

Production of Cellulose II from Native Cellulose by Near- and Supercritical Water Solubilization

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We explored conditions for dissolving microcrystalline cellulose in high-temperature and high-pressure water without catalyst and in order to produce cellulose II in a rapid and selective manner. For understanding reactions of microcrystalline cellulose in subcritical and supercritical water, its solubilization treatment was conducted using a continuous-flow-type microreactor. It was found that cellulose could dissolve in near- and supercritical water at short treatment times of 0.02–0.4 s, resulting in the formation of cellulose II in relatively high yield after the treatment. Next, characteristics of the cellulose II obtained were investigated. As a result, it was confirmed that the relative crystallinity index and the degree of polymerization of the cellulose II were high values ranging from 80 to 60% and from 50 to 30%, respectively. From these findings, it was suggested that this method had high potential as an alternative technique for the conventional cellulose II production method.

KEYWORDS: Cellulose II; native cellulose; cellulose I; Supercritical water; solubilization

INTRODUCTION

Cellulose is a linear syndiotactic homopolymer composed of D-anhydroglucose units, which are linked together by $\beta(1,4)$ -glycosidic bond linkages. Each of the D-anhydroglucose units possesses three hydroxyl groups at C-2, C-3, and C-6 positions, so cellulose seems to have high affinity to water. However, it does not dissolve in common solvents or water at ordinary state because it crystallizes by intra- and intermolecular hydrogen bond linkages. The presence of these hydrogen bond linkages is responsible for chain stiffness and stability of the conformation of cellulose.

It is well known that cellulose exists in several crystal modifications. The cellulose I is called native cellulose, and most of the celluloses existing in nature have the crystal modification. With the statistics 1996,⁽¹⁾ the production amount of native cellulose I fiber in the world is about 2000 million tons annually. This material has been utilized for industries of fibers, foods, pharmaceuticals, etc., mainly as a fiber itself and organic filler in terms of its physical properties. Cellulose II is also an important material called a manmade fiber. **Table 1** shows some important physical properties of cellulose I and cellulose II.⁽²⁾ The physical and chemical properties of this material are quite different from those of native cellulose, which probably results from the difference in the crystal structure between cellulose I and II. For example, the degree of

Table 1. Some Important Physical Properties of Cellulose I and Cellulose II (2)

property	cellulose I	cellulose II
DP	103–104	250–450
X-ray crystallinity/%	50–75	25–40
density/g cm ⁻³	1.53–1.89	1.49–1.55
breaking strength (dry)/cN tex ⁻¹	26–50	14–61
elastic modulus (dry)/cN tex ⁻¹	2–11	8–40
water vapor regain at 65% rel. humidity/%	7–8	12–14

polymerization (DP) and X-ray crystallinity of the cellulose II is much lower than those of the cellulose I. Also, the water absorbency of the cellulose II is higher than that of the cellulose I. Using these properties, the cellulose II has been employed in the extensive areas of films, fibers, foods, and cosmetics.

However, it hardly exists in nature except for celluloses in marine biomass, so it must have been produced from native cellulose by derivatizing and dissolving using various solvent systems, as shown in **Table 2**. About 2.3 million tons of cellulose II is produced annually (rayon, 2.0 million tons; cellulose acetate, 230 thousand tons; and cuprammonium cellulose, about 40 thousand tons) ⁽¹⁾. Cellulose II is also utilized extensively in the areas of films, foods, fibers, etc. There are two conventional methods for cellulose II production, namely the viscose method and the cuprammonium method. In the viscose method, viscose rayon is produced in the following manner: First, wood pulp is mercerized in 18–19% aqueous sodium hydroxide (NaOH) solution at room temperature (18–25 °C) for 24 h. In this process, a strong chemical interaction takes place between cellulosic hydroxyl groups and the NaOH dipoles, resulting in cleavage of intra- and intermolecular

