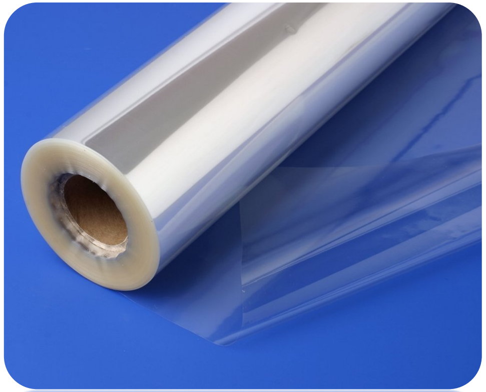
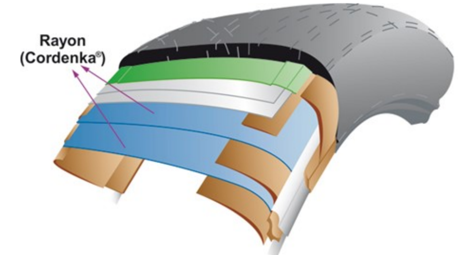
Aalto University
School of Chemical
Engineering

Cellulose: Regeneration

CHEM-E2140 - Cellulose Based Fibres
Michael Hummel

Cellulose products



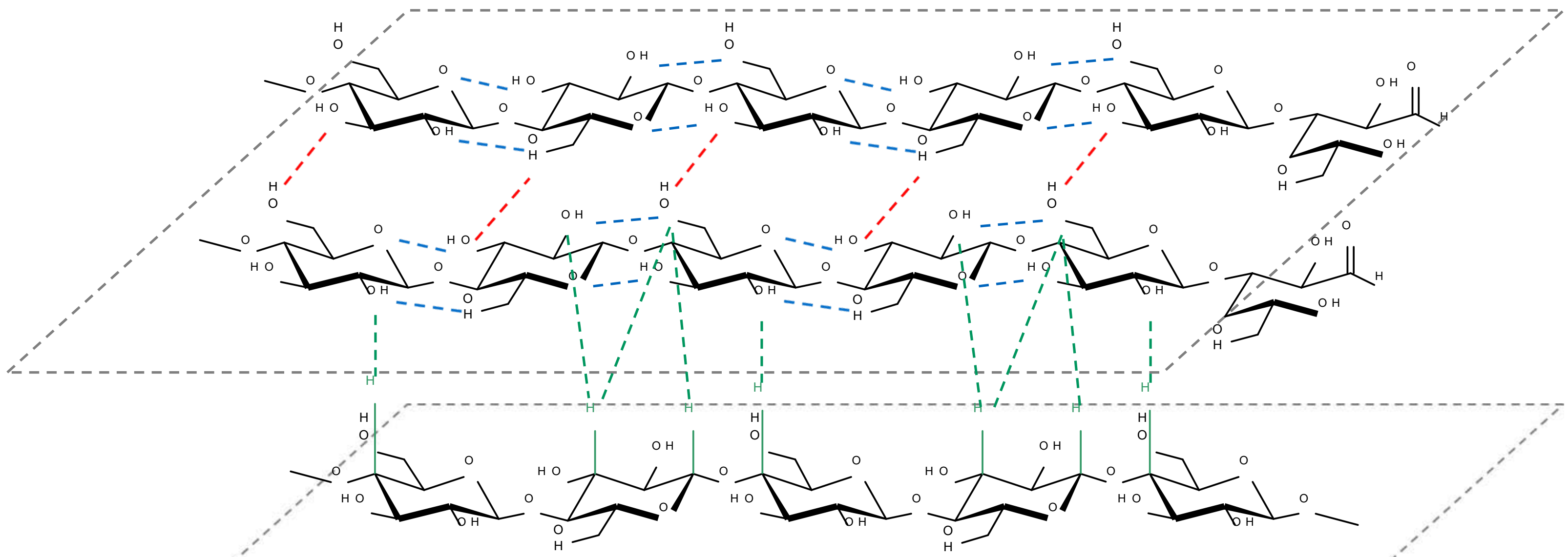


Learning outcomes

After this lecture you know

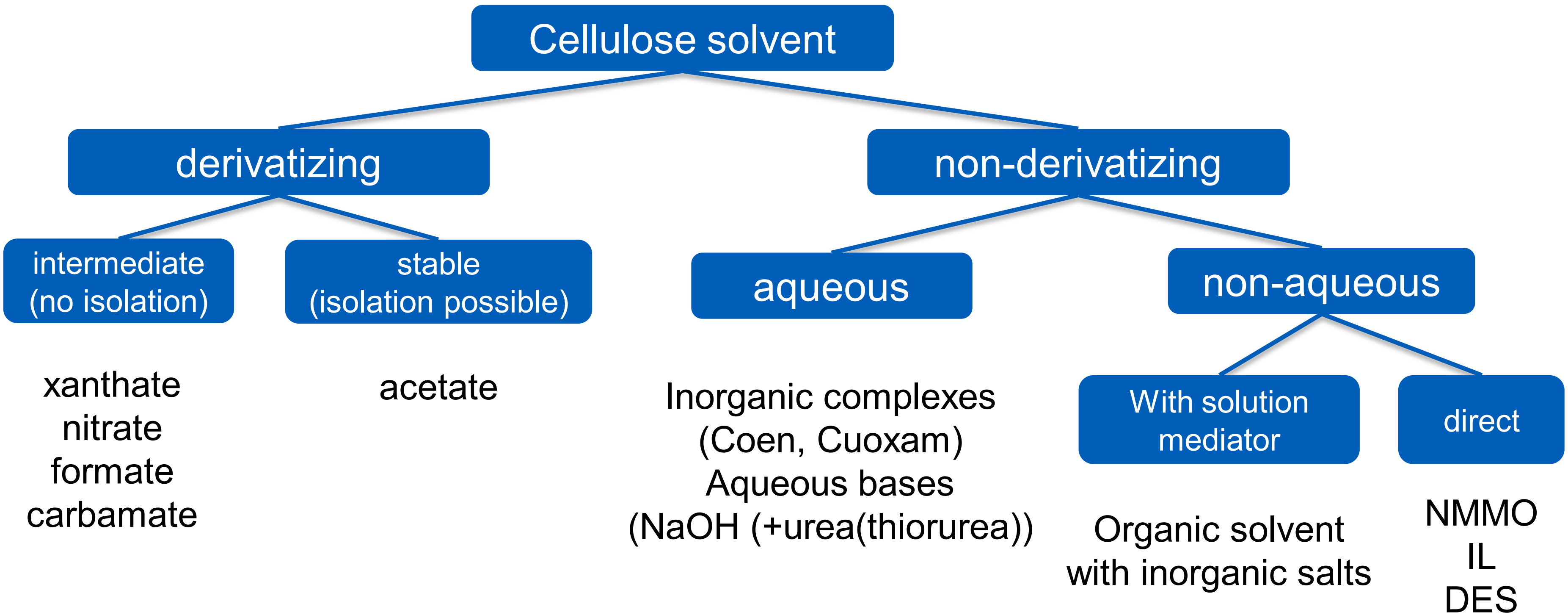
- **a history of man-made cellulosic fibers**
- **different cellulose solvents**
- **how to classify the quality of a cellulose solvent**
- **difference between regeneration and coagulation**

Non-covalent bonds in cellulose



O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain
intersheet H-bond

Cellulose dissolution - overview

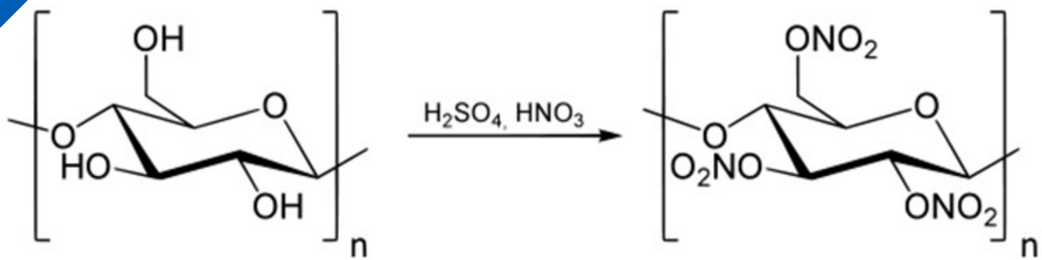


Regeneration **Coagulation**

History of cellulose solvents

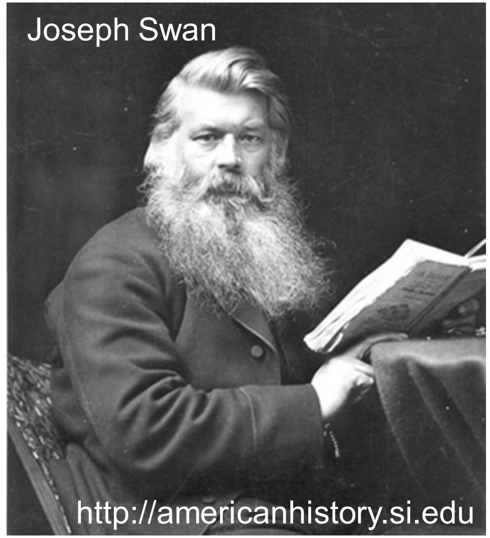
1846: Cellulose nitrate

derivatizing



= guncotton, highly flammable

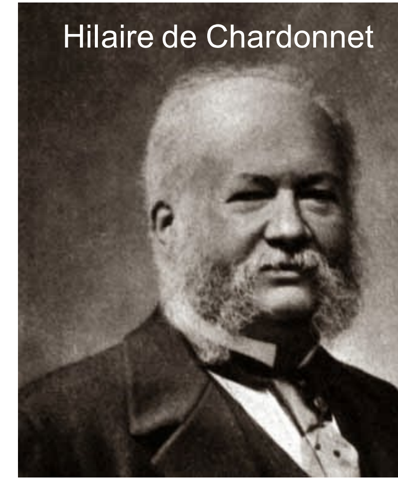
Swan developed the process to spin cellulose nitrate and de-nitrate the cellulose using ammonium bisulfate; yet he did not pursue this process further



1889: Chardonnet silk

Paris world exhibition 1889

Cover illustration by Albert Edelfelt

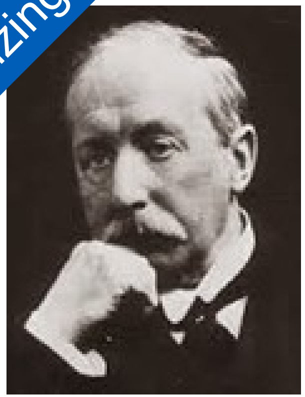


Hilaire de Chardonnet

Developed spinning of cellulose nitrate to a commercial level.
Nowadays called the Father of "Father of Rayon" and the founder of the MMCF industry

