New Class of Cellulose Fiber Spun from the Novel Solution of Cellulose by Wet Spinning Method

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SYNOPSIS

A novel cellulose solution, prepared by dissolving an alkali-soluble cellulose, which was obtained by the steam explosion treatment on almost pure natural cellulose (soft wood pulp), into the aqueous sodium hydroxide solution with specific concentration (9.1 wt %) was employed for the first time to prepare a new class of multifilament-type cellulose fiber. For this purpose a wet spinning system with acid coagulation bath was applied. The mechanical properties and structural characteristics of the resulting cellulose fibers were compared with those of regenerated cellulose fibers such as viscose rayon and cuprammonium rayon commercially available. X-ray analysis shows that the new cellulose fiber is crystallographically cellulose II, and its crystallinity is higher but its crystalline orientation is slightly lower than those of other commercial regenerated fibers. The degree of breakdown of intramolecular hydrogen bond at $C_3[X_{am}(C_3)]$ of the cellulose fiber, as determined by solid-state cross-polarization magic-angle sample spinning (CP/MAS) ^{13}C NMR, is much lower than others, and the NMR spectra of its dry and wet state were significantly different from each other, indicating that cellulose molecules in the new cellulose fiber are quite mobile when wet. This phenomenon has not been reported for so-called regenerated cellulose fibers.

INTRODUCTION

Since Kamide and his collaborators first demonstrated that cellulose samples, regenerated from its cuprammonium solution under specialized conditions, can completely dissolve in 8–10 wt % aq. sodium hydroxide (NaOH) solution at 4°C and that the solubility of the cellulose against aq. NaOH solution is mainly governed by the degree of the breakdown of intramolecular hydrogen bonds,[1] much effort has been made to prepare such an alkali-soluble cellulose directly and economically from natural cellulose. Although the so-called steam explosion technique has been widely applied to wood chips and bagasse in order to separate ligno-components from cellulosic components, this technique has not been applied to pure cellulose.[2] Kamide et

al. succeeded in preparing alkali-soluble cellulose by applying the steam explosion treatment as a method for the breakdown of intramolecular hydrogen bonds on almost pure celluloses such as soft wood pulp and hard wood pulp.[3,4] They also clarified the specific solvation structure of 8–10 wt % aq. NaOH solution as a cellulose solvent[5] and the structural change of the alkali-soluble cellulose during its dissolution into the aq. NaOH solution.[6] In addition Kamide et al.[1,7] proved that in the alkali-soluble cellulose–aq. NaOH and the alkali-soluble cellulose–aq. lithium hydroxide systems cellulose was dissolved molecularly without forming a derivative or complex.

On the one hand, in the regenerated cellulose fiber industry, so-called viscose rayon and cuprammonium rayon, which were industrialized during the early 1900s, still occupy a sole and exclusive position, although their processes have problems with the possible discharge of toxic gases and substances from their spinning systems. To meet these environmental problems, many organic solvent systems such as

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dimethylformamide (DMF)-nitrogen oxide,[8] N-methyl-morpholine N-oxide-water,[8] dimethylsulfoxide-paraformaldehyde,[10] liquid ammonia-ammonium thyocyanate-water,[11] chloral-DMF-pyridine,[12] and dimethylacetamide-lithium chloride[13] systems aiming at a closed process for the regenerated fiber production have been investigated. Although an industrial spinning system has been developed using N-methyl-morpholine N-oxide-water as cellulose solvent, most of the systems seem to be still unsuccessful from an industrial viewpoint, partly because of the high toxicity of the solvent itself, the production of the explosive by-products, and the difficulty in solvent recovery. In addition, with some exceptions in most of these organic solvents as well as in viscose and cuprammonium cellulose solutions, cellulose dissolves as a derivative or complex, requiring the chemical regenerating process besides neutralization and refining processes when these systems are employed to produce the regenerated cellulose fiber. This situation creates an interesting and important research field, that is, the utilization of the novel cellulose-aq. alkali solution, which seems not to bring about any serious hazards and requires no chemical regeneration process in producing fibers, films, and so on. If a new class of fibers, films, membrane, and other products could be obtained by using the novel cellulose solution system, it would have a paramount and important impact on the cellulose chemical industry.