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Table 2. Typical Derivatizing and Dissolving Systems for Cellulose

classification	system	typical composition
acid	H ₃ PO ₄ /H ₂ O	>85%
alkali	CS ₂ /NaOH/H ₂ O	18–19% NaOH, CS ₂ /Cell = 30–35%(w/w)
	NaOH/H ₂ O	8–9% NaOH
metal complex	[Cu(NH ₃) ₄](OH) ₂	Cu/NH ₃ = 1/6–7 (mol/mol)
organic solvent	DMAC/LiCl	Cell/DMAC/LiCl = 6/86/8
	DMF/N ₂ O ₄	Cell/DMF/N ₂ O ₄ = 8/15/77

hydrogen bond linkages to form the sodium cellulose I intermediate (Cell–ONa). Next, the intermediate reacts with carbon disulfide (CS₂) at 20–30 °C for 1–2 h to form hydrophilic cellulose xanthogenate (viscose, Cell–O–C(S)–SNa). This derivative is then decomposed to cellulose II, sulfate, and CS₂ by neutralization of NaOH. In the cuprammonium method, the cellulose II is obtained by dissolution of cotton linter (cellulose I) in cuprammonium solution and subsequent solidification and regeneration of the dissolved intermediate. In the viscose method, the toxic hydrogen sulfide (H₂S) arises a little. However, the enormous cost is necessary to lower the amount of H₂S emission to the standard value in the countries in which the environmental standard is severe, such as North America (3). Therefore, the production of rayon (cellulose II) has been successively driven into the ground. Moreover, even in the other conventional methods for production of cellulose II, they have utilized alkali, acid, metal complex, and organic solvent so as to improve the reactivity of cellulose, which caused the increase of cost for their waste treatments. For such reasons, the discovery of a new solvent that has low impact to the environment became urgent for developing a manufacturing system of cellulose II.

As one of the techniques that these problems will be able to solve, use of water at near the critical point ($T_C = 374.2$ °C, $P_C = 22.1$ MPa) as a reaction medium can be focused on. In near- and supercritical water, it is possible that physical properties of water such as density and dielectric constant can be changed in the extensive range between gas and liquid by manipulating temperature and pressure. This is because the diffusion coefficient of water increases at supercritical state, resulting from the weakening of the interaction among water molecules, namely hydrogen bond linkages, while the diffusion coefficient of water is low due to the cluster formation under hydrothermal and lower temperature conditions.

To date, we have studied elucidating reaction pathways and the mechanism of cellulose (4–6) and its related compounds (7–13) in subcritical and supercritical water. On the cellulose reaction, it was found that cellulose could be rapidly hydrolyzed to form water-soluble celooligosaccharides and glucose in a relatively selective manner in supercritical water, while pyrolysis products such as 5-hydroxymethyl-2-furaldehyde (5-HMF) and 2-furaldehyde were mainly formed in subcritical water(4–5). Kinetic study on the cellulose reaction clarified that the rate of decomposition of cellulose in supercritical water became much faster than that expected from the rate in subcritical water (5–6). The direct observation of cellulose-water phase in high-temperature and high-pressure water using a diamond anvil cell (DAC) also indicated that cellulose I can dissolve in this water (6). Furthermore, we found that a large amount of cellulose-like material was precipitated in the aqueous product solution on its decantation process after near- and supercritical water treatment (6). Here, we conducted solubilization experiments of microcrystalline cellulose in near- and supercritical water more in detail and tried to explore an optimum condition for high yield of the cellulose-like material. Also, we clarified that the characteristics of the cellulose-like precipitates obtained by the near- and supercritical water solubilization treatment.

MATERIALS AND METHODS

Experimental Methods. Microcrystalline cellulose from Merck (Avicel No. 2331; mean particle size, 20–100 μm; a viscosity average degree of polymerization (DP_V), 230; a relative crystallinity (χ_c), 77.8%) was used in this study. Cellulose solubilization treatment was conducted at 320–400 °C, 25–33 MPa and 0.02–0.6 s using a continuous-flow-type microreactor shown in **Figure 1**. Cellulose-water slurry of 10 wt % was rapidly heated to the reaction temperature by mixing four volumes of near- and supercritical water at the mixing point, which was connected to the reactor. The slurry passed through the reactor was quickly quenched with a cooling jacket having a direct cooling system. This rapid-heating and quick-quenching method enabled us to estimate the accurate volume of the reactor. The residence time in the reactor was calculated by eq 1.

$$\tau = \frac{V \cdot \rho}{F \cdot \rho_0} \quad (1)$$

where V is the reactor volume of the reactor, F is the flow rate of the fluid introduced in the reactor, ρ is the water density at the reaction condition, and ρ_0 is the water density at ambient temperature and pressure.

