

# Change of Morphological Properties in Drawing Water-Swollen Cellulose Films Prepared from Organic Solutions. A View of Molecular Orientation in the Drawing Process

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**ABSTRACT:** Drawable water-swollen cellulose films were prepared by coagulating in water two different cellulose organic solution systems. The drawability of the water-swollen films was dependent on the rate of coagulation. Transparent films prepared by the slow coagulation showed good drawability and had a maximum draw ratio of 2.0. However, the drawn films maintained the highly noncrystalline state even after dried at 50°C under vacuum. X-ray analysis and polarized FT-IR measurements performed under a saturated deuterium oxide vapor of these dried drawn films, prepared by slow coagulation, showed that their noncrystalline regions (more than 80%) as well as crystalline regions (less than 20%) were highly oriented by the drawing process. Furthermore, meridional intensity curves in the X-ray diffraction exhibited interesting patterns even though the drawn sample was highly noncrystalline. In fact, they are quite different from those in regenerated cellulose II fibers. However, despite this increase in draw ratio and in the orientation of the chains, the number of crystalline domains in the films did not increase significantly. This may perhaps be attributed to the three-dimensional network structure resulting from the intermolecular hydrogen bonds between chains which are maintained through the drawing process and which can hinder the crystallization of cellulose. © 1999 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 37: 451–459, 1999

**Keywords:** cellulose; drawing; orientation; crystallization; intermolecular hydrogen bond

## INTRODUCTION

The preparation of fibers and films with high modulus and strength has been extensively investigated for various polymers. To obtain such polymeric materials, both a highly molecular orientation and a high degree of crystallinity are required. In many cases, the preparation of such high-performance materials requires that a drawing procedure be employed as the most common method to promote the orientation of polymer

chains. In addition, the drawing treatment enhances not only the orientation but also the crystallinity in the drawn polymers.<sup>1</sup>

Recently, new organic solvents, such as N-methylmorpholine N-oxide (MMNO)<sup>2–5</sup> and dimethylacetamide(DMAc)/lithium chloride(LiCl),<sup>6,7</sup> have been used to dissolve cellulose to prepare novel cellulosic products with improved mechanical properties when compared to materials prepared by the conventional viscose process. The fine structure and tensile properties of these new cellulosic fibers prepared from these cellulose solutions have been characterized.<sup>8,9</sup> However, such reports treat only fibrous products and do not provide any information about films.

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How to orient and crystallize chains simultaneously during the drawing process is the key factor in improving the mechanical properties of cellulose film as well as fibers. Thus far, the investigations into the drawing process for cellulose after fixation of the superstructure as films have been considered difficult, because of a lack in drawability that is hindered by intermolecular hydrogen bonds. There have been few reports about the drawability of intermolecular hydrogen bonded chains in cellulosic films obtained from the new organic solutions. For polyamides, the formation of the intermolecular hydrogen bonds was reported to lead to a maximum draw ratio that is far below that expected.<sup>10</sup> Since intermolecular hydrogen bonds largely restrict the mobility of polymer chains, celluloses having many intermolecular hydrogen bonds are expected to exhibit less drawability. In order to achieve a high draw ratio, these intermolecular hydrogen bonds need to be dissociated during the drawing process. The energy required to dissociate such a hydrogen bond is quite high. Indeed, the dissociate energy for approximately 20 hydrogen bonds is assumed to correspond to that of a covalent bond.<sup>10</sup> Thus, the hydrogen bond interaction in cellulose is too strong and it inhibits the conventional drawing of the cellulose films coagulated from the solutions. Only when the hydrogen bond interaction in a specimen of cellulose is suppressed prior to drawing, it should be possible to successfully draw the film. Thus, an investigation into the drawability of cellulose films should provide some interesting information on the changes in the crystalline and amorphous regions of cellulose associated with the drawing process. In addition, the preparation of drawable cellulose films should also provide some valuable insights into any cellulose-structural changes occurring during the drawing process.

In this study, we have firstly produced highly water-swollen and transparent cellulose films for drawing. These films were found to be predominantly amorphous as obtained by a particular precipitation method from the MMNO and DMAc/LiCl solutions. Secondly, the drawability of these films was investigated to establish any correlation between the orientation and crystallinity in the samples. Thirdly, the change in the supermolecular structure of the water-swollen cellulose produced by drawing was examined.

