

Solubility of Cellulose III in Sodium Hydroxide Solution

B. LASZKIEWICZ^{1,*} and J. A. CUCULO²

¹Technical University of Lodz, 90-924 Lodz, Poland; ²North Carolina State University, School of Textiles, Raleigh, North Carolina 27695

SYNOPSIS

Studies on cellulose III solubility have been conducted in 8.5% NaOH solution with and without the presence of added substances, such as acrylamide, acrylic acid, acrylonitrile, and thiourea. The highest value of cellulose III solubility was obtained as a result of the introduction of thiourea and acrylamide in a 5% ratio of NaOH into NaOH solution. Moreover, dissolving conditions proved to be of great importance. Cellulose III introduced into NaOH solution and repeatedly frozen and unfrozen three times dissolved 50% (dissolving with 5% thiourea). The soluble cellulose fraction showed significantly lower molecular mass in comparison with its insoluble fraction. Comparative studies on cellulose crystallinity using the CP/MAS ¹³C-NMR method showed a satisfactory compatibility of results with determinations obtained from the X-ray method. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Cellulose solubility in solutions of alkaline metals has been investigated for many years¹ and is still under study.^{2,3} The above problem elicits great interest due to its practical importance. Successful attainment of concentrated, stable cellulose solutions in NaOH or in other alkaline metal hydroxides could possibly eliminate the viscose process as a method for manufacturing fibers. This process, very harmful to the environment, could be replaced by direct dissolution of cellulose in an inexpensive, common solvent, e.g., sodium hydroxide solution. The formation of cellulose fibers based on the so-called direct solvents has been studied in many laboratories.⁴ Particular attention should be given to such solvents as NH₃/NH₄SCN,⁵⁻⁷ zinc chloride,⁸ *N*-methylmorpholine-*N*-oxide,⁹ and aqueous solution of sodium hydroxide. *N*-Methylmorpholine-*N*-oxide has been recognized by many authors as a direct cellulose solvent. Earlier this year, the first commercial facility producing cellulosic fibers via this solvent has come on stream. The fiber will be produced by Courtaulds Fibers as "Tencel." This solvent is fully recoverable in a closed loop, ecologically attractive process. Fiber processing based on the

above solvent has developed very slowly due to its high cost and to the unusual, high spinning temperature required.

The remaining cellulose solvents and their respective fiber-forming processes were investigated only on a laboratory scale. They are, nevertheless, very interesting from a technological point of view despite the fact that concentrated cellulose solutions in these solvents show high viscosity. Aqueous sodium hydroxide solution is one of the cheapest cellulose solvents. This solvent is not ideal, however. It only dissolves cellulose of a relatively low molecular mass, making it impossible to obtain fibers with satisfactory properties. Solutions containing cellulose with a degree of polymerization (\overline{DP}) of over 250 are unstable and cellulose precipitates relatively rapidly from these solutions.

The current objectives were to investigate, first, cellulose III solubility in sodium hydroxide solution and, second, the influence of selected organic compounds on the solubility, as well as to study the DP and structure of cellulose fractions precipitated from the solution.

EXPERIMENTAL

Materials

Cellulose III with a \overline{DP} of 590, determined by the viscometric method in cadoxen solution, was used

* To whom correspondence should be addressed.

Table I Solubility of Cellulose III

Sample	Conditions of Solubility		Mass of Cellulose III after Treatment (g)				Fraction of Dissolved Cellulose III (%)	\overline{DP} Dissolved Fraction of Cellulose III	\overline{DP} of Insoluble Fraction of Cellulose III	
	Temp (°C)	Time (h)	Solvent (mL)	Mass of Cellulose Sample (g)	Fraction Precipitated from Solution	Insoluble Fraction				Mass of Both Fractions
1	-5	6	150 mL NaOH	3.5020	0.3800	3.1066	3.4866	11.29	212	614
2	-5	6	150 mL NaOH 5% AM	3.6543 3.6451	0.5083 0.6949	3.0702 2.8823	3.5784 3.5772	15.98 20.93	263 194	624 562
3	-5	6	150 mL NaOH 5% TU	4.0158 3.8073	0.6684 0.5096	3.2405 3.1920	3.9089 3.7616	19.31 16.16	201 203	586 589
4	-5	6	150 mL NaOH 5% AA	4.1053	0.3537	3.7153	4.0690	9.49	239	568
5	-5	6	150 mL NaOH 5% AN	4.0942	0.4986	3.5143	4.0129	14.16	232	577