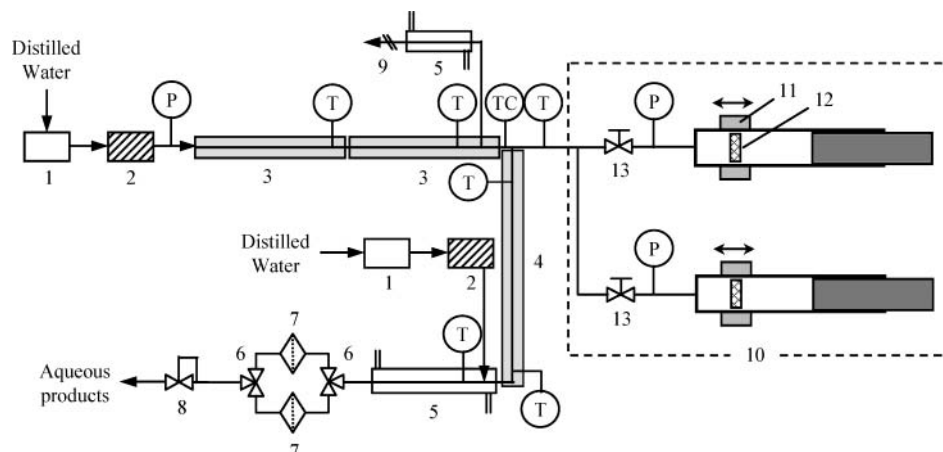


Figure 1. Schematic representation of a continuous flow-type microreactor for near- and supercritical water treatment of cellulose: (1) degassing unit, (2) HPLC pump, (3) preheater, (4) reactor, (5) cooling jacket, (6) three-way valve, (7) in-line filter, (8) backpressure regulator, (9) relief valve, (10) slurry feed pump, (11) permanent magnet, (12) static mixer, (13) needle valve.

The product solution quenched by the cooling jacket was passed through inline filters of 0.5- μm pore size (NUPRO, Model SS-4TF-05). In this part, solid fraction such as unreacted cellulose or residue was recovered, and the water-soluble portion that passed through this filter was depressurized at a backpressure regulator (TESCOM, Model 26-1721-24) and then collected in a sampling bottle for a given time.

Analytical Methods. After the solubilized treatment, the aqueous product solution was decanted at 20 °C for several hours. If white precipitate appeared in the solution, it was separated from the water-soluble portion, dried at 60 °C for 24 h, and then weighed, W_p . Yield of the precipitate, Y_p , was calculated by eq 2.

$$Y_p = \frac{W_p}{W_0} \quad (2)$$

Water-soluble products were quantified by a high performance liquid chromatography (HPLC) system (Thermoquest Co. Ltd., Model AS3000) with a refractive index detector (ERC, Model 7515A RI detector). Detailed analytical procedure had described in our previous work (6). Product yield, Y_i , was determined by eq 3.

$$Y_i = \frac{W_i}{W_0} \quad (3)$$

Here, Y_i and W_i represent general forms of a yield and a carbon weight of the product i , respectively. The Y_0 is a yield of the water-soluble oligosaccharides (cellohexaose, cellopentaose, cellotetraose, cellotriose, and cellobiose), Y_{Glc} is a yield of glucose, and the Y_D indicates a combined yield of the degradation products of glucose, that is, fructose, erythrose, glycolaldehyde, glyceraldehyde, dihydroxyacetone, pyruvaldehyde, 1,6-anhydro- β -D-glucose, and 5-HMF.