## EXPERIMENTAL

### Film Preparation

The cellulose sample used was bleached cotton linters with a degree of polymerization of 1300. The cellulose was dried before use under vacuum at 40°C. Cellulose films were prepared from two different solvent systems, N-methylmorpholine N-oxide (MMNO) provided by Nippon Nyukazai Co. and N,N-dimethylacetamide(DMAc)/LiCl, in the following manner:

#### *Films from the MMNO Solution*

The dried cellulose (0.15 g) was mixed with 8.0 g of MMNO and 60 mg of *n*-propyl gallate.<sup>3</sup> The mixture was heated to 120°C with constant stirring. Following complete dissolution of the cellulose, 12 ml of dimethyl sulfoxide was added to the solution while cooling to 80°C.<sup>11</sup> The resulting solution was filtered and poured onto a flat glass plate. The cellulose solution on the plate was then coagulated in water at 2°C for 12 h. The coagulated film was washed for several days with running water to remove all solvent. Thus, the highly water-swollen cellulose films precipitated from MMNO solution were obtained.

#### *Films from the DMAc/LiCl Solution*

First, LiCl dried at 105°C was dissolved in anhydrous DMAc to give a concentration of 5% (w/w) solution. Dissolution of cellulose was taken by a swelling procedure followed by solvent exchange technique.<sup>12</sup> Cellulose was treated in water overnight and filtered to remove the water. Then the cellulose was immersed in methanol and filtered to remove excess methanol. After four repetitions of the methanol treatments, more than five solvent-exchanges with DMAc were carried out. The cellulose swollen by DMAc was then dissolved in the DMAc/LiCl solution with stirring at room temperature for 3 weeks. The resulting solution was then centrifuged and filtered to remove any insoluble portion. The actual concentration (wt%) of cellulose in the solution was determined by weighing a small portion of the dried cellulose film obtained by regenerating a certain amount of the solution, typically, about 1.3 wt%. Films from the DMAc/LiCl solution were prepared by the following slow precipitation technique.<sup>13</sup> The solution was poured into a glass petri dish with a flat bottom and placed in a closed box containing water. In this manner, saturated water vapor slowly

diffusing into the solution was used to precipitate the cellulose. It was allowed to stand in this manner at room temperature for several days until the precipitation, under a saturated water vapor atmosphere, was complete. After the precipitated film (at this stage fixation of the superstructure as a film appeared to be completed) was washed with running water for several days to remove the solvent, a highly water-swollen transparent film was obtained. The two types of water-swollen films obtained from both the MMNO and DMAc/LiCl solutions were stored in water until needed.

Drawn cellulose films were studied at desired draw ratios and compared with undrawn films. The undrawn films were prepared by air-drying without any restraints overnight on a glass plate. The films were then dried under high vacuum at 40–50°C for more than 24 h. Drawn films were prepared as follows: water-swollen cellulose films were cut into strips of approximately 30 mm length and 5 mm width. These water-swollen specimen were then clamped in a manual stretching device and elongated uniaxially to the desired draw ratio ( $\lambda$ ) ranging from  $\lambda = 1.0$  to 2.0 at room temperature. The drawing process was performed while the sample was in a water-swollen state. Following air-drying, the drawn specimen in the stretching device, it was vacuum-dried at 40–50°C for more than 24 h. The thickness of the dried films was varied depending on the solution volume used to produce the coagulated films. The thicknesses of the dried films for X-ray measurements was about 80  $\mu\text{m}$ , while for infrared spectroscopy, the thickness was less than 10  $\mu\text{m}$ .

### Measurements

The density of the cellulose films was obtained by pycnometry using a mixture of *p*-xylene and carbon tetrachloride at 30°C. Prior to measurements being made, the dried specimens were cut into fragments, washed with ethanol, vacuum-dried at 40°C for more than 1 day, and were then subjected to an ultrasonic treatment for 5 min in carbon tetrachloride. The degree of crystallinity obtained from the density measurement was calculated on the basis of reported density values for crystalline cellulose II (1.610  $\text{g}/\text{cm}^3$ )<sup>14</sup> and amorphous cellulose (1.481  $\text{g}/\text{cm}^3$ ).<sup>15</sup> The calculation was performed using eq. (1):

$$X = (1/\rho_a - 1/\rho)/(1/\rho_a - 1/\rho_c) \quad (1)$$

where  $\rho$  is the density of the specimen,  $\rho_a$  is the density of the amorphous region,  $\rho_c$  is the density