In this article we attempt to prepare a new class of filament type, but not staple-type cellulose fiber, using the novel cellulose solution by a wet spinning method with acid coagulation bath and elucidate some characteristic features of the new fiber in its morphology, mechanical properties, and supermolecular structure, in comparison with some commercially available regenerated cellulose filament-type fibers.

EXPERIMENTAL

Material

Alkali-Soluble Cellulose Sample

An alkali-soluble cellulose sample (the viscosity-average degree of polymerization $P_v = 331$, solubility $S_a = $ ca. 100%) was prepared by applying the steam explosion treatment on a soft wood (mainly white spruce) pulp [Alaska Pulp, U.S.A., α-cellulose content, 90.1 wt %, $P_v = 1060$)] under the conditions of water vapor pressure $P = 2.9$ MPa and the treating

time $t = 30$ s with water content of the original cellulose of 100%, as described in the previous papers.[1,3]

Cellulose-Aq. Alkali Solution

A 50-g of alkali-soluble cellulose (water content about 8–12 wt %) in dry base was dispersed into 950 g of a given concentration of 9.1 wt % aq. NaOH solution, precooled at 4°C, stood for 8 h with intermittently mixing by a home mixer, and the resultant solution was subjected to centrifugation at 7500 rpm for 60 min in order to exclude the slightly remaining undissolved part and to carry out the degasification at 4°C. The solution thus obtained was immediately employed to wet spinning of cellulose fiber.
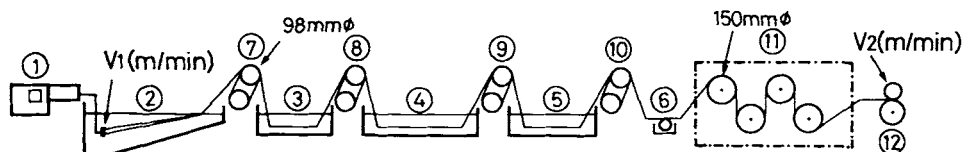
Wet Spinning

Selection of Coagulants

In order to select roughly the appropriate coagulants for multifilament spinning, the cellulose solution obtained earlier was introduced into a glass syringe (inner diameter, 11 mmϕ) with a needle (length, 10 mm; inner diameter, 0.255 mmϕ) as a spinneret, and the solution was extruded with an aid of a plunger-piston-type extruder (Microfeeder, Furue Science Co., Japan) into coagulation bath (length, 43 cm) containing various coagulants at the extruding speed v_1 of 120 cm/min, and a resultant monofilament was rolled up in a water bath at the take-up speed v_2 of 120 cm/min (draft ratio $D_r = v_2/v_1 = 1.0$). Aqueous solutions of sulfuric acid (H_2SO_4), hydrochloric acid (HCl), acetic acid (CH_3COOH), and phosphoric acid (H_3PO_4), and their several salts were examined as coagulants. In most cases the temperature of coagulation bath was about 15°C because higher temperature tended to gelatinize the cellulose solution. For the strong acids such as aq. H_2SO_4 and HCl the spinning test was also carried out at the lower temperature (ca. 5°C) of the coagulation bath. During the experiments coagulation state and spinnability were observed for each coagulant and the total assay was made as follows: (×) too weak coagulation with no spinnability; (△) weak coagulation but forming spinnable fiber (unstable taking-up); (○) proper coagulation and good spinnability; (××) too strong coagulation with forming frail coagulated fiber (impossible taking-up).

