# Crystalline Character of Native and Chemically Treated Egyptian Cottons. I. Computation of Crystallinity, Disorder Parameter, Orientation Factor, and Spiral Angle

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## Synopsis

Computer data processing and electronic monochromatization of x-rays were employed for determining crystallinity, disorder parameter, Hermans' orientation factor, as well as DeLuca and Orr spiral angle of native, mercerized and urea-treated cottons. The results indicate the values for the degree of crystallinity to vary significantly between cottons. Increase in disorder on mercerization is confirmed. The effect of urea treatment is not so well defined. The differences in Hermans' x-ray orientation factor are significant at the 1% level between cottons and at the 10% level between treatments. Besides, from a critical analysis of the values obtained, it is shown that the spiral angle $\phi$ in the method of DeLuca and Orr is probably a direct estimate of the mean inclination of the crystallites to the fiber axis, while Hermans' orientation angle $\beta$ is a complex function of other parameters as well. The computer programs which could be applied to other polymers are included.

## INTRODUCTION

Egyptian cottons, on account of their long and fine staple, are among those in greatest demand in the world market. What exactly endows them with their particularly desirable characteristics for use in fabrics of superior quality still remains largely a mystery. Any serious attempt to resolve this question will have to take into account the growth conditions of both the cotton plant and the fibers. It would be of considerable interest, however, to study the crystalline character of the cotton fibers in the collapsed state after the bolls open and correlate it to their tensile strength which is of paramount importance in textile processing. For the purpose of the present study, the term "crystalline character" comprises three aspects, viz., degree of crystallinity, crystallite orientation, and crystallite sizes as measured by x-ray diffraction techniques. Results on the first two aspects are reported here, and the last will be reported in part II.

It is now widely accepted that the degree of crystallinity based on the simplified "crystalline–amorphous system" is not very meaningful and that

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a critical study of the fine structure of cellulosic fibers must make use of relatively recent concepts such as paracrystallinity[1] and disorder function.[2,3] Crystallinity of cotton cellulose is reexamined here in the light of disorder function. Similarly, though Hermans and co-workers[4] and DeLuca and Orr[5,6] arrived at two independent estimates of crystallite orientation from the observed line profile, no attempt seems to have been made so far to correlate the two. These methods are appraised here together, leading to some interesting interpretations.

In textile manufacture, chemical finishing plays an important role as it helps to promote properties such as water repellency, crease resistance, flame resistance, better dyeing, etc. Mercerization is a most widely known process. Urea has been used in cellulose textile finishing, often in combination with other chemicals, particularly caustic soda. References to urea treatment are however scanty in current literature. At times the results reported seem to be contradictory. Rebenfeld[7] studied the effect of urea and mercerization on the mechanical properties of single fibers. He concluded that different cottons responded differently to identical chemical treatments. Preston and co-workers[8] noted a marked increase in the swelling action of cellulosic fibers by urea treatment. Katz and Seiberlich[9] found higher swelling in caustic soda in the presence of urea, but Jeffries and Warwicker[10] concluded that the changes in mercerization produced by urea were only slight. Therefore, it was felt desirable to have a fresh look at the urea treatment of the cotton fibers. Thus, in the present investigation, the changes that take place in the crystalline character on mercerization with or without prior urea treatment are critically examined.

## EXPERIMENTAL

### Samples and Treatments

Five varieties of Egyptian cottons, viz., Menoufi, Giza 69, Giza 66, Ashmouni, and Danderah, were chosen for this study, and two more cottons, K6 and Sea Island, were included for comparison.

The cottons were first dewaxed by benzene in a Soxhlet apparatus for 6 hr, then washed and boiled in 1% sodium carbonate solution for 1 hr, and finally washed and dried. Then the cotton samples were divided into four parts. The first part was examined under x-rays (vide infra) without further treatment. The second part was treated with 60% urea solution (w/v) in slack form for 1/2 hr at 27°C, then washed, and dried at 105°C for 1 hr. The third part was mercerized in 25% (by weight) NaOH solution for 5 min at 27°C, washed and neutralized by 1% acetic acid solution for 10 min, then washed and dried as before. The fourth part was subjected to both treatments: urea followed by mercerization as described before. The fibers were not dried between the two treatments but only washed.

