

# X-Ray Study of Crystallinity and Disorder in Ramie Fiber

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## SYNOPSIS

The degree of crystallinity and the disorder parameter in ramie fibers treated with various concentrations of aqueous NaOH solutions at room temperature ( $\sim 30^\circ\text{C}$ ) and at  $0^\circ\text{C}$ , respectively, have been analyzed by the wide-angle x-ray diffraction method of Ruland and Vonk.<sup>9-11</sup> The results appear to suggest the presence of highly distorted crystalline regions that are first affected by lower concentrations of alkali. At higher concentrations of mercerizing strength it is observed that the lattice conversion to cellulose II is accompanied by a decrease in the degree of crystallinity and an increase in the disorder parameter values. The tensile properties of the fibers corroborate the results. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

It is generally argued that cellulose fibers display three-dimensional order of varying degrees of perfection.<sup>1,2</sup> In a simplified two-phase model, the supramolecular structure of a polymer is considered as a system of crystalline (ordered) and amorphous (disordered) phases. The term "degree of crystallinity" refers to a numerical measure of the order existing in the sample. The concept of crystallinity as a gross physical property is valuable, as the physical and mechanical properties of polymers are profoundly dependent on it. However, the partially crystalline polymers may contain various types of lattice defect that are classified in general as disorders of the first and second kinds.<sup>3</sup> Both types of disorder cause local displacements of atoms, group of atoms, or molecules from their positions in an ideal lattice. However, in disorders of the first kind, the magnitude of the displacement is independent of the location in the crystal and long-range order is preserved, while in disorders of the second kind, the displacements appear to increase with the distance from any chosen origin, and the long-range order is destroyed. Thermal motions, localized point defects such as vacancies, interstitials, or solute atoms or molecules, chain ends, etc., produce disorders

of the first kind, while packing disorder of chain molecules and paracrystallinity generate disorders of the second kind.

The assessment of order in cellulose by x-ray diffraction method is usually a complex procedure because it involves a separation of the observed intensity distribution into two parts, namely, the contributions due to crystalline and the amorphous components. The diffuse scattering by various lattice defects referred to above and the broadening of reflections by small crystallite size render the solution of the problem still more difficult. Hermans and Weidinger<sup>4,5</sup> were the first to use x-ray method in cellulose, and estimated the crystallinity in native and mercerized ramie to be 70% and 50%, respectively. They assumed a two-phase system and defined an arbitrary but precise method to resolve the crystalline, the amorphous, and the background contributions in the observed pattern. Based on the work by Hermans and Weidinger, various integration methods have been proposed and used successfully by a number of workers for different cellulose samples.<sup>3,6</sup> Simpler methods based on a crystallinity index function relating the intensity of the principal interferences and that at a simultaneously varying minimum in the diffractogram have also been suggested.<sup>3,6</sup> A method based on profile fitting to account for peak overlap and distortion has also been used to estimate crystallinity in cellulose.<sup>7,8</sup> By fitting Cauchy and Gaussian function to the diffraction profiles, Hindeleh et al.<sup>8</sup> estimated the crystallinity in ramie to be 72%. The best approach to date for

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the evaluation of both crystallinity and disorder in polymers has been described by Ruland.<sup>9-11</sup> The applications of Ruland's method in cellulose have been reported by several workers.<sup>12-15</sup> Viswanathan and co-workers<sup>12,13</sup> observed that mercerization increases the disorder of the original cellulose. Sotton<sup>14</sup> and Fink et al.<sup>15</sup> observed that mercerization in cotton cellulose decreases both degree of crystallinity and disorder parameter. It is, thus, seen that in the x-ray methods of measurement the inherent difficulties as referred to above led to several approximations. Consequently, the contradictory nature of the results, their interpretation, and evaluation are still today a matter of discussion and subject of continuing study. In the present work we report the results of the systematic studies of crystallinity and disorder in ramie fibers treated with alkali of various concentrations at room temperature ( $\sim 30^\circ\text{C}$ ) and at  $0^\circ\text{C}$ , respectively, by using the improved method due to Ruland and Vonk.<sup>9-11</sup>