Multifilament

Multifilament spinning of the cellulose solution was carried out by using a wet spinning machine (see Fig. 1), constructed by the authors. ① is a plunger-

Figure 1 Schema of multifilament spinning machine: ① plunger-piston-type extruder with stainless cylinder (inner diameter, 50 mmϕ); ② first coagulation bath (length, 80 cm); ③ second coagulation bath (length, 50 cm); ④ water bath (length, 100 cm); ⑤ boiling water bath (length, 50 cm); ⑥ oiling roll; ⑦–⑩ Nelson-type rollers (diameter, 98 mmϕ); ⑪ roll heaters (diameter, 150 mmϕ); ⑫ take-up device.

piston-type extruder with a stainless cylinder (inner diameter, 50 mmϕ) having cooling jacket (JP-H model micro-feeder, Furue Science Co., Japan); ② the first coagulation bath (length; 80 cm); ③ the second coagulation bath (length, 50 cm); ④ the water bath (length, 100 cm); ⑤ the boiling water bath (length, 50 cm); ⑥ the oiling roll; ⑦–⑩ the Nelson-type rollers (diameter, 98 mmϕ); ⑪ the roll heaters (diameter, 150 mmϕ); and ⑫ the take-up device. Two spinnerets with different hole number (50 and 100) but with same diameter (0.06 mmϕ) for each hole were used. The cellulose solution prepared at 4°C was introduced into the cylinder cooled at 5°C, and the air was excluded carefully from the system, then extruded at the speed v_1 (2.55–22.5 m/min) into the first coagulation bath (20 wt % aq. H_2SO_4 at 5°C). The coagulated fiber was rolled up at the speed of v_2 (5.5–24.0) at Nelson roll ⑦ dipped into the second coagulation bath (water, 20°C), passed through the washing baths again (water, 20 and 95°C), and after oiling the fiber was dried at roll heaters (first roller, 180°C; second roller 130°C; third roller, 120°C; fourth roller, 30°C) and finally taken up. The spinning conditions employed for each experiment are summarized in Table II.

Analyses

The Viscosity-Average Degree of Polymerization of Cellulose

The viscosity-average degree of polymerization P_v of original alkali-soluble cellulose and the cellulose fibers spun in this study was determined from the limiting viscosity number [η] in cadoxen [cadmium oxide–ethylenediamine–NaOH–H_2O (5 : 28 : 1.4 : 165.6 weight ratio)] at 25°C by using the following equation[14]:

$$[\eta] = 1.84P_w^{0.76} \tag{1}$$

where P_w is the weight-average degree of polymerization.

Mechanical Properties

Denier of fibers was estimated with the assumption that the cross section of the fiber is true circle, by weighing the dried fiber with 90 cm in length. Tensile strength and elongation of the dried fibers were estimated according to the procedure (constant rate stretching method) described in JIS-L-1013-1981-7.5.

Scanning Electron Microscopic (SEM) Observation

The coagulated fiber samples before drying were directly immersed into liquid nitrogen and subjected to lyophilization. Onto the lyophilized fiber samples, gold was sputtered by using a metal evaporating apparatus (Fine coat ion sputter JFC-1100, JEOL Ltd., Japan), and the sputtered samples were observed on a field emission type scanning electron microscope (S-800 type field emission scanning electron microscope, Hitachi, Japan) and photographed.

X-ray Diffractometry

X-ray diffraction patterns of the samples were recorded on a X-ray diffractometer (Rotor Flex RU-200PL, Rigaku Denki Co., Ltd., Japan) with a scintillation counter. For the tablet of the powdered fiber samples the reflection method was applied and the crystallinity $X_c(X)$ was estimated by Segal's method,[15] using the following relations:

$$X_c(X) = 100[I(002) - I_{am}]/I(002) \tag{2}$$

Here, $I(002)$ and I_{am} mean the peak intensities, corresponding to (002) plane ($2\theta = 21.7°$) and amorphous ($2\theta = 16.0°$). Apparent crystal size (ACS) was estimated through use of Scherrer's equation.[16]

$$ACS = 0.9\lambda/\cos\theta \cdot \beta \tag{3}$$

with

$$\beta = (B^2 - b^2)^{1/2} \qquad (4)$$

Here, λ is the wavelength of the incident X-ray (1.5418 Å); θ, the diffraction angle corresponding to the (002) and (10$\bar{1}$) planes; b, the instrumental constant (0.2°), and B, the half value width in radians of the diffraction angle of the (002) and (10$\bar{1}$) planes.

