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Crystalline structure of cellulose

Eero Kontturi
Department of Bioproducts and Biosystems
School of Chemical Engineering
Aalto University

CHEM-E2140

Assignment

Answer the questions in front of you in “Before the lecture” column

Learning outcome

After this lecture, you will be able to :

- Distinguish molecular vs. supramolecular structure with cellulose
- Recognize the crystalline polymorphs of cellulose
- Explain why the polymorphic structure matters

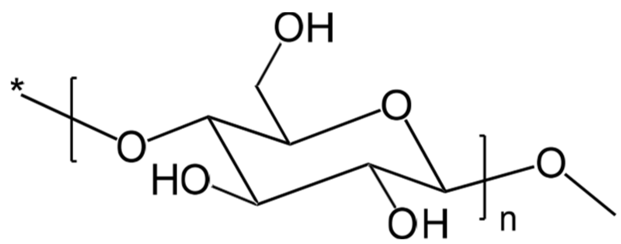
Contents

(1) Cellulose structure: molecular vs. supramolecular
(2) Crystalline forms of cellulose:
 - Cellulose I_{α} and I_{β}
 - Cellulose II
 - Cellulose III_{I} and III_{II}

(3) Implications of the crystalline structure

Recap: cellulose

- Cellulose is a polysaccharide biosynthesized in nature
- Main structural (load bearing) component of all plants
- The most abundant biopolymer on earth (10^{12} tons produced per year)



- Poly (1,4-β-D-glucopyranose)
- Linear homopolymer
- Forms semi-crystalline microfibrils
- Recalcitrant
- Insoluble

Supramolecular structure of cellulose

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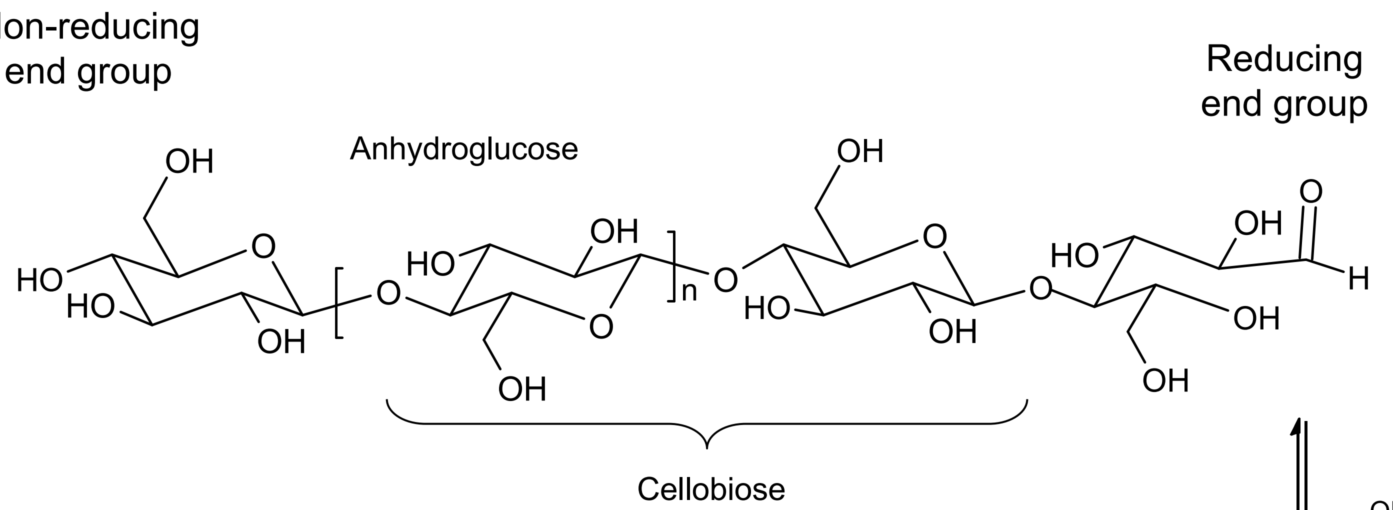
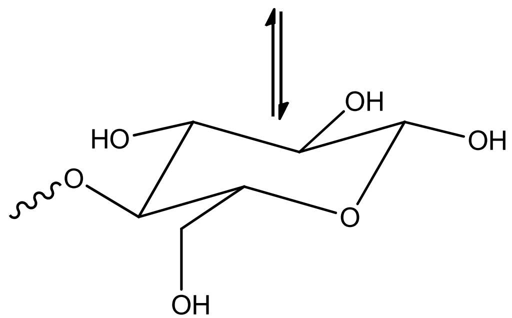
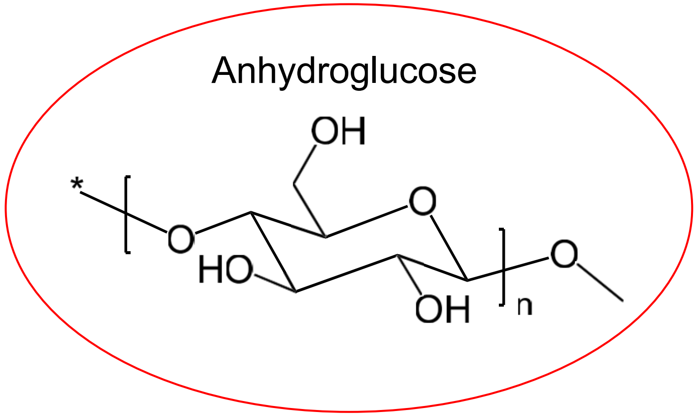
Molecular structure of cellulose

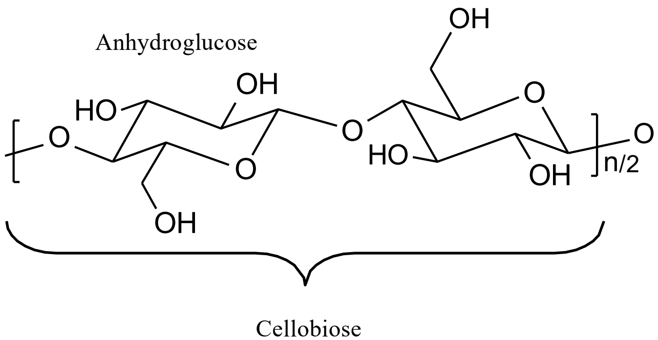




- Reducing end group is in equilibrium with a cyclic hemiacetal

Note on the molecular structure





- Often cellobiose is presented as the repeating unit (n/2) of cellulose
- In a cellulose crystal, the adjacent anhydroglucose units are twisted 180º with respect to each other