1892: The viscose process

derivatizing

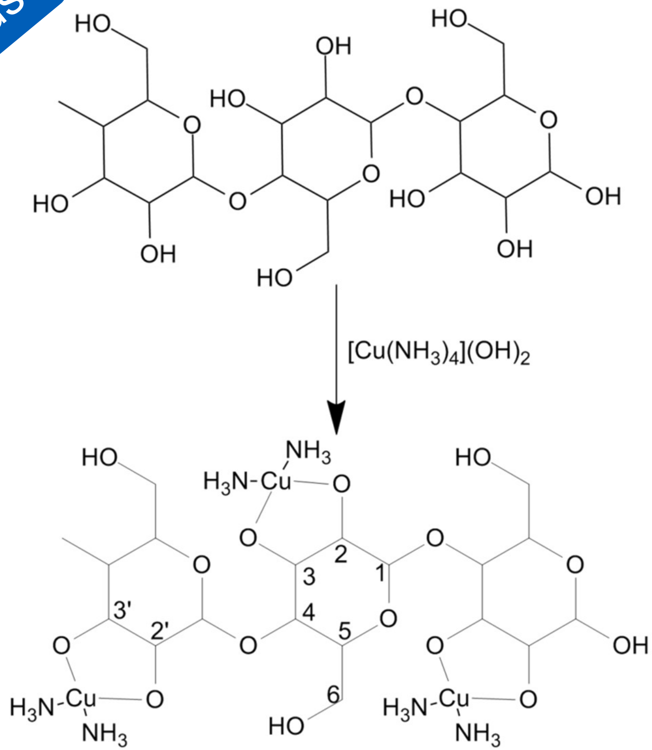


1892: Charles Frederick Cross, Edward John Bevan, Clayton Beadle file a patent describing today's viscose process

1905: Courtauld Fibres installs first commercial viscose plant in Coventry, UK

1857: Schweizer’s reagent

aqueous



wikipedia.com

Schweizer's reagent is an alkaline solution of copper sulfate in ammonia, $[Cu(NH_3)_4]\ (OH)_2.3H_2O$, named after Matthias Eduard Schweizer (1818-1860)

1934: direct dissolution

direct

Patented Jan. 9, 1934 — 1,943,176

UNITED STATES PATENT OFFICE

1,943,176

CELLULOSE SOLUTION

Charles Graenacher, Basel, Switzerland, assignor to Society of Chemical Industry in Basle, Basel, Switzerland

No Drawing. Application September 16, 1931, Serial No. 563,218, and in Switzerland September 27, 1930

21 Claims. (Cl. 260—100)

This invention relates to new cellulose solutions and the application thereof for making various products chemically or mechanically, and necessary, with suitable anhydrous diluents or other suitable additions. As such additions may be named, for example, substances having a re-

Charles Graenacher: father of direct solvents:

organic solvents that are capable of dissolving cellulose without derivatization or additional solubilization-mediator

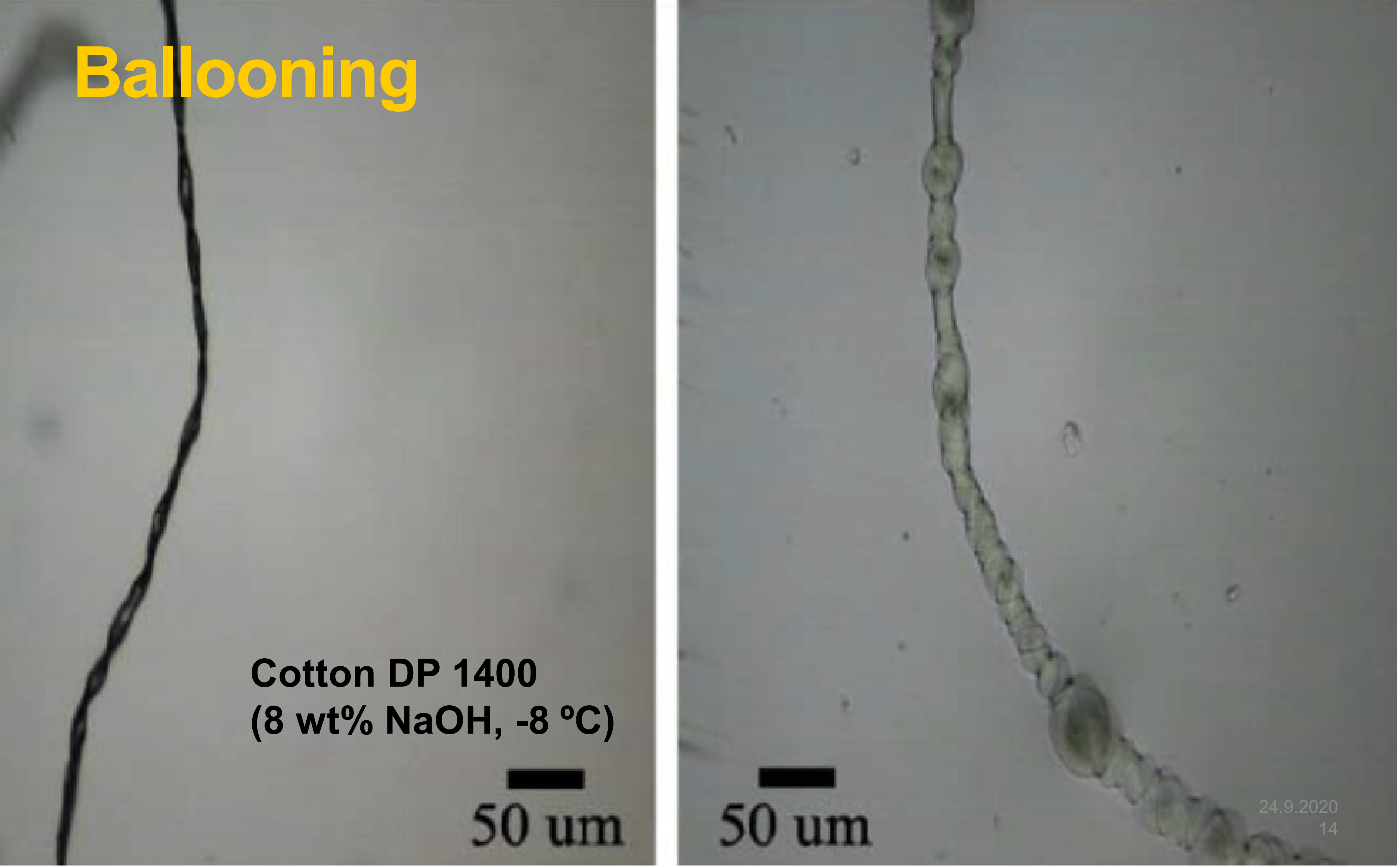
Types of cellulose (dissolution and) regeneration

Cellulose swelling: gross structure of cellulose as a moiety of particles, fibers, or a film (i.e., solid cellulosic phase) maintained, despite significant changes of physical properties and an increase in sample volume due to uptake of the swelling agent

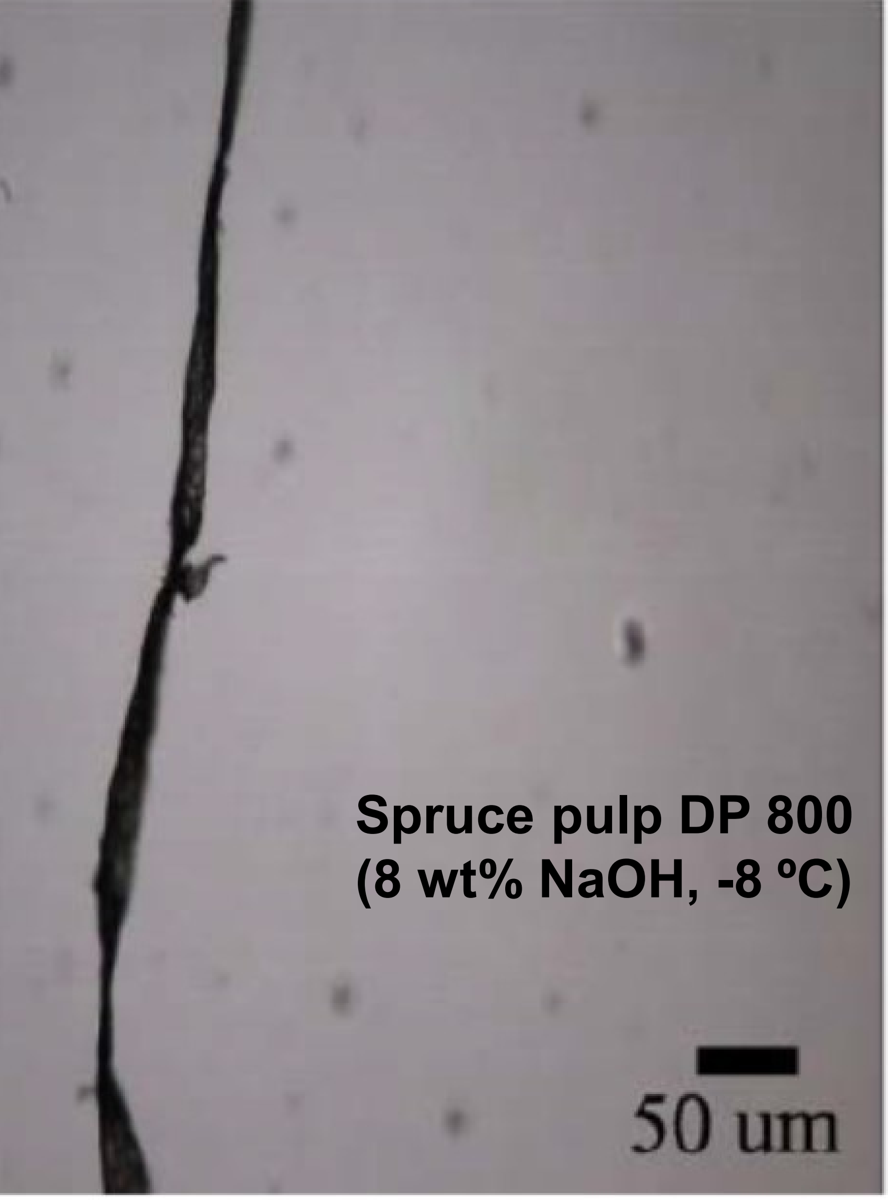
Cellulose dissolution: transition from a two-phase system to a one-phase system (clear solution), in which the original supramolecular structure of cellulose is destroyed