## Crystallinity and Disorder Parameter Measurements

A method of estimating crystallinity developed by Ruland[2] for polypropylenes and adapted by Viswanathan and Venkatakrishnan to cellulosic fibers[11] was used in the present study. The equipment consisted of a Philips x-ray generator PW 1010, a wide-angle goniometer PW 1050, and a diffractometer PW 1051. By using the texture goniometer PW 1078 for transmission geometry of compressed powdered cotton,[12] scattered radiation was measured point by point from $s = 0.04$ to $0.70$ ($= 2 \sin \theta/\lambda$) corresponding to $2\theta = 3°$ to $65°$ at equal intervals of $s = 0.003$. The combination of Ni-filtered Cu radiation, proportional counter, and single-channel pulse-height analyzer gave a satisfactorily high peak-to-background ratio.

The observed intensities, corrected for specimen absorption and air scatter,[13] were used, by means of a program written in FORTRAN II for IBM 1620 computer (Appendix I), to determine the areas $A_t$ of the curve $s^2 I(s)$ versus $s$ for four chosen ranges of $s_0 - s_p$. Correction for polarization, normalization of intensities to electron units,[14] and substraction of incoherent scattering were also included in this program. Following the procedure described earlier,[2,11] the areas of the crystalline peaks $A_c$ were measured by planimeter for the four chosen ranges of $s_0 - s_p$. From these values of $A_c$ and the computed values $A_t$ of the total area under the $s^2 I(s)$ versus $s$ curves, the values of the disorder parameter $k$ and the degree of crystallinity $X_{cr}$ were evaluated by another program (Appendix II) which also gave the variation of $X_{cr}$ between the four ranges of $s_0 - s_p$.

## Crystallite Orientation Measurements

The texture goniometer adapted by Viswanathan and Venkatakrishnan[12] for fiber bundles was used for the azimuthal scanning of the reflections. The intensity readings were taken at intervals of 5 degrees by the fixed time method (64 sec).

### *Hermans' Orientation Factor*

By means of a computer program (Appendix III), Hermans' x-ray orientation factor $f_x$ and the mean inclination $\beta$ to the fiber axis, for cellulose I and II, were then evaluated according to the relations

$$\overline{\sin^2 \alpha} = \frac{\int_0^{\pi/2} F(\alpha) \sin^2 \alpha \cos \alpha \, d\alpha}{\int_0^{\pi/2} F(\alpha) \cos \alpha \, d\alpha} \tag{1}$$

$$\overline{\sin^2 \beta} = 2 \overline{\sin^2 \alpha_4} = \overline{\sin^2 \alpha_0} + \overline{\sin^2 \alpha_3} \tag{2}$$

$$f_x = 1 - {}^3/_2 \overline{\sin^2 \beta} \tag{3}$$

where $\alpha_4$, $\alpha_0$, and $\alpha_3$ are the azimuthal angles along the (002) arc for cellulose I and the (101) and (10$\bar{1}$) arcs for cellulose II, respectively, and $F(\alpha)$ is

the intensity at $\alpha$ expressed as percentage of the peak after substracting a background assumed to be linear and equal to the intensity at azimuthal angle = 90°. These calculations are also included in the same program. The overlapping (021) and (10$\bar{1}$) arcs for cellulose II were resolved by the method described by Venkatakrishnan[15] before the calculation of $f_x$.

### DeLuca and Orr Method

Assuming the observed azimuthal diffraction line profile to be a resultant of two equal Gaussian intensity distributions, according to DeLuca and Orr, observed intensities $I_1$ and $I_2$ at azimuthal angles $\epsilon_1$ and $\epsilon_2$, expressed as percentages of the maximum intensity at $\epsilon = 0$, are governed by the theoretical expressions

$$I_1 \exp (H^2 \epsilon_1{}^2) = \cosh (2H^2 \epsilon_1 \phi) \qquad (4)$$

$$I_2 \exp (H^2 \epsilon_2{}^2) = \cosh (2H^2 \epsilon_2 \phi) \qquad (5)$$

where $H^2 = (\ln 2/\alpha^2)$. The spiral angle $\phi$ and the half-intensity angle $\alpha$ of crystallite orientation were obtained through a computer program (Appendix IV) for solving the above two equations, i.e., by assigning different values for $H^2$ till identical values are obtained for $\phi$ from the two equations. This program had been written and used earlier by one of the authors.[16] The (002) arc was analyzed for cellulose I. For cellulose II, both the (002) and (10$\bar{1}$) arcs were scanned independently.