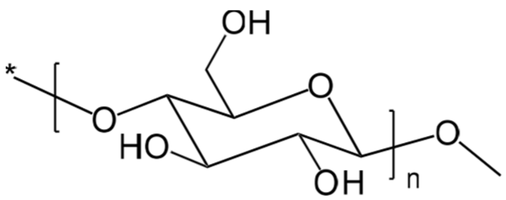
→ Therefore, cellobiose drawn this way is often presented as the repeating unit

- However, cellulose does not need to be inside a crystal (it can be, e.g., in solution)

→ **Anhydroglucose is the actual repeating unit (monomer) of cellulose**

Molecular *vs.* supramolecular structure

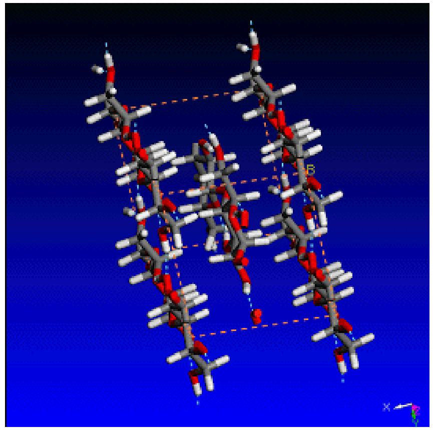
Molecular structure



- $(1\rightarrow4)$-β-D-glucopyranose
- high native DP (~5000-15000)

Structure revealed:
Freudenberg
Liebigs Ann. Chem. **1928**, *461*, 130.
Haworth *Nature* **1930**, *126*, 438.

Supramolecular structure



- individual cellulose chains linked together by intermolecular bonding

Structure revealed (cellulose I_{α} ja I_{β}):
Nishiyama et al.
J. Am. Chem. Soc. **2002**, *124*, 9074.
J. Am. Chem. Soc. **2003**, *125*, 14300.

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https://presemo.aalto.fi/e2140structure

Then answer the relevant question

Crystalline forms (polymorphs) of cellulose

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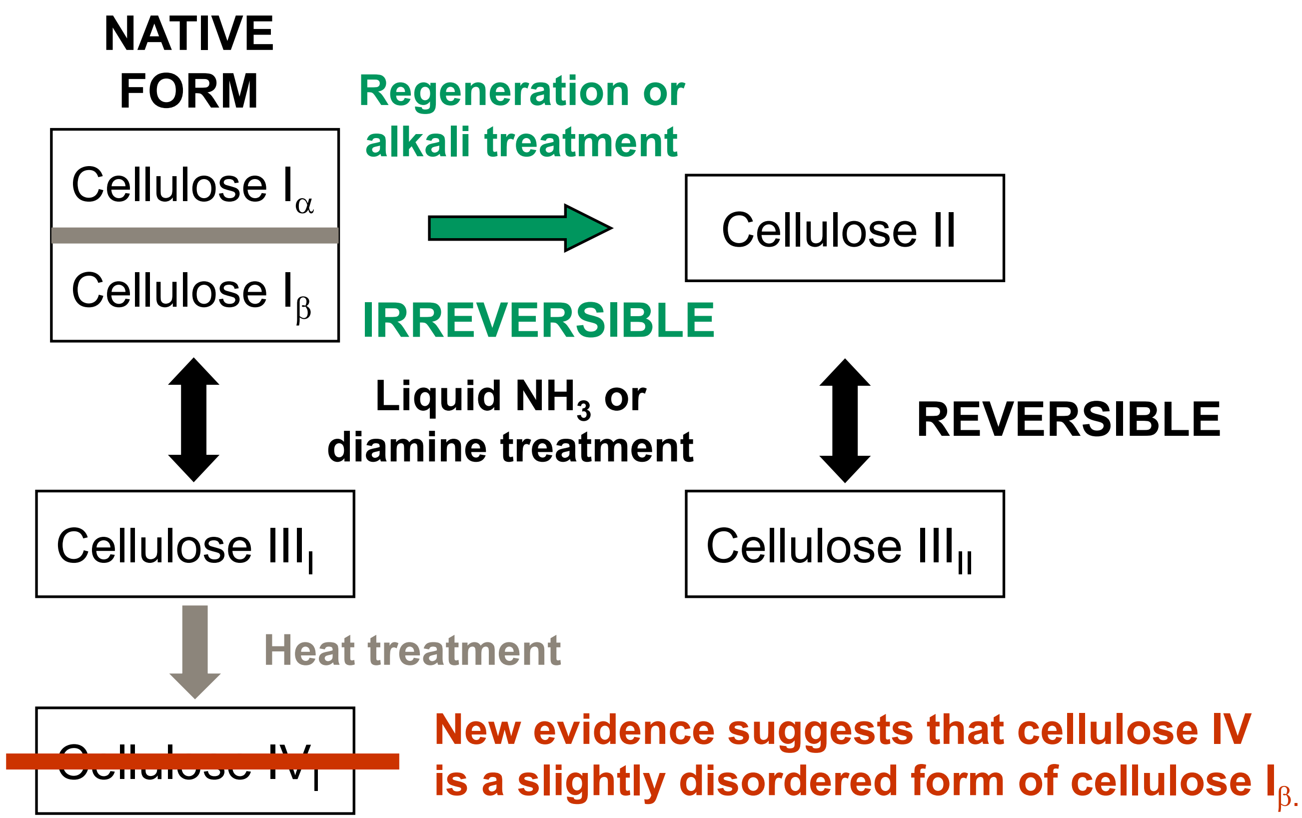
Cellulose polymorphs



Methods for measuring crystalline form and crystallinity of cellulose

- X-ray diffraction
- Solid state Nuclear Magnetic Resonance (NMR) spectroscopy
  specifically: cross-polarization magic angle spinning (CP-MAS) ^{13}C NMR

Most applied methods, generally regarded as the most reliable

- Electron diffraction
- Neutron scattering
- IR spectroscopy
- Raman spectroscopy

