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Inter- and Intramolecular Order in Regenerated Cellulose

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Introduction

It is well known that the degree of molecular order in cellulose samples regenerated from viscose depends not only on the origin of the cellulose and its molecular weight, but also quite markedly on the conditions prevailing during the regeneration and on subsequent after-treatments.[1]

In the course of other work on the properties of cellulose gels[2] we have had occasion to examine the degree of order of regenerated cellulose as a function of various treatments given after the completion of the regeneration. The effects of drying, steaming, and conditioning in aqueous alkali were followed by three known techniques, viz.: (1) x-ray analysis, (2) density determinations, and (3) D_2O exchange measured by infrared analysis. Further information regarding the inter- and intramolecular bonding in cellulose was obtained by measuring the accessibility to solutions of NaOD in D_2O by infrared analysis. On the basis of these studies some new aspects of the structure and properties of regenerated cellulose are formulated and discussed.

Preparation and Conditioning of Bulk Gels and Thin Films of Regenerated Cellulose

For the preparation of thick sheets of bulk cellulose gel by regeneration from viscose, slow processing is essential in order to avoid irregularities in the sheet. Isotropic gels were therefore prepared as follows. The viscose (textile rayon grade, courtesy of the Skenandoa Rayon Company, Utica, N. Y.) was poured into a mold composed of two unglazed 12 × 12 cm.^{2} porcelain plates separated by a Plexiglas spacer of 3 mm. Prior to assembling, the plates were steeped in 15% ammonium sulfate solution for one day in order to remove all air. The filled mold was then immersed again in the 15% ammonium sulfate coagulating bath, which was agitated by a magnetic stirrer. A heavy weight was placed on the upper plate to keep the mold together. Slow coagulation by diffusion required about 48 hr., after which time the ammonium sulfate solution was replaced by a 10% sulfuric acid solution. After 10 hr. the regeneration was complete. The fresh gel was treated with a 2% sodium sulfide solution to remove residual sulfur, and then washed repeatedly with distilled water. The appearance of the sheet of about 2 mm. thickness was slightly opaque but quite regular over the whole area. Thin films were cast from a layer of viscose on a glass plate in the usual manner, the same sequence of baths as described above being used for the coagulation, regeneration, desulfuration, and washing, respectively.

The fresh gels (marked A in the following) were subsequently treated as follows: (1) sample drying of the thin films in air at 65% R.H. (samples marked B); (2) steaming of the thin films in 100°C. steam for 4 hr. (samples marked C); (3) extraction and conditioning of the bulk gels in aqueous NaOH solutions (samples marked D). In this last case, the first step of the treatment consisted in alternate immersions in 10% NaOH at 3°C. for the day and in distilled water for another day. After each cycle the wet weight was determined. To prevent oxidative

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degradation and formation of carboxyl groups all solutions were deaerated by boiling and saturated with nitrogen before use. The flasks were stoppered and kept in the dark. Figure 1 shows the wet weights as a function of the number of cycles in 10% alkali (Curve I). The initial increase in wet weight is a reproducible effect which probably is related to the dissolution of low molecular weight cellulose.

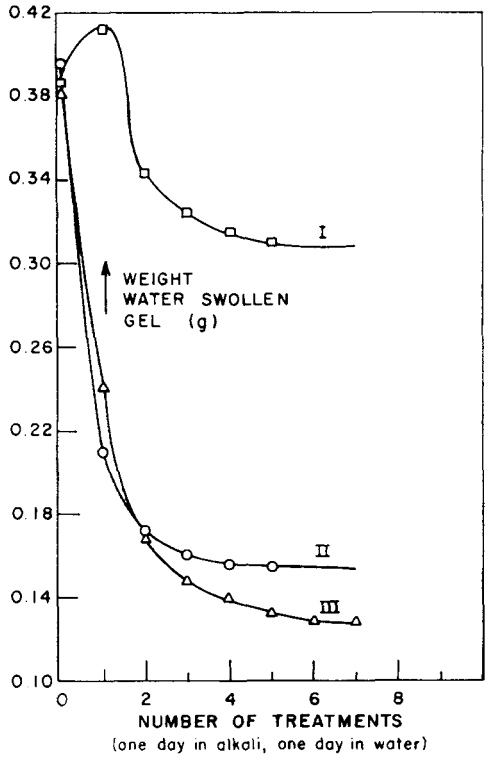

Fig. 1. The extraction-conditioning treatment at 3°C., used in obtaining type D cellulose gels: (I) extraction in 10% NaOH; (II) conditioning in 20% NaOH; (III) combined treatment, 3 days in 10% NaOH and repeatedly in 20% NaOH (type D gels).