## THEORETICAL BASIS OF X-RAY METHOD

Ruland<sup>9,10</sup> assumed that the fraction of crystalline material in the specimen can be given by

$$x_c = \frac{\int_{s_0}^{s_p} s^2 I_c(s) ds}{\int_{s_0}^{s_p} s^2 I(s) ds} \cdot K(s_0, s_p, D, \overline{f^2}) \quad (1)$$

where  $s = 2 \sin \theta / \lambda$  is the magnitude of reciprocal lattice vector,  $2\theta$  being the scattering angle and  $\lambda$  the wavelength of x-ray radiation.  $I$  and  $I_c$  represent, respectively, the intensity of total coherent scattering and the coherent intensity scattered from the crystalline phase.  $\overline{f^2}$  is a mean square atomic scattering factor for the polymer.  $D$  is the lattice imperfection factor.  $s_0$  and  $s_p$  represent the lower and upper limit of integration for the finite and relatively large angular range. The coefficient  $K$  allows for the loss in intensity due to lattice imperfection and is given by

$$K = \frac{\int_{s_0}^{s_p} s^2 \overline{f^2} ds}{\int_{s_0}^{s_p} s^2 \overline{f^2} D ds} \quad (2)$$

Ruland<sup>9,10</sup> argues that all kinds of disorders can be lumped together in one Gaussian lattice-imperfection factor given by

$$D = \exp(-ks^2) \quad (3)$$

where

$$k = k_T + k_1 + k_2 \quad (4)$$

$k_T$  accounts for thermal motion,  $k_1$  for other disorders of the first kind, and  $k_2$  for disorders of the second kind.

Following Vonk,<sup>11</sup> Eq. (1) can be written as

$$R(s_p) = \frac{1}{x_c} + \frac{k}{2x_c} s_p^2 \quad (5)$$

where  $K$  has been approximated as

$$K = 1 + \frac{k}{2} s_p^2 \quad (6)$$

and

$$R(s_p) = \frac{\int_{s_0}^{s_p} I s^2 ds}{\int_{s_0}^{s_p} I_c s^2 ds} \quad (7)$$

Thus, assuming a linear plot of  $R$  versus  $s_p^2$ , both  $x_c$  and  $k$  can be obtained from Eq. (5).

## EXPERIMENTAL

### Sample Preparation

Degummed (2-3% gum content) and bleached ramie fibers were used for the present study. The fibers were suitably combed and cut to 10 cm length. These were then treated with aqueous sodium hydroxide solutions of various concentrations (w/w) at room temperature ( $\sim 30^\circ\text{C}$ ) and at  $0^\circ\text{C}$ , respectively, for 1 h. After treatment, the fibers were washed and air dried. The details of the procedure were as described elsewhere.<sup>16</sup> To get alkali cellulose, after NaOH treatment the samples were carefully pressed to remove the excess of alkali and then air dried. The above fiber samples were then cut into small pieces and finely powdered.

### Experimental Data and Calculation

The intensity data for the finely powdered and randomized fiber samples were obtained over a wide range of scattering angle ( $s \sim 0.06 \text{ \AA}^{-1}$ – $1.1 \text{ \AA}^{-1}$ ) in a Phillips x-ray diffractometer (PW 1710) using Ni-

filtered  $\text{CuK}\alpha$  radiation at 40 KV and 20 mA. The calculations were made according to the procedure described by Vonk<sup>11</sup> using a Cyber 180 computer. The x-ray scattering curve of ramie fiber heated to 300°C for 1 h was taken as amorphous standard for all samples. The incoherent scattering was calculated on the basis of chemical composition of cellulose as  $\text{C}_6\text{H}_{10}\text{O}_5$ . For 18% alkali-treated and air-dried soda cellulose complex the composition taken was that of soda cellulose III,<sup>17</sup>  $\text{C}_6\text{H}_{10}\text{O}_5$ , NaOH,  $2\text{H}_2\text{O}$ .