Native cellulose:
cellulose I_α
cellulose I_β

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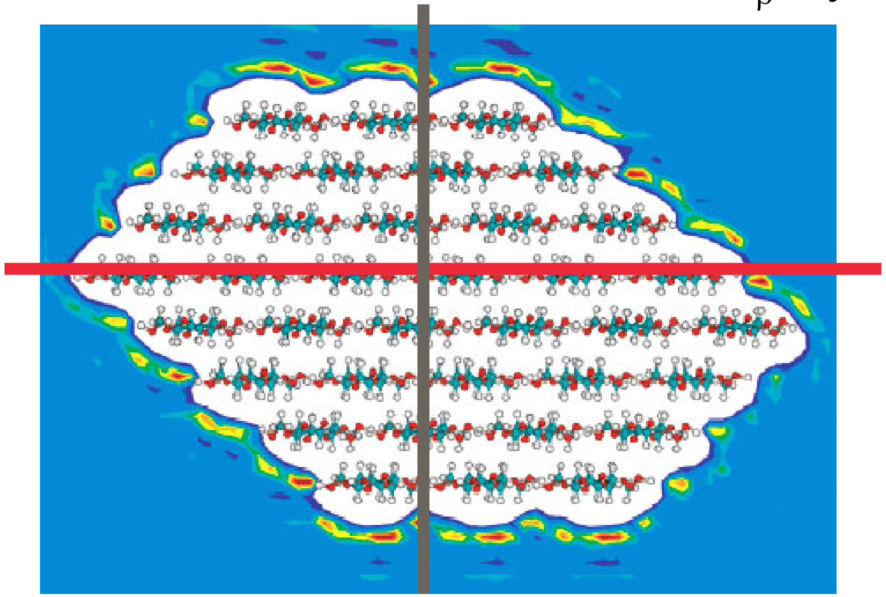
Cellulose I crystal

Cellulose chains form sheets which are connected with each other

Radial cross section of a cellulose I_{β} crystallite:



6 × 6 model (not confirmed!)
→ 36 cellulose chains

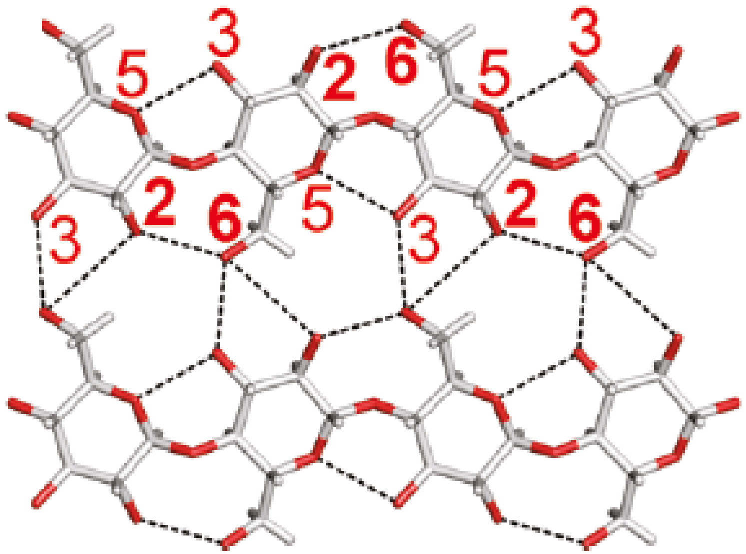
Within the sheets:
hydrogen bonds

Between the sheets:
van der Waals bonds

Cross sectional image taken from: Gross and Chu *J. Phys. Chem. B* **2010**, *114*, 13333.

Cellulose I: hydrogen bonding

Sheet in cellulose I



Main hydrogen bonds:

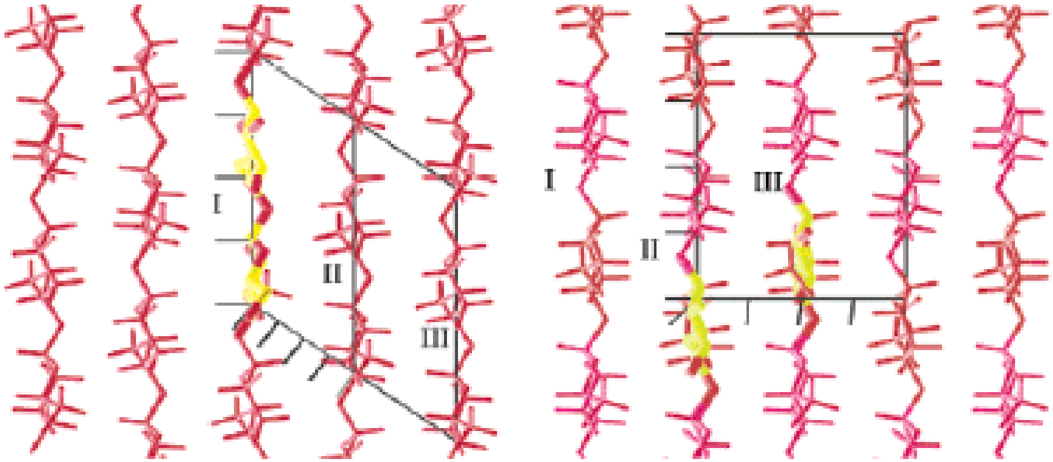
- 3→5 intramolecular bond lends rigidity to the cellulose chain
- 2→6 intramolecular bond
- 3→6 intermolecular bond keeps the sheets together

NOTE: Cellulose chains in cellulose I crystals run parallel

Distinction between I_α and I_β

Two forms of native crystalline cellulose exist: I_α and I_β.

Atalla and Vanderhart *Science* **1984**, *223*, 283.



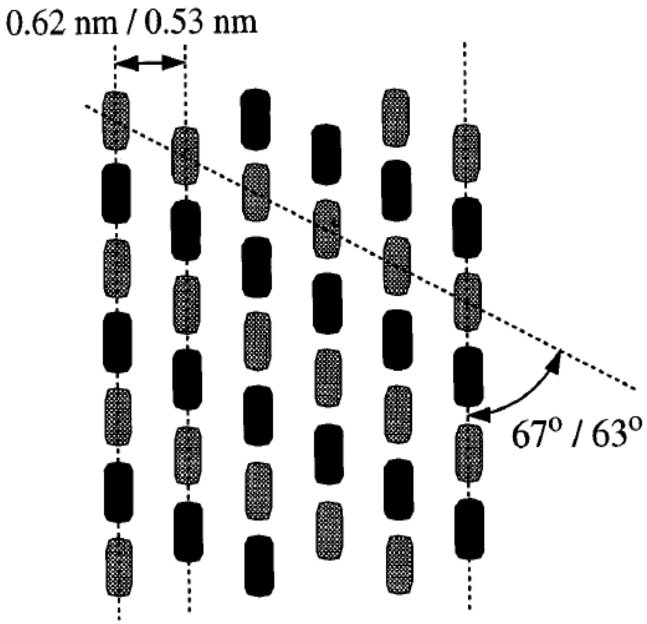
I_α: one chain triclinic
- dominant in, e.g., bacterial cellulose and algae

I_β: two chain monoclinic
- dominant in higher plants (e.g. wood, cotton)

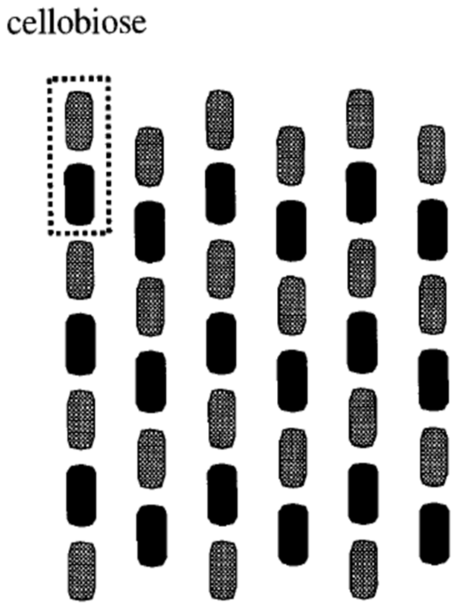
Crystallographic details in 1Å resolution (cellulose I_α ja I_β):

Nishiyama et al.
J. Am. Chem. Soc. **2002**, *124*, 9074.
J. Am. Chem. Soc. **2003**, *125*, 14300.