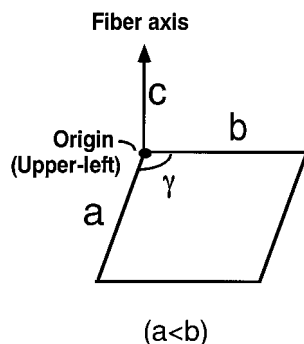
of the crystalline region, and  $X$  is the crystallinity of the cellulose film.

Wide-angle X-ray diffraction (WAXD) photographs were taken on flat film using nickel-filtered  $\text{CuK}\alpha$  radiation produced by a Rigaku RINT-2500HF X-ray generator at 40 kV and 40 mA. The WAXD intensity curves with a scanning speed 0.5°/min were measured by a transmission method using a scintillation counter at 40 kV and 200 mA through the angular range  $2\theta$  for the equatorial and the meridional scan to the drawing direction;  $2\theta = 5\text{--}35^\circ$  and  $10\text{--}80^\circ$ , respectively. The instrumental broadening was corrected by using Si powder as a standard material. The crystallinity from the WAXD intensity curve was calculated assuming that the area ratio was given by the crystalline region area divided by the total area.<sup>16</sup> To avoid complications due to contributions from the sample orientation in this measurement, the sample was cut into small pieces which were placed in a glass capillary of 1 mm diameter. Then, the measurements were carried out using a fiber attachment. The crystallite orientation parameter,  $\pi$ , for drawn films was estimated using eq. (2):

$$\pi = (180 - H^\circ)/180 \quad (2)$$

where  $H^\circ$  is the half-width of the azimuthal intensity distribution for the meridional reflection at the (004) plane. Another methodology for the orientation parameter  $\langle P2(\cos\theta) \rangle$ <sup>17</sup> is not well established for meridional reflections of cellulose and both methods provided with almost the same values.<sup>18</sup> In addition to the above reasons, since our cellulose specimens were highly noncrystalline and thus their crystallites may be assumed considerably small and imperfect, we decided to use the half-width method to estimate the orientation of the specimens.<sup>19,20</sup> Cellulose lattice parameter notations were made according to the general crystallographic rule as shown in Figure 1. According to this rule, the *c*-axis coincides with the molecular chain axis and the *b*-axis is larger than the *a*-axis for a monoclinic unit cell.<sup>21</sup>

Fourier transform infrared (FT-IR) spectra of drawn films prepared from the DMAc/LiCl solution were obtained using a Perkin Elmer Spectrum 2000 spectrometer system equipped with a polarizer. Thirty-two scans were averaged and the resolution was 2  $\text{cm}^{-1}$ . To observe the crystalline and noncrystalline regions in the specimens, FT-IR spectra for drawn specimens before



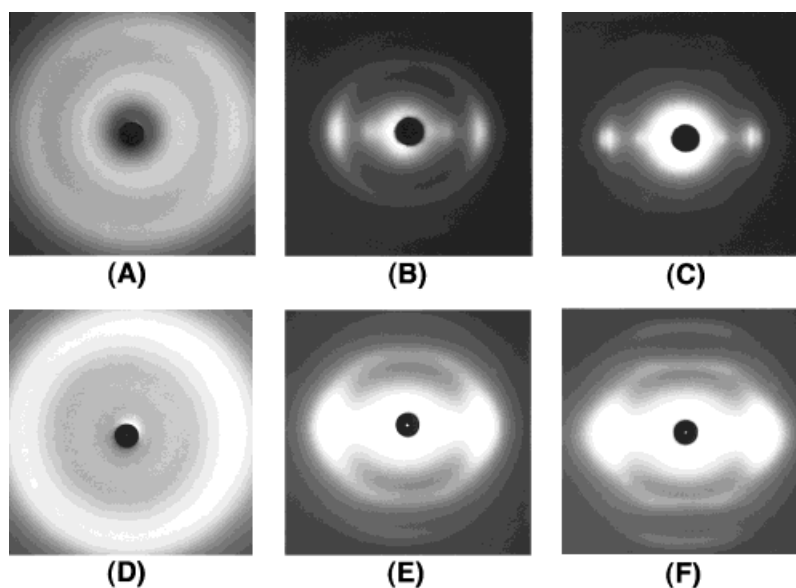
**Figure 1.** Notation for the lattice constant for the cellulose II crystal unit cell. The  $c$ -axis corresponds to the molecular chain axis, while the  $b$ -axis is longer than the  $a$ -axis.