The crystalline orientation for the fiber bundle sample placed on fiber specimen attachment was estimated by transmission method. In this procedure scintillation counter was held constant at $2\theta = 20.0°$ [(10$\bar{1}$) plane] and the fiber bundle sample was revolved perpendicular to the direction of the incident X-ray and the X-ray diffraction intensities at azimuth angles ψ were recorded. Orientation parameter f was estimated by the following equation:[17]

$$f = \{1 - (\psi_{1/2}/180)\} \qquad (5)$$

Here, $\psi_{1/2}$ denotes the half value width of the azimuth angle, expressed in degrees. As reference, those for the commercial regenerated fibers (viscose rayon and cuprammonium rayon) were also estimated.

Solid-State CP/MAS ^{13}C NMR Measurement

CP/MAS ^{13}C NMR spectra of the fiber obtained here as well as the commercial regenerated fibers were recorded both at dry and wet states on a Fourier transform (FT) NMR spectrometer (FX-200, JEOL Ltd., Japan) under the following operating conditions: 50.1 MHz for ^{13}C nucleus; data points, 8192 (4096 zero-filling); accumulation, 500; pulse width, 5 μs; contact time, 2 ms; pulse interval, 5.1 s; spectral width, 20,000 Hz; acquisition time, 102.4 ms. From the spectra the degree of breakdown of the intramolecular hydrogen bond at C_3-hydroxyl groups in glucopyranose unit, χ_{am} (C_3) was estimated by the following equations proposed in our previous work:[18]

$$\chi_{am}(C_3) = 100 \times I_h(C_4)/\{I_h(C_4) + I_l(C_4)\} \qquad (6)$$

The ratio of the value at dry and wet states $\Delta\chi$ [$= \chi_{am}(C_3)_{wet}/\chi_{am}(C_3)_{dry}$] was also calculated as a measure of molecular mobility in the fiber when wet.

RESULTS AND DISCUSSION

Selection of Coagulants

Table I collects the results on coagulation and spinnability tests on cellulose monofilament spin-

ning from the novel cellulose solution. Clearly a wide variety of coagulants can be employed for this novel cellulose solution although the coagulation and spinnability are strongly dependent on the spinning conditions such as the extruding speed, hole number and its diameter of spinneret, length of coagulation bath and take-up speed, and so on. When we use the coagulation bath controlled at 15°C aq. H_2SO_4 with concentration of 3–15 wt %, aq. HCl with concentration of 3–10 wt %, aq. CH_3COOH with concentration with 5–15 wt %, and aq. H_3PO_4 with concentration of 5–15 wt % were proved to be applicable to the wet spinning of the novel cellulose solution. Aqueous solutions of the sodium and ammonium salts of these acids with wide range of concentration also enable us to make new cellulose fiber. Magnesium, calcium, and zinc salts of these acids seem not to be used as effective coagulants. At coagulation temperature of 5°C the proper concentration range of the strong acids as coagulant seems to shift to higher concentration region. For example, the proper concentration range for aq. H_2SO_4 lies between 10 and 30 wt %. Because the novel cellulose solution must be finally neutralized in the process of the wet spinning and the stock temperature of the cellulose solution is ca. 5°C, a 20 wt % aq. H_2SO_4 controlled at 5°C was adopted as the coagulant for the multifilament spinning of the novel cellulose solution.