With continued treatment in 10% alkali, recrystallization takes place, and the gel becomes more compact. In total, about 36% of the cellulose is lost during this extraction procedure. If one exposes the freshly regenerated cellulose to a similar treatment with 20% alkali, no loss in cellulose content is found, but there is a considerably higher loss in water content (Curve II of Fig. 1). This was ascribed to a penetration of the cellulose crystallites by the alkali which caused an "annealing" to higher crystallinity when subsequently the alkali was washed out with water. The samples marked D were obtained by a combination of the two conditioning procedures, i.e., they were first exposed to three cycles in 10% alkali and then to seven cycles in 20% alkali (Curve III in Fig. 1).

Determination of Inter- and Intramolecular Order

X-Ray Analysis. The x-ray diffraction pattern of regenerated cellulose is usually considered to be due to a superposition of the scattering of the relatively small crystallites (100–300 A. in length and 5–10 glucose units in thickness), and the scattering of an amorphous cellulose matrix in which the crystallites are embedded. The crystallites are, however, not defined, and a gradual transition from crystalline to completely disordered (amorphous) regions is often assumed. The assignment of a certain percentage crystallinity to a cellulose sample then becomes rather arbitrary, and it may, at most, serve as a relative measure of order referred to a certain method of analysis. To determine this rather arbitrary percentage crystallinity from the x-ray pattern, Hermans and Weidinger[3] compare the integrated intensity of the diffraction maxima, d_2, with the intensity of the diffuse scattering as measured by the height $A-$ (Fig. 2). Since the height $A-$ has to be estimated this method may give rise to some uncertainty, especially if the crystalline reflections are not very well resolved. Several other methods for estimating the so-called "x-ray crystallinity" exist,[4,5] but they represent no considerable improvement.

For our work a Norelco recording x-ray diffractometer, equipped with a Geiger counter, was used. The dried gels were disintegrated by grinding very gently to prevent crystallite breakdown and embedded in a thin layer of silicon grease on the flat sample holder, exposing an area of roughly $^3/_4 \times {}^1/_2$ in. to the x-ray beam. The beam was Ni-filtered, and scattering due to residual hard x-rays was eliminated by repeating the run with 0.3 mm. Al foil in front of the counter. This thickness absorbs 98% of the CuKα radiation but transmits 91% of the harder radiation. A third scanning without sample provided the background due to air scattering. Compton and thermal scattering were estimated by comparison with the work of Hermans and Weidinger.[3]

The weight fractions X of crystalline material were calculated from the diffractograms of untreated cellulose (A) and the NaOH-conditioned sample (D) (see Fig. 3), from the relations

$$I_{cr,D}/I_{cr,A} = X_D/X_A$$

$$A_{m,D}/A_{m,A} = (1 - X_D)/(1 - X_A) \qquad (1)$$

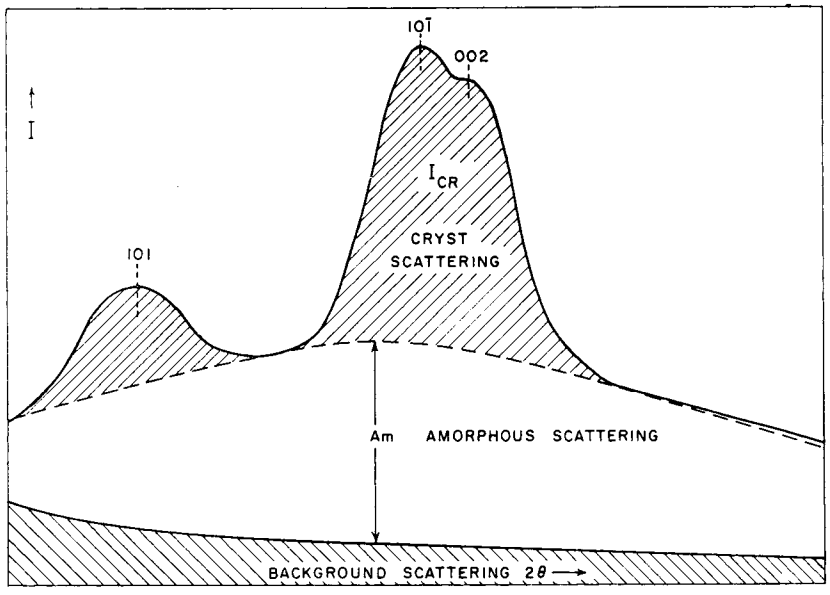

Fig. 2. Schematic x-ray diffractogram of regenerated cellulose.

These relations hold if the irradiated mass of the two samples and the intensity of the x-ray beam have been the same in both experiments. These conditions were fulfilled within a few per cent in our case. This calculation (see Table I) as well as Figure 3 show that the conditioning treatment of sample D has very considerably increased the x-ray crystallinity. The very pronounced increase in resolution and decreased half width of the diffraction peaks of sample D indicates that the crystallites have become better ordered and/or larger than in sample A. The effect is larger than found by other workers[3] due to our extensive conditioning treatment, which seems to be ideal for growing larger and more perfect cellulose crystallites.