## RESULTS AND DISCUSSION

### Crystallinity and Disorder Parameter

The crystallinity values and the disorder parameters for the seven varieties of cotton before and after treatments, viz., swelling in urea, mercerization and swelling in urea followed by mercerization, are given in Table I. It is seen that, among the native cottons, Sea Island has the highest crystallinity (0.65) and Giza 69, the lowest (0.56). On urea treatment, Sea Island still retains the highest crystallinity (0.63), but the poorest crystallinity (0.50) is exhibited by Giza 66 and *not* by Giza 69. Of the mercerized samples, with or without urea pretreatment, Ashmouni shows the highest crystallinity (0.62), whereas Danderah exhibits the lowest value (0.56). Ashmouni and Giza 69 show strikingly higher crystallinity on mercerization, and in this sense these two cottons show distinctly a different trend from the rest of the cottons.

A similar inference can also be drawn from the values of the disorder parameter $k$. Whereas the mean value for $k$ is calculated to be 3.0 for cellulose I (native and urea-treated samples) and 3.6 for mercerized cottons (with and without prior urea treatment), Giza 69 and Ashmouni show the highest increases in the disorder parameter. These differences in behavior could perhaps be attributed to "variations in the conditions of natural deposition of cellulose on the inner surface of the primary wall of the cotton

TABLE I
Degree of Crystallinity $X_{cr}$ and Disorder Parameter $k$ for Native and Treated Cotton Fibers

| Cotton | Native cotton | | Urea-treated cotton | | Mercerized cotton | | Urea-treated and Mercerized cotton | | $X_{cr}$ Mean |
|---|---|---|---|---|---|---|---|---|---|
| | $X_{cr}$ | $k$ | $X_{cr}$ | $k$ | $X_{cr}$ | $k$ | $X_{cr}$ | $k$ | |
| Menoufi | 0.59 | 3.5 | 0.62 | 3.5 | 0.58 | 3.9 | 0.56 | 3.2 | 0.59 |
| Giza 69 | 0.56 | 2.4 | 0.56 | 2.5 | 0.59 | 3.4 | 0.60 | 3.5 | 0.58 |
| Ashmouni | 0.59 | 2.6 | 0.59 | 2.5 | 0.63 | 3.9 | 0.61 | 4.0 | 0.61 |
| Danderah | 0.59 | 2.6 | 0.55 | 3.0 | 0.57 | 3.5 | 0.55 | 3.3 | 0.57 |
| Giza 66 | 0.62 | 3.2 | 0.50 | 2.8 | 0.60 | 4.2 | 0.56 | 3.4 | 0.57 |
| Sea Island | 0.65 | 3.4 | 0.63 | 2.8 | 0.60 | 3.8 | 0.60 | 3.9 | 0.62 |
| K 6 | 0.61 | 3.9 | 0.60 | 3.3 | 0.58 | 3.4 | 0.62 | 3.9 | 0.60 |
| Mean | 0.60 | | 0.58 | | 0.59 | | 0.59 | | 0.59 |

fibers,[17] and such a hypothesis could only be confirmed through inter-disciplinary investigations.

A statistical analysis of variances between cottons and between treatments has been carried out, and the results are presented in Table II. It is seen that the variance due to interaction is considerably larger than the variance due to error in measurement of the degree of crystallinity from two observations on any given cotton for a specific treatment. Since it is neither possible nor feasible to investigate critically the causes for the "interaction," the variances between treatments and between cottons have been assessed only against interaction variance rather than error variance. Thus, it is concluded from Table II that the changes in the degree of crystallinity are significant at 10% between cottons and not significant between different treatments. However, this does not mean that the crystallinity of individual cottons remains unaffected by any treatment; on the contrary, from the same analysis it could be inferred that any difference between the mean values of two cottons, based on two measurements for each, exceeding 0.03 is quite significant.