### Determination of Cellulose I and Cellulose II Fractions

The extent of conversion to cellulose II in the mercerized sample was determined using the equation<sup>18</sup>

$$I_p = \alpha I_1 + (1 - \alpha) I_2 \quad (8)$$

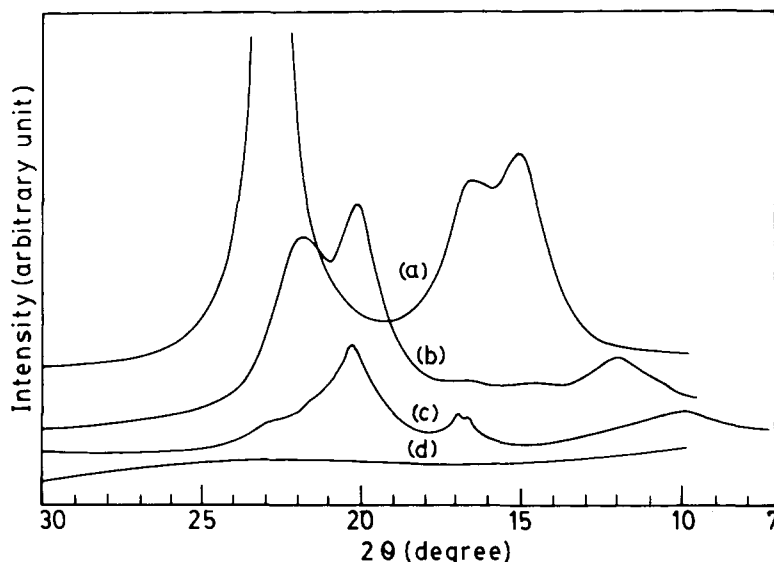
where  $I_1$  and  $I_2$  are the measured intensities at  $2\theta = 15^\circ$  of cellulose I and cellulose II samples, respectively.  $I_p$  represents the corresponding intensity for the composite sample and  $\alpha$  denotes the fraction of cellulose I in the sample. The conversion to cellulose II was assumed to be approximately complete for 30% NaOH sample at room temperature (R.T.) and 12% NaOH sample at 0°C.

### Measurement of Tensile Properties

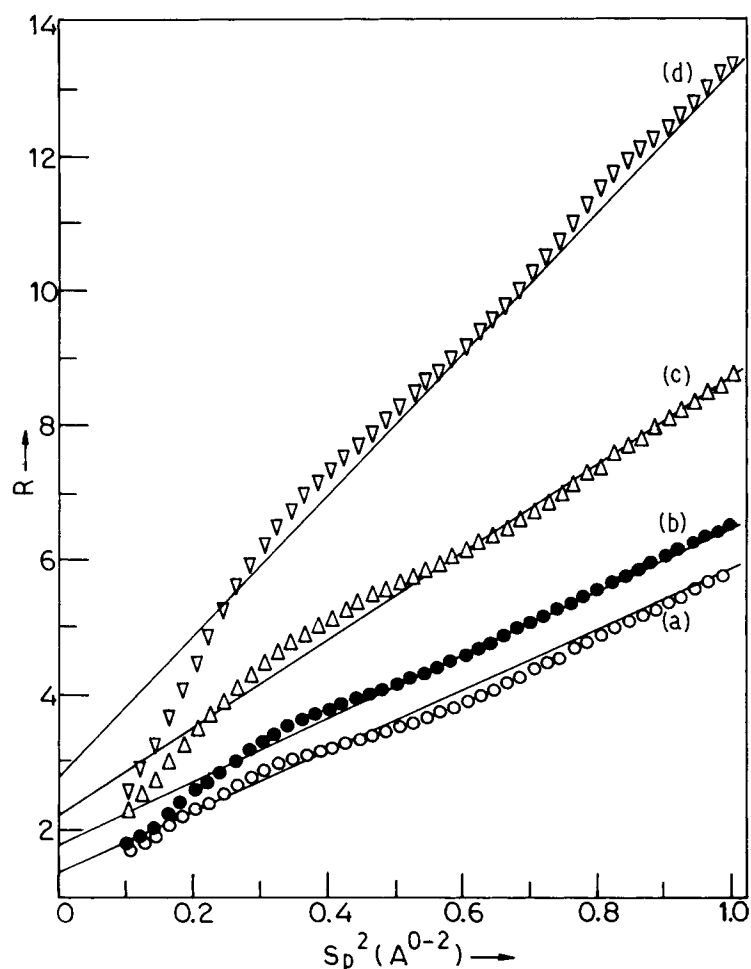
The tensile properties of the fibers were measured by an Instron Tensile Tester (model 1185) at a gauge length of 1 cm and crosshead speed of 1 mm/min.