Density Determinations. P. H. Hermans, J. J. Hermans, and D. Vermaas[6] have made a detailed study of the densities of various cellulose samples. They have shown that to a first approximation the expected increase in density with increasing crystal-

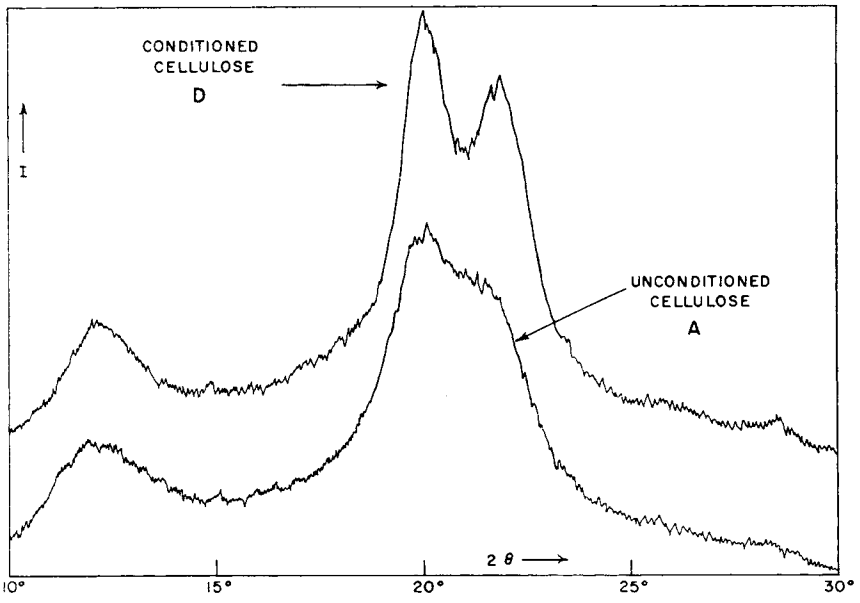

Fig. 3. X-ray diffractogram of type A and type D bulk gels, after drying. Vertically displaced for clarity.

TABLE I
Characteristics of Molecular Order in Regenerated Cellulose

	Type A		Type B, film	Type C, film	Type D, bulk
	Bulk	Film			
X-ray crystallinity (dry), %	35	—	—	—	47
Density (dry), g./ml.	1.517	—	—	—	1.557
Crystallinity from density (dry), %	(35)[b]	—	—	—	74
Infrared accessibility (wet), %	81.5	87	83	80	69
Infrared crystallinity (wet), %[a]	27.5	19	25	30	40

[a] The data obtained refer to wet samples (D_2O exchange), although the subsequent infrared measurements are made on dried samples.

[b] Assumed value according to the x-ray data.

linity occurs. They also showed that a number of organic liquids, including benzene, do not penetrate into dry cellulose and can therefore be used as immersion media for pycnometer determinations of the density of dry cellulose.

Samples of type A and D were dried in a vacuum oven at 115°C. until constant weight was obtained (after 2 days), and their densities measured at 25°C. in dry benzene. The results are given in Table I. The value found for type A sample is slightly less than the value 1.519 reported for isotropic model filaments[6] prepared in much the same way as our bulk gels A. The very high value of 1.557 found in type D samples again reflects the strong effect of the conditioning procedure used in this case. To calculate the percentage crystallinity of type D cellulose from these data, we have to assume that the amorphous and crystalline weight fractions each have a characteristic and constant density ρ and that their contributions to the observed density are additive. In that case we have

$$(1 - X_D)/(1 - X_A) = [\rho_A/(\rho_{cr} - \rho_D X_D)/\rho_D(\rho_{cr} - \rho_A X_A)] \quad (2)$$

where $\rho_{cr} = 1.583$ is the density of crystalline regions in regenerated cellulose, calculated from the unit cell. If one now inserts in eq. (2) the value $X_A = 0.35$ found from the x-ray data, one calculates X_D to be 0.74, which is much higher than the value of 0.47 obtained directly from the x-ray data (see Table I).

This discrepancy might be attributed to the arbitrariness of the x-ray crystallinity method, but it is also possible that the assumption of equal density of the amorphous phase in the two samples is incorrect. Experimental evidence supporting this latter view will be given in the next section. It then follows that density is a poor crystallinity index for regenerated cellulose samples.