TABLE II
Analysis of Variance of Crystallinity for Different Cottons and Treatments

|  | Sum of squares | Degree of freedom | Variance | $F$-ratio |
|---|---|---|---|---|
| Between cottons | 0.0212 | 6 | 0.003533 | 2.16 |
| Between treatments | 0.0034 | 3 | 0.001133 | 0.69 |
| Interaction | 0.0295 | 18 | 0.001639 | |
| Total between replicate | 0.0541 | 27 | | |
| Within replicate | 0.0112 | 28 | 0.000400 | |
| Total | 0.0653 | 55 | | |

Incidentally, it is worth mentioning here that owing to the better resolution of overlapping reflections through the use of a pulse-height discriminator and proportional counter in this study, the line separating the crystalline peaks form the continuous scatter is probably closer to the "valleys" in the $s^2I(s)$ versus $s$ curve. This could, therefore, as pointed out earlier,[11] account for the higher crystallinities than was the case when only a nickel filter and Geiger-Müller counter were employed.

## Crystallite Orientation

### Hermans' X-Ray Orientation Factor

The values obtained for the x-ray orientation factor $f_x$ according to Hermans' procedure and the corresponding values for the inclination $\beta$ of the crystallite axis to the fiber axis are indicated in Table III. A statistical analysis summarized in Table IV reveals that the difference in orientation

TABLE III
X-Ray Orientation Factor $f_x$ and Inclination $\beta$ of Crystallite Axis to Fiber Axis

| Cotton | Native cotton | | Urea-treated cotton | | Mercerized cotton | | Urea-treated and mercerized cotton | | Mean |
|---|---|---|---|---|---|---|---|---|---|
| | $f_x$ | $\beta°$ | $f_x$ | $\beta°$ | $f_x$ | $\beta°$ | $f_x$ | $\beta°$ | $f_x$ |
| Menoufi | 0.701 | 26.52 | 0.694 | 26.85 | 0.702 | 26.47 | 0.718 | 25.70 | 0.704 |
| Giza 69 | 0.687 | 27.18 | 0.689 | 27.10 | 0.680 | 27.37 | 0.663 | 28.30 | 0.680 |
| Ashmouni | 0.647 | 29.02 | 0.643 | 29.20 | 0.667 | 28.12 | 0.669 | 28.02 | 0.657 |
| Danderah | 0.623 | 30.08 | 0.645 | 29.12 | 0.644 | 29.15 | 0.649 | 28.93 | 0.640 |
| Giza 66 | 0.623 | 30.08 | 0.645 | 29.12 | 0.656 | 28.62 | 0.651 | 28.83 | 0.644 |
| Sea Island | 0.654 | 28.70 | 0.662 | 28.33 | 0.675 | 27.75 | 0.677 | 27.65 | 0.667 |
| K 6 | 0.699 | 26.62 | 0.721 | 25.55 | 0.722 | 25.50 | 0.700 | 26.57 | 0.711 |
| Mean | 0.661 | | 0.671 | | 0.678 | | 0.675 | | 0.672 |

between cottons is highly significant at the 1% level and that the differences between treatments are significant at the 10% level. This clearly emphasizes the greater importance of the orientation measurements than crystallinity measurements, for example, in the understanding of phenomena of tensile behavior of cotton fibers. From the error variance of Table IV, it is also seen that a difference of 0.005 in the x-ray orientation factor between the mean values for two cottons based on two observations on each is quite significant. Also, it is found that the orientation factor $f_x$ is considerably higher for the mercerized samples than for native cottons, the mean values being 0.678 and 0.661, respectively. Swelling in urea per se tends to improve the orientation, though not to the same extent as mercerization.

TABLE IV
Analysis of Variance of X-Ray Orientation Factor for Different Cottons and Treatments

| | Sum of squares | Degree of freedom | Variance | $F$-ratio |
|---|---|---|---|---|
| Between cottons | 0.036696 | 6 | 0.006116 | 25.48 |
| Between treatments | 0.002024 | 3 | 0.000675 | 2.81 |
| Interaction | 0.004328 | 18 | 0.000240 | |
| Total between replicate | 0.043048 | 27 | | |
| Within replicate | 0.000302 | 28 | 0.000011 | |
| Total | 0.043350 | 55 | | |

Giza 69 is a notable exception to this general trend: the orientation factor for Giza 69 remains unaltered on urea treatment, but is considerably lowered on mercerization (−0.007), especially so for the sample treated with urea prior to mercerization (−0.024). The extent to which each cotton is affected by the treatments seems to be a characteristic of the cotton. Therefore, as was pointed out by Rebenfeld,[7] different cottons may have to be considered as unique fiber types for the purpose of a physical, as opposed to a statistical, understanding of their properties such as breaking tenacity or extension at break. Such a physical understanding, in order to be complete, however, does not only require the basic data on crystallinity and orientation factor referred to in this study, but also a precise knowledge of the crystallite sizes, which will be reported in Part II of this work.