Properties of New Fibers

Table II collects the spinning conditions (extruding speed v_1, take-up speed v_2, draft ratio D_r, and shear stress γ), P_v, mechanical properties [denier (d), tensile strength (TS), and tensile elongation (TE) at dry state] and structural characteristics (χ_c (X), ACS, f, χ_{am}(C_3) (at dry and wet), $\Delta\chi$[$= \chi_{am}(C_3)_{wet}/\chi_{am}(C_3)_{dry}$]) of the new fiber obtained. For comparison the mechanical and structural properties of typical commercial regenerated fibers (viscose rayon and cuprammonium rayon) are also shown.

Physical and Mechanical Properties

As seen in Figure 2, the cross section of the lyophilized new cellulose fiber (F-4) is almost a true circle. Its very thin and coarse skin is not the structure constituted of the densely coagulated molecules as seen in viscose rayon, and it is rather more porous than inner part. The inner structure of the new fiber is also very porous with average pore size of 110 nm. The whole appearance of the other fibers spun here was almost the same as those shown in the figure. This means that as-spun new cellulose fiber might

Table I   Results of the Coagulation and Spinnability Tests

Anion	Conc. (wt %)	Cation							
		H^+ 5°C	H^+ 15°C	Na^+ 15°C	NH_4^+ 15°C	Mg^{2+} 15°C	Ca^{2+} 15°C	Zn^{2+} 15°C	Al^{3+} 15°C
SO_4^{2-}	1	X	X	X	X	X	—	X	X
	3	X	O	X	△	X	—	△	△
	5	△	O	△	O	△	—	△	△
	10	O	O	O	O	△	—	XX	XX
	15	O	O	O	O	XX	—	XX	XX
	20	O	XX	O	O	XX	—	XX	XX
	30	O	XX	O	O	XX	—	XX	XX
Cl^-	1	X	X	X	X	X	X	X	X
	3	O	O	X	△	X	X	△	O
	5	O	O	△	O	△	△	△	XX
	10	O	O	△	O	XX	△	△	XX
	15	O	XX	O	O	XX	XX	XX	XX
	20	XX	XX	O	XX	XX	XX	XX	XX
	30	XX	XX	XX	XX	XX	XX	XX	XX
CH_3COO^-	5	O	O	△	△	XX	—	△	XX
	7	O	O	O	△	XX	—	△	XX
	10	O	O	O	O	—	XX	XX	XX
	15	O	O	O	O	—	XX	XX	XX
	20	O	XX	O	O	—	XX	XX	XX
PO_4^{3-}	5	O	O	△	△	△	—	△	XX
	10	O	O	O	O	△	—	△	XX
	15	O	O	O	O	XX	—	XX	XX
	20	O	XX	O	O	XX	—	XX	XX

be a kind of coagulated gel containing a large amount of solvent.

P_v of the fibers is of the same order as that of the starting alkali-soluble cellulose. TS of the new fibers ranges from 1.53–1.82 g/d, which is in the same range as that of regenerated fibers; but the TE is smaller than those for the regenerated fibers. The shear rate $\dot{\gamma}$ on the solution imposed when the solution comes out through the spinneret tends to result in the higher TS in the $\dot{\gamma} \le 10^4$ s^{-1}, but an excess shear rate seems not to be preferable to obtain the fiber with the higher TS. TS of the fiber may not be influenced by draft ratio $D_r (= v_2/v_1)$ within this experimental conditions.