## RESULTS AND DISCUSSION

Figure 1 shows the typical x-ray diffractograms of a few samples. Native and mercerized ramie fibers exhibit the well-known cellulose I and cellulose II patterns, respectively, while the air-dried alkali cellulose (18% NaOH at R.T.) shows broad peaks near  $10^\circ$  and  $20.3^\circ$  ( $2\theta$ ) similar to those reported for soda cellulose I.<sup>19</sup> It is known<sup>17</sup> that soda cellulose I formed from ramie in 12.5–19% NaOH gives, on drying, soda cellulose III. On drying soda cellulose I, the equatorial spacing, especially of the  $(1\bar{1}0)$  plane, decreases with loss of water. The similarity of unit cell parameters in Na-cellulose I and III suggests<sup>20</sup> that only marginal changes in crystalline packing and other structural features occur during such transformation. The fiber heated at 300°C produces a pattern similar to that of an amorphous scattering curve.<sup>18</sup> Figures 2 to 4 show plot of  $R$  versus  $s_p^2$  for different samples. Figure 5 shows the stress-strain curves of raw ramie, air-dried soda cellulose, and mercerized ramie (18% NaOH at R.T.). The results of the measurements are given in Tables I and II. It is observed from Table I that the degree of crystallinity ( $x_c$ ) decreases with increase in concentration of alkali both at R.T. and at 0°C. The disorder parameter ( $k$ ) initially decreases significantly (viz. 8% NaOH-treated fibers at R.T.), then increases steadily with the increase in conversion to cellulose II. The effect is similar for samples treated at 0°C, except that the conversion to cellulose II starts at a much lower concentration of NaOH. The disorder parameter is seen to be considerably higher



**Figure 1** Some typical x-ray diffractograms of ramie: (a) untreated; (b) mercerized; (c) air-dried soda cellulose complex (18% NaOH at R.T.); (d) heat treated at 300°C for 1 h.

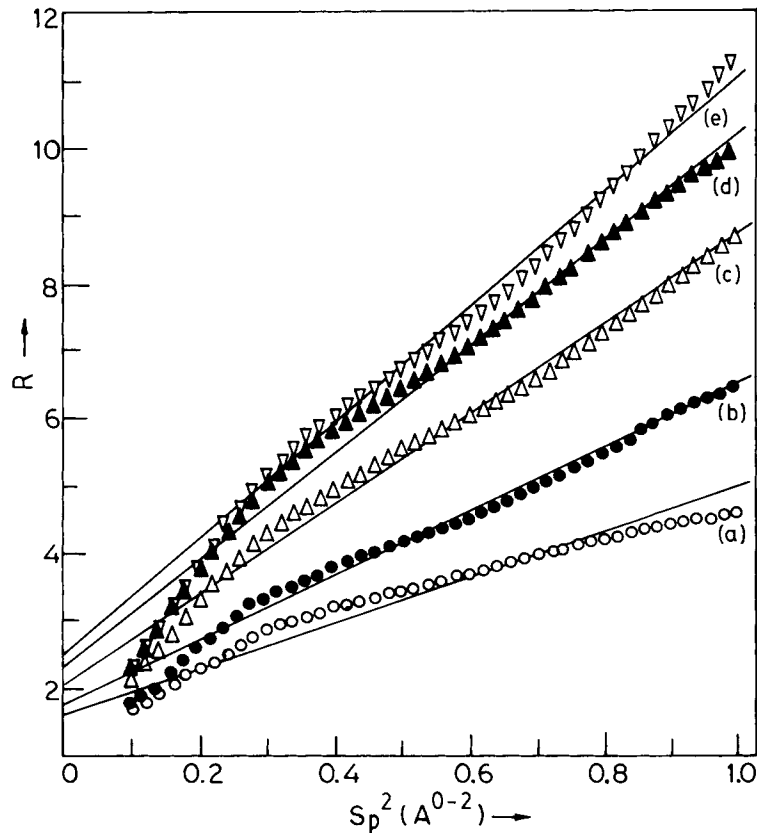


**Figure 2**  $R(s_p)$  vs.  $s_p^2$  plots of alkali-treated ramie at 0°C: (a) untreated; (b) 6% NaOH; (c) 9% NaOH; (d) 12% NaOH.