## DeLuca and Orr Method

The line profiles obtained in the orientation studies of the cotton K6 were somewhat abnormal, in the sense that the Gaussian distribution analysis was beset with certain practical difficulties, and therefore require to be

TABLE V

50% X-Ray Angle ψ, Spiral Angle φ, and Half-Intensity Angle α of Crystallite Orientation for Different Cottons and Treatments for Cellulose I

| Cotton | Native cotton (002) | | | Urea-treated cotton (002) | | |
|---|---|---|---|---|---|---|
| | ψ | φ | α | ψ | φ | α |
| Menoufi | 27.5 | 13.58 | 15.40 | 26.9 | 13.47 | 15.74 |
| Giza 69 | 28.5 | 14.25 | 16.57 | 27.8 | 13.94 | 15.67 |
| Ashmouni | 30.5 | 15.29 | 17.20 | 30.4 | 15.14 | 17.62 |
| Danderah | 32.4 | 16.20 | 17.00 | 31.1 | 15.56 | 16.94 |
| Giza 66 | 32.2 | 16.07 | 17.45 | 31.8 | 15.99 | 17.09 |
| Sea Island | 29.1 | 14.16 | 18.61 | 28.4 | 14.13 | 17.60 |

TABLE VI

50% X-Ray Angle ψ, Spiral Angle φ, and Half-Intensity Angle α of Crystallite Orientation for Different Cottons and Treatments for Cellulose II

| Cotton | Mercerization (002) | | | Urea + Mercerization (002) | | | Mercerization ($10\bar{1}$) | | | Urea + Mercerization ($10\bar{1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ψ | φ | α | ψ | φ | α | ψ | φ | α | ψ | φ | α |
| Menoufi | 23.5 | 10.61 | 18.35 | 22.6 | 9.09 | 19.31 | 21.6 | 10.13 | 15.45 | 20.8 | 8.98 | 16.56 |
| Giza 69 | 25.3 | 11.29 | 19.88 | 25.4 | 11.45 | 20.07 | 22.3 | 10.37 | 15.88 | 22.7 | 10.74 | 16.53 |
| Ashmouni | 27.0 | 12.62 | 21.16 | 23.9 | 11.03 | 22.31 | 25.2 | 12.10 | 17.47 | 22.0 | 9.83 | 17.54 |
| Danderah | 28.1 | 13.71 | 19.41 | 27.2 | 11.22 | 22.26 | 26.5 | 12.98 | 18.25 | 24.4 | 11.03 | 18.84 |
| Giza 66 | 27.8 | 13.26 | 18.31 | 27.7 | 12.94 | 20.32 | 25.7 | 12.43 | 14.77 | 24.8 | 12.02 | 17.40 |
| Sea Island | 23.8 | 9.73 | 18.77 | 24.4 | 11.44 | 19.44 | 22.3 | 9.31 | 18.12 | 21.8 | 10.31 | 18.19 |

studied separately in greater detail. Tables V and VI give a summary of
the results obtained for the remaining six cottons, through an application
of the DeLuca and Orr method to the azimuthal scan of the (002) diffrac-
tion arc of cellulose I and to the (10$\bar{1}$) as well as (002) diffraction arcs of
cellulose II. Besides the two angles $\phi$ and $\alpha$ defined by DeLuca and Orr,
the values obtained for the 50% x-ray angle $\psi$ from the experimental
azimuthal profiles are also included in Tables V and VI for comparison.
Both $\psi$ and $\phi$ are invariably larger for cellulose I than for cellulose II of the
same cotton, while the crystallite orientation angle is smaller for cellulose I
than for cellulose II, except for the notably opposite trend observed for
Giza 66 (native to mercerized).

Between $\psi$ and $\phi$, pooling together all the values for both celluloses I and
II, a correlation coefficient of 0.981 is found to exist if (10$\bar{1}$) reflections for
cellulose II are taken into account, whereas a slightly lower correlation
coefficient, of 0.966, is observed if (002) reflections for cellulose II are con-
sidered. Duckett and Tripp,[18] investigating single fibers of six native
cottons, have shown almost a similar relation between the 50% x-ray angle
and spiral angle. Thus, it seems reasonable to assume that the 50% x-ray
angle of the observed azimuthal intensity distribution gives a simple and
practical estimate of the spiral angle for both celluloses I and II by the use
of the regression equation $\phi = 0.597\psi - 2.981$ obtained from the data
presented in this work.