Solid residue trapped in the filtration part was dried at 60 °C for 24 h and subsequently weighed, W_R . Conversion of cellulose, X , was determined from the weight change of cellulose before and after the treatment by eq 4.

$$X = 1 - \frac{W_R}{W_0} \quad (4)$$

Measurement of Macromolecular Characteristics of the Precipitate. The precipitate that appeared in the aqueous product solution was analyzed by an X-ray diffraction (XRD) analyzer (MAC Science Co. Ltd., Model M18XHF22-SRA) using Mo-K α radiation (wavelength, 0.71423 nm). Relative crystallinity index of the precipitate, χ_c , was determined by the following equation with Segal's method (14):

$$\chi_c = \frac{I_{(200)} - I_{\text{am}}}{I_{(200)}} \quad (5)$$

The content of amorphous region in the precipitate, χ_{am} , was calculated as

$$\chi_{\text{am}} = 1 - \chi_c \quad (6)$$

where $I_{(200)}$ and I_{am} mean peak intensities corresponding to (200) plane ($2\theta = 9.98^\circ$) and amorphous ($2\theta = 8.40^\circ$) for cellulose I. For cellulose II, $I_{(200)}$ and I_{am} are $2\theta = 9.00^\circ$ and 6.00° , respectively.

Viscosity-average degree of polymerization, DP_v , of the precipitate was determined as follows (15). A solid sample of 0.5 g (dry basis) was added in 1.5 mL of cadoxen solution (cadmium oxide/ethylene-diamine/NaOH/H₂O=5/28/166/14 (w/w/w/w)) at 25 °C. To swell and dissolve the precipitate into the cadoxen solution, it was maintained at less than 10 °C for 24 h with stirring. After the dissolution, a viscosity-average molecular weight of the precipitate, M_v , was evaluated by determining a limiting viscosity number, $[\eta]$, using the Mark-Houwink-Sakurada equation described in eq 7. The DP_v was obtained by eq 8

$$[\eta] = 1.84 \cdot M_v^{0.76} \quad (7)$$

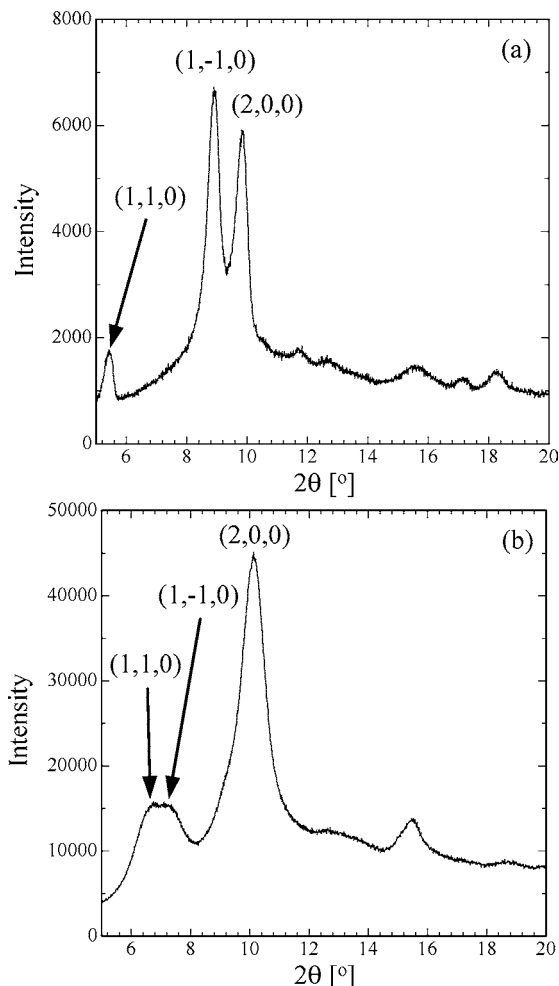


Figure 2. X-ray diffraction patterns of (a) the precipitate recovered from the supercritical water treatment at 380 °C, 30 MPa, and 0.17 s and (b) the untreated native cellulose I.