Distinction between I_α and I_β



triclinic
Iα



monoclinic
Iβ

Baker et al. *J. Struct. Biol.* **1997**, *119*, 129.

Distinction between I_α and I_β

- Cellulose I_β is the predominant form in higher plants (wood, cotton etc.) and tunicate (cellulose in tunicate animals)
- Cellulose I_α is the predominant form in algae and in cellulose emitted by microbes (bacterial cellulose)

NOTE: Cellulose I_α and cellulose I_β ALWAYS coexists with each other in nature, usually within the same microfibril.

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Then answer the relevant question

Regenerated cellulose: cellulose II

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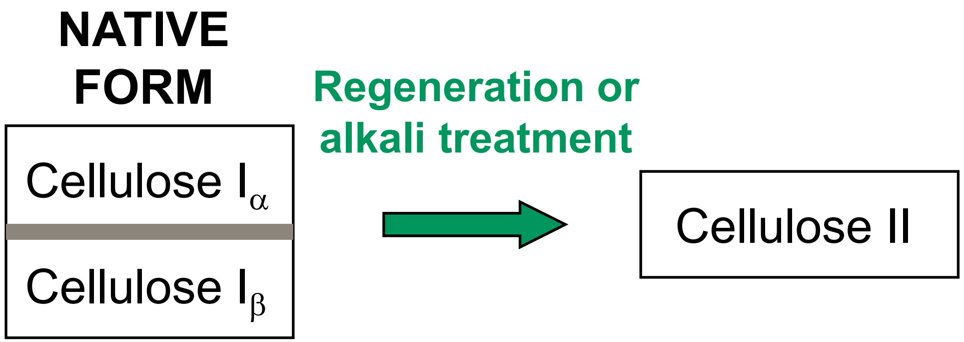
Emergence of cellulose II



“Man-made” form of cellulose

Preparation by: - dissolving the cellulose / regeneration

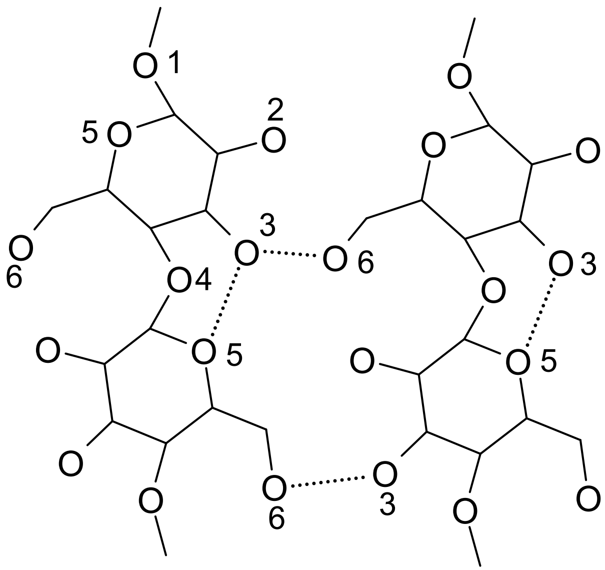
- swelling in concentrated alkali (e.g. > 10% NaOH)

Silk-like texture of cellulose II materials means that they are widely applied in textile industry.

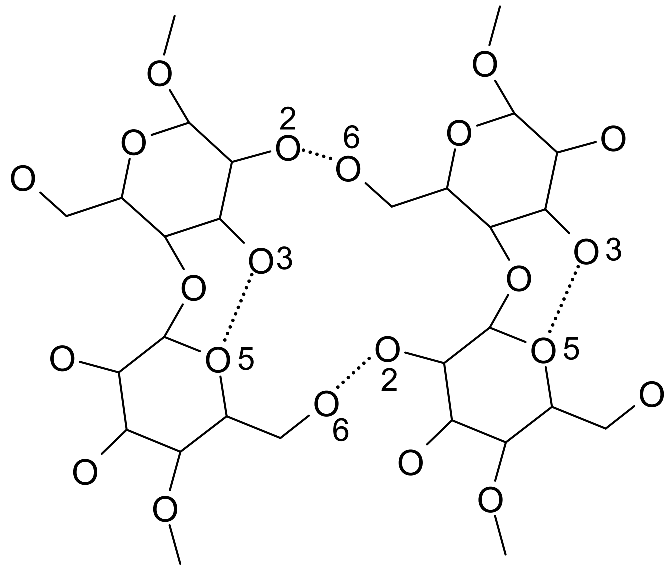
Distinction between cellulose I and II

Note: hydrogens have been omitted to enhance clarity

Cellulose I



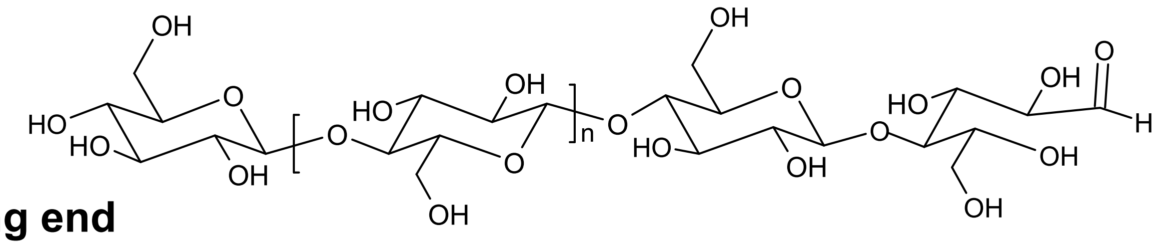
Cellulose II

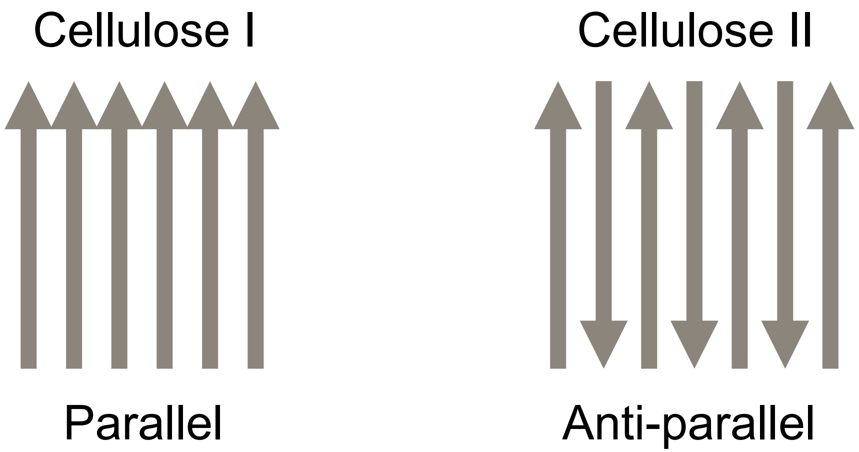


Hydrogen bonding patterns within the sheets are different.