Structural Characteristics

A typical new fiber (F-1) is crystallographically cellulose II revealing two characteristic X-ray diffraction peaks at 20.0° for (10$\bar{1}$) plane and at 21.7° for

Table II   Spinning Conditions of Cellulose Fibers from Cellulose–aq. NaOH

Sample Code	Spinneret (n/holes)	v_1 (m·min^{-1})	v_2 (m·min^{-1})	D_r	$\dot{\gamma}$ (10^3 s^{-1})	P_v	Denier	TS (g·d^{-1})	TE (%)	χ_c (X) (%)	ACS/Å (002)	ACS/Å (10$\bar{1}$)	χ_{am} (C$_3$) (%) f (%)	Dry	Wet	$\Delta\chi$
F-1	100	2.55	6.7	2.6	5.8	312	57	1.56	6.3	65	34	35	83	40	37	0.93
F-2	50	4.5	5.5	1.2	10	306	53	1.82	7.3				81	49	41	0.84
F-3	100	4.5	10.8	2.4	10	313	69	1.71	4.3	67	32	34	83	45	36	0.80
F-4	50	22.5	24.0	1.1	50	326	84	1.53	7.3				79	42	39	0.93
VR[a]						381	75	1.44	18.1	60	29	33	84	54	52	0.96
CuR[b]						752	75	2.05	9.1	61	36	37	87	76	73	0.96

[a] Viscose rayon.
[b] Cuprammonium rayon.

(a)

(b)

$\overline{2\mu m}$ $\overline{2\mu m}$
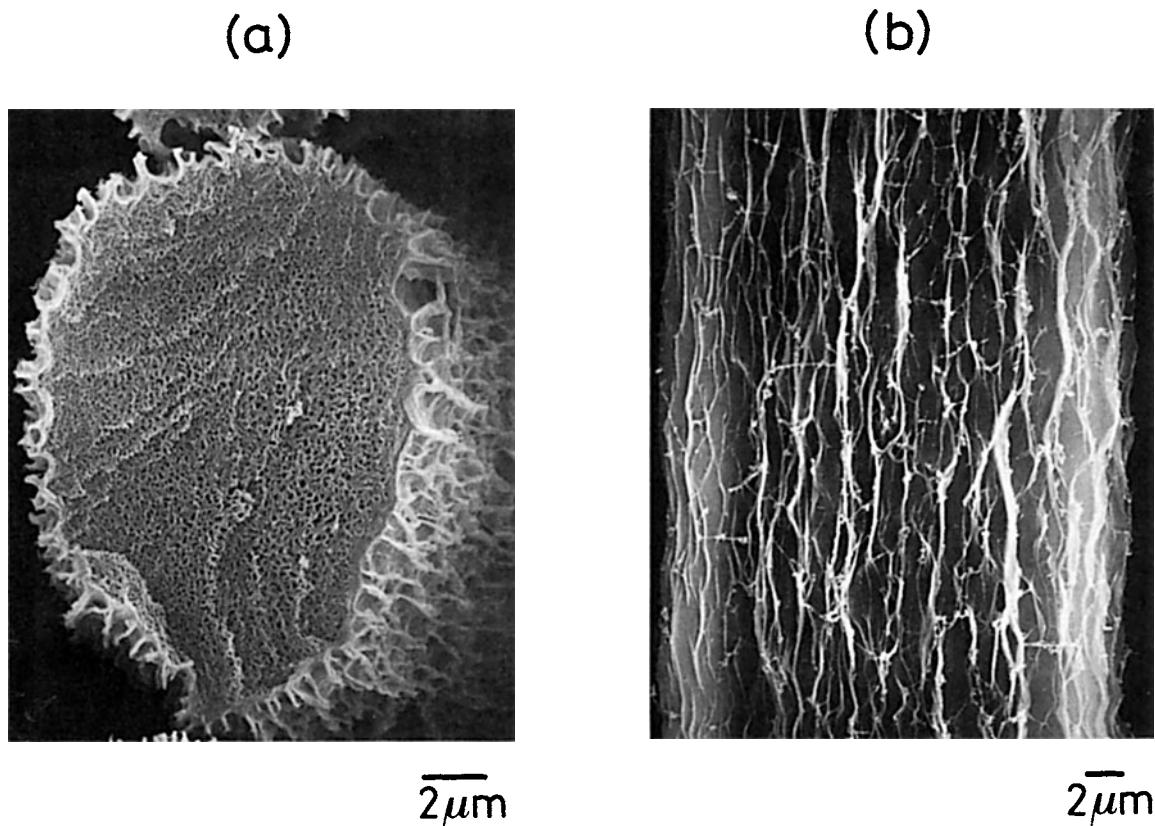
Figure 2   SEM micrographs of the lyophilized fiber of as-spun fiber F-4: (a) cross-sectional view, (b) side face view.