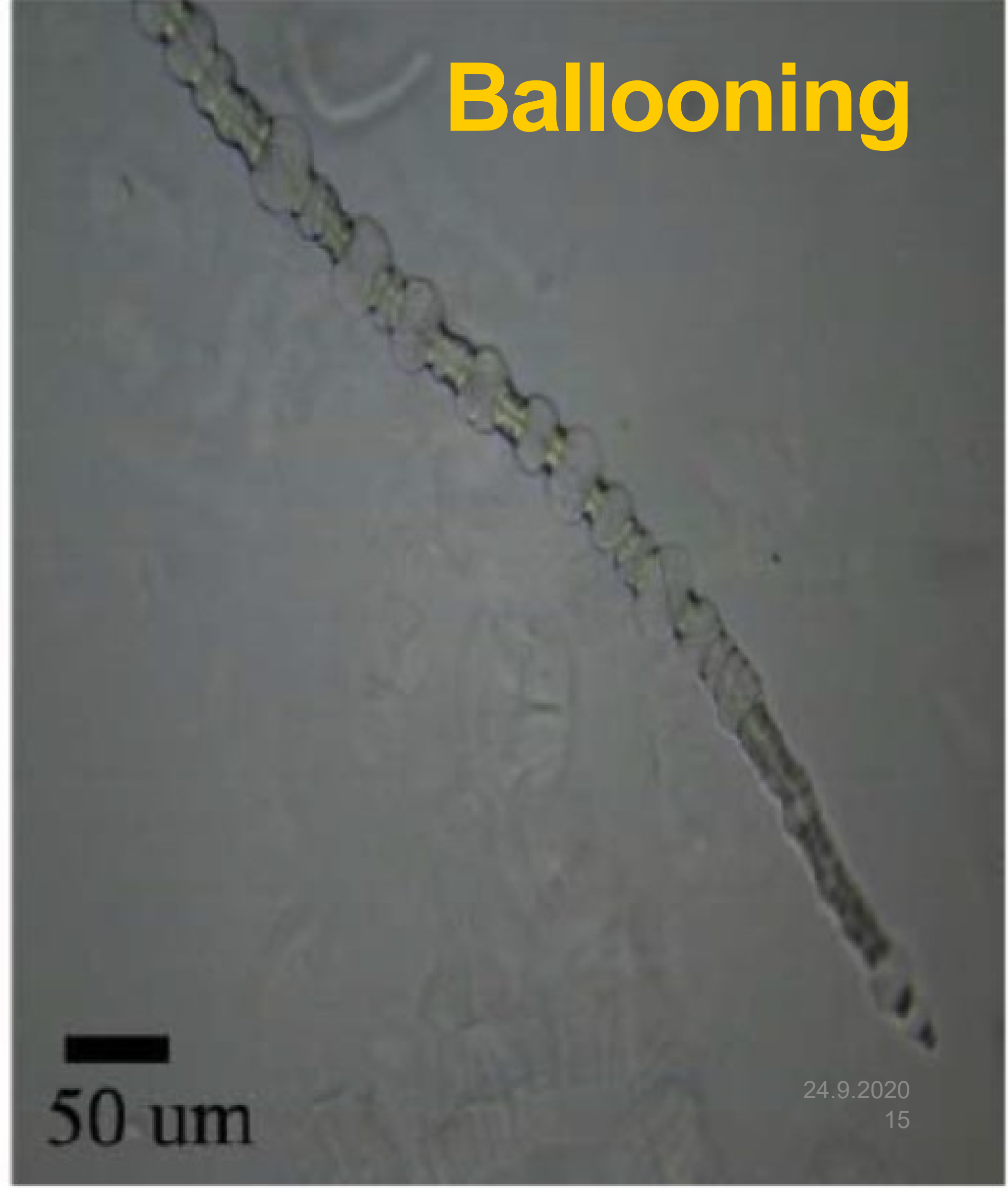
<u>However, there is often no clear-cut borderline between a swelling process and a dissolution process</u>

Ballooning

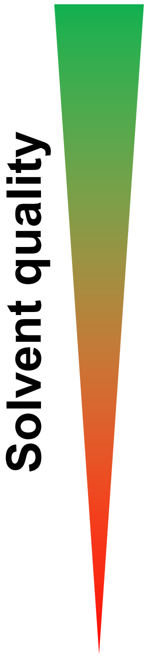


Cotton DP 1400
(8 wt% NaOH, -8 ºC)

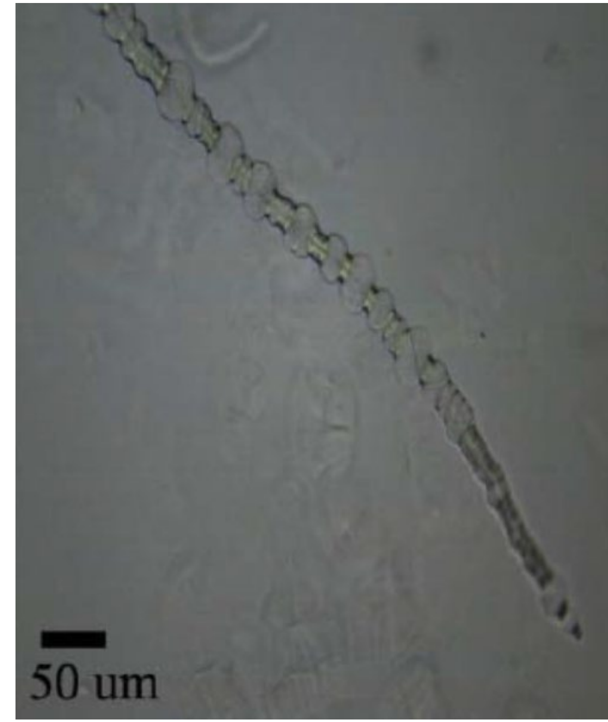

Spruce pulp DP 800
(8 wt% NaOH, -8 ºC)
50 um


Ballooning
50 um

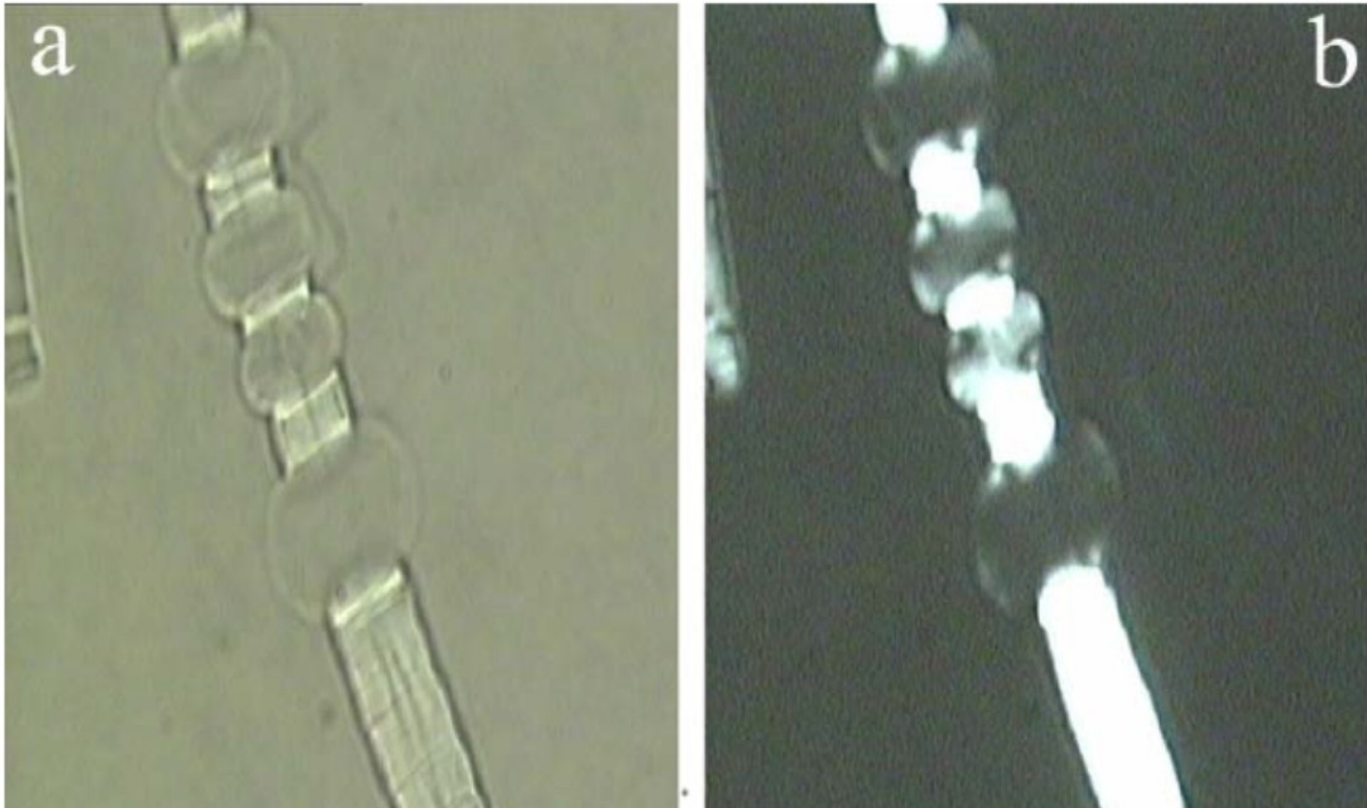
Swelling and dissolution



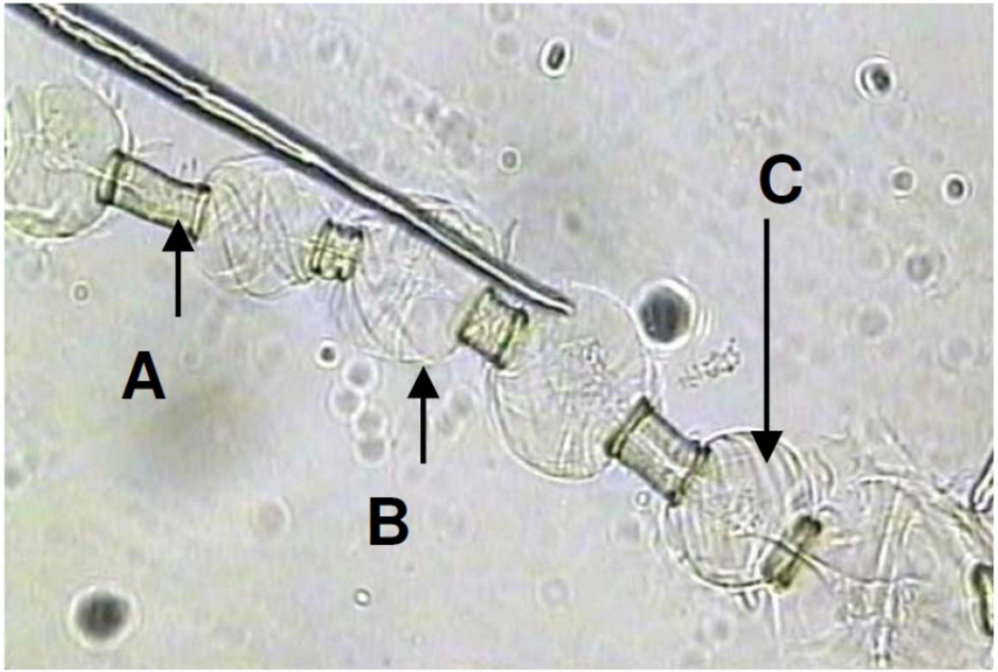
- **Mode 1:** Fast dissolution by disintegration into rod-like fragments
- **Mode 2:** Large swelling by ballooning and then dissolution of the whole fiber
- **Mode 3:** Large swelling by ballooning and partial dissolution of the fiber, still keeping its fiber shape
- **Mode 4:** Homogeneous swelling and no dissolution of any part of the fiber
- **Mode 5:** No swelling and no dissolution (non-solvent)