and after deuteration were also compared under the same measurement condition.<sup>22</sup> The deuteration of the films were carried out in a home-made IR sample holder under a saturated deuterium oxide vapor. Infrared spectra obtained under these conditions were reproducible. The IR spectrum for the noncrystalline regions was obtained by subtraction of the deuterated spectrum from the original spectrum. The infrared dichroism,  $D$ , was determined by ratioing the vertical absorption intensity to the parallel absorption intensity at  $1159\text{ cm}^{-1}$ . This peak band which can be used to estimate the orientation, is attributed to anti-

symmetrical bridge C–O–C stretching band. In particular, the band can be interpreted as representing molecules aligned parallel to the molecular axis.<sup>23</sup> Then the angle,  $\gamma$ , between the direction of the transition moment and the chain axis was calculated.<sup>24</sup>

## RESULTS AND DISCUSSION

Slowly coagulated cellulose films from both MMNO and DMAc/LiCl solutions were obtained in a highly water-swollen state. These water-swollen cellulose films were transparent and composed of approximately 93 wt% water and 7 wt% cellulose prior to drawing. Figure 2 shows WAXD photographs for undrawn water-swollen cellulose films cast from both MMNO and DMAc/LiCl solutions together with photographs for dried uniaxially drawn specimens at the draw ratio ( $\lambda$ ) 1.5 and 2.0, respectively. The pattern for the undrawn water-swollen specimens exhibited predominantly noncrystalline regions and a diffuse water ring ( $2\theta = \text{ca. } 28^\circ$ ). The undrawn films after dried showed strong Debye rings corresponding to the (110) and (020) plane, however, the (1 $\bar{1}$ 0) plane was only faintly observed. In contrast, the intensity of the (1 $\bar{1}$ 0) plane was somewhat increased on the equator, when the photographs as the edge view were recorded with the direction of



**Figure 2.** WAXD photographs for drawn cellulose films from MMNO solution: (A) undrawn water-swollen state; (B) draw ratio 1.5; (C) draw ratio 2.0 and from DMAc/LiCl solution; (D) undrawn water-swollen state; (E) draw ratio 1.5; (F) draw ratio 2.0.

**Table I.** Crystallite Orientation Parameter,  $\pi$ , Estimated from Azimuthal WAXD Pattern at (004) Plane for Drawn Cellulose Films from Organic Solutions

Draw Ratio	Orientation Parameter ( $\pi$ )	
	MMNO	DMAc/LiCl
1.0	0.00	0.00
1.5	0.67	0.56
2.0	0.89	0.88

X-ray beam parallel to the film surface. These observations for the undrawn films indicate that the cellulose crystallites are oriented at random with respect to the axis perpendicular to the film surface. Additionally, the (110) plane of the cellulose crystallite presumably must have the uniplanar orientation parallel to the film surface. For both samples obtained from each solvent system, increasing the draw ratio produced WAXD photographs showing a higher degree of orientation. The changes in the patterns mirror the crystallite orientation parameters which also increased with draw ratio as shown in Table I. A few slight reflection planes can also be discerned in the WAXD photographs for the films made in both solvent systems and they can probably be attributed to contributions from low crystalline regions (see Table II) in the sample. However, the photographs for the cellulose films made from DMAc/LiCl solution are slightly different from those obtained from MMNO. The drawn films from MMNO [Fig. 2(C)] exhibited the typical diffraction pattern for the crystal structure of an oriented crystalline phase of cellulose II, which is characterized by clearly identified patterns for the (110) and (020) planes. On the other hand, the photographs for the drawn films from DMAc/LiCl [Fig. 2(F)] exhibited more diffused patterns than those obtained for MMNO films. This seems to support the idea that films drawn from DMAc/LiCl solution contain more noncrystalline regions than do films drawn from MMNO.