(002) plane, as observed for viscose rayon and cuprammonium rayon (Fig. 3). Table II (column 11–14) shows that (1) the crystallinity X_c of the new fibers is relatively high ranging 0.65–0.67, compared with those (ca. 0.6) of the commercial regenerated
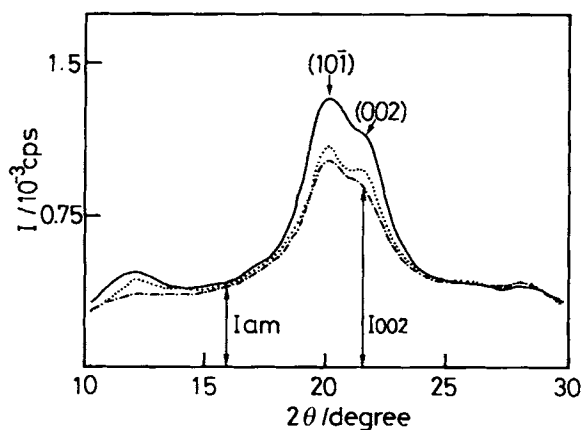
Figure 3   X-ray diffraction patterns of a typical new fiber (F-1) (———), viscose rayon (- - -); and cuprammonium rayon (- - - -).

fibers; (2) the new fibers have orientation parameter f ranging 0.79–0.83 which is considerably lower than those of commercial regenerated fibers; and (3) ACS increases in the order: cuprammonium rayon > new fiber > viscose rayon.

Figure 4(a) and 4(b) show CP/MAS ^{13}C NMR spectra of a typical new fiber, viscose rayon and cuprammonium rayon at dry and wet states, respectively. The spectral shape in the NMR spectra of these fibers at dry state is different from sample to sample. This tendency is most distinct for C_4 carbon peak region, suggesting that there are several molecular packing (or ordering) states in the molecules. C_4 carbon peak region might reflect the possibility of the formation of $O_3 \cdots O_5'$ intramolecular hydrogen bond, as pointed out previously.[1] A close analysis revealed that the degree of the breakdown of intramolecular hydrogen bond at C_3 position X_{am} (C_3) for the new fiber is significantly smaller, indicating the higher degree of formation of $O_3 \cdots O_5'$ intramolecular hydrogen bond, as shown in column 15 of Table II. This is in some sense very comparative to the results obtained by X-ray analysis, which revealed higher crystallinity for the new fiber. When
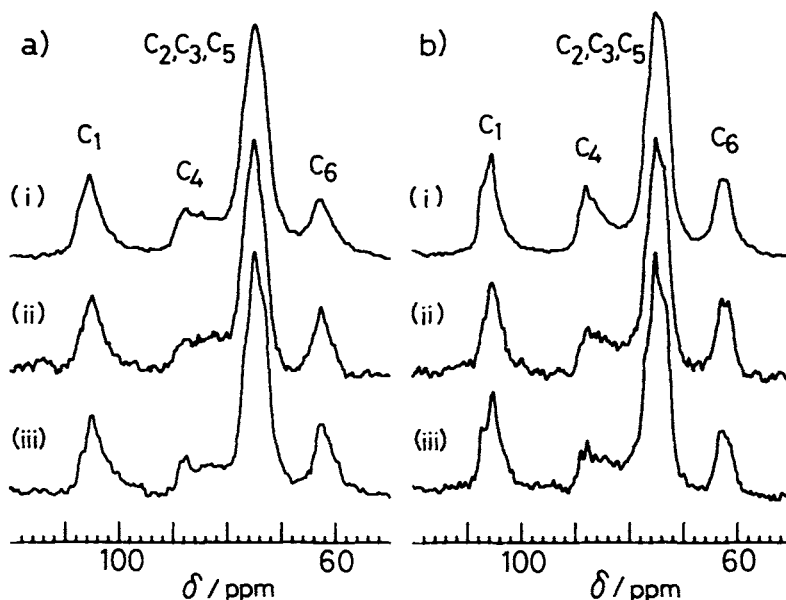
Figure 4 CP/MAS ^{13}C NMR spectra of cellulose fibers at (a) dry and (b) wet state: (i) typical new fiber (F-1), (ii) viscose rayon, and (iii) cuprammonium rayon.