AM, acrylamide; AA, acrylic acid; TU, thiourea; AN, acrylonitrile. The \overline{DP} of control cellulose III was 548.

in the dissolution work. Cellulose III was obtained from powdered cellulose I with a \overline{DP} of 660 as shown below:



Liquid ammonia at -42°C was added dropwise onto cellulose I contained in a Dewar vessel. Subsequently, it was slowly evaporated over a period of 3 days. The resulting cellulose III was placed in a flask covered with 8.5% aqueous NaOH solution and then stored at -5°C for 6 h. As shown in Table I, certain organic compounds (5% w/w based on solid NaOH) were added to some of the solutions. The second series of cellulose III samples (Table II) was stored at -38°C for a period of 15 h. At these conditions, the samples solidified. Following this, the samples were thawed with warm water and refrozen. This was repeated three times. Following the final thaw, the samples were centrifugated at a speed of 7000 rpm to separate undissolved cellulose. Next, the dissolved cellulose was precipitated from solution using 3% sulfuric acid. It was washed with ethyl alcohol and dried at 60°C . The quantity of cellulose dissolved was determined gravimetrically.

Methods

Viscosity-average \overline{DP} of Cellulose

P_v was determined by the limiting viscosity number in cadoxen solution at 20°C , using the following equation⁴:

$$[\eta] = 1.84 P_v^{0.76}$$

where P_v is the weight-average DP.

Solubility (S_0) of Cellulose

The solubility of cellulose was calculated as a percentage using the following equation:

$$S_0 = 100 \times (W_1 - W_2) / W_1$$

where W_1 is the weight of the cellulose sample before the solubility test, and W_2 , the weight of the cellulose-insoluble sample.

X-ray Diffractometry

X-ray diffraction patterns of the samples were recorded on a X-ray diffractometer by the reflection

Table II Solubility of Cellulose III

Sample	Solvent	Mass of Cellulose Sample (g)	Mass of Cellulose Sample after Treatment (g)			Dissolved Fraction (%)
			Fraction Precipitated from Solution	Insoluble Fraction	Mass of Both Fractions	
Cellulose I	10 mL NaOH	0.3504	0.1154	0.2293	0.3447	34.56
Cellulose III	10 mL NaOH	0.3653	0.1434	0.2069	0.3503	43.36
Cellulose III	10 mL NaOH 1% TU	0.3574	0.1606	0.1940	0.3546	45.72
Cellulose III	10 mL NaOH 3% TU	0.5489	0.3662	0.1655	0.5317	69.85
		0.6428	0.3320	0.3064	0.6384	52.33
Cellulose III	10 mL NaOH 5% TU	1.5321	0.7260	0.7572	1.4832	50.57

TU, thiourea.

method. The crystallinity was estimated by Segal et al.'s method¹⁰ using the following equation:

$$CI = 100 \times [I(002) - I_{am}] / I(002)$$

where $I(002)$ is the peak intensity corresponding to the (002) plane at $2\theta = 22.8^\circ$ for cellulose I and at $2\theta = 21.1^\circ$ for cellulose III. I_{am} is the peak intensity of the amorphous fraction at $2\theta = 16^\circ$ for cellulose I and of $2\theta = 12^\circ$ for cellulose III.

Solid-state CP/MAS ¹³C-NMR Measurement

CP/MAS ¹³C-NMR spectra were recorded on a Bruker MSL-300-type FT-NMR. Measurement conditions were the following: rotation angle of 56° to a magnetic field with a frequency of 2.5 kHz; relaxation time, 6 s; resonance frequency, 75.968 MHz; cross-polarization contact time, 1000 s; measurement temperature, 25°C; scanning number, 113–440 impulse; and pulse width, 29.411 Hz.

The degree of breakdown of the intramolecular hydrogen bonds (value χ_{am}) at C2, C3, and C6 of the hydroxyl groups in the glucopyranose unit was defined by Kamide and co-workers and estimated using equations proposed in the literature.¹¹ CP/MAS ¹³C-NMR was also used to estimate cellulose crystallinity according to the method suggested by Zbankov et al.¹²

RESULTS

Cellulose solubility in sodium hydroxide solutions depends on many factors: first of all, on the cellulose

molecular mass and its crystallinity, the concentration of the NaOH solution, and also on the temperature. The data in Table I show that addition of organic compounds to the NaOH solution can have a substantial impact on cellulose solubility. However, as yet, no satisfactory explanation of this phenomena has been given.¹³ Attempts to explain this phenomenon of increased cellulose solubility in sodium hydroxide solutions containing specific organic compounds have not been very convincing. Nevertheless, this phenomenon is real. The introduction of acrylamide or thiourea into sodium hydroxide solutions results in an increase of cellulose solubility of ca. 50% at -5°C (Table I). The effect is less dramatic when applied in the temperature cycling technique (Table II).