Distinction between cellulose I and II

Cellulose chain has a direction:

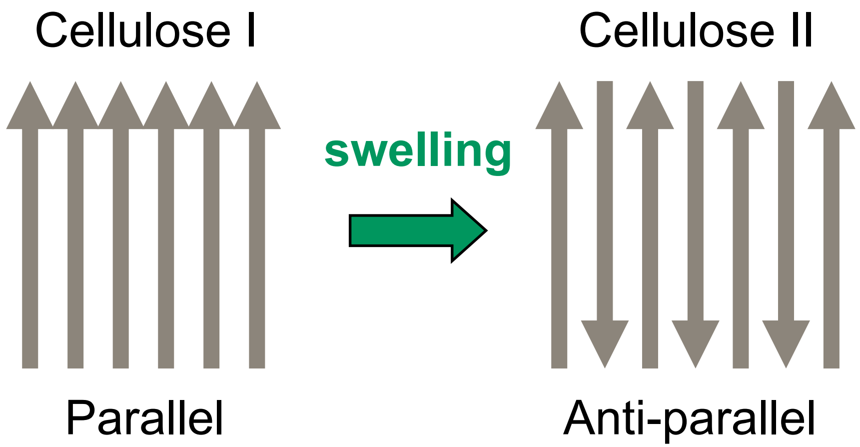




Dilemma of anti-parallel cellulose II

Cellulose II preparation by: (a) dissolving the cellulose / regeneration
(b) **swelling in concentrated alkali**

How is it possible for the cellulose chains to transform from parallel to anti-parallel without dissolution?

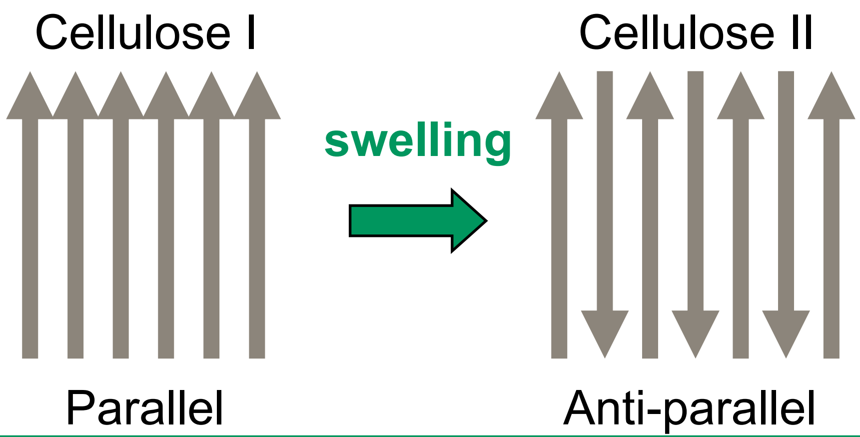


Dilemma of anti-parallel cellulose II

- Cellulose crystals in parallel microfibrils run in opposite direction
- NaOH swells the crystals
- Anti-parallel arrangement is thermodynamically more favourable than parallel arrangement

→ **HYPOTHESIS:**

Cellulose chains in parallel microfibrils intermingle and form new antiparallel crystals



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Then answer the relevant question

Cellulose III

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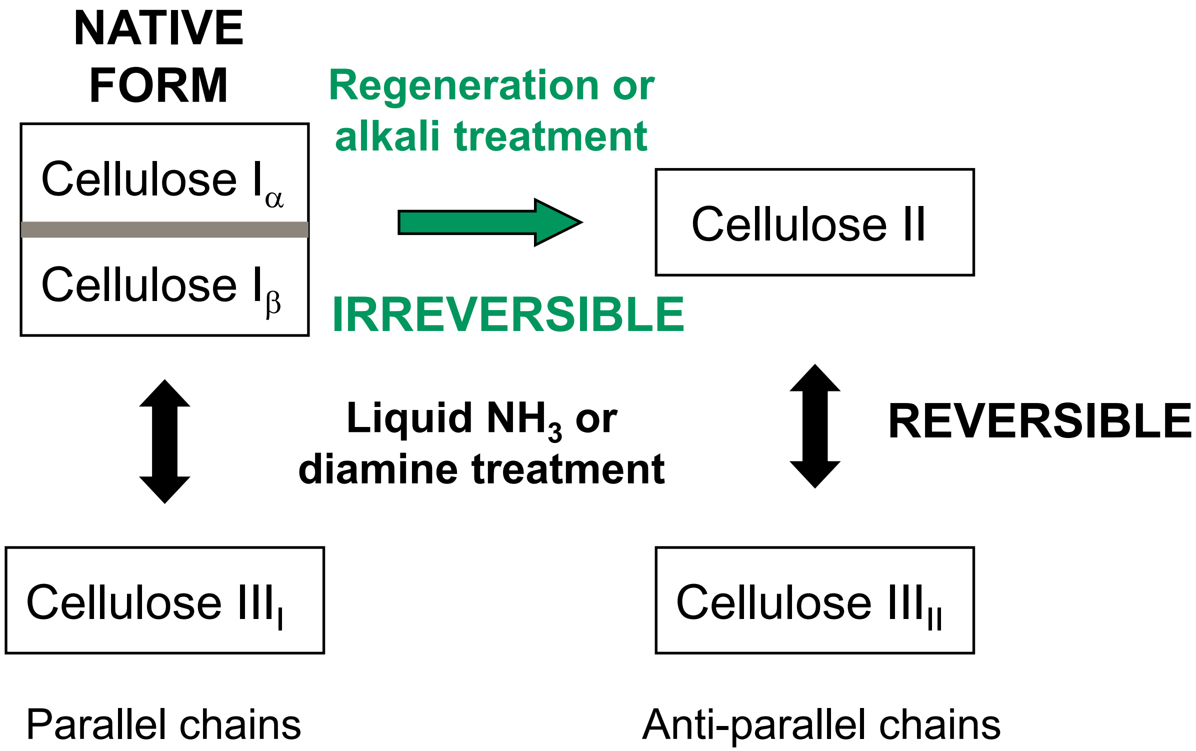
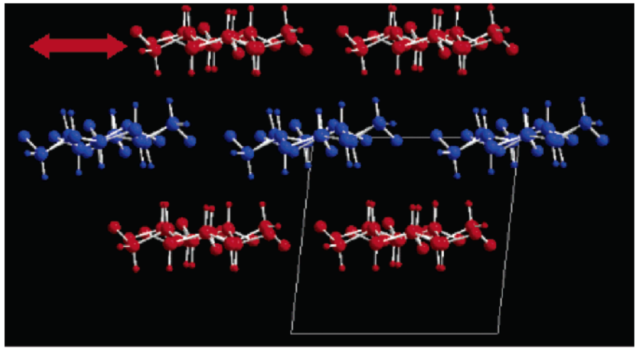
Conversion to cellulose III