D_2O Exchange and Infrared Analysis. A third method which furnishes information regarding the molecular order in cellulose samples is a combination of D_2O exchange and infrared analysis.[1] On immersion of a cellulose sample, all accessible OH groups on the cellulose chains will exchange and become OD groups. The exchange is measured by infrared analysis from the characteristic stretching vibrations at 3100 to 3500 cm.$^{-1}$ for OH and 2300 to 2600 cm.$^{-1}$ for OD (see Fig. 4).

The experimental technique followed by us was adapted from the work of Marrinan and Mann.[7] Cellulose films of about 10 μ thickness were mounted in a remodeled microliquid cell of a Baird Associates double-beam infrared spectrometer equipped with a 60° lithium fluoride prism. Two microscope cover glasses were used as windows (etched to decrease reflection), separated by a Plexiglas spacer, the center part of which was cut out to allow space for the cellulose film. Inlet and outlet tubes to the interior of the cell were provided by small Teflon tubings closely fitting into two small holes drilled sideways in the spacer. The film was clamped at top and bottom by means of a perforated nylon ring fitting at the inside of the cut-out hole in the spacer. Air tight seals were obtained with lead gaskets and some grease. Nitrogen, carefully dried over an array of P_2O_5 tubes was used to flush out excess D_2O and to dry the film. With a hypodermic syringe small amounts of 99.5% D_2O (about 0.3 ml.) were injected into the cell, left there for about 7 min. and flushed out with the dried nitrogen. This process was repeated five times, after which the cell was installed in the spectrometer while the dry nitrogen was passing through. After about 7 min., the transmittance in the neighborhood of 3600 cm.$^{-1}$ no longer decreased, which was taken as an indication of dryness. A difference spectrum was then taken using two etched cover glasses in the reference beam. To obtain thin sections of the never-dried bulk gels A and D, 10 μ slices were cut from strips of gel with a thickness of 1–2 mm.

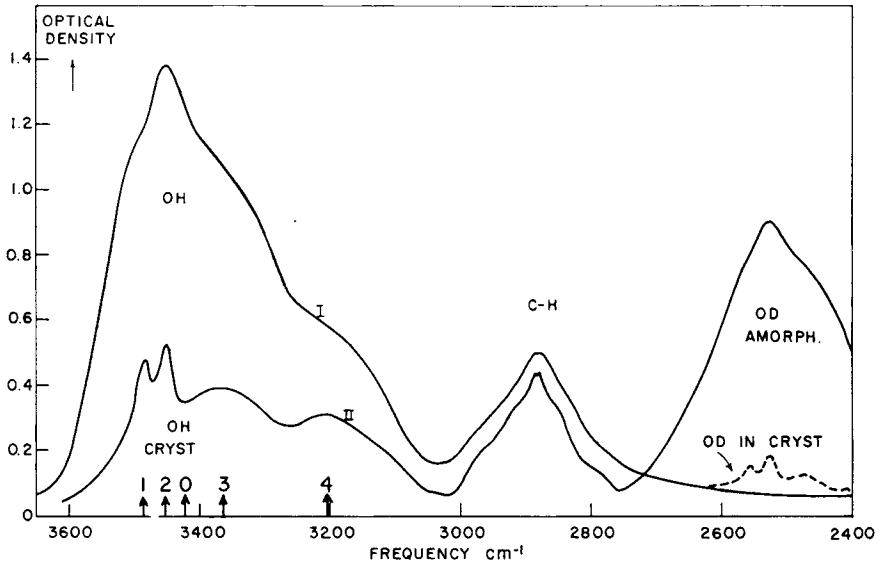

Fig. 4. Infrared spectra of regenerated cellulose (I) and deuterated cellulose (II).

This was accomplished by first gluing the gel onto a piece of wood with a pressure-sensitive cement (Eastman 910 cyanoacrylate adhesive), keeping the gel wet all the time, and slicing with a microtome.

From the spectra the accessibilities to D_2O were calculated from the optical densities, log I_0/I, in the OD band at 2530 cm.$^{-1}$ and in the OH band at 3360 cm.$^{-1}$. This is according to Marrinan and Mann, who found these particular points in the spectrum to be insensitive to orientation effects. From Beer's law one has for the ratio of the optical densities at these points:

$$\frac{\log (I_0/I)_{OD}}{\log (I_0/I)_{OH}} = \frac{K_{OD}X_{OD}}{K_{OH}X_{OH}} \qquad (3)$$

$$X_{OD} + X_{OH} = 1$$

where $K_{OD}/K_{OH} = 1.11$ as determined by the authors quoted[7] by a second independent method. The X_{OD} values obtained on the bulk gels as well as the films are listed in Table I as infrared accessibilities. In Figure 5 the amorphous OD bands of the A and D type samples are plotted after correction for the differences in irradiated mass and accessibility. It appears that the type D sample shows more absorption at the low wave number end of the band. Since an O—D--O bond is stronger,[8] the larger the difference in wave number with the free O--D stretching frequency at 2580 cm.$^{-1}$,[8] it follows that in type D gels there is a higher percentage of stronger O—D--O bonds than in type A gels. We can conclude therefore that the alkali conditioning procedure does not only decrease the D_2O accessibility, due to the higher crystallinity, but also causes a closer packing (shorter O—D--O bonds) in the so-called amorphous regions. Since this closer packing should be paralleled by a density increase