in the case of air-dried alkali cellulose than the corresponding washed sample. It is seen from Table II that the tenacity of the fibers decreases while percent of extension at break increases appreciably in mercerized and air-dried alkali cellulose samples. The tenacity value is lower in the case of soda cellulose, which shows the lower value of degree of crystallinity and higher value of disorder parameter, as expected.

For a better understanding and meaningful discussion of the above results it is necessary at this stage to consider briefly the various views regarding the fine structure of cellulose such as the fringed-fibrillar model,<sup>21</sup> crystal-defect model,<sup>22,23</sup> paracrystalline model,<sup>24,25</sup> and folded chain model.<sup>26,27</sup> The fringed-fibrillar model is a typical two-phase system in which perfect crystalline domains are interspersed with amorphous regions. This simple model is very useful in explaining the various properties of cellulose. The crystal-defect concept, on the other hand,

is essentially a one-phase crystalline structure where the lattice imperfections can account for those properties normally attributed to amorphous regions. However, for crystalline fractions smaller than 0.8, Ruland<sup>10</sup> concluded that there exists a segregation into ordered and disordered domains (a two-phase concept). The paracrystalline nature of cellulose has been shown by x-ray studies.<sup>24</sup> However, the chain folding in cellulose still remains disputed. Recently, Nishimura and Sarko,<sup>19</sup> while studying the mechanism of mercerization in ramie, suggested that the overall morphology of ramie fiber could be subdivided into three regions: the highly oriented amorphous one, another consisting of small and distorted crystalline region, and a third consisting of a well-ordered crystalline region. They considered the interface between crystallites as amorphous regions, where the degree of chain orientation was similar to that in crystalline phase but



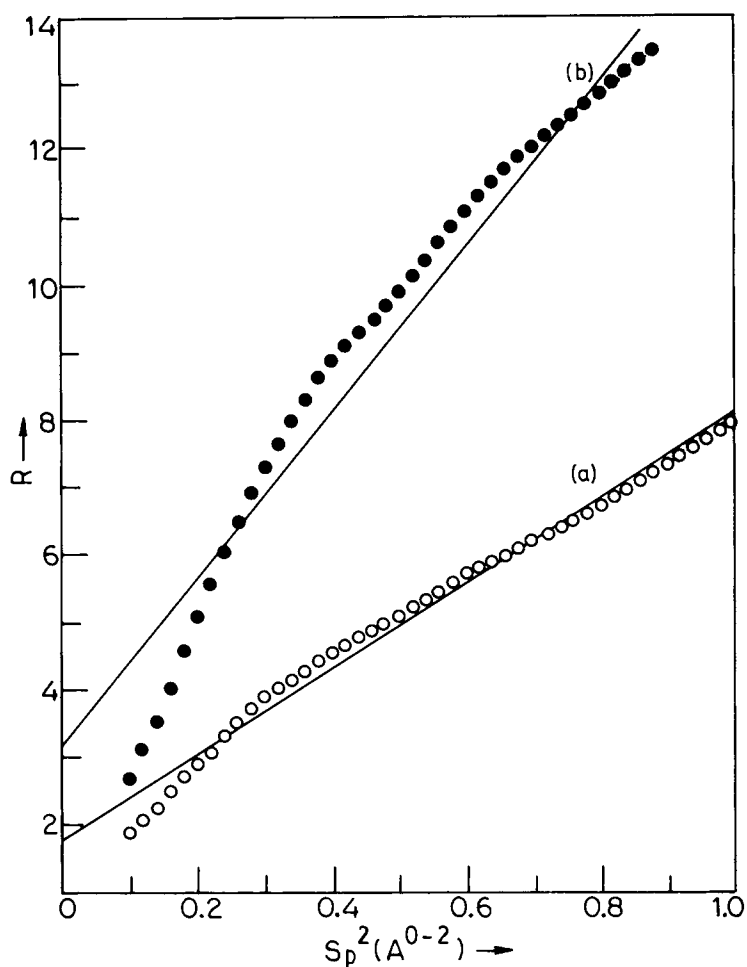
**Figure 3**  $R(s_p)$  vs.  $s_p^2$  plots of alkali-treated ramie at room temperature: (a) 8% NaOH; (b) 12% NaOH; (c) 15% NaOH; (d) 18% NaOH; (e) 25% NaOH.