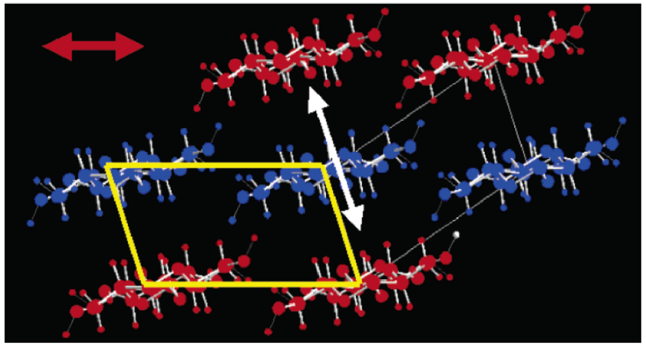
Hess and Trogus *Ber.* **1935**, *B68*, 1986–1988.

Conversion: cellulose $I_\beta \rightarrow$ cellulose III

Cellulose I_β

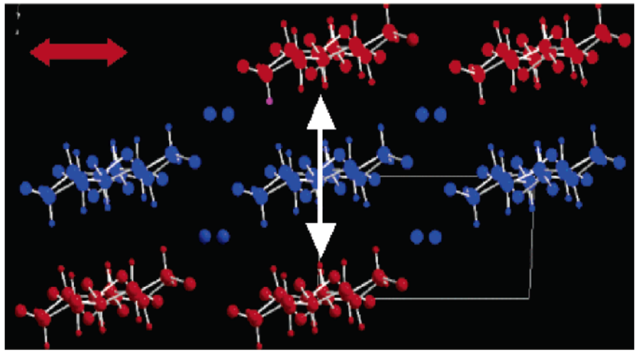


Cellulose III_I



NH_3 (l)

Ammonia-cellulose I complex

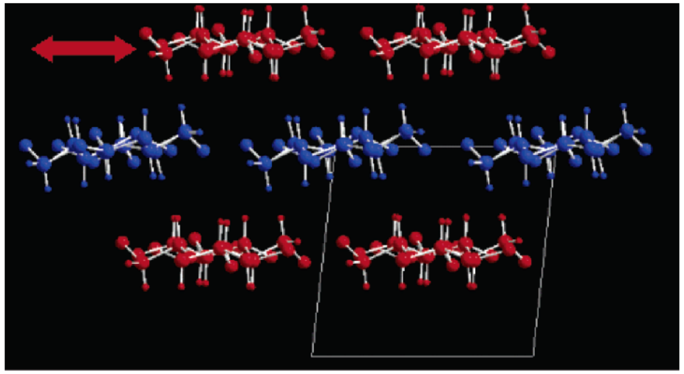


NH_3 removal
(e.g. evaporation)

Wada et al. *Macromolecules* **2006**, *39*, 2947.

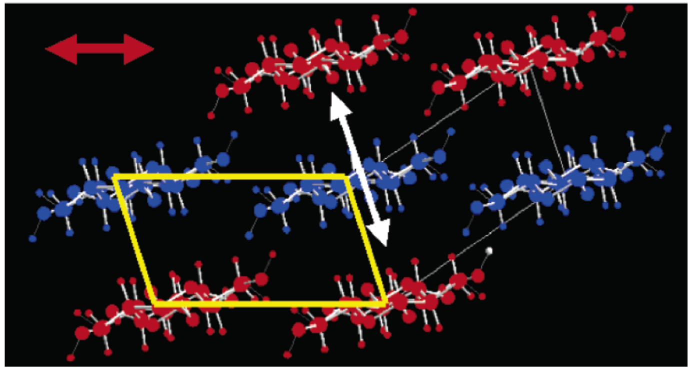
Distinction: cellulose I and cellulose III

Cellulose I_β



- Hydrogen bonds only between cellulose molecules within the sheets
- van der Waals bonds between the sheets