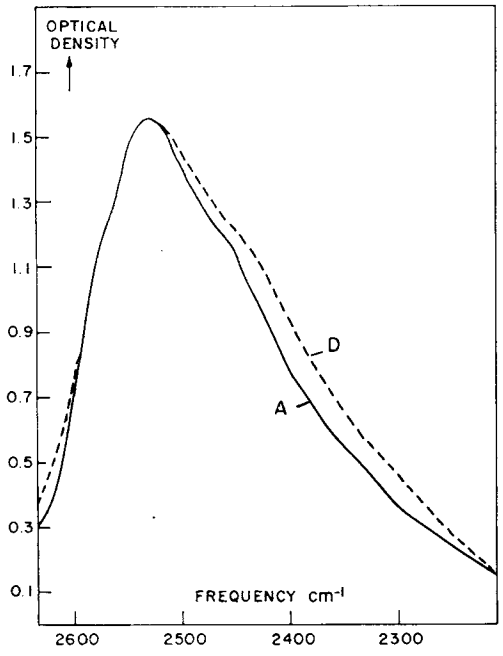

Fig. 5. The O-D--O band in the infrared spectrum of (——) type A gels and (- -) type D gels. Deuteration in wet state; samples dried before taking the spectra.

in the amorphous regions, we find here an explanation for the unexpectedly large crystallinity of type D cellulose as obtained from the density data when we assumed that the amorphous density is the same in the original and conditioned gel samples, respectively.

Mann and Marrinan[1,7] have shown that in liquid-phase deuteration the penetration of D_2O goes beyond that of vapor-phase deuteration. Knowing the ratio of the optical densities of the crystalline hydroxyl groups, they could stop the vapor-phase deuteration as soon as the spectrum of the crystalline hydroxyls was obtained. On subsequently carrying out a liquid phase deuteration they ascribed the increase in accessibility to a penetration of the crystallites. In this way, they found that in type A cellulose about 33% of each crystallite is deuterated, whereas for a cellulose similar to our type D, only 23% of each crystallite is deuterated in the liquid D_2O treatment. With this information one can estimate on IR crystallinity from the accessibility data by using the relation:

$$A = \sigma\alpha + (100 - \alpha) \qquad (4)$$

where A is accessibility, α is per cent infrared crystallinity, and σ is the fraction of the crystallites accessible to the liquid D_2O. Comparing these infrared crystallinities of A and D samples with the x-ray values (see Table I), the infrared values are found to be lower. This is to be expected. since the x-ray method measures the crystallinity of dried cellulose, which is higher than that of wet cellulose, as measured by the infrared method which is based on D_2O accessibility. Independent proof for this is found[7] in rehydrogenating the dried deuterated film (see Fig. 4). A small amount of resistant OD groups remained, apparently trapped in the crystallites, thus showing that the drying of the film has increased the crystallinity. It should be pointed out, however, that the difference may also, at least partly, be caused by the different techniques used in obtaining the crystallinities.

Exchange with NaOD in Heavy Water and Infrared Analysis. The studies of accessibility of cellulose regenerated at thin films were extended to solutions of sodium deuteroxide (NaOD) in heavy water. The solutions were prepared by adding heavy water (99.5%) with a hypodermic syringe to weighed amounts of solid NaOD (supplied by Volk Radiochemical Company, Chicago, Ill.) in rubber-capped weighing bottle. Five NaOD solutions in heavy water were prepared: 4.1, 6.0, 8.2, 12.3, and 16.4 wt.-% NaOD which corresponds to 1.1, 1.7, 2.4, 3.8, and 5.2*M* solutions respectively.

The treatments of the cellulose films were made in the infrared microcell by repeated injections of fresh portions (0.2 ml.) of NaOD solution with a hypodermic syringe. For a 0.5-hr. treatment five injections were made, for a 1-hr. treatment eight injections, and for a 2-hr. treatment, 15 injections. The remaining NaOD washed out with repeated D_2O injections, and the film dried by a gentle stream of dry nitrogen which continued during recording of the infrared spectra. Films with three different pretreatments were studied: (A) never-dried film, (B) film dried in air, and (C) never-dried film steam-treated for 2 hr. The accessibility of these different films were evaluated from the infrared spectra as previously described, and the infrared crystallinity calculated according to Mann and Marrinan.[7] The accessibilities and crystallinities for the different film samples are given in Table II. The steam-conditioned film was treated for deuterium exchange in a never-dried state. The rate of exchange is fast enough to give—within the experimental accuracy of 1%—constant values after 1 hr. treatment. This agrees with D_2O exchange measurements of Frilette, Hanle, and Mark.[9] All data recorded in Table II refer to 1- and 2-hr. treatments.