they run in both directions. A study of mass-order distribution indicates that cellulose fibers can be characterized by a series of intermediate stages of ordered arrangement of chains that intervene between the perfectly crystalline and amorphous regions.<sup>28</sup>

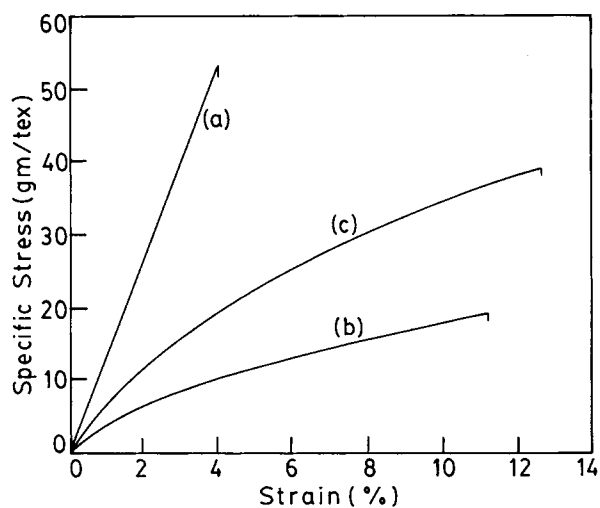
It is evident from Table I that in the room temperature treatment below 12% NaOH, the swelling is mainly intercrystalline, as there is no appreciable change in crystal lattice. The marked decrease in disordered parameter ( $k$ ) at 8% NaOH treatment can be explained by assuming the existence of the regions of intermediate order, which may be termed distorted crystalline regions.<sup>29</sup> The low concentration of alkali may cause further disorder in these regions, increasing the amorphous fraction. With the increase in concentration of alkali, the more orderly crystalline regions are affected, and conversion to cellulose II occurs. The decrystallization and increase in  $k$  values seem to be directly related to the amount of cellulose II conversion (Table I). It is well known that the intracrystalline swelling agent penetrates the cellulose I lattice and converts it into

soda cellulose which, on washing, yields cellulose II structure. The conversion to cellulose II involves rotation of D-glucose residues about the glycosidic link and a rearrangement of hydrogen bonding network.<sup>16</sup> The lattice energy of cellulose I must be overcome for this short-range adjustment. The swelling is likely to increase the interchain spacing accompanying increase in distortion and diminution of cohesion among them, thereby providing enough degree of freedom for mutual short-range adjustment. This suggests that decrystallization must precede the formation of cellulose II and should be directly related to the fraction of cellulose II present in the sample. Native cellulose I is known to be in a metastable state, while cellulose II is a more stable structure.<sup>30,31</sup> Moreover, when cohesion among the chains, during swelling, is diminished, they may behave in the normal way as isolated chains and tend to coil up under the influence of thermal motion, as expected. This chain folding is also likely to contribute to the increase in the degree of disorder.

In the air-dried alkali cellulose samples (Table I), the degree of crystallinity is seen to be lower and



**Figure 4**  $R(s_p)$  vs.  $s_p^2$  plots of air-dried soda cellulose complex at room temperature: (a) 8% NaOH; (b) 18% NaOH.