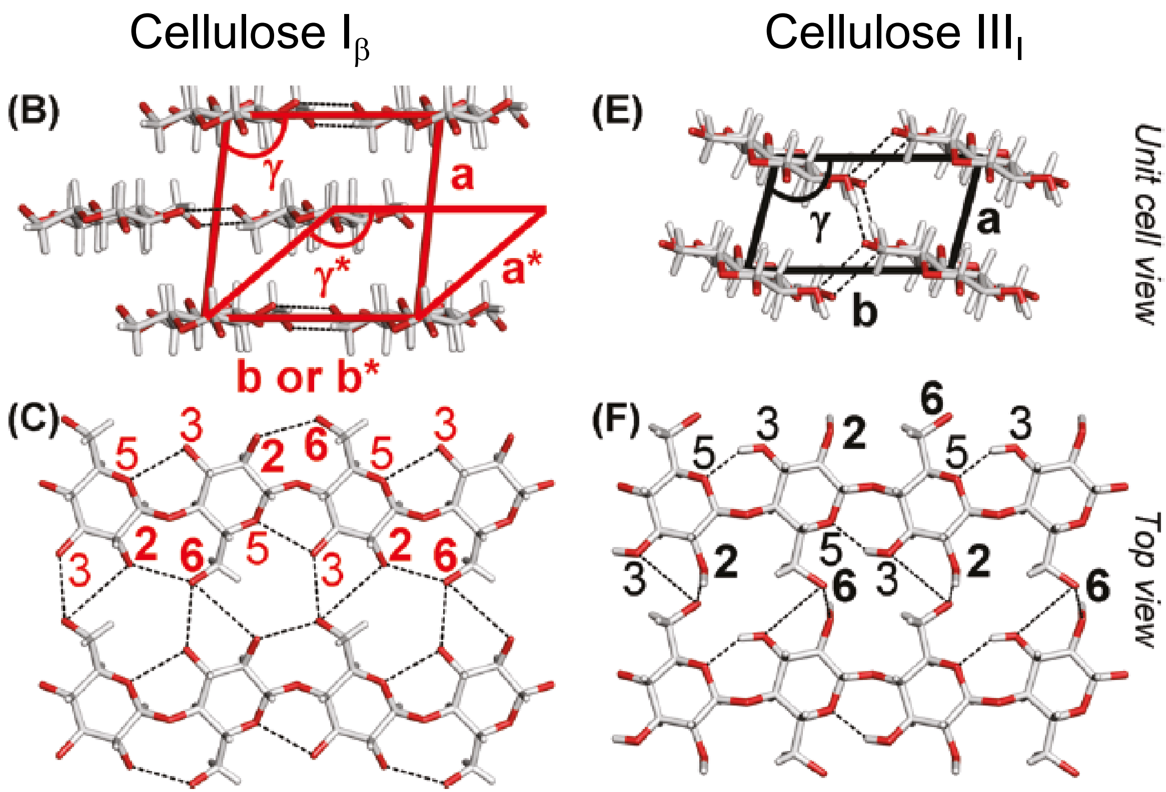
Cellulose III_I



- Hydrogen bonding also between the sheets

Wada et al. *Macromolecules* **2006**, *39*, 2947.

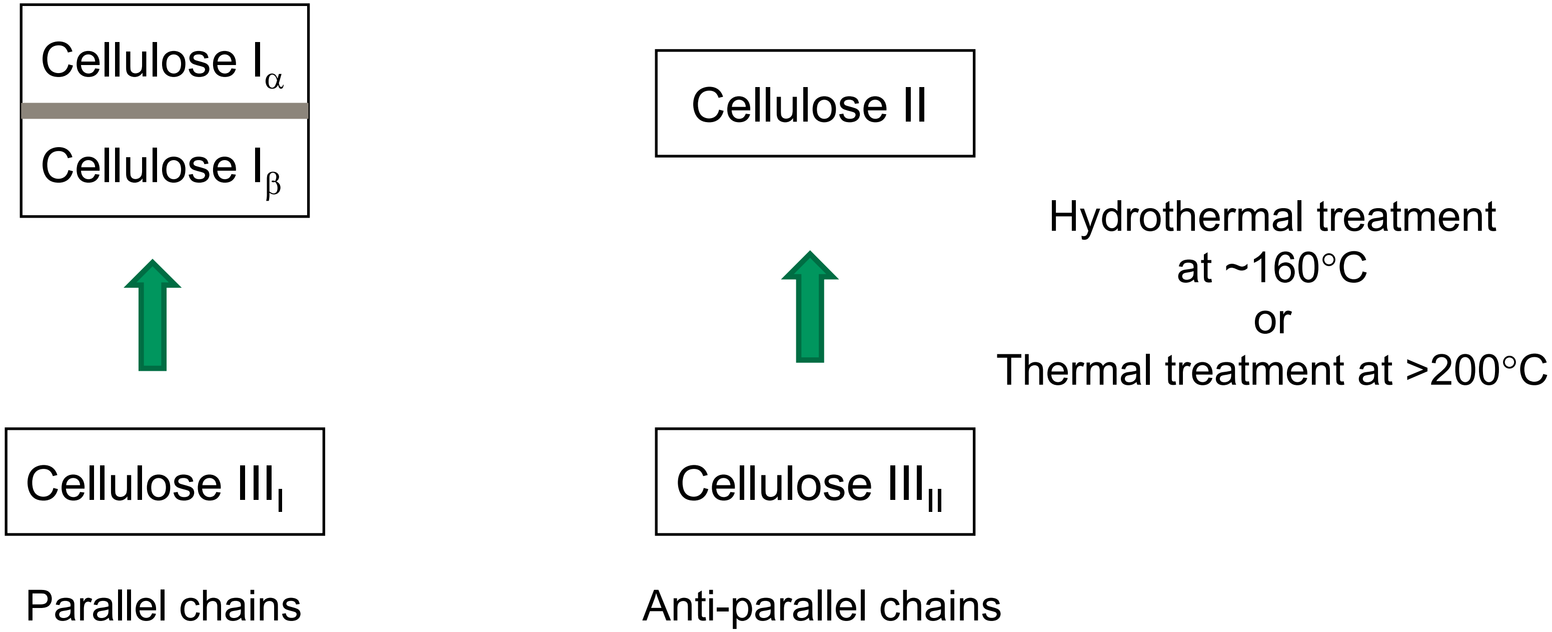
Distinction: cellulose I and cellulose III



Chundawat et al. *J. Am. Chem. Soc.* **2011**, *133*, 11163.

Reversibility of cellulose III conversion

- Cellulose III can be converted back to its starting material



Chanzy et al. *Carbohydr. Res.* **1987**, *160*, 1.
Wada et al. *Macromolecules* **2001**, *34*, 3271.

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Then answer the relevant question

Cellulose IV

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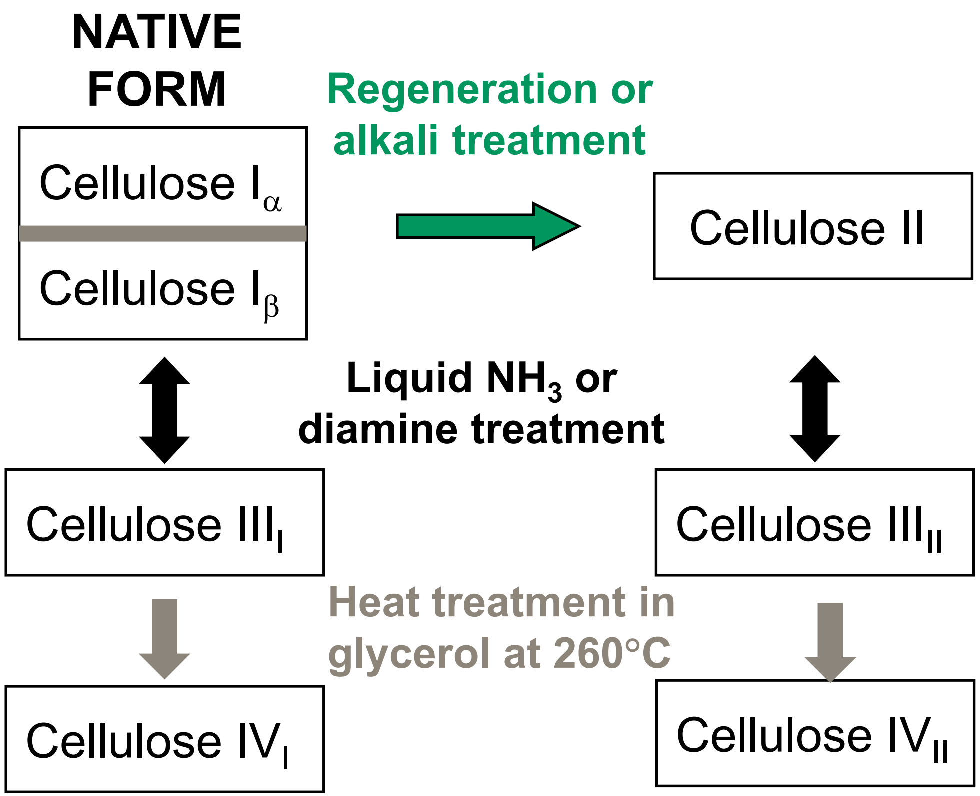
Conversion: cellulose III → cellulose IV



Hutino and Sakurada *Naturwissenschaften* **1940**, *28*, 577.