TABLE II
Accessibility and Crystallinity of Regenerated Cellulose Films in Solutions of NaOD in D_2O Measured by Infrared Analysis

	Film A		Film B		Film C	
NaOD in D_2O, %	Accessibility %	Crystallinity, %	Accessibility, %	Crystallinity, %	Accessibility, %	Crystallinity, %
0	87	19	83	25	80	30
4.1	96.5	5	—	—	—	—
6.0	98	3	—	—	—	—
8.2	98	3	96	6	95.5	7
12.3	—	—	98	3	97.5	4
16.4	100	0	100	0	100	0

It should be noted that 100% accessibility is obtained only in 16.4% NaOD solutions for all three film samples. The infrared spectra contain four well defined absorption bands in the region 3200 to 3500 cm.$^{-1}$ (*1* to *4* in Fig. 4) which are all assigned to OH stretching vibrations of hydrogen-bonded

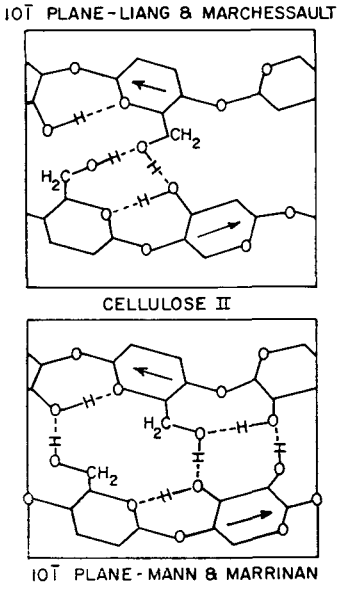

Fig. 6. Proposed intra- and interchain hydrogen bonds the 10$\bar{1}$ planes of cellulose II lattice according to Mann and Marrinan[10] and Liang and Marchessault.[11]

hydroxyl groups.[10,11] Two of these bands (*1* and *2* in Fig. 4) are assigned to OH groups involved in intrachain hydrogen bonds (OH--O_5') and the other two (*3* and *4* in Fig. 4) to interchain hydrogen bonds, as shown in Figure 6. The relative intensities of these four absorption bands were measured in relation to the saddle point between 2 and 3 (marked *0* in Fig. 4). The intensity ratios were found to be a function of the nonaccessible fraction of the cellulose treated with NaOD-solutions, as shown in Figure 7 for never-dried film (Type A). The relative intensities of the first two bands (1 and 2) tend to increase at high accessibilities while those of the other two (3 and 4) change less, if at all. With the proposed assignments of the four absorption bands, this would mean that the intrachain hydrogen-bonded OH-groups are more resistant against deuterium exchange than the interchain bonded groups.

Discussion and Conclusions

It is now well established that the degree of molecular order varies widely among native celluloses of different biological origin.[13] Similar variations for regenerated celluloses, due to methods of preparation and conditioning, are verified in these studies. If the regeneration of cellulose from viscose is made very slowly as in the case of bulk gels (A in Table I), its infrared crystallinity (27.5%) is considerably higher than that of a thin film (A, 19%) regenerated instantaneously by immersion in

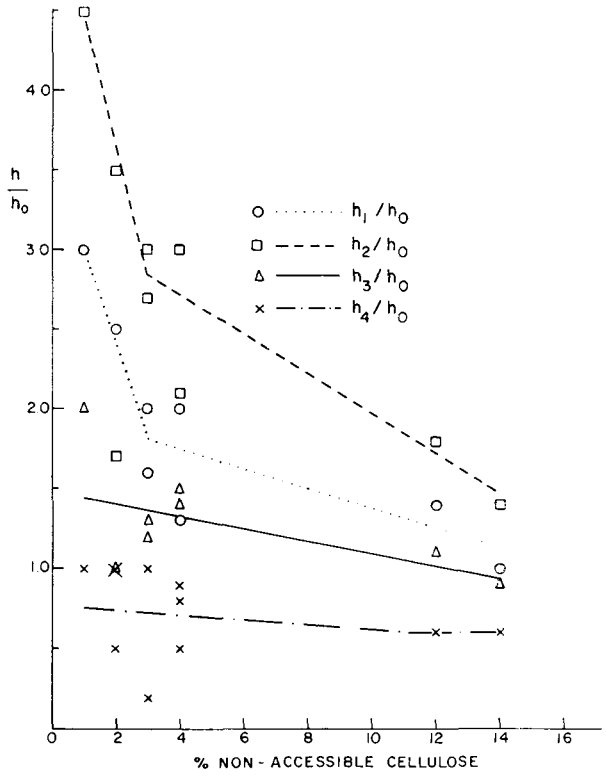

Fig. 7. Intensity ratios h/h_0 of infrared absorption bands for OH stretching vibrations in regenerated cellulose at different accessibilities (cf. Fig. 4 and text).