No necking of the sample was observed while deforming the water-swollen cellulose films by the uniaxial elongating process. In addition, the maximum draw ratios were fairly low when compared with other synthetic polymers. This indicates that cellulose  $\beta$ -glucan single chains may not undergo a crystalline transformation from folded to fibrous chains during the drawing process.

When the water-swollen cellulose films from MMNO coagulated at 20°C were elongated at room temperature, the draw ratio reached a maximum of 1.3. In contrast, when coagulation was performed at 2°C, the resulting films had a maximum draw ratio of 2.0 and the films formed were mechanically strong and more transparent than those coagulated at a higher temperature. Thus, the properties of drawn water-swollen cellulose film from MMNO seem to be dependent upon the coagulation-temperature. Slow coagulation attributed to the lower temperature of the coagulant gave the swollen cellulose films with a greater drawability. Similar results were obtained in a cellulose/liquid ammonia/ammonium thiocyanate solution system.<sup>25</sup> It has also been reported that cellulose products with improved physical properties were obtained by using coagulants at reduced temperatures. The same behavior has also been reported for gel spun of poly(vinyl alcohol).<sup>26</sup>

The crystallinity measured for the drawn cellulose films are listed in Table II. The crystallinity for an undrawn MMNO film was higher when coagulated at 20°C than at 2°C. The former films were weak and translucent because of the higher crystallinity, suggesting that the coagulating temperature may also affect the optical properties of the formed film. Films coagulated at 20°C also exhibited a clearly phase separation between the coagulated-film face and the glass surface. These film texture characteristics may partially explain the lower drawability of these films. As previously noted, the slow coagulation process with water may provide a favorable environment that pro-

**Table II.** Change in Crystallinity for Drawn Cellulose Films Determined from Density and WAXD Pattern Methods<sup>a</sup>

Specimen	Draw Ratio	Crystallinity (%)	
		Density	WAXD
MMNO	Undrawn	17.9	23.6
	1.5	19.5	23.9
	2.0	20.4	24.9
DMAc/LiCl	Undrawn <sup>b</sup>	27.8	
	Undrawn	13.8	18.2
	1.5	15.4	18.9
	2.0	16.3	20.1

<sup>a</sup> In MMNO, the drawing process was performed for samples coagulated at 2°C.

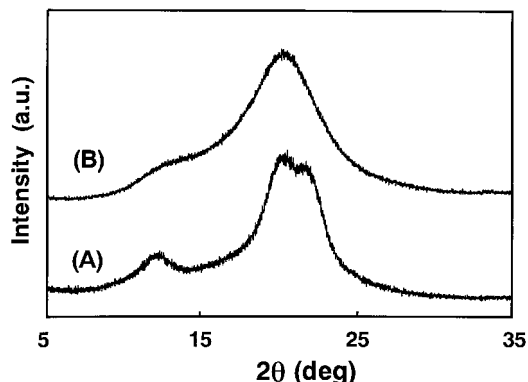
<sup>b</sup> Coagulated at 20°C.

motes good drawability for water-swollen cellulose films. The films coagulated in saturated water vapor at room temperature from DMAc/LiCl solution had the same drawability as films coagulated with water at the lower temperature from MMNO. Film precipitation in a saturated water-vapor atmosphere produced slower coagulation. The films exhibited drawability only as long as they were in a water-swollen state or in a never-dried state. Once the cellulose films were dried they no longer exhibited any drawability. However, when immersed again in water, they started to exhibit the drawability that no longer reached the maximum. Although a nonaqueous coagulant system such as methanol also gave transparent methanol-swollen films, such films did not exhibit any great drawability. It is also noteworthy that only these films swollen in water and coagulated resulted in highly drawable cellulose films. This suggests that cellulose interacts with water in a unique manner, which influences the formation of the hydrogen bonds which strongly contribute to the supermolecular structure found in the swollen cellulose state.