The structure of cellulose has a noticeable influence on cellulose solubility. On the bases of the current experiments, it is clear that cellulose III has a higher solubility than that of cellulose I at comparable molecular mass. This is related, presumably, to the fact that cellulose III has a lower degree of crystallinity (Table V) than that of cellulose I. However, The $-\text{CH}_2\text{OH}$ conformation may also be different.

Our experiments also indicate that in aqueous NaOH solutions of cellulose the fractions of relatively lower molecular mass are being dissolved, as expected from the general rules of polymer solubility. X-ray examination (Fig. 1) indicates that the cellulose III used in these experiments has much lower crystallinity than that of the initial cellulose I. Moreover, fractions of cellulose IIIB dissolved in aqueous NaOH solution and then precipitated and

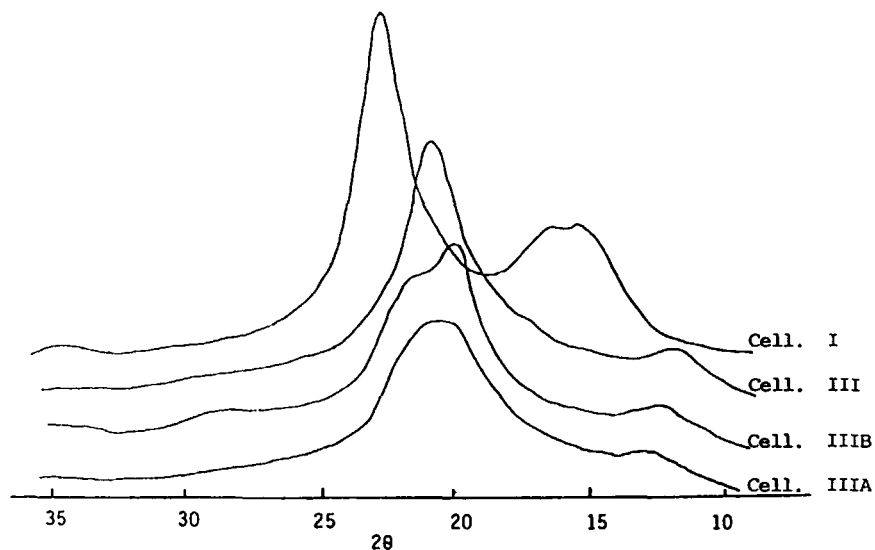


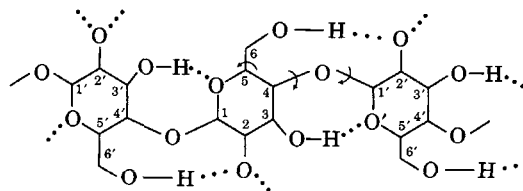
Figure 1 X-ray diffraction of celluloses I and cellulose III.

dried at 60°C have changed their structure from that of the initial cellulose III used for the dissolution experiment (Table III). This is reflected in the change of the main band at scattering angle $2\theta = 24.0^\circ$, characteristic of cellulose III. The precipitated, dried sample has two peaks of X-ray scattering—one at the angle $2\theta = 20.0^\circ$ and the other at angle $2\theta = 22.0^\circ$. These data show that under the experimental conditions used partial rearrangement of cellulose III into cellulose I has taken place.

Conclusions concerning cellulose solubility may also be made based on spectrograms of solid cellulose using cross-polarization magic angle sample spinning (CP-MASS) ^{13}C -NMR.¹⁴⁻²¹

In the cellulose macromolecule, conformational changes are related to a rotation center around carbon bonds $\text{C}'1 - \text{O} - \text{C}4$, i.e., with glycosidic bonds between the glucose rings. The main factor influencing the magnetic features of carbon atoms C1 and C4, respectively, is related to the conformational changes of $\text{C}'1 - \text{O} - \text{C}4$ groups. These changes are

predominantly controlled by intramolecular hydrogen bonds between the hydrogen atom linked with the C3 OH group and the oxygen atom from the adjacent glucose ring:



The intramolecular hydrogen bonds of $\text{O}3\text{H} \cdots \text{O}'5$ type, as shown above, forms a seven-element ring in which carbon atoms C3 and C4 form the conjugated system of π electrons placed on the oxygen atom together with σ electrons of orbital $\text{C}-\text{O}$ bonds. When electrons of the above system are mobile, carbon C4 has the character of a cation, and carbon C3, of an anion.² In the case where intramolecular co-actions are lower and carbon C4 does not take part in the building up of a seven-element ring, the density of electrons at C4 is still lower than that at C3, which is reflected in the displacement of the NMR peak in the direction of the lower magnetic field. Hence, partially broken intramolecular hydrogen bonds of cellulose III samples can be considered, taking into account the magnetic field built around the C4 carbon atom able to create a heterogeneous magnetic field. This heterogeneous magnetic field, depending on intensity changes, conditioned by the hydrogen bonds $\text{O}3-\text{H} \cdots \text{O}'5$ and $\text{O}6\text{H} \cdots \text{O}'2\text{H}$ in cellulose I, will be displaced in the direction of higher values according to the

Table III X-ray Characteristics of Structure Changes in Cellulose III

Sample	Position of Peaks at 2θ				
	1	2	3	4	5
Cellulose I	—	15	—	22.8	34.8
Cellulose III	11.8	—	21.1	—	—
Cellulose IIIA	12.2	—	20.7	28.0	34.8
Cellulose IIIB	12.2	—	20.5	28.0	34.8

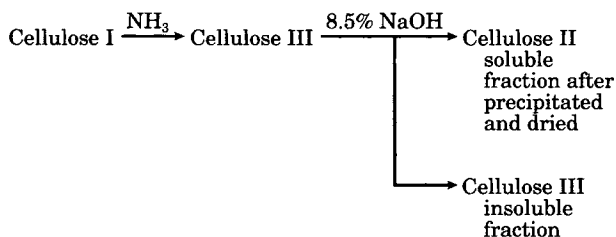
quantitative increase of hydrogen bonds. The above conclusions are entirely justified by the experimental results presented in Table IV and also on the spectrograms shown in Figure 2.

On the bases of the presented spectrograms and the values of magnetic field displacements, it can be concluded also that magnetic field displacement characteristic of C1 and C6 is observed. The heights of peaks for C2, C3, and C5 are also changed due to cellulose treatment with a liquid ammonia and as a result of cellulose III dissolving. These changes can be explained by the fact that in cellulose there are intramolecular hydrogen bonds²²⁻²⁴ of O2H · · · O'6 and O6H · · · O'2 types.

CP/MAS ¹³C-NMR spectra of all the pertinent cellulose samples are presented in Figure 2. Comparison of particular spectra showed that the cellulose I spectrum differs considerably from the spectra of the remaining samples. The peak attributed to carbon C1 appears in cellulose I at 105.0 ppm as a single peak. In cellulose III, it is also a single peak, but the magnetic field of C1 is slightly displaced toward the higher values (lower value of ppm, see Table IV), this being possible evidence for a change of conformation in a cellobiose fragment of cellulose macromolecule resulting from a rotation of the glycosidic bonds C'1 — O — C4. Only in the case of the cellulose IIIB sample, i.e., for the fraction dissolved in 8.5% NaOH, then precipitated with 3% H₂SO₄ and dried at 60°C, the peak C1 expressed as a doublet with displacement values of 106.9 and 105.1 ppm appeared. This doublet confirms considerable structural changes in the above-mentioned cellulose sample and is characteristic of the cellulose

II structure, where a higher quantity of intramolecular hydrogen bonds occurs in comparison to cellulose III.

This structural change in cellulose can be expressed as



On the other hand, the cellulose III fraction that was not dissolved (cellulose IIIA sample) did not undergo any considerable structural changes despite some changes in hydrogen bonds linked with carbon atoms C2, C3, and C5 expressed as a single sharp peak with a displacement value of 74.6 ppm and responsible for the presence of the hydrogen bonds of O3 — · · · O'5 type. In the case of cellulose I, in the above displacement region, three peaks of 74.8, 72.2, and 71.4 ppm occur (see Table IV). In the initial cellulose I, there are two peaks characteristic of the C4 magnetic field, respectively, at 88.8 and 83.7 ppm. They undergo displacement and change of intensity under the influence of liquid ammonia until they finally attain displacement values of 87.7 and 84.1 ppm. The wide peak for cellulose I at 83.7 ppm represents the carbon C4 magnetic field mainly in the cellulose amorphous region.¹⁹ For cellulose III, the peak is displaced and corresponds to the lower magnetic field, i.e., with 84.1 ppm. At the same time, the