measured at wet state, the peak separation as a whole for all samples becomes better than that at dry state. For example, each two sharp peak components at 107.4 and 105.4 ppm for C_1 carbon peak region and 89.2 and 88.1 ppm for C_4 carbon peak region are clearly detectable. C_6 carbon peak region of viscose rayon splits into two peaks by wetting. The whole spectral shape for C_4 carbon peak region of the new fiber at wet state is relatively sharper than that of others. As seen in column 16 of Table II, $X_{am}(C_3)$ for all samples decreases more or less by wetting. This indicates that $O_3 \cdots O_5'$ intramolecular hydrogen bond in the new fiber as well as the commercial regenerated cellulose fibers apparently increases, although the degree of the increase is very conspicuous only for the new cellulose fiber obtained here. It is quite astonishing that the wet treatment facilitates the molecular mobility in so-called disordered region of new fibers even if they have higher crystallinity and higher degree of intramolecular hydrogen bond. This result may correspond to the experimental facts that the new fiber is totally very porous. Horii et al.[19] reported the similar NMR spectral change in natural cellulose by wetting. They suggested that the molecular chains in amorphous region of natural cellulose is partially ordered in a water-swollen state, but those chains are distorted through drying, and the strain can be released when cellulose becomes wet again. On the contrary they found that the CP/MAS ^{13}C NMR spectrum of cellulose II was not changed by wetting, and they ex-

plained this phenomenon by their assumption that the structure of the amorphous region in cellulose II has no regularity both in the wet and dry state. But NMR spectra of the new cellulose fibers spun in this study (cellulose II) show remarkable change in C_4 region by wet treatment. These spectral changes may be caused by the temporary formation of intermolecular hydrogen bond between O_5 oxygen and water molecules or by the intramolecular hydrogen bond formation accompanying rearrangement of cellulose molecules in wet state. Note that the NMR spectral change caused by wet treatment also takes place for the so-called commercial regenerated fibers, more or less. This seemingly opposes the results reported by Horii et al.,[19] but we believe that the higher order of coagulated structure may play an important role on the molecular mobility induced by the interaction with polar solvent.

CONCLUSION

A cellulose dope prepared from an novel alkali-soluble cellulose-9 wt % aqueous sodium hydroxide solution was subjected to wet spinning, for the first time, using aq. H_2SO_4 as a coagulation bath. The mechanical properties and structural characteristics of the resulting novel cellulose fibers were compared with commercial regenerated cellulose fibers such as viscose rayon and cuprammonium rayon. The novel cellulose fiber reveals cellulose II crystal form

from X-ray analysis, and the crystallinity is higher but its crystalline orientation is slightly lower than the commercial regenerated fibers. The degree of breakdown of intramolecular hydrogen bond at $C_3[X_{am}(C_3)]$ of the cellulose fiber, determined from CP/MAS ^{13}C NMR, is much lower than others, and the CP/MAS ^{13}C NMR spectra of its dry and wet state were significantly different from each other, indicating that cellulose molecules in the novel cellulose fiber is quite mobile. This phenomenon has not been reported for so-called regenerated cellulose fibers.

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