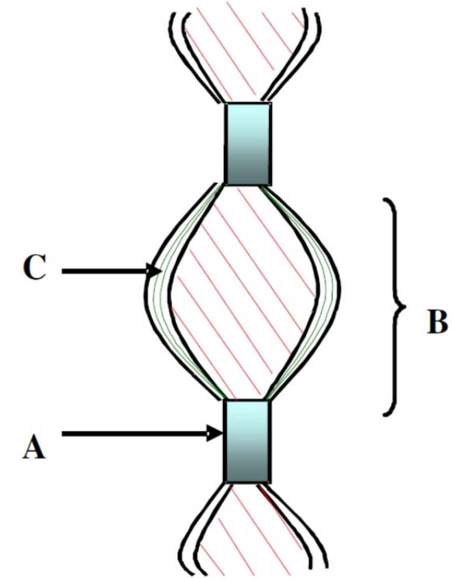


Mode 2: Balloning



Mode 2: Balloning



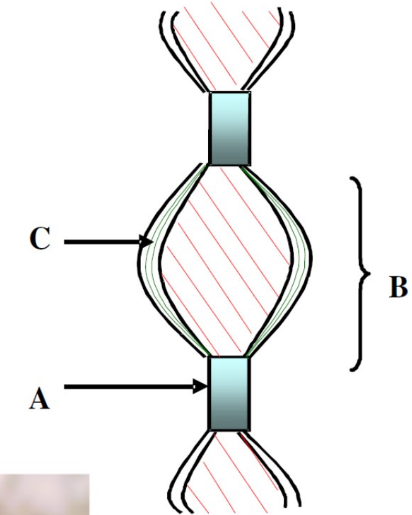


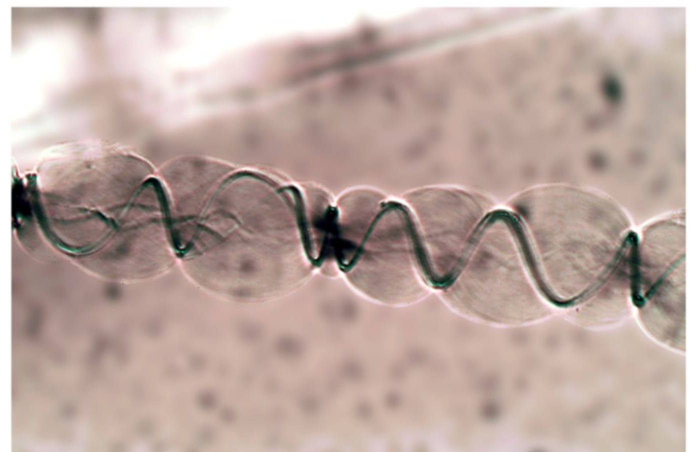
A: unswollen fiber
B: dissolution and ballooning
C: undissolved P and S1 cell wall encapsulating dissolved cellulose

Navard, Cuissinat. 7th International Symposium "Alternative Cellulose : Manufacturing, Forming, Properties", Sep 2006, Rudolstadt, Germany. 7 p., 2006. <hal-00579326>

Mode 2: Balloning

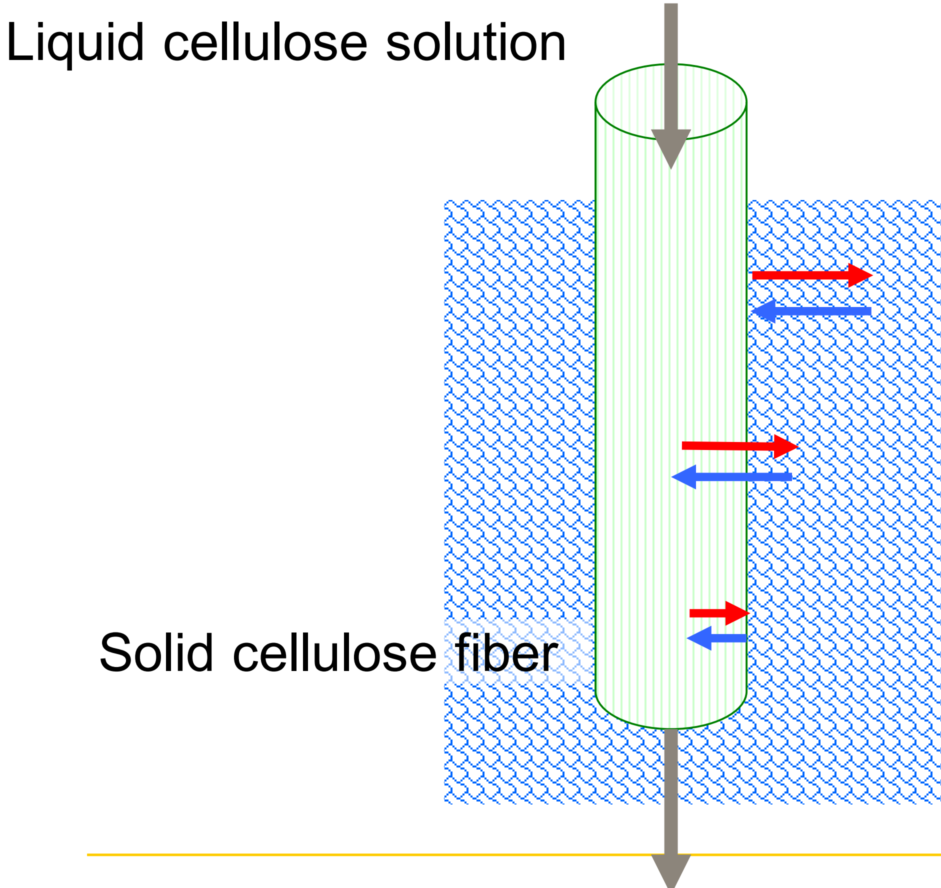
- Phase 1: balloon formation
- Phase 2: balloon bursting
- Phase 3: dissolution of the un-swollen sections
- Phase 4: dissolution of the balloon membrane scraps





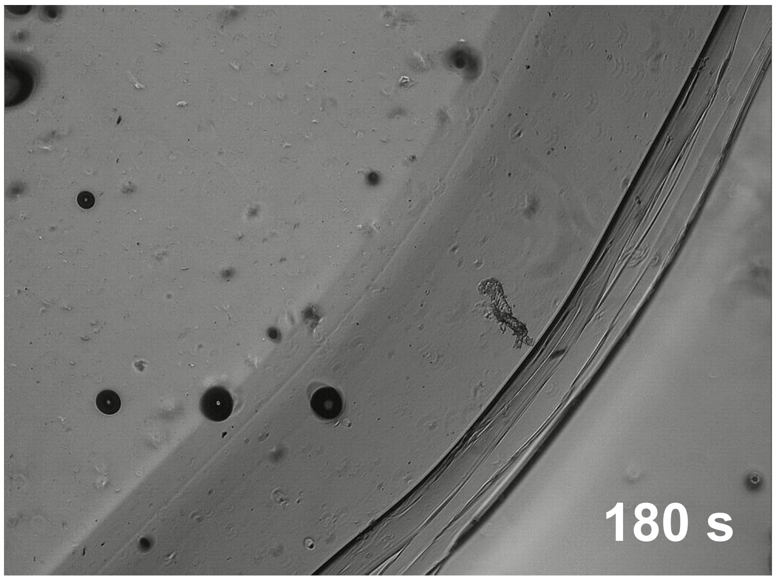
Coagulation/regeneration
≠
inverse of dissolution

Regeneration / coagulation



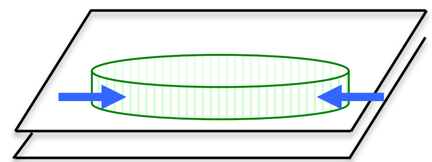
- Cellulose solution immerges into coagulation bath
- Solvent and anti-solvent diffusion
  - filament-water interface
  - in coagulation bath
  - in fiber body
- Structure formation; fiber morphology

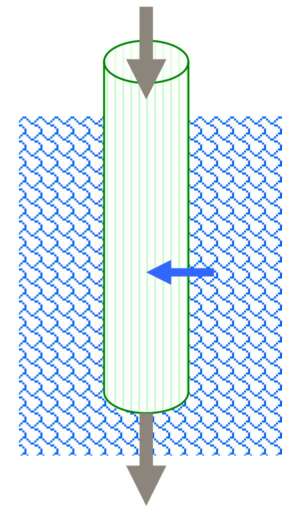
Regeneration / coagulation



Regeneration / coagulation proceeds from the surfaces towards the center of the solution