$$DP_v = \frac{M_v}{162} \quad (8)$$

RESULTS AND DISCUSSION

Formation of Cellulose II. On the solubilization treatment of cellulose at 355–400 °C, 25–33 MPa, and 0.02–0.22 s, aqueous product solution collected right after this treatment was a quite clear liquid, but white cellulose-like precipitate formed during decantation for several hours at 20 °C. Here, XRD patterns of all the precipitates formed were recorded. **Figure 2a** shows a typical XRD pattern of the precipitate obtained at 380 °C, 30 MPa, and 0.17 s. For comparison, the diffraction pattern of untreated native cellulose I was shown in **Figure 2b**. In general, the specific peaks in the XRD pattern of a crystalline solid reflect its crystal structure. The XRD pattern of untreated cellulose I had three specific diffraction peaks at angles of 7.4, 7.6, and 10.1°, while the precipitate had three specific peaks at angles of 6.0, 9.0, and 9.9°, and there was no peak originating from the crystal structure of the untreated cellulose I. All the precipitates obtained in this study had almost the same diffraction patterns. It was confirmed that the XRD pattern of the precipitate was consistent with that of the commercial cellulose II (15). From these analytical results, it can be considered that the crystal structure of the precipitates is not the cellulose I crystal form, but the cellulose II crystal form. This result indicates that the crystal structure of native cellulose can be rearranged to that of cellulose II through the treatment in near-

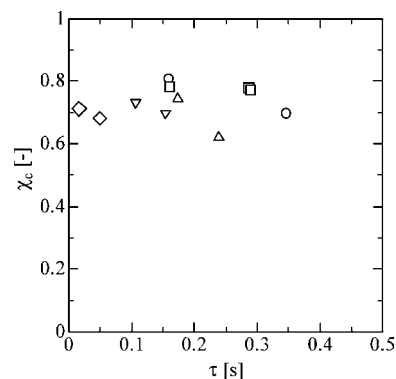
Table 3. Product Distributions after Near- and Supercritical Water Treatment of Cellulose and Subsequent Decantation

T (°C)	P (MPa)	ρ (g cm ⁻³)	τ (s)	X (C%)	product yield/C%			
					Y_P	Y_O	Y_{Glc}	Y_D
355	25	0.61	0.21	52.1	6.1	25.0	2.0	19.0
360	33	0.63	0.22	45.9	26.1	6.7	9.0	4.1
375	25	0.50	0.18	64.8	12.2	13.4	19.9	17.7
375	33	0.58	0.15	59.0	20.4	20.2	11.4	6.1
385	25	0.31	0.16	82.9	33.3	14.1	20.8	12.4
380	30	0.53	0.17	76.2	39.3	16.7	16.4	3.8
400	25	0.17	0.02	99.0	51.0	14.1	20.8	12.4
			0.05	98.6	0.2	27.1	37.4	35.3
			0.15	99.8	n.d.	14.5	42.6	43.7

and supercritical water, where cellulose I crystal can rapidly dissolve into water at near- and supercritical state by the cleavage of intermolecular hydrogen bond linkages to form a large number of cellulose molecules, followed by the aggregation and recrystallization to the cellulose II crystal during the decantation after the near- and supercritical water treatment.

Product Distribution of Near- and Supercritical Water Treatment of Native Cellulose. Table 3 shows the product distributions after near- and supercritical water treatment of cellulose and subsequent decantation of the aqueous product solution. In the case of the subcritical water treatment at 320 °C and 25 MPa, cellulose II was hardly obtained, and water-soluble saccharides were mainly yielded, suggesting that cellulose mainly hydrolyzes heterogeneously on its surface region without swelling or dissolving. In near-critical water treatment (360–385 °C), hydrolysis of cellulose took place with partial dissolution of cellulose into high-temperature water. This phenomenon became remarkable at high-pressure conditions. At 375–380 °C, a large amount of cellulose II (12–39% in yield) could be formed when the conversion of cellulose was about 50%. In supercritical water (e.g., 400 °C and 25 MPa), cellulose disappeared within an extremely short residence time of 0.02 s and its hydrolysates (cellulose II and water-soluble saccharides) could be obtained in relatively high yield (about 50%).