It is also seen from Tables V and VI that all the three angles derived
from (10$\bar{1}$) reflections are without exception smaller than those derived
from (002) reflections for mercerized cottons. This indicates that, al-
though both regenerated celluloses and mercerized cottons have the same
crystal structure of cellulose II, in regenerated cellulosic fibers the orienta-
tion of (002) planes is usually more pronounced than that of (10$\bar{1}$) planes,
as stated by Hermans and co-workers[4]; the opposite is true for the mer-
cerized cotton fibers. Similar inference could be drawn from the data
published by Venkatakrishnan.[15]

## Orientation Factor—Spiral Angle Relationship

A comparison of the results obtained by the two methods of determining
x-ray orientation brings out some striking features. First of all, it is clear
that the increase in orientation factor observed on mercerization is achieved
mostly at the expense of the spiral angle: the mean angle of inclination of
the cellulose crystallites to the fiber axis decreases on mercerization, despite
the fact that the dispersion of the crystallites about the spiral angle is
higher in many cases. On mercerization, Giza 66 shows the highest in-
crease in the orientation factor, 0.033, as against an average increase of
0.016. This is reflected in the exceptionally large reductions both in the

crystallite orientation angle from 17.45° to 14.77° and in the spiral angle from 16.07° to 12.43°. Secondly, a very significant correlation coefficient of 0.91 is found to exist between Hermans' orientation angle $\beta$ and DeLuca's spiral angle $\phi$ for cellulose I. The correlation is somewhat poorer (0.76) for cellulose II, whether based on (10$\bar{1}$) or (002) reflections. There is no significant correlation between $\beta$ and $\alpha$. This is only to be expected, since the crystallite orientation angle is only a measure of the dispersion of the crystallites about the spiral angle for which $\beta$ is another estimate just like $\phi$.

From the regression equation of $\phi$ upon $\beta$, viz., $\phi = 0.74\beta - 6.26$ for cellulose I, the spiral angle $\phi$ for the best oriented naturally occurring cellulosic fibers, ramie ($\beta = 8.35°$), works out to be very nearly zero. Thus, although both the methods purport to estimate the same parameter, viz., the inclination of the crystallite axis to the fiber axis, even for the best oriented ramie entirely different values are obtained. This inconsistency may perhaps be explained only on the basis that in Hermans' method the angle $\beta$ refers to the inclination of the cellulose *molecular chain* to the fiber axis, i.e., the chain direction and the crystallite axis are assumed to be parallel. However, recently it has been shown by the present authors[19] that a cellulose molecule is probably helical, with the molecular chain spiralling around the helical axis at an angle of 7.85°. That the DeLuca and Orr spiral angle for ramie could indeed be nearly zero is seen from the observation of steep S-spirals,[20] which apparently do not vary from the peripheral layers to the core of the fiber, and also from the total absence of azimuthal splitting even for the (040) reflection for ramie.[21]

## CONCLUSION

The mean value for the degree of crystallinity for seven cottons, in the native and chemically treated forms, is found to be 0.59, and Hermans' orientation factor is 0.672. For both the parameters, the differences between cottons are much more pronounced than between treatments.

From a scrutiny of the values obtained for $\beta$ and $\phi$, the view is put forward that $\beta$ is a resultant of both the inclination of the cellulose chain to the crystallite axis and the inclination of the crystallite to the fiber axis, whereas $\phi$ is the mean inclination of the crystallite to the fiber axis. In either case, structural reversals and convolutions in fibers are not taken into account. Ramie is a special instance where $\phi$ is nearly zero and $\beta$ is the inclination of the cellulose chain to the crystallite axis, which is almost parallel to the fiber axis.

It may also be noted that the easily evaluated 50% x-ray angle $\psi$, though devoid of any physical significance, could be used to estimate the spiral angle through an appropriate regression equation between $\psi$ and $\phi$.