Shell-core formation

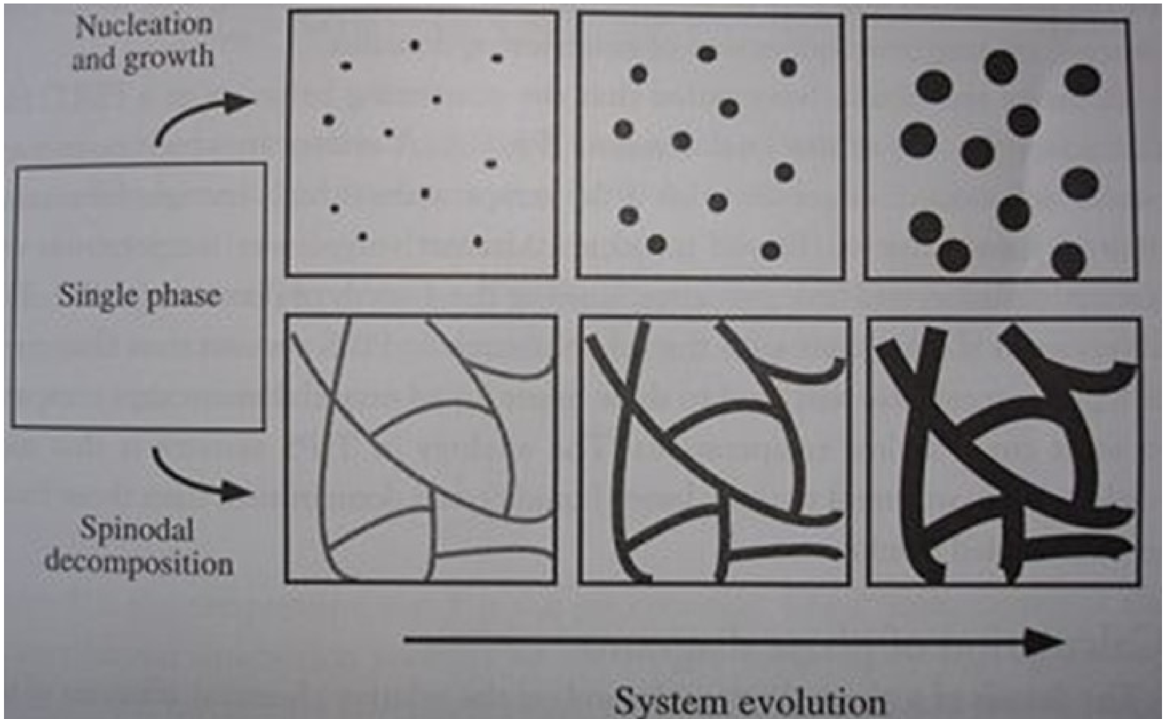




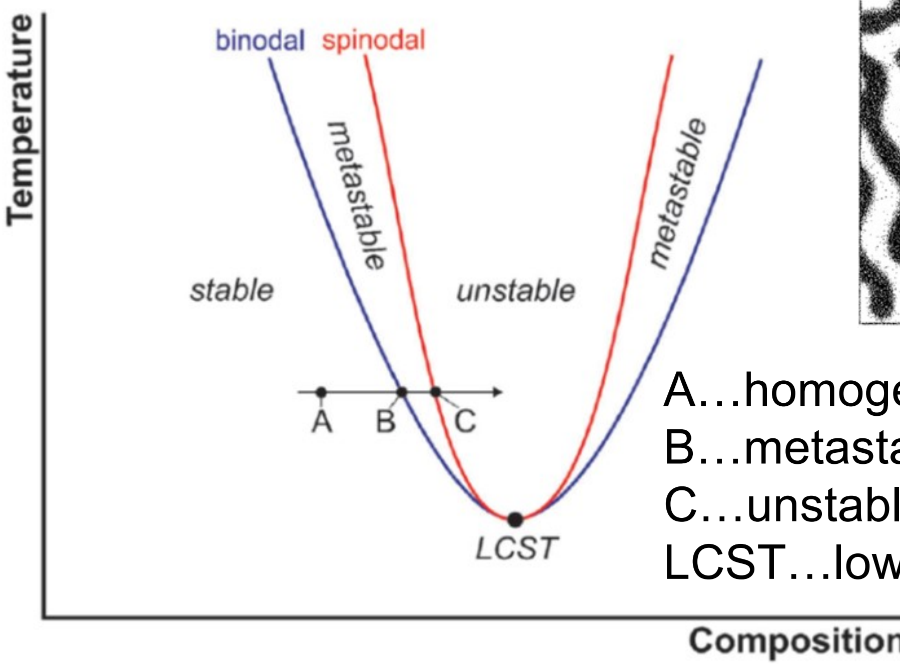
Spinodal decomposition vs. Nuleation & growth

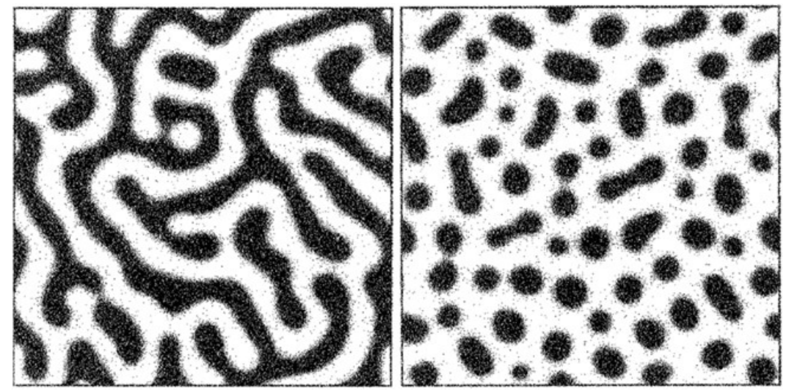
How does matter solidify from a melt/solution?

Spinodal decomposition vs. Nuleation & growth



Spinodal decomposition vs. Nuleation & growth





A…homogeneous region, stable solution
B…metastable solution; binodal demixing = nucleation
C…unstable solution, phase separation inevitable
LCST…lower critical solution temperature

Gebauer *et al.* Chem. Soc. Rev. 2014, 43, 2348.
García-Ojalvo, *et al.* Europhys. Lett., 1998, 42, 125.

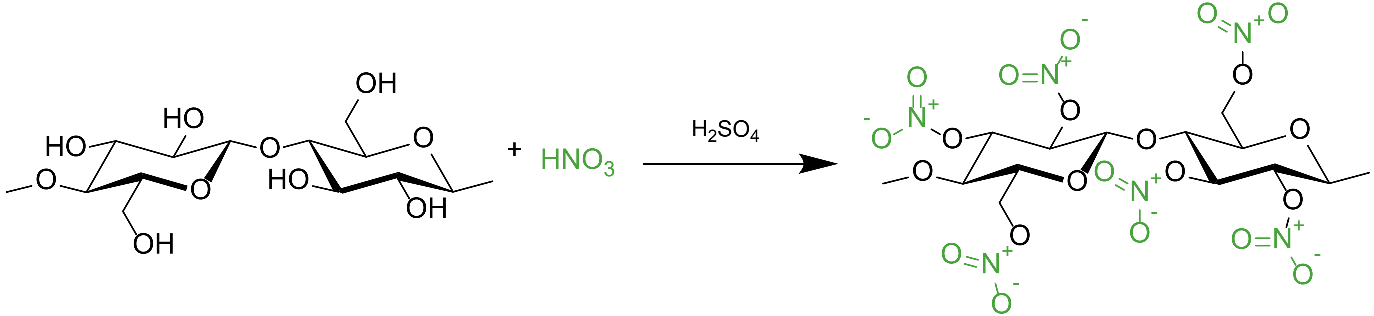
Summary questions

- **Why cellulose dissolution?**
- **What is the difference between spinodal decomposition and nucleation & growth?**

Regeneration

Intermediate Derivatization

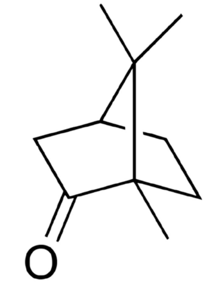
Cellulose nitrate



- Alternatively in DMF/N_2O_4
- Cellulose nitrate soluble in ether/ethanol/acetone
- Solution spun through nozzles into regeneration bath containing $(NH_4)(HSO_4)$
- Flammable ("mother-in-law silk")

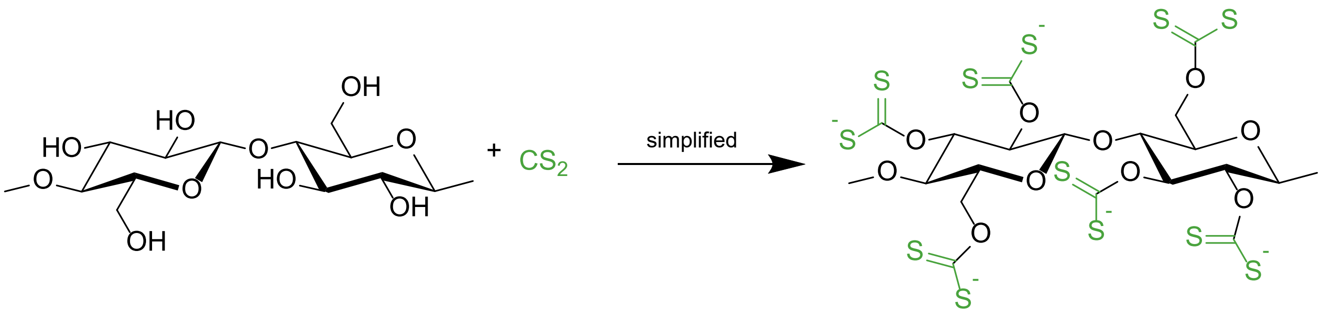
Cellulose nitrate - Celluloid

Celluloid = thermoplast containing cellulose nitrate and camphor



1856 first created by Alexander Parkes; called it Parkesine
1870 John Wesley Hyatt patents it as „Celluloïd“ to be sold through the Celluloid Manufacturing Company

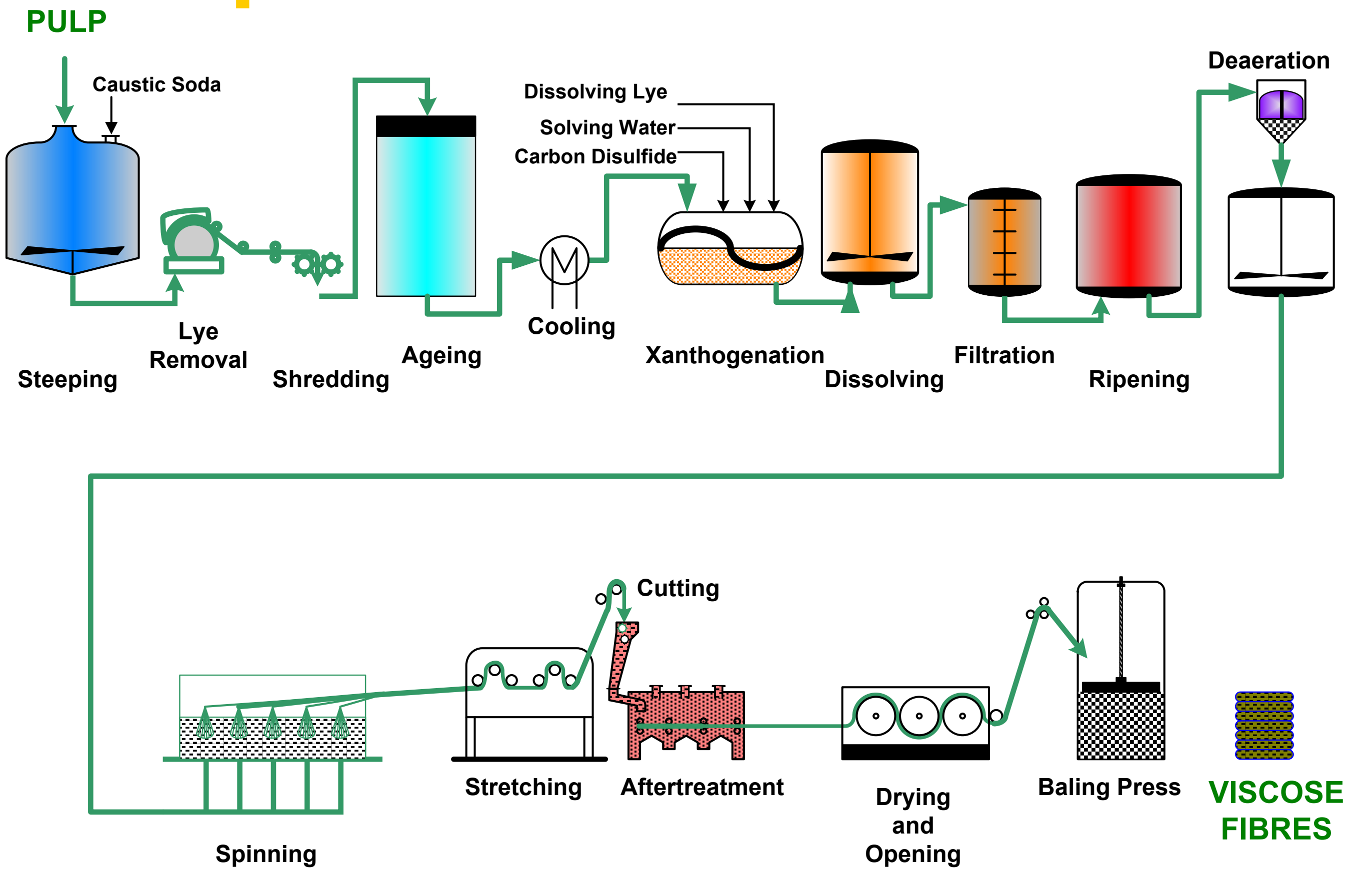
Xanthate (viscose)