an acid bath. By repeated swelling with aqueous alkali and deswelling in water of the bulk gel (D in Table I) its crystallinity is further increased to 47 and 40%, as measured by x-ray diffraction and D_2O exchange + infrared analysis, respectively. A smaller stepwise increase in infrared crystallinity for regenerated film (19% for A in Table I) is caused by drying (25% for B) and steam treatment (30% for C).

The crystallinity value (74%) derived from density for dried bulk gel (D in Table I) after alkali conditioning lies far above the x-ray and infrared values (47 and 40%). The values of 74% was calculated with the assumption that the density of the amorphous cellulose was unaffected by the alkali conditioning. The infrared spectra for the deuterated gels before and after conditioning (Fig. 5) have shown that this is probably not true. The OD absorption band for amorphous cellulose after alkali conditioning is shifted by about $\Delta\nu = 20$ cm.$^{-1}$ towards lower wave numbers indicating shorter O—D--O bonds (R). Using known relations of $\Delta\nu$ to R from hydrogen-bonded solids.[14] we find tentatively that the $\Delta\nu$ values measured in Figure 5 would mean a shortening of the O—D--O

bonds by 0.98% at $R > 2.8$ A. and by 0.23% at $R > 2.8$ A. Assuming that the amorphous cellulose is hydrogen-bonded in three dimensions, we find that the measured shortening of the hydrogen bonds would mean a volume contraction by 0.7 to 2.9%. With corrections of this magnitude for the density of the amorphous cellulose, we can explain most of the discrepancy in the crystallinity values derived from density measurements (Table I). Based on these data, we are justified to conclude that the intermolecular order in both amorphous and crystalline regions of a cellulose sample can be varied with the regeneration process and the after-treatment applied. One method, e.g., bulk density, is therefore not sufficient for an estimate of the per cent crystallinity in a cellulose sample. The accessibility data (cf. Fig. 6 and Table II) combined with the intensity ratios for the four infrared absorption bands as a function of NaOD concentration in D_2O (Fig. 7), have tentatively been interpreted to mean that the three types of OH-groups along the cellulose chains have different accessibility: the two absorption bands (*1* and *2* in Fig. 4) assigned to hydroxyl groups on carbon atom No. 3 (OH_3), intrachain hydrogen-bonded to the adjacent ring oxygen (O'_5), remain relatively stronger at higher NaOD concentrations than the other two (*3* and *4* in Fig. 4) which are assigned to interchain hydrogen-bonded OH-groups (cf. Figs. 6 and 7). If it is the hydrogen bonding which causes the higher resistance to deuterium exchange, we may conclude that the intramolecular order is retained longer with progressive swelling than the intermolecular order. This is not expected, because the two intrachain hydrogen bonds are weaker than the two interchain bonds, to judge from their location in the spectrum (see Fig. 4). It is conceivable, however, that the intrachain hydrogen bonds in this reaction are more resistant than expected from their strength, because breaking of one hydrogen bond would require the disordering of adjacent chain units as well, i.e., a cooperative effect within chain segments. The observed effects are well in line with the lower reaction rate for OH_3 groups measured in etherification reactions of alkali cellulose.[15] Steric effects on the accessibility of the OH-groups on carbon atom 3 can also affect their reaction rates, both in etherification reactions and deuterium exchange processes.

It has been stated in the literature that regenerated cellulose is completely accessible to reactions already at very low concentrations (about 1%) of NaOH in aqueous solution.[12] We have, however, measured a gradual increase in accessibility with increasing NaOD concentration from 4 to 12% with complete deuterium exchange at 16% NaOD (cf. Table II).

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Synopsis

Cellulose was regenerated from technical viscose as bulk gels and thin films (never dried) and then conditioned by repeated swelling with sodium hydroxide solutions and steam treatments. These extraction and conditioning treatments of the gels increased the crystallinity and decreased the accessibility to water as measured by x-ray, infrared, and density measurements. The density of the gels increased more during these treatments than one would expect from the increase in crystallinity as measured from x-ray diffraction. Supported by the combined density, infrared, and D_2O-exchange data, this was taken as evidence that the conditioning also gives a closer packing or an increased order in the so-called amorphous regions. Both steam-conditioning and drying decreased the accessibility of thin films as measured by a combination of infrared analysis and swelling with sodium deuteroxide solutions in heavy water (NaOD in D_2O). Reports in the literature that regenerated cellulose is completely accessible in dilute aqueous alkali solutions (about 1%) have not been verified. The intensity ratios of the different infrared absorption bands were measured during the gradual swelling and exchange with NaOD of increasing concentrations from 1 to 16% in D_2O.