## Data Required for Programs in Appendices

### Appendix I

| | |
|---|---|
| S(I) | $s$ values at equal intervals |
| DS | interval of $s$ |
| P(I), D(I) & R(I) | lists of polarization factor, incoherent scatter, and observed intensity as functions of $s$ |
| J, K, L, N | limits for the four ranges of $s_0\text{-}s_p$ |
| TH, WT | thickness (cm) and weight (g) of the pressed polymer specimen |
| X | square of the sum of atomic numbers for a monomer unit |
| Y | number of monomer units per gram divided by the cross-sectional area of the pressed specimen |
| Z | absolute intensity of incoherent scatter from a monomer unit |

### Appendix II

| | |
|---|---|
| M | number of values of the disorder parameter |
| XI(I, J) | readings of the disorder function for the four ranges of $s_0\text{-}s_p$ |
| FK(I) | values of disorder parameter |
| A, B, C, D | areas $A_t$ of the intensity curve for the four ranges (output data of Appendix I) |
| E, F, G, H | measured areas $A_c$ of the crystalline peaks for the four ranges |

### Appendix III

| | |
|---|---|
| N | number of azimuthal intensity readings |
| EPS | angular interval between successive intensity readings |
| F(I, J) | azimuthal intensity readings |

### Appendix IV

| | |
|---|---|
| H | initial value of $H^2$ to solve the two equations |
| DELH | increment of $H^2$ |
| X, Y | intensities $I_1$ and $I_2$ at azimuths $\epsilon_1$ and $\epsilon_2$ |
| EPS, GAM | azimuthal angles $\epsilon_1$ and $\epsilon_2$ |

# Appendix I

```
C     X RAY CRYSTALLINITY & DISORDER PARAMETER FOR POLYMERS   PART 1
      DIMENSIONS%200□,R%200□,P%200□,D%200□,RP%200□
      DIMENSIONS2%200□,RU%200□,RUS%200□,RD%200□
      READ1,J,K,L,N
      READ2,DS,X,Y,Z
      READ3,%S%I□,I#1,N□
      READ3,%P%I□,I#1,N□
      READ3,%D%I□,I#1,N□
      DO10I#1,N
 10   S2%I□#S%I□**2
100   READ4,TH,WT
      READ5,%R%I□,I#1,N□
      RA#0.
      DO20I#1,N
      RD%I□#R%I□*P%I□
      RP%I□#RD%I□*S2%I□
 20   RA#RA&RP%I□
      T#%RA-%RP%I□&RP%N□□/2.□*DS
      CC#%X*WT□/%Y*TH□
      ALPHA#%Z-CC□/T
      DO30I#1,N
      RU%I□#%ALPHA*RD%I□□-D%I□
 30   RUS%I□#%S2%I□*RU%I□
      RSA#0.
      RSB#0.
      RSC#0.
      RSD#0.
      DO40I#1,J
 40   RSA#RSA&RUS%I□
      DO50I#J,K
 50   RSB#RSB&RUS%I□
      DO60I#K,L
 60   RSC#RSC&RUS%I□
      DO70I#L,N
 70   RSD#RSD&RUS%I□
      AT1#%RSA-%RUS%1□&RUS%J□□/2.□*DS
      AT2#%RSB-%RUS%J□&RUS%K□□/2.□*DS
      AT3#%RSC-%RUS%K□&RUS%L□□/2.□*DS
      AT4#%RSD-%RUS%L□&RUS%N□□/2.□*DS
      A#AT1
      B#A&AT2
      C#B&AT3
      D#C&AT4
      PUNCH6,%RUS%I□,I#1,N□
      PUNCH7,A,B,C,D
      GO TO 100
 1    FORMAT%4I4□
 2    FORMAT%4F12.6□
 3    FORMAT%10F8.4□
 4    FORMAT%2F6.4□
 5    FORMAT%16F5.0□
 6    FORMAT%10F8.4□
 7    FORMAT%4F10.5□
      END
```