Effect of reaction temperature to the formation of cellulose II was examined. At 355–375 °C, the higher the reaction pressure was from 25 to 30 MPa (or 33 MPa), the higher the yield of cellulose II became. At 380–385 °C, however, the yield of cellulose II at a constant conversion of cellulose did not change even if reaction pressure varied. This result was explained as follows: The trend that cellulose immediately disappears in near- and supercritical water probably resulted from two things. One is the increase of the reactivity of high-crystalline cellulose. The higher the temperature becomes, the larger the kinetic energies of cellulose molecules that form a crystal structure become. As a consequence, the intermolecular interaction among the cellulose molecules such as the hydrogen-bond linkage seems to become weaker with increasing temperature. Another point is that properties of water can greatly change at around the critical point of water. Each water molecule forms a conjugated group with a few molecules under high water dense condition like subcritical state, because it has hydrophilic interactions among water molecules. As temperature elevates and reaches around the near-critical region (360–385 °C and 25–33 MPa), water density and dielectric constant decrease, but the hydrophobicity of water becomes strong and diffusion coefficient also becomes high. These changes can permit cellulose to dissolve partially into near-critical water. In supercritical water, the diffusion coefficient of hydrophobic

**Figure 3.** The relative crystallinity index (χ_c) of cellulose II as a function of treatment time (τ). Symbols: \circ , 370 °C and 25 MPa; \triangle , 375 °C and 25 MPa; \square , 380 °C and 30 MPa; ∇ , 385 °C and 25 MPa; \diamond , 400 °C and 25 MPa.

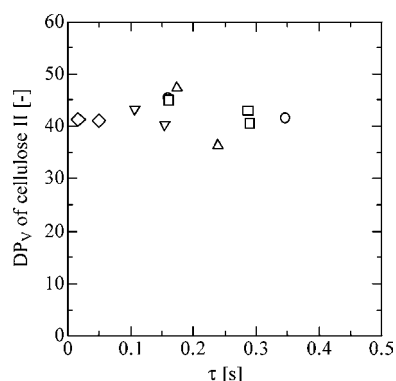
water molecules becomes higher than that in near-critical water, and thus a large part of hydrogen bond linkages in cellulose are cleaved. Accordingly, cellulose can rapidly dissolve in supercritical water.

As to effect of reaction pressure to the formation of cellulose II, it can be explained by the following. In this experiment, cellulose-water slurry was quickly heated by mixing with preheated water at the mixing part, as shown in Figure 1. On the typical reactions at 355–375 °C, the preheated water is at supercritical state (380–390 °C), but its hydrophobicity and diffusion coefficient vary drastically around the critical point of water, so penetration of water molecules being at supercritical state to the inside of crystalline cellulose will facilitate with an increase of reaction pressure, resulting in the difference in the degree of dissolution of cellulose. By contrast, on the reaction at near- and supercritical water, temperature of the preheated water ranges from 400 to 430 °C, and its hydrophobicity and diffusion coefficient become higher than that around the critical point of water. However, pressure dependence of the water properties at a constant temperature in supercritical water becomes small compared with the case of those at near the critical point, so the effect of pressure to the formation of cellulose II seems to decrease in supercritical water.