The crystallinity of cellulose has, to date, been estimated from its WAXD intensity curves. In general, for other polymers densities have been used to calculate their crystallinity. We have therefore applied the density method to our cellulose specimens. The crystallinity for films from MMNO and DMAc/LiCl, calculated from their densities, did not change significantly in ranges from 17.9 to 20.4% and from 13.8 to 16.3%, respectively, with increasing the drawing ratio as shown in Table II. In addition, the crystallinities determined by the density method were slightly lower than those calculated from the X-ray method for both solvent systems. Since cellulosic films may contain micro voids that are not penetrated by the solvent medium, the density measurement for such films could give lower values<sup>27-29</sup> than expected. FT-IR measurements could also provide with the crystallinity index by the amounts of remaining hydroxyl groups in the drawn films after deuteration of the sample specimen, since deuterium oxide may not be able to penetrate into all the crystalline and paracrystalline regions, but the very surface of them. The ratio of the remaining hydroxyl groups to the total amounts was slightly decreased from 12.7 to 10.6%, which is the opposite behavior to the above results from X-ray and density measurements. This indicates that the surface condition of crystallites or paracrystalline domains may be asso-

ciated with the deuteration for hydroxyl groups. Thus, the crystallinity for cellulose samples may be slightly dependent on the measurement method. Nonetheless, these results show that the density method might be helpful in giving an estimate of the crystallinity in cellulose. In any case, it should be also noted that the crystallinity of the undrawn films was relatively low as indicated by the diffuse WAXD patterns for these samples. The more interesting result is that the crystallinity did not change significantly even while the draw ratio increased. Also in general, the crystallinity of crystalline polymers can be increased by drawing since this promotes orientation of the polymer chains. However, in the present case for cellulose films, coagulated and drawn from organic solutions, increase of molecular orientation did not result in greater crystallization. Orientation in the crystalline regions resulting from stretching did not produce a corresponding increase in crystallinity. A possible explanation being the presence of stable intermolecular hydrogen bonds in the cellulose films formed during the drawing process after coagulation. In other words, intermolecular hydrogen bonds may contribute to orientation of the chains but hinder crystallization. Hydroxypropyl cellulose has exhibited the same behavior with regard to orientation and crystallization during the drawing process.<sup>30</sup> Therefore, another novel method is needed if we wish to increase the crystallinity of the oriented cellulose films by the drawing process.

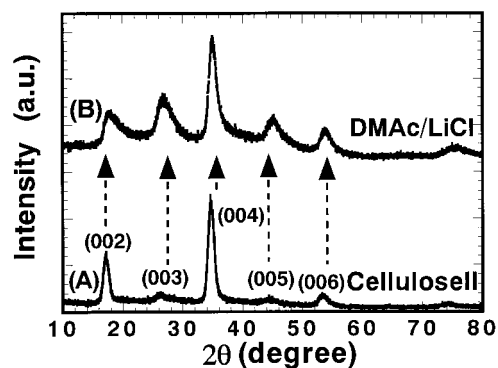
The equatorial WAXD intensity curves for the drawn films ( $\lambda = 2.0$ ) both MMNO and DMAc/LiCl are shown in Figure 3. They revealed that the intensity profile, for films drawn from MMNO, was compatible with crystalline cellulose II, whereas the diffuse intensity profile obtained for DMAc/LiCl films indicated they contain considerably more amorphous regions. Since the water coagulation of cellulose dissolved in MMNO solution would be faster, the regenerated cellulose film from MMNO solution generally produced higher degree of crystallinity than did films coagulated from other solution systems.<sup>8</sup> On the other hand, significant crystalline diffractions were not observed in the profiles from DMAc/LiCl films, indicating that the slower-coagulated films may produce crystallites of a small size or with many imperfections in the crystalline structures. The meridional scan of WAXD was employed to analyze the order along the fiber direction for the drawn samples. Meridional intensities of cellu-



**Figure 3.** Equatorial intensity curves for the WAXD patterns for drawn films (draw ratio,  $\lambda = 2.0$ ) prepared from MMNO (A), and DMAc/LiCl (B) solution. The a.u. indicates arbitrary unit.