Conversion: cellulose III → cellulose IV – credible evidence

Recent evidence from FT-IR spectroscopy, solid state NMR spectroscopy, X-ray diffraction and diffraction simulations:

Wada et al. *Biomacromolecules* **2004**, *5*, 1385.
Newman *Cellulose* **2008**, *15*, 769.

- Credible proof that cellulose IV_I is not a genuine allomorph
- Cellulose IV_I is seen as a distorted form of cellulose I_β

Some implications of the crystalline forms of cellulose

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Elastic modulus

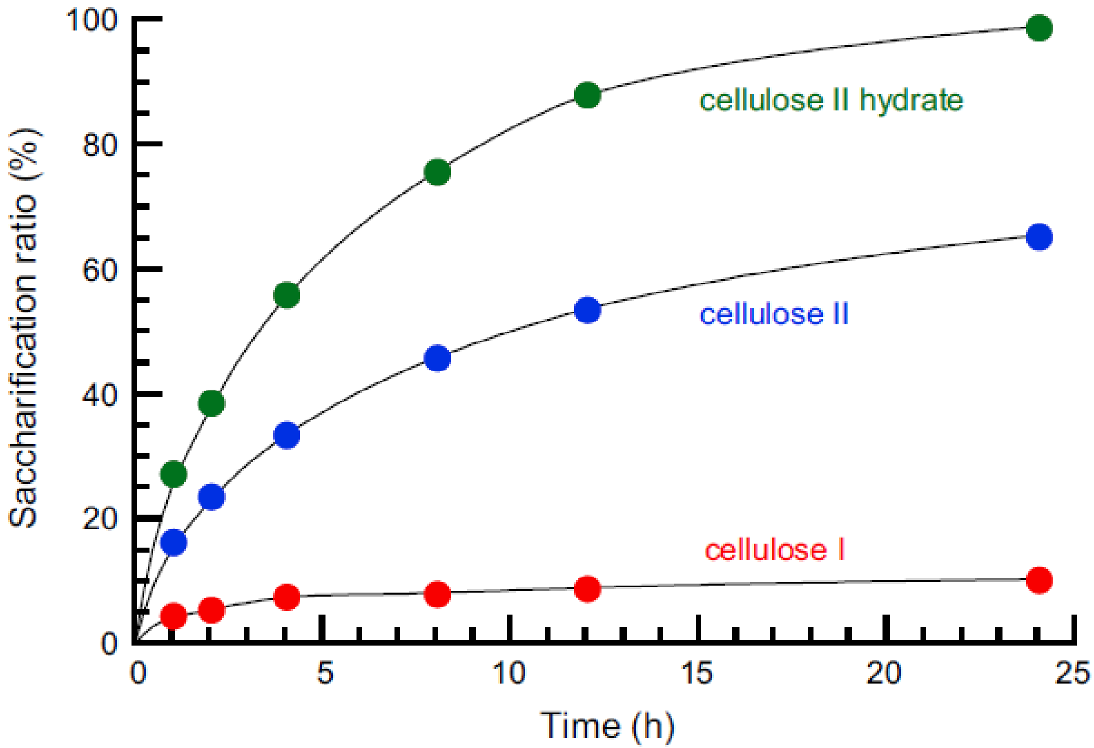
Form	Elastic modulus
Cellulose I	138 GPa
Cellulose II	88 GPa
Cellulose III_I	87 GPa
Cellulose III_{II}	58 GPa

The values are estimates for pure crystalline forms (based on XRD data)

→ Native cellulose I is decidedly stiffer and stronger than the "man-made" forms

Nishino et al. *J. Polym. Sci. B* **1995**, *33*, 1647.

Hydrolytic degradation: cellulose I *vs.* II



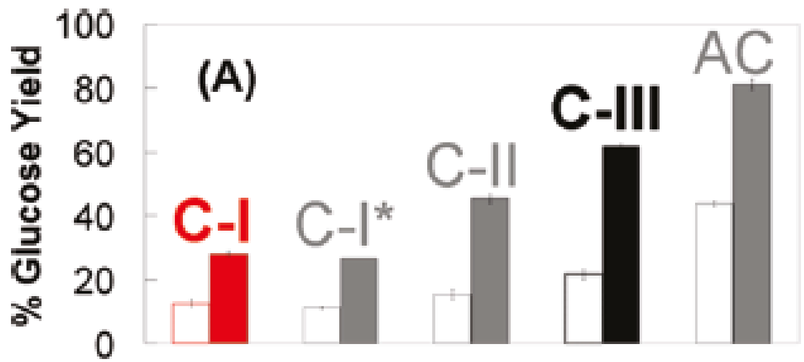
Hydrolysis of cellulose II is much faster and proceeds to a greater extent than that of cellulose I.

NOTE: Cellulose II hydrate is a form of cellulose II with water molecules inside its crystalline lattice.

Wada et al. *Polym. Degrad. Stabil.* **2010**, *95*, 543.

Hydrolytic degradation: cellulose I *vs.* III

Glucose yield from enzymatic hydrolysis of different cellulose allomorphs



C-I: cellulose I
C-I*: ammonia-cellulose complex
C-II: cellulose II
C-III: cellulose III
AC: amorphous cellulose

Chundawat et al. *J. Am. Chem. Soc.* **2011**, *133*, 11163.

Summary on cellulose polymorphs

- Cellulose exists in several crystalline polymorphs:
  - cellulose I_α and I_β (native forms)
  - cellulose II (prepared regeneration or alkaline treatment)
  - cellulose III_I and III_{II} (prepared by liquid ammonia treatment)

- Cellulose polymorphs are physically different and they differ in reactivity

NOTE: Cellulose is virtually never 100% crystalline; it is semi-crystalline. Semi-crystallinity will be a key issue in the lecture on cellulose morphology

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Then answer the relevant question

Assignment

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