# Appendix II

```
C       X RAY CRYSTALLINITY & DISORDER PARAMETER FOR POLYMERS   PART II
        DIMENSIONX%60,4□,AC%4□,XI%60,4□,Y%60□,FK%60□
        READ2,M
        DO5I#1,M
    5   READ11,%XI%I,J□,J#1,4□
        READ12,%FK%I□,I#1,M□
    1   READ11,A,B,C,D
        READ11,E,F,G,H
        AC%1□#E/A
        AC%2□#F/B
        AC%3□#G/C
        AC%4□#H/D
        DO3CI#1,M
        DO15J#1,4
   15   X%I,J□#XI%I,J□*AC%J□
        SUM#0.
        DO20J#1,4
   20   SUM#SUM&X%I,J□/4.
        VAR#C.
        DO25J#1,4
   25   VAR#VAR&%SUM-X%I,J□□**2
   30   Y%I□#SQRTF%VAR/4.□
        SMALL#Y%1□
        IND#1
        DO40I#2,M
        IF%SMALL-Y%I□□40,40,45
   45   SMALL#Y%I□
        IND#I
   40   CONTINUE
        AM#%X%IND,1□&X%IND,2□&X%IND,3□&X%IND,4□□/4.
        PUNCH14,AM,FK%IND□,SMALL
        GOTC1
    2   FORMAT%I3□
   11   FORMAT%4F10.4□
   12   FORMAT%16F5.2□
   13   FORMAT%4F10.5,2X,3F10.5□
   14   FORMAT%3F10.5□
        END
```

## Appendix III

```
     X RAY ORIENTATION FACTOR FOR CELLULOSE I & II
     DIMENSIONC%90□,SC%90□,F%90,2□
     DIMENSIONF1%90,2□,F2%90,2□,F3%90,2□,F4%90,2□
     DIMENSIONB1%2□,D1%2□,AO%2□
     READ3,N,EPS
     A#0.
     T#3.14159/180.
     DO101I#1,N
     TA#T*A
     S#%SINF%TA□□**2
     C%I□#COSF%TA□
     SC%I□#S*C%I□
  10 A#A&EPS
 200 CONTINUE
     IF%SENSE SWITCH1□30,100
  30 AO%2□#AO%1□
     J#1
     GO TO 40
 100 DO50J#1,2
  40 READ1,%F%I,J□,I#1,N□
     B#0.
     D#0.
     DO20I#1,N
     F1%I,J□#F%I,J□-F%N,J□
     F2%I,J□#F1%I,J□*100./F1%1,J□
     F3%I,J□#F2%I,J□*SC%I□
     F4%I,J□#F2%I,J□*C%I□
     B#B&F3%I,J□
  20 D#D&F4%I,J□
     B1%J□#B
     D1%J□#D-50.
  50 AO%J□#B1%J□/D1%J□
     SINB#AO%1□&AO%2□
     FX#1.-1.5*SINB
     SINB1#SQRTF%SINB□
     BETA#ATANF%SINB1/SQRTF%1-SINB□□
     BETA#BETA/T
     PUNCH2,FX,BETA
     GO TO 200
   1 FORMAT%10F8.3□
   2 FORMAT%2F10.6□
   3 FORMAT%I3,F3.0□
     END
```

## Appendix IV

```
C       ORIENTATION & SPIRAL ANGLES ASSUMING GAUSSIAN DISTRIBUTIONS
      1 READ5,H,DELH
        READ5,EPS,GAM
        READ5,X,Y
        PI#3.14159
        T#PI/180.
        EPS1#EPS*T
        GAM1#GAM*T
        EPS2#EPS1*EPS1
        GAM2#GAM1*GAM1
     10 D1#2.*H*EPS1
        D2#2.*H*GAM1
        C1#X*EXPF%H*EPS2□
        C2#Y*EXPF%H*GAM2□
        C12#C1*C1
        C22#C2*C2
        IF%C12□22,20,20
     20 IF%C22□22,23,23
     23 X1#C1&SQRTF%C12-1.□
        X2#C2&SQRTF%C22-1.□
        FI1#LOGF%X1□/D1
        FI2#LOGF%X2□/D2
        AF#ABSF%FI1-FI2□
        IF%SENSE SWITCH1□11,12
     11 PRINT15,H,FI1,FI2,AF
        PAUSE
        IF%SENSE SWITCH2□1,12
     12 CONTINUE
        IF%AF-1.E-04□14,14,22
     14 ALPH2#LOGF%2.□/H
        ALPHA#SQRTF%ALPH2□/T
        FG1#FI1/T
        FG2#FI2/T
        PRINT25,EPS,GAM,X,Y,H,FG1,FG2,ALPHA
        PUNCH25,EPS,GAM,X,Y,H,FG1,FG2,ALPHA
        GO TO1
     22 H#H&DELH
        GOTO10
      5 FORMAT%2F8.4□
     15 FORMAT%4F10.5□
     25 FORMAT%8F9.5□
        END
```

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