Characteristics of Cellulose II. Relative crystallinity index of the precipitate (χ_c) was calculated by eq 4, based on the XRD pattern. Figure 3 shows the relationship between the χ_c of the cellulose II and the treatment time (τ). At a high-pressure of 30 MPa, the χ_c value became high (about 80%) when the conversion of cellulose reached 80–90%. This value was higher than those of regenerated celluloses obtained by the viscose method and the cuprammonium methods, as shown in Table 2. Even at lower pressure condition of 25 MPa, the χ_c values were still maintained at a high level ranging from 60 to 80%. The reason for this result is probably because of the difference in the dissolution mechanism of cellulose between this method and the viscose and cuprammonium methods. According to the works of Okajima et al. (18) and Yamane et al. (19), there are two dissolution types in the dissolution mechanism of cellulose, namely a direct type and an indirect type. In dilute NaOH aqueous solution, dissolution of cellulose is the direct type, while it is the indirect type with the formation of any complex and derivative in viscose solution and cuprammonium solution. Moreover, it is natural that the crystallinity of the regenerated cellulose obtained by the dilute alkali treatment becomes higher than that obtained by the viscose and cuprammonium methods. Considering this knowledge, it can be expected that dissolution of cellulose in near- and supercritical water seems to be the

Table 4. Characteristics of Cellulose II and Its Production Efficiency: Comparison of This Method with the Typical Production Methods of Regenerated Celluloses

method	starting material (DP_V)	time for cellulose dissolution and treatment conditions	properties of cellulose II	
			DP_V	χ_c
near- and supercritical water treatment (this work)	microcrystalline cellulose (230)	0.02–0.22 s H ₂ O (355–400 °C)	30–50	60–80%
viscose method (27)	wood pulp (700–800)	(1) 24 hrs 18–19% NaOH/H ₂ O, 18–25 °C (2) 1–2 hrs CS ₂ , 20–30 °C	300–350	27–40%
cuprammonium method (76)	cotton linter (800–2, 600)	several hrs [Cu(NH ₃) ₄](OH) ₂	450–550	40.8%

**Figure 4.** The viscosity-average degree of polymerization (DP_V) of cellulose II as a function of treatment time (τ). Symbols: \circ , 370 °C and 25 MPa; \triangle , 375 °C and 25 MPa; \square , 380 °C and 30 MPa; ∇ , 385 °C and 25 MPa; \diamond , 400 °C and 25 MPa.

direct type, and therefore the cellulose II obtained by this treatment has high crystallinity.

The DP_V of the cellulose II were also measured. **Figure 4** shows a plot of DP_V of the cellulose II versus the treatment time (τ). The DP_V of the cellulose II was about 40 (ranging from 30 to 50) in all the reaction conditions. This result can be explained by the reaction mechanism of microcrystalline cellulose in near- and supercritical water that we had proposed (20). A cellulose particle is composed of many cellulose microfibrils. This microfibril consists of crystalline region (100–150 nm long) and amorphous region (several nanometers long). Microcrystalline cellulose used in this study mainly consists of the crystalline region, which is an aggregate of linearly-connected several crystallites having DP_V of 30–50. When the cellulose is treated with near- and supercritical water, it can be considered that each microfibril itself dissolves and then hydrolyzes to several crystallites, or that each microfibril hydrolyzes to several crystallites and then dissolves (20).

Comparison of this Method with the Conventional Techniques. Here, production efficiency of this method and characteristics of the cellulose II produced in this study were compared with those of the conventional ones. **Table 4** summarizes the result. It can be found that this method has some advantages from the environmental point of view: (1) An environmentally benign solvent (water) is employed in this method, (2) this method is the rapid one-pot production method of cellulose II, and (3) this method can produce cellulose II with high crystallinity and relatively high DP . Considered from these points, it can be said that this method has high potential as a new effective production method of cellulose II and that this treatment can synthesize new cellulosic materials with middle molecular weight, which may be applicable to many research fields. However, the DP of the cellulose II obtained

was low (up to 50) even at the optimum condition. This is because cellulose rapidly converts to oligosaccharides and monosaccharides in high-temperature water. To solve this problem, it is necessary to take any countermeasure to prevent the dissolved cellulose from hydrolyzing to the saccharides. We will report a result of this matter in a future paper.

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Received for review September 26, 2002. Revised manuscript received June 8, 2003. Accepted June 25, 2003. Financial support provided by a Grant-in-Aid for Scientific Research on Priority Area “Mechanism of hydrolysis in Supercritical Water” (#11450295) from the Ministry of Education, Culture, Sports, Science and Technology.

JF025989I