The few data available now seem to indicate that hydroxyl groups assigned to intrachain hydrogen bonds in crystalline regions are more resistant to deuterium exchange than hydroxyl groups assigned to interchain hydrogen bonds. Based on these studies the concepts of crystallinity, order, and accessibility to water and swelling agents for regenerated cellulose are discussed.

Résumé

On a régénéré de la cellulose à partir de viscose technique sous forme de gels compacts et de minces films (jamais sèchés) et amenés aux conditions requises par gonflement répété à l'aide des solutions de soude et par traitements à la vapeur. Ces extraction et conditionnement des gels augmentent la cristallinité et diminuent l'accès à l'eau comme l'indiquent les mesures aux rayons-X, à l'infra-rouge et de densité. La densité de ces gels augmente pendant ces traitements de manière plus importante qeu prévu à partir de l'augmentation de cristallinité mesurée par diffraction aux rayons-X. En tenant compte des données obtenues par la densité, l'infra-rouge et les échanges de D_2O, on peut considérer comme évident que le conditionnement produit également un tassement plus serré ou un ordre supérieur dans les régions dites amorphes. Le conditionnement à la vapeur aussi bien que le sèchage diminue l'accessibilité des films fins comme on a pu le mesurer en combinant l'analyse infra-rouge et le gonflement par des solutions de deutéroxyde de soude dans l'eau lourde (NaOD dans D_2O). Les données de la littérature n'ont pas été vérifiées en ce qui concerne l'accessibilité totale de la cellulose régénérée dans des solutions aqueuses de soude (environ 1%). Les rapports d'intensité des différentes bandes d'absorption infra-rouge ont été mesurés pendant le gonflement graduel et l'échange de NaOD en concentrations croissantes de 1 à 16% dans le D_2O. Les quelques données disponibles à l'heure actuelle semblent indiquer que les groupes hydroxyles issus des ponts-hydrogène entre les chaîne dans les régions cristallines sont plus résistants à l'échange avec le deutérium que les groupes hydroxyles issus des ponts d'hydrogène entre les chaînl- En se basant sur ces études on discute les concepts de cristae. linité, d'arrangement et d'accessibilité à l'eau et des agents de gonflement pour la cellulose régénérée.

Zusammenfassung

Cellulose wurde aus technischer Viskose als Gel und als dünner Film (ohne Trocknen) regeneriert und dann durch wiederholtes Quellen in Natriumhydroxydlösung und Dampfbehandlung konditioniert. Diese Extraktion und Konditionierung der Gele erhöhte die Kristallinität und setzte die Angreifbarkeit durch Wasser herab, wie Röntgen-, Infrarot- und Dichtemessungen zeigten. Die Dichte der Gele nahm durch diese Behandlung stärker zu als nach der durch Röntgenbeugung bestimmten Kristallinitätszunahme zu erwarten gewesen wäre. Gestützt auf die Gesamtheit der Dichte-, Infrarot- und D_2O-Austauschergebnisse wurde der Schluss gezogen, dass die Konditionierung auch eine dichtere Packung oder bessere Ordnung der sogenannten amorphen Bereiche liefert. Sowohl Dampfkonditionierung als auch Trocknung setzte die durch eine Kombination von Infrarotanalyse und Quellung in Natriumdeuteroxydlösungen in schwerem Wasser (NaOD in D_2O) gemessene Angreifbarkeit dünner Filme herab. Literaturangaben, dass verdünntes, wässriges Alkali (etwa 1%) regenerierte Cellulose vollständig durchdringt, konnten nicht bestätigt werden. Das Intensitätsverhältnis der verschiedenen Infrarotabsorptionsbanden wurde während der fortschreitenden Quellung und des Austausches mit NaOD bei Konzentrationen von 1 bis 16% in D_2O gemessen. Die wenigen bis jetzt erhaltenen Ergebnisse lassen erkennen, dass die den Wasserstoffbrücken innerhalb einer Kette in kirstallinen Bereichen zugeordneten Hydroxylgruppen gegen Deuteriumaustausch beständiger sind als die den Wasserstoffbindungen zwischen den Ketten zugeordneten Hydroxylgruppen. Auf Grundlage dieser Untersuchungen werden die Annahmen über Kristallinität, Ordnung und Angreifbarkeit durch Wasser und Quellungsmittel für regenerierte Cellulose diskutiert.

End of Symposium