Table IV Comparison of the ¹³C Chemical Shifts of the Sharp Spectral Features in Celluloses I and III

Sample	Chemical Shifts (ppm)			
	C1	C4	C2, 3, 5	C6
Cellulose I	105.0 (5.3) ^a	88.8 (2.9)	74.8 (9.6)	64.9 (3.7)
		83.7 (1.4)	72.2 (8.8)	62.5 (2.1)
			71.4 (8.5)	
Cellulose III	104.8 (4.9)	87.7 (1.6)	75.7 (8.6)	62.1 (4.1)
		84.1 (1.5)	73.5 (10.1)	
Cellulose IIIA	104.8 (3.9)	87.2 (1.5)	74.6 (10.3)	62.3 (3.9)
		84.5 (1.5)		
Cellulose IIIB	106.9 (3.9)	87.4 (2.7)	74.7 (12.9)	62.4 (5.5)
	105.1 (4.4)			

Cellulose IIIA, insoluble fraction of cellulose III; Cellulose IIIB, soluble fraction of cellulose III and precipitated.

^a Intensity (in parentheses).

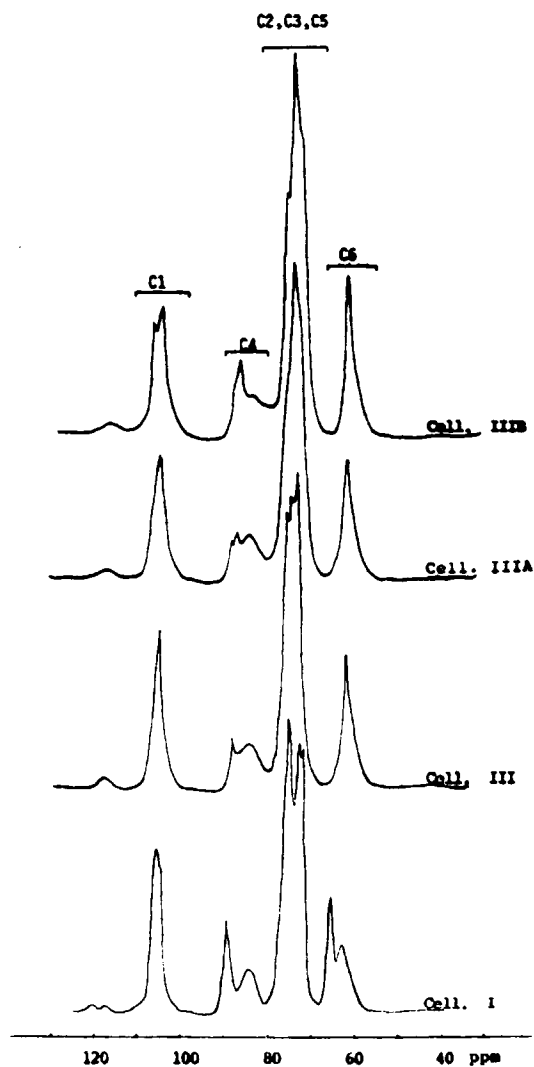


Figure 2 CP/MAS ^{13}C -NMR spectra of cellulose.

peak is considerably wider, reflecting the fact that cellulose III has undergone structural changes connected with a decrease in degree of order (Table V).

This is confirmed by X-ray examination and by the crystallinity index computed from the field below the curve of a wide peak C4 with a displacement value of 84.1 ppm.

As can be seen from Figure 2 and the values presented in Table V, the degree of disorganization increases for the cellulose III fraction (Fig. 2, curve Cell.IIIA) not dissolved in 8.5% NaOH. On the other hand, in the soluble cellulose III fraction that was precipitated from a solution and dried (Cell.IIIB curve), an increased degree of macromolecule order was noticed. This was reflected in the collapse of the C4 peak at 84.1 ppm in cellulose III and in the simultaneous appearance of a sharp peak at 87.4 ppm in cellulose IIIB.

The displacement value at which the peak determining the C4 magnetic field in cellulose IIIB appears is different from the C4 value for cellulose I. This change can probably be explained by the fact that the soluble cellulose III fraction, during the process of precipitation and during drying, attained a structure different from that of cellulose I. The resulting macromolecule conformation corresponds probably with that of cellulose II.