- Cellulose xanthate soluble in caustic solution
- Solution spun through nozzles into regeneration bath containing H_2SO_4 / Na_2SO_4 and additives

YouTube: The production of viscose fibres at Kelheim Fibres GmbH
https://www.youtube.com/watch?v=zcxcPVX5ejY

Viscose process



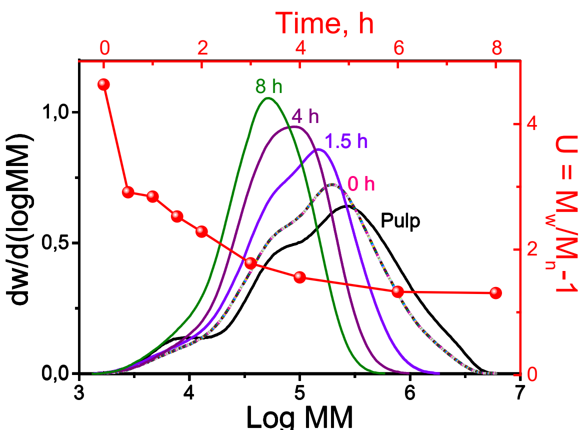
Viscose process

Steeping (alkalization):

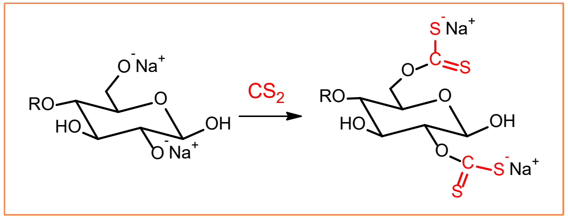
conversion to cellulose-II lattice

$$Cell - OH + NaOH \longrightarrow Cell - O^{-}Na^{+} + H_2O$$

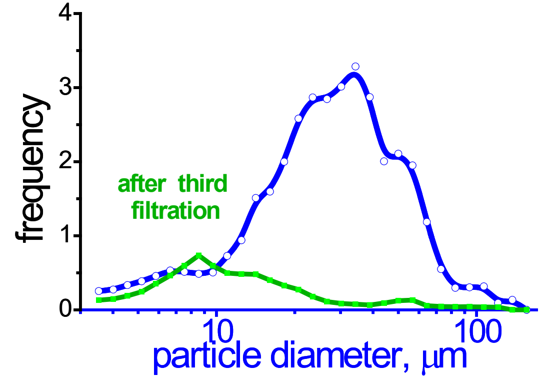
Ageing (DP adjustment)



Xanthation

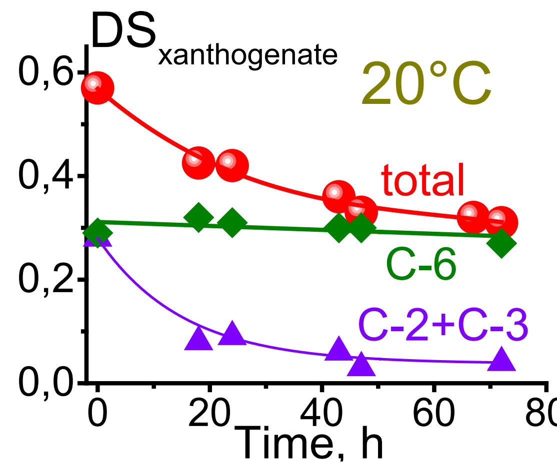


Viscose Filtration



Ripening

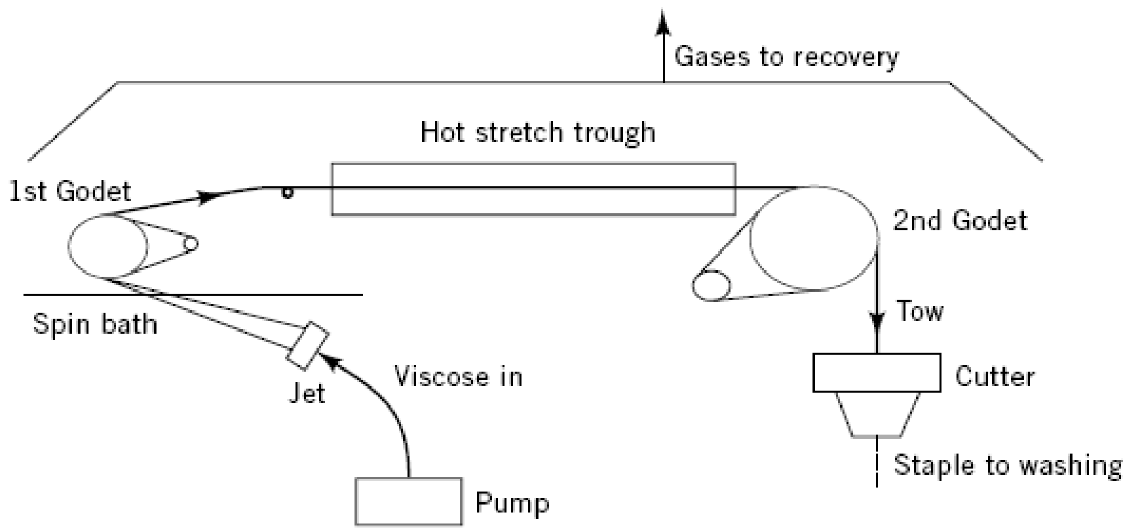
$$2CS_2 + 6\ NaOH \rightarrow$$
$$Na_2CS_3 + Na_2CO_3 + Na_2S + 3H_2O$$



Schwaighofer, A. et al. *Anal Bioanal Chem* (2011) 400:2449-2456

Viscose process

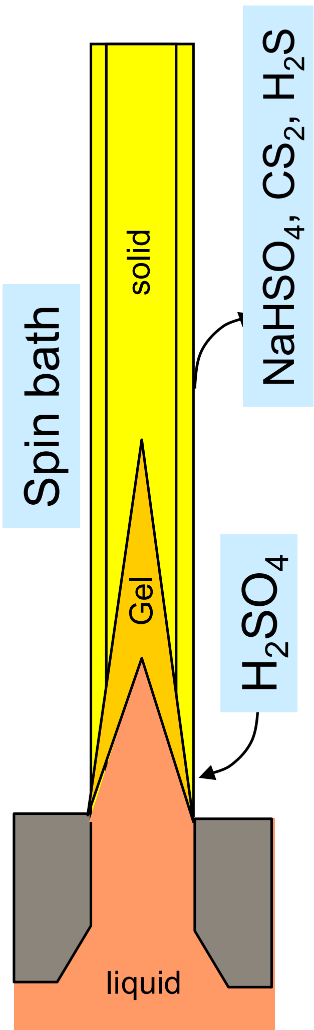
Spinning
↓
Stretching
↓
Cutting
↓
Washing
↓
Drying



Viscose process

- Each spinning position has up to 200.000 holes for staple fibres.
- The diameter of the typically round shaped holes is between 40 and 90 mm.
- Spinning velocity is slow in wet spinning, only 12 to 20 m/min.
- The viscose is pumped through the spinnerets into the spinbath where it coagulates.

Viscose regeneration



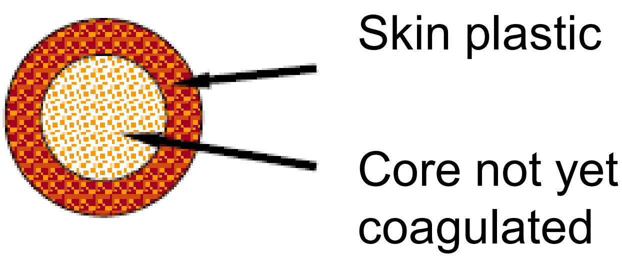
Prim. Structure Formation

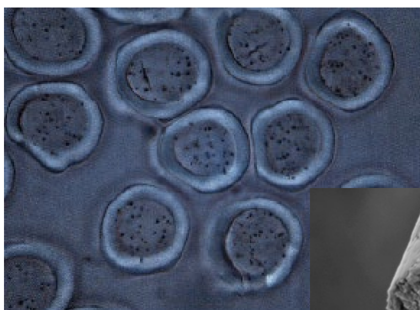
- Coagulation

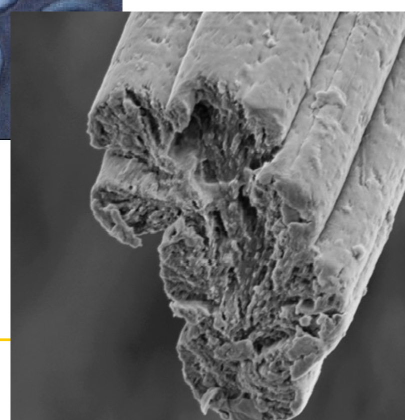
Second. Structure Formation

- Dehydratation, densification
- Regeneration
- Orientation, crystallization

Viscose regeneration: Skin core structure







- Skin show higher orientation; smaller sized crystallites
- Core less oriented
- Skin thickness can be increased by additives which retard coagulation

Viscose – High tenacity variations through delayed regeneration

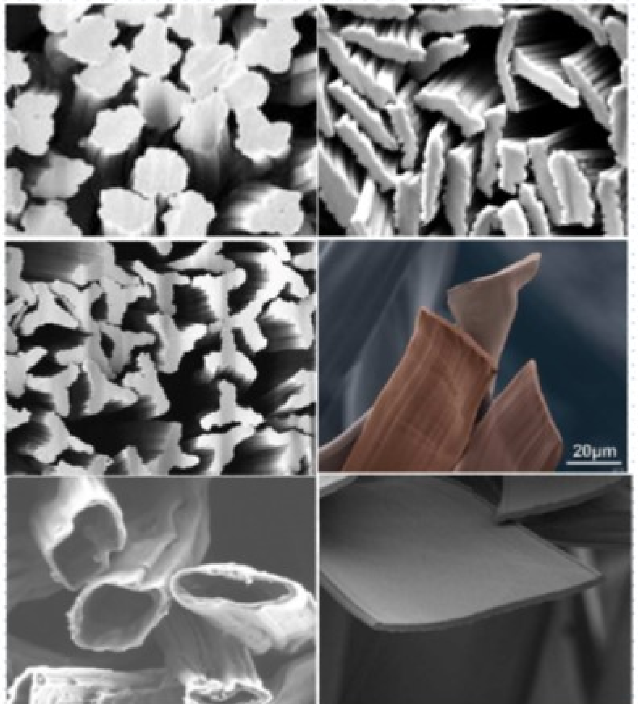
Modifiers in viscose to delay regeneration

