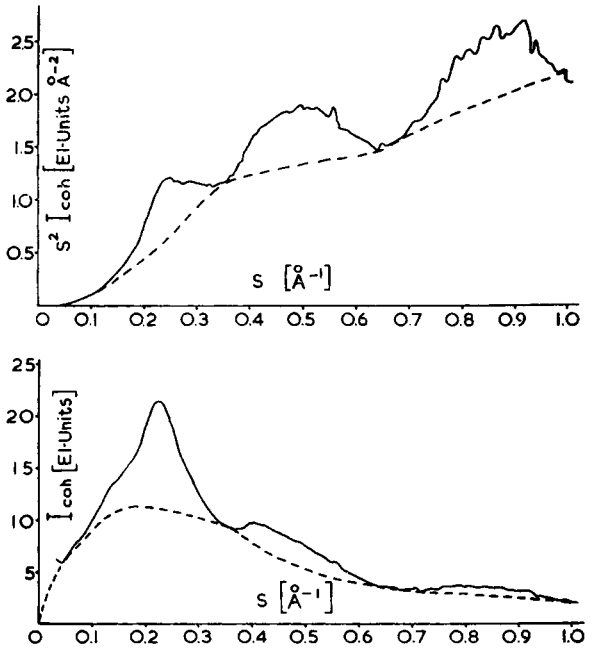

Fig. 4. Plots of (*a*) $s^2I(s)$ vs. s and (*b*) $I(s)$ vs. s for ball-milled amorphous cellulose. Dewaxed Karnak cotton, dried for 3 hr at 110°C, ball-milled for 48 hr.

lite sizes is shown graphically in Figure 5 for all the samples. It may be inferred that the degree of crystallinity correlates far better with the lateral sizes of the crystallites than with the crystallite length and that the length itself tends to increase with its lateral dimensions, the notable exceptions being native ramie and mercerized, subsequently hydrolyzed Karnak and ramie. It appears from the data that a combination of mercerization and hydrolysis would make the crystallite length equal to its lateral size, about 85 Å.

Finally, it is interesting to compare the values for the crystallite dimensions obtained in this study with those reported by other workers from x-ray line-broadening measurements and electron microscopic investigations. Whereas the crystallite lengths are of the same order, the lateral sizes tend to be significantly different. This could be attributed above all to the influence of mechanical action on the crystallite sizes. Thus Betrabet et al.[13] found the microfibrils of untreated cotton to be 110 Å wide and hardly 25 Å thick, when the purified fibers were beaten in water in a blender and the specimens for electron microscopy were prepared by allowing the slurry to dry on the grids and subsequently coated with gold–palladium. When the fibers were given a more rigorous treatment of disintegration under water by use of an ultrasonic generator and the aqueous suspension mixed with uranium acetate was sprayed on to carbon-coated specimen grids, Manley[14, 15] found that both native and regenerated celluloses consist ultimately of an identical basic structural element, viz., a filament, 35 Å wide, termed protofibril, essentially a quasi-single crystal. Similarly prolonged ball-milling reduces the size very considerably so that only a peak corresponding to 11 Å, i.e., roughly of the same order as the unit cell dimensions, is observed in wide-angle x-ray diffraction in the present study. Indeed, in this

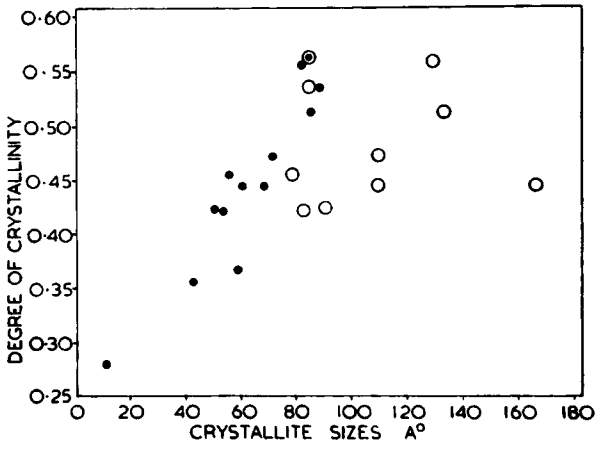

Fig. 5. Correlation between the degree of crystallinity and the crystallite sizes: (●) lateral dimensions; (○) crystallite lengths.

sense, the sample could be considered amorphous, although the crystallinity and order are appreciable. The values in Table II could differ from others also because of the entirely different procedures adopted for estimating the background intensity.

SUMMARY

From the foregoing, it is clear that the "degree of crystallinity" and "order" are not synonymous. Thus mercerization tends to increase the disorder in native cellulose without affecting the degree of crystallinity, while hydrolysis increases the degree of crystallinity without affecting the disorder. Hydrolysis of a mercerized cellulose restores the original order but with an increase in the degree of crystallinity.

A correlation exists between the degree of crystallinity and the crystallite dimensions, particularly the lateral. This holds true even in the case of the small but perfect cellulose crystallites in the polynosic rayon and the ball-milled amorphous sample which exhibits an appreciable crystallinity.

The authors are grateful to Mr. K. Sreenivasan, F. T. I., Director, South India Textile Research Association, Coimbatore, for his interest in the work, to Professor R. S. Krishman, F. Inst. P., Indian Institute of Science, Bangalore, for his very valuable suggestions, and to Mr. R. Ramakrishnan for his assistance in the calculations.

The amorphous sample was kindly provided by Dr. T. Radhakrishnan of the Ahmedabad Textile Industry's Research Association, Ahmedabad, India.

References

1. R. Hosemann and S. N. Bagchi, *Direct Analysis of Diffraction by Matter*, North Holland, Amsterdam, 1962.
2. R. Bonart, R. Hosemann, F. Motzkus, and H. Ruck, *Norelco Reptr.*, **7**, 81 (1960).
3. A. Viswanathan and V. Venkatakrishnan, *Proceedings of the 7th Joint Technical Conference*, Ahmedabad Textile Industry's Research Assn., India, 1965, Section B, 41.
4. W. Ruland, *Acta Cryst.*, **14**, 1180 (1961).
5. W. Ruland, *Faserforsch. Textiltech.*, **18**, 59 (1967).
6. A. Viswanathan and V. Venkatakrishnan, Norelco Reptr., **13**, 48 (1966).
7. H. Ruck and H. Krassig, *Norelco Reptr.*, **7**, 71 (1960).
8. N. Norman, *Acta Cryst.*, **10**, 370 (1957).
9. J. Krogh-Moe, *Acta Cryst.*, **9**, 951 (1956).
10. P. H. Hermans, *Physics and Chemistry of Cellulosic Fibers*, Elsevier, Amsterdam, 1949.
11. P. H. Hermans and A. Weidinger, *Text. Res. J.*, **31**, 558 (1961).
12. H. Ruck, *Norelco Reptr.*, **7**, 75 (1960).
13. S. M. Betrabet, E. H. Daruwalla, and H. T. Lokhande, *Text. Res. J.*, **36**, 684 (1966).
14. R. St. J. Manley, *Nature*, **204**, 1155 (1964).
15. R. St. J. Manley, *J. Polym. Sci. B*, **3**, 691 (1965).

Received May 3, 1968