In cellulose III, the peak characteristic of C4 occurs at a lower displacement than that of cellulose I. Further, in cellulose I, in the region of the magnetic field typical for carbon C6, a rather broad doublet with displacement values of 64.9 and 62.5 ppm is observed; on the other hand, in cellulose III, a single peak at 62.1 ppm appears, confirming that the ammonia treatment of cellulose I produces a change of magnetic field characteristic of carbon C6. It is presumably related to the change in rotation of the C5—C6 bond. The characteristic feature is that displacement values of the C6 peak are different for cellulose III insoluble and soluble fractions and they appear, respectively, at 62.3 ppm (Cell.IIIA) and 62.4 ppm (Cell.IIIB). These insignificant changes

Table V Changes in Crystallinity and in Degree of Breakdown of the Intramolecular Hydrogen Bonds by Liquid Ammonia Treatment of Cellulose

Sample	X-ray CI (%)	^{13}C -NMR CI (%)	Degree of Breakdown of the Intramolecular Hydrogen Bonds		
			χ_{am} (C2)	χ_{am} (C3)	χ_{am} (C6)
Cellulose I	45	49	-28	70	64
Cellulose III	31	30	8	57	62
Cellulose IIIA	24	19	38	50	59
Cellulose IIIB	36	40	12	74	57

Cellulose IIIA, insoluble fraction of cellulose III; cellulose IIIB, soluble fraction of cellulose III and precipitated; CI, crystallinity index; χ_{am} , breakdown of the intramolecular hydrogen bonds at C2, 3, and 6.

in values of a peak position characteristic of the carbon C6 magnetic field result probably from different values of hydrogen bondings $O6H \cdots O'2$ being in the cellulose samples (see values presented in Table V).

By comparing values of the crystallinity index of all samples, it is apparent that the highest crystallinity index is that of cellulose I. At the same time, cellulose I shows the highest values of χ_{am} (C3, 6), indicating that cellulose I has the highest number of intramolecular hydrogen bonds. Cellulose III has considerably lower values of χ_{am} , which corresponds to lower crystallinity. The lowest value of the crystallinity index is shown by the insoluble fraction of cellulose III (Cell.IIIA sample). The above sample shows also the lowest values of χ_{am} (C2, 3, 6), related very probably to the large structure effected during the temperature sequence of the sample in 8.5% NaOH solution. These changes are a relatively permanent event through the drying process. Hence, it is characteristic that the soluble fraction of cellulose III (Cell.IIIB sample) with a substantially lower molecular mass shows higher crystallinity compared with the cellulose IIIA sample and, at the same time, has higher values of χ_{am} (C3) and lower value of χ_{am} (C2).

This confirms that the quantity of the hydrogen bonds of $O2H \cdots O'6$ type decreased in this case as compared to the cellulose IIIA sample, and for the hydrogen bonding of $O3H \cdots O'5$, substantially increased.

CONCLUSIONS

The experiments have indicated that introduction of acrylamide and thiourea into NaOH solution generates an increase of cellulose solubility at the temperature of -5°C . The cellulose III fraction being dissolved at this temperature shows lower molecular mass in comparison with the insoluble cellulose fraction. The way of dissolving has an impact on the cellulose solubility. In case of three times repeated freezing and unfreezing of the cellulose III sample at temperature -38°C , cellulose III solubility increases significantly even up to 40%. When thiourea is introduced into 8.5% NaOH in a 5% ratio, cellulose III solubility increases up to 52%. Cellulose III solubility under the described conditions of dissolving is higher than is cellulose I solubility. Measurements of crystallinity of the examined cellulose samples made using X-ray diffractometry and spectra of CP/MAS ^{13}C -NMR differ from each other insignificantly in value terms; nevertheless, the ob-

tained results are entirely compatible. This is evidence that the NMR method is very useful for the determination of cellulose crystallinity. Based on the CP/MAS ^{13}C -NMR spectra analysis, it was found that the soluble fraction of cellulose III differs in the structure, conformation, and quantity of intramolecular hydrogen bonds from the cellulose IIIA fraction that is not dissolved in aqueous 8.5% NaOH solution. Besides, it has been recorded that solubility and insolubility in NaOH solutions as well as conditions of precipitation and drying have, presumably, an impact on the quantity of hydrogen bonds in the cellulose sample.

The cellulose fraction dissolved in 8.5% NaOH and then precipitated from the solution and dried has the structure of cellulose II and more hydrogen bonds for particular $\chi_{am(C3)}$ in comparison with the insoluble fraction.

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