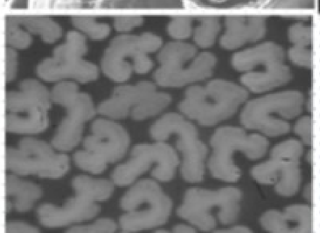
- Zn salts
- Organic modifiers
- Mixed modifiers
- Formaldehyde

Plasticizing coagulation bath

- Hot water or steam
- Hot, diluted sulfuric acid solution

Viscose variations



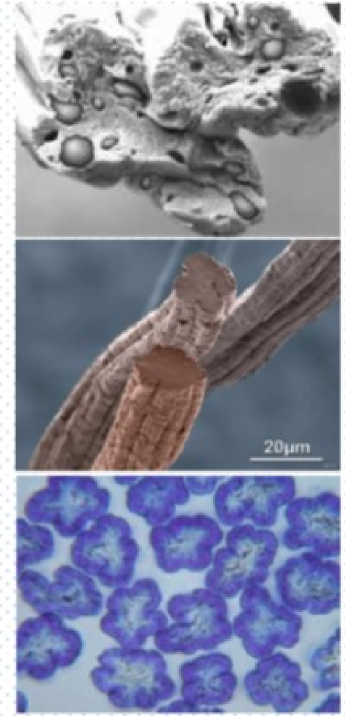


a) 7 types of cross-sections

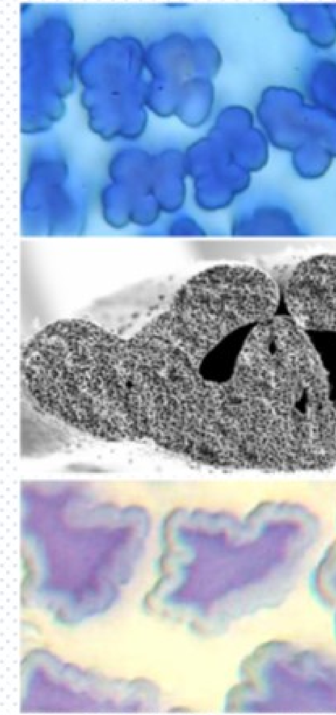
Standard	Flat (1:5)
Trilobal	Superflat (1:20)
Hollow	Smooth (1:40)
Letter shaped	

b) Titer (diameter):
0,5dtex–28dtex, (7–48µm)

c) Fibre length:
3–120mm; endless tow



d) Incorporation of particles/ chemicals
Pigments,
Microcapsules,
Ion exchange additives,
...



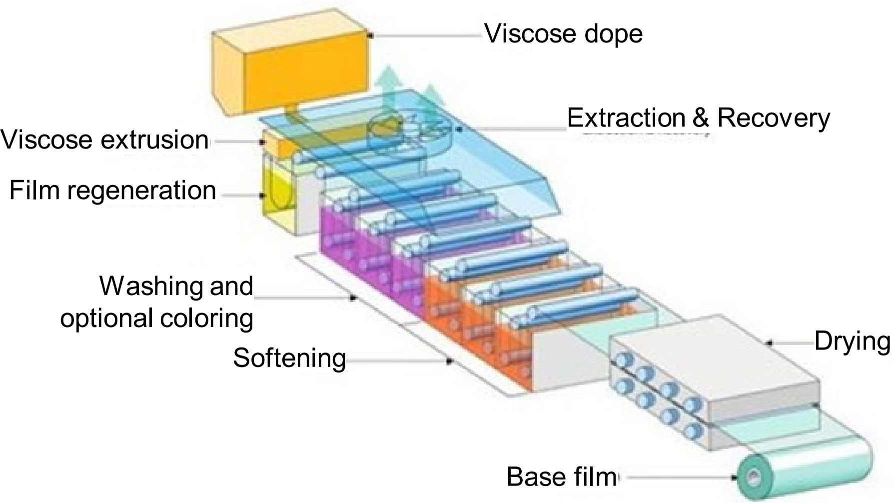
e) Polymer blends

f) Coating, impregnation
Inorganic polymers
Biopolymers
Modified biopolymers
Synthetic polymers

Viscose variations

H. Harms “Acel Symposium", Helsinki, May 19, 2017

Viscose – Cellophane



Good barrier properties regarding air and grease

Coating needed to decrease water permeability

Viscose – Cellophane

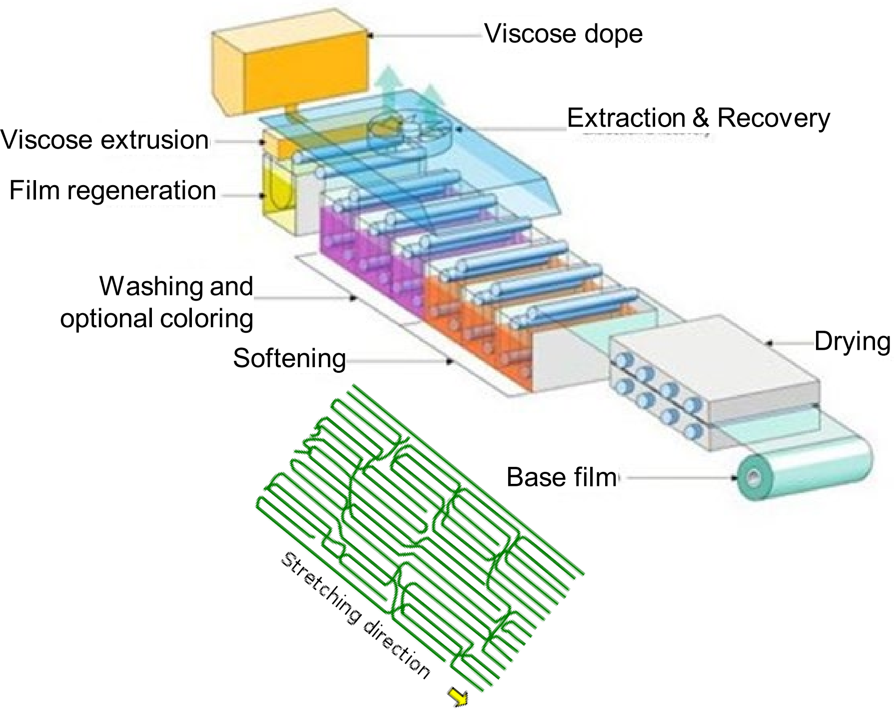


TABLE II

Mechanical Anisotropy of Test Specimens

Specimen	Tensile dynamic modulus $E_\delta \times 10^3$, kg/mm²[a]						
	$\delta = 0°$[b]	$\delta = 10°$	$\delta = 20°$	$\delta = 30°$	$\delta = 45°$	$\delta = 60°$	$\delta = 90°$[b]
C-1-D_{ex}	7.7	7.6	7.3	6.8	6.0	5.6	5.4
C-1-D_{el}	6.2	6.2	6.1	5.6	5.3	4.7	4.7
C-1-D_{st}	5.4	5.3	5.2	4.5	4.4	4.0	3.7
C-1-W	0.21	0.20	0.18	0.14	0.11	0.09	0.08
C-2-D_{ex}	7.7	7.2	7.0	6.8	6.3	5.9	5.5
C-2-D_{el}	6.8	6.4	6.4	5.6	5.2	4.7	4.5
C-2-D_{st}	5.6	5.4	5.0	4.6	4.3	3.9	3.9
C-2-W	0.20	0.20	0.17	0.15	0.11	0.09	0.08
C-3-D_{ex}	6.7	6.6	6.5	6.1	5.5	5.5	5.4
C-3-D_{el}	6.0	5.7	5.6	5.4	4.7	4.5	4.6
C-3-D_{st}	5.0	4.9	4.7	4.5	4.1	4.0	3.8
C-3-W	0.16	0.16	0.14	0.12	0.10	0.09	0.08

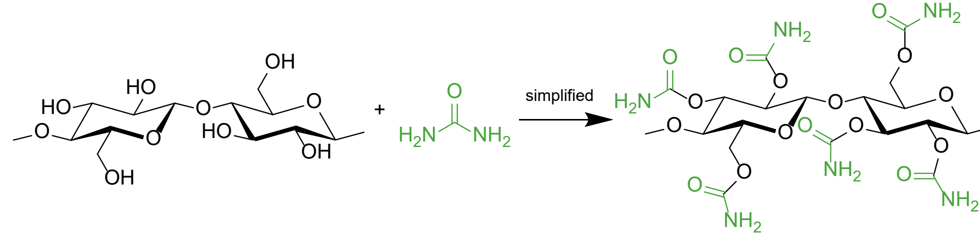
[a] Measured by the Viscoelastic spectrometer at 20°C. The modulus is the real part of the tensile complex dynamic modulus at 11.0 cps.

[b] The angle 0° corresponds to the x_3 axis (the machine direction); and 90° corresponds to the x_2 axis (the transverse direction) within the film plane; δ is the angle between the direction of tensile deformation and the machine direction.

Aalto University
School of Chemical Engineering

Nomura *et al. J. Polym. Sci. A-2,* **1969,** 7, 325-355

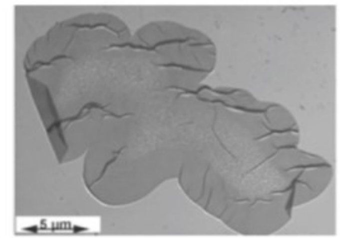
Carbamate

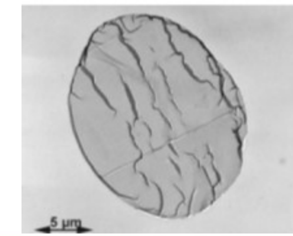


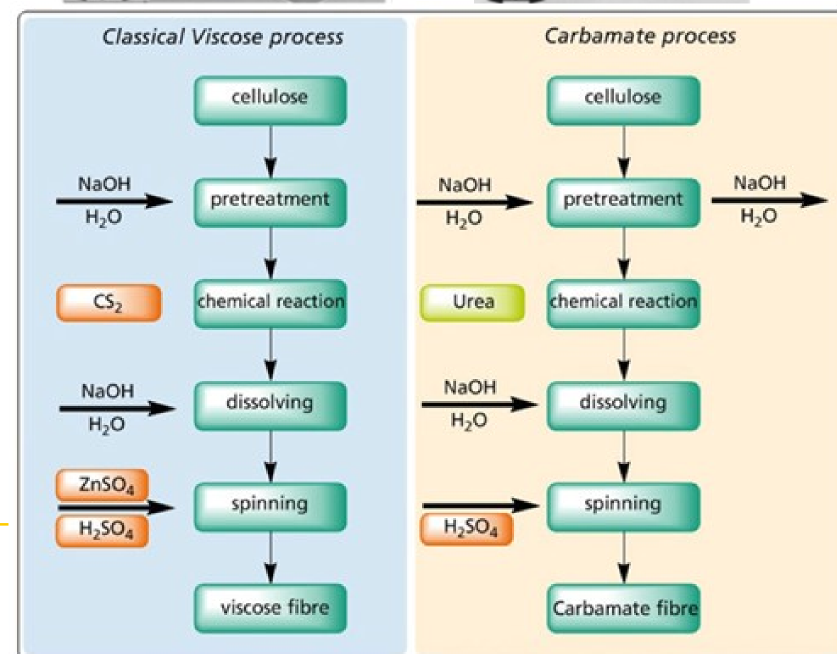
Initial development by Neste Oy (Ekman et al. Lenz. Ber. 1984 57, 38-40.