**Figure 5** Stress-strain curves of ramie fibers: (a) untreated; (b) air-dried soda cellulose complex; (c) mercerized (18% NaOH at R.T.).

the disorder parameter is higher than in the corresponding washed samples. With 8% NaOH at room temperature, the reaction takes place mainly in the intercrystalline regions, as discussed earlier. Assuming the existence of distorted crystalline regions, the presence of sodium ions in these regions is quite likely to disturb further the structural state and, consequently, increases  $k$  and lowers  $x_c$  values. At higher concentration of 18% NaOH, the  $\text{Na}^+$  ions penetrate the interchain spaces in the crystalline regions, resulting in the formation of soda cellulose, as indicated by the x-ray pattern. Swelling is induced by the water molecules surrounding the sodium ions. At any particular NaOH concentration, various hydrates of sodium hydroxide exist in equilibrium with free water. The varying degree of hydration of each individual alkali ion may lead to the formation of disordered soda cellulose, according to Warwicker's concept of 'sheet' of cellulose chains.<sup>32,33</sup> Yokota<sup>34</sup>

**Table I Degree of Crystallinity ( $x_c$ ) and Disorder Parameter ( $k$ ) in Alkali-Treated Ramie**

Treatment	$x_c$	$k$ ( $\text{\AA}^2$ )	Approx. Fraction of Cellulose	
			Cell. I	Cell. II
Untreated	0.71	6.3	1.00	—
8% NaOH (R.T.)	0.63	4.3	1.00	—
12% NaOH (R.T.)	0.57	5.3	0.90	0.10
15% NaOH (R.T.)	0.49	6.4	0.19	0.81
18% NaOH (R.T.)	0.43	6.7	0.08	0.92
30% NaOH (R.T.)	0.40	6.8	—	1.00
6% NaOH (0°C)	0.57	5.4	0.87	0.13
9% NaOH (0°C)	0.45	5.9	0.46	0.54
12% NaOH (0°C)	0.35	7.2	—	1.00
8% NaOH (R.T.) (unwashed and air dried)	0.56	7.0	—	—
18% NaOH (R.T.) (unwashed and air dried)	0.31	7.6	—	—

and Nishimura and Sarko<sup>19</sup> suggested that the transformation from cellulose I to Na-cellulose I might proceed without decrystallization, i.e., crystal-to-crystal phase transformation. From the above results it appears that swelling, before the formation of soda cellulose lattice, causes decrystallization of cellulose I lattice limited by the cohesive forces between the cellulose chains. The decrystallization perhaps provides the necessary degree of freedom to cellulose chains for short-range adjustment leading to conversion to soda cellulose. The observations<sup>19</sup> that the formation of Na-cellulose I is facilitated by lower crystallinity of the original cellulose and that both Na-cellulose I and cellulose II have an antiparallel chain arrangement support the above hypothesis. Once soda cellulose is formed, the transformation from soda cellulose to cellulose

II structure may proceed without further decrystallization. It was interesting to note during these studies that there was not much difference in the integrated crystalline scattering of air-dried soda cellulose and that of the corresponding washed samples. The lower value of  $x_c$  in the air-dried soda cellulose compared to that of the corresponding washed sample might probably be due to the highly disordered structure of soda cellulose.

## CONCLUSIONS

The results show that the simple two-phase model of completely ordered and disordered phases has little validity for ramie fiber. The existence of intermediate order regions, such as highly distorted crystalline regions, has to be considered for a satisfactory explanation of the phenomenon of swelling. The alkali, with concentrations less than the mercerizing strength, affects the highly distorted crystalline regions, thereby reducing the distortion significantly. At higher concentrations of mercerizing strength, the disorder parameter increases and the degree of crystallinity decreases along with the conversion of structure from cellulose I to cellulose II. From the above results, the cellulose II may be considered as a more disordered structure than cellulose I. Though the temperature has a pronounced effect on swelling, the effects of alkali treatments at room temperature and at 0°C, respectively, are similar as far as changes in crystallinity and disorder parameters are concerned. The air-dried soda cellulose complex appears to be a more disordered structure than the native and mercerized cellulose. The results also suggest that decrystallization prior to the formation of soda cellulose perhaps provides the necessary degree of freedom to cellulose chains for short-range adjustment. The results further indicate that the degree of crystallinity and the disorder parameter are closely related to the tensile properties of the fibers.

**Table II Tensile Properties of Ramie Fibers**

Sample	Tenacity (g/tex)	Percent Extension at Break
Raw ramie	51.6	3.9
Mercerized ramie (18% NaOH treated at R.T.)	38.4	12.6
Air-dried soda cellulose (18% NaOH treated at R.T.)	18.3	10.4

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