lose are affected by the disorder of the neighboring chains, which is symmetry for the chain axis. So far, studies<sup>31,32</sup> based on the meridional profile of cellulose crystal have been limited because cellulose polymorphs provide with almost the same meridional patterns. However, the present results demonstrated that our drawn cellulose sample, which is highly ordered and noncrystalline, gave an interesting profile for the meridional scan. Figure 4 shows meridional WAXD patterns of the drawn cellulose film together with commercial available cellulose II fiber as a conventional regenerated cellulose. The meridional profile of cellulose II fiber exhibited two distinct peaks of (002) and (004) plane at  $2\theta = 17.2^\circ$  ( $d = 0.516$  nm) and  $34.7^\circ$  ( $d = 0.259$  nm), respectively. The odd-order reflections of (003) and (005) were not significantly observed, indicating that this cellulose II fiber was assumed to be the  $P2_1$  space group.<sup>14</sup> In contrast, the profile of the drawn cellulose exhibited a quite interesting pattern when compared with that for cellulose II fiber. The most striking characteristics were the presence of reflections of  $2\theta = 26.54^\circ$  ( $d = 0.336$  nm) and  $44.83^\circ$  ( $d = 0.202$  nm), which correspond to the odd-order reflections of (003) and (005) planes which have not so far recognized in the conventional regenerated cellulose II crystalline form. This indicates that the drawn, ordered and noncrystalline cellulose film may possess a space group similar to  $P1$ , differing from the case for the typical regenerated cellulose II with a space group of  $P2_1$ . In addition, the reflection corresponding to (004) in the drawn cellulose appeared in a slightly higher angle at  $2\theta = 34.89^\circ$  ( $d = 0.257$  nm). The meridional reflections in the profile of the drawn cellulose were

broadened considerably as compared in Figure 4, indicating that the structure of the drawn cellulose film along the chain direction may have a certain disorder. This also supports the hypothesis that the drawn cellulose was composed of the ordered noncrystalline regions. From the view point of crystallization focusing on the molecular structure of cellulose, the behavior of the primary OH group located at the C(6) position of a glucose unit was assumed to make up the extent of crystallization, as well as the final morphology of cellulose.<sup>33</sup> Considering that the drawn cellulose film contained more than 80% of noncrystalline regions, the conformation of C(5)–C(6) and the resulting intermolecular hydrogen bonds in the present cellulose molecules may differ from those in the crystallites. In the noncrystalline region, rotational positions of the C(6) hydroxyl groups may be considered as indeterminate or totally nonoriented, whereas all of those are identical in the crystallites. Thus, our drawn film may be in the differential state of the intermolecular hydrogen bonding between C(6) hydroxyl groups and adjacent chains. Accordingly, the resulting structure of the drawn cellulose film exhibited the ordered noncrystalline state, which may restrain the two-fold screw axis along its fiber direction. Less symmetry attributed to such a sequence of the unequal conformation at the O(6) rotational position with respect to the O(5) and the C(4) in a  $\beta$ -glucan chain of the drawn cellulose may lead to the development of the above characteristic meridional reflections corresponding to odd-order ones which are not seen in cellulose II crystal.<sup>34</sup> In addition, the reflection at  $34.89^\circ$ , appearing at a higher diffraction angle than that for (004) in



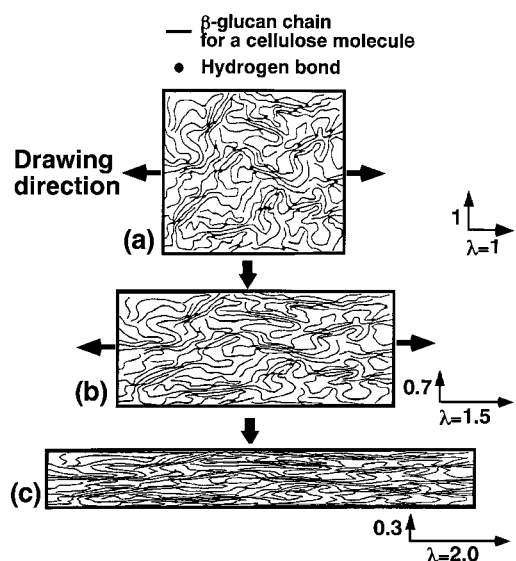
**Figure 4.** Meridional intensity curves for the WAXD patterns for cellulose II fibers (A), and drawn films (draw ratio,  $\lambda = 2.0$ ) prepared from DMAc/LiCl solution (B). The a.u. indicates arbitrary unit.

cellulose II, indicates displacement of the chain conformation angles. Thus, the interesting characteristics of the meridional WAXD pattern of the drawn cellulose including the broadened reflections are presumably attributed to the  $\beta$ -glucan chain arrangement in the ordered noncrystalline regions.

In order to confirm the changes in orientation for the molecular chains of cellulose, we obtained polarized FT-IR spectra for the noncrystalline regions of drawn films prepared from DMAc/LiCl solution. The orientation of the molecular chains was determined from the band at  $1159\text{ cm}^{-1}$  as described in the experimental section. As a result, the uniaxial drawing was indicated to urge the molecular chain orientation to the stretching direction in the  $\gamma$  range from  $0^\circ$  to  $38.5^\circ$ . This analysis for the behavior will be elaborated on in a future paper.<sup>24</sup> In the crystalline regions, the orientation parameter,  $\pi$ , from WAXD patterns at (004) plane listed in Table I showed that the orientation of the crystallites increased along with increasing the draw ratio. Consequently, the crystalline regions may be oriented continually during the drawing process. In conclusion, the results from FT-IR and X-ray analysis demonstrated that the drawn films ( $\lambda = 2.0$ ) have the high orientation yet the bulk of the film is noncrystalline.

## CONCLUSIONS

This study presents some interesting features with regard to the changes in morphological properties of water-swollen cellulose during the drawing process. We want to emphasize that the degree of crystallinity did not show any significant change with increasing draw ratio, whereas the molecular chains become highly oriented. This behavior for cellulose is quite different from that of other polymers that do not exhibit secondary interactions such as hydrogen bonding.<sup>1</sup> A schematic mechanism is shown in Figure 5 to explain this unique orientation behavior of the water-swollen cellulose during the drawing process. Figure 5(a) illustrates the structure of amorphous cellulose as proposed by Kondo and Sawatari.<sup>33</sup> Cellulose molecules are depicted as semiflexible chains. Domains engaged in intermolecular hydrogen bonding are randomly distributed in the amorphous cellulose. For other polymers, when regions are oriented and reaggregated with the chains aligned simultaneously by some physical force due to uniaxial drawing, then the regions



**Figure 5.** Schematic representation of the cellulose structure during the drawing process: (a) undrawn state; (b) drawn slightly; (c) maximum drawn state ( $\lambda = 2.0$ ). Horizontal arrows show the draw ratio, and vertical arrows show the shrinkage ratio.

spontaneously crystallize into crystalline regions. However, the present case of drawing a water-swollen cellulose would appear to be quite different and may be considered as an analogy of the above mechanism in the following manner. Initially, the undrawn cellulose film can be regarded as a mixture of amorphous regions containing a small amount of junction zones including hydrogen bonded and crystalline domains that show no orientation. Next, the cellulose molecules would exist as semiflexible chains as illustrated in Figure 5(a). As the drawing process proceeds [Fig. 5(b) and (c)], the width of the drawn films will exhibit a certain amount of shrinkage after drying. The orientation of cellulose  $\beta$ -glucan chains increases as the draw ratio increases, as can be seen in Figure 5(b) and (c). When the draw ratio reaches the maximum, the cellulose chains containing the amorphous or noncrystalline regions and junction zones are highly oriented, as confirmed by WAXD patterns and polarized FT-IR spectra. Despite these changes, the intermolecular hydrogen bonds linking adjacent cellulose chains to each other in the original amorphous regions may not be dissociated but remain intact during the drawing process. Furthermore, hardly any oriented crystallization of cellulose chains occurs. Since most of the oriented chains are restricted by the hydrogen-bonded domains, the de-



gree of the crystallinity should have an almost constant value at any draw ratio. After these changes, the sturdy three-dimensional network structure of cellulose  $\beta$ -glucan chains formed by the intermolecular hydrogen bonding may still hinder crystallization during drawing. It should also be noted that cellulose swollen in water may actually show weakened interaction between the cellulose chains as is the case for a favorable plasticizer, and consequently water-swollen cellulose can exhibit better drawability than films prepared using conventional methods. To crystallize the drawn cellulose while maintaining its higher orientation, will require a novel modification in the drawing methods that can control the formation of intermolecular hydrogen bonds. In addition, using the degree of orientation to determine the noncrystalline regions in the film is also becoming important in predicting the mechanical properties of films or fibrous materials.<sup>35</sup> Further studies on drawn cellulose films containing a significant amount of highly oriented noncrystalline regions may also prove valuable.

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