Regeneration in acidic spin bath.

Conditioned fiber strength comparable to viscose; extremely low wet strength



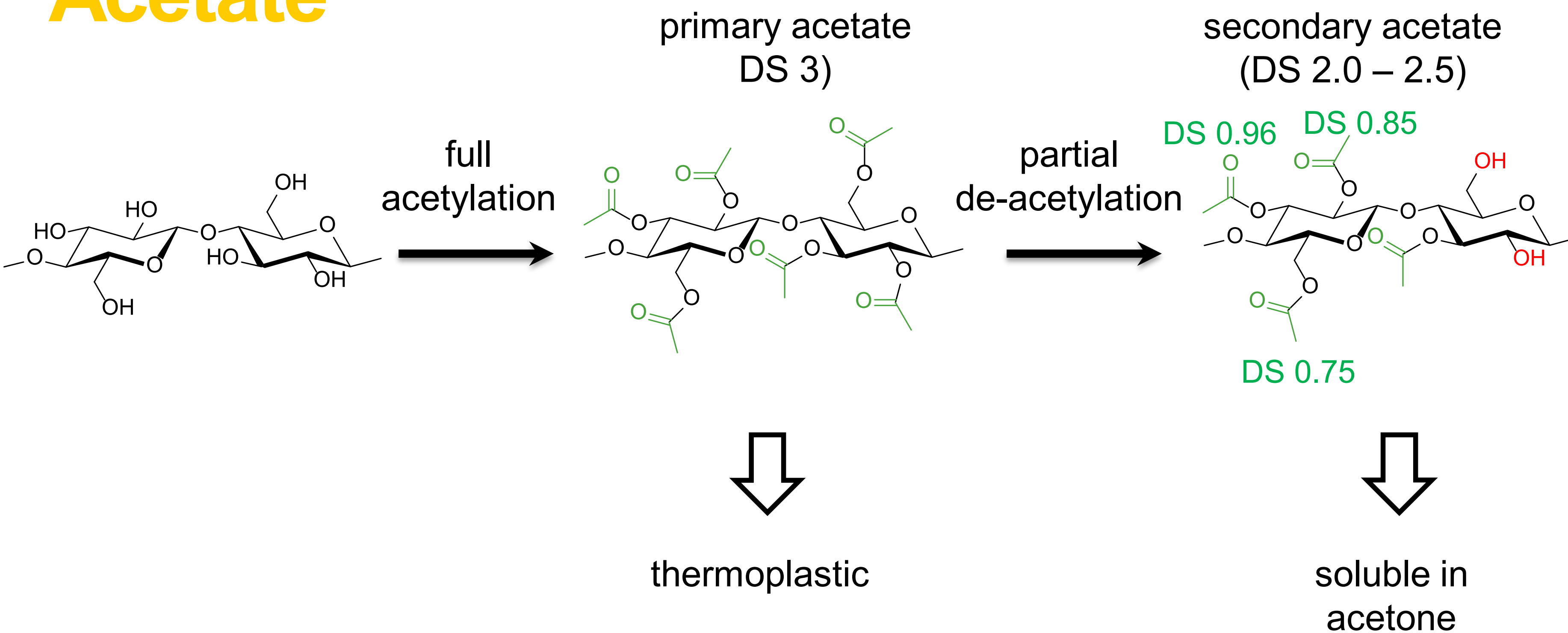




Fink *et al. Cellulose*, **2014,** 21, 31-51

Stable derivatives

Acetate



Fischer *et al. Macromol. Symp.* 2008, 262, 89–96

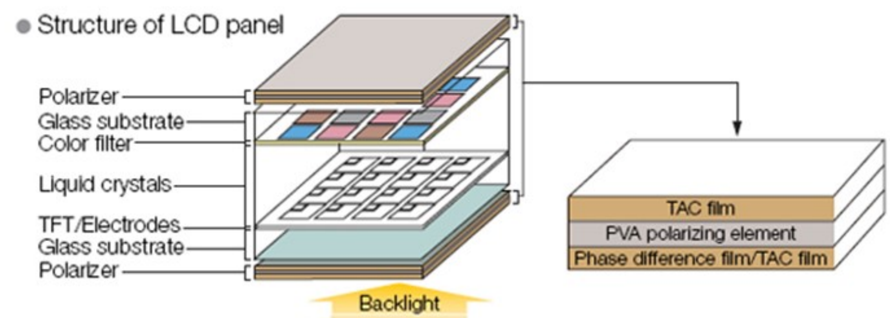
Acetate

Melt processed:

- Frames for glasses
- First Lego bricks (today acrylonitrile butadiene styrene)
- TAC films for LCD

Solution spun:

- Fiber tows for cigarette filters
- Fortisan fibers: spun as secondary acetate and subsequently saponified; high orientation of cellulose molecules enables high mechanical properties



Fortisan: regenerated CA

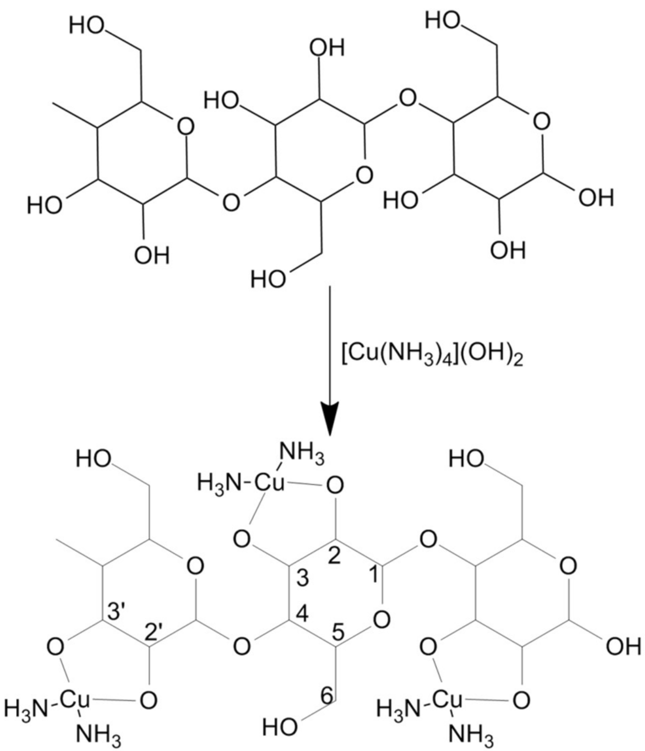
CA fiber is spun and then stretched under steam, resulting in high molecular orientation

The fiber is then saponified (de-acetylated = regenerated) to yield pure cellulose with high strength (cf. next lecture)

Coagulation

Non-derivatizing – aqueous

Metal complexes

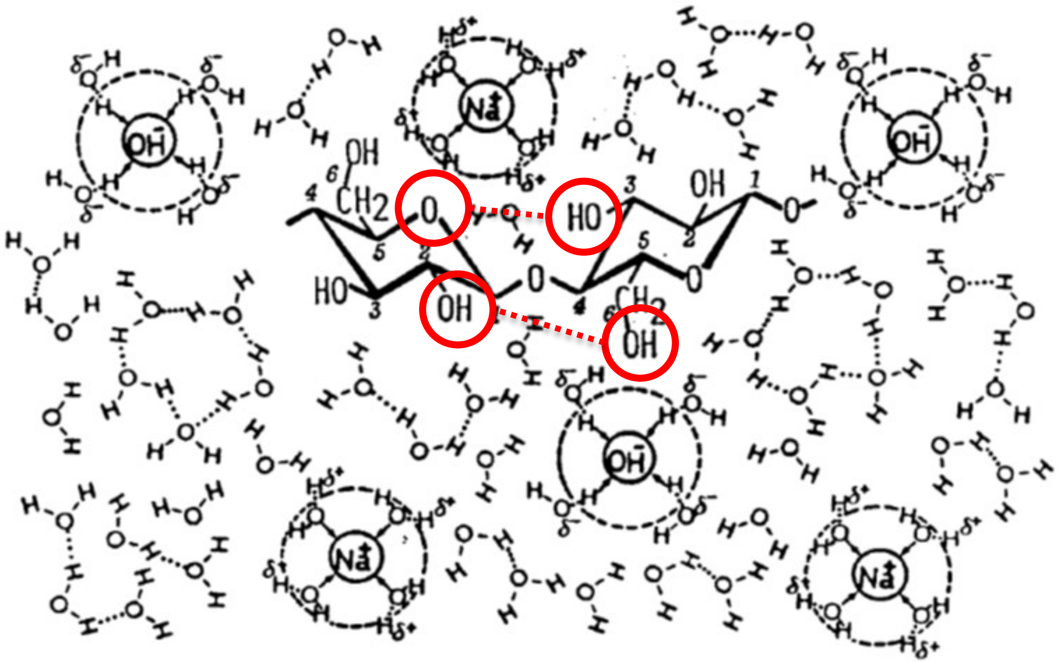


- Cuoxam: tetraammine diaqua copper hydroxide, $[Cu(NH_3)_4(H_2O)_2](OH)_2$
- Cuen: Copper(II) ethylenediamine hydroxide
- Nioxam ($[Ni(NH_3)_6][OH]_2$)
- Zincoxen ($[Zn(NH_2(CH_2)_2NH_2)_3][OH]_2$)
- Cadoxen ($[Cd(NH_2(CH_2)_2NH_2)_3][OH]_2$)
- Nitren ($[Ni(NH_2CH_2CH_2)_3N][OH]_2$)
- Pden ($[Pd(NH_2(CH_2)_2NH_2)][OH]_2$)
- Ferric sodium tartrate complex $Na_6[Fe(III)(C_4H_3O_6)3]$

Dissolution through complex formation; spun into acidic spin bath which causes de-complexation and regeneration of cellulose

Commercial cupro fiber (Cuoxam, tradename Bemberg™ fiber) produced on a scale of ca. 25 000 t/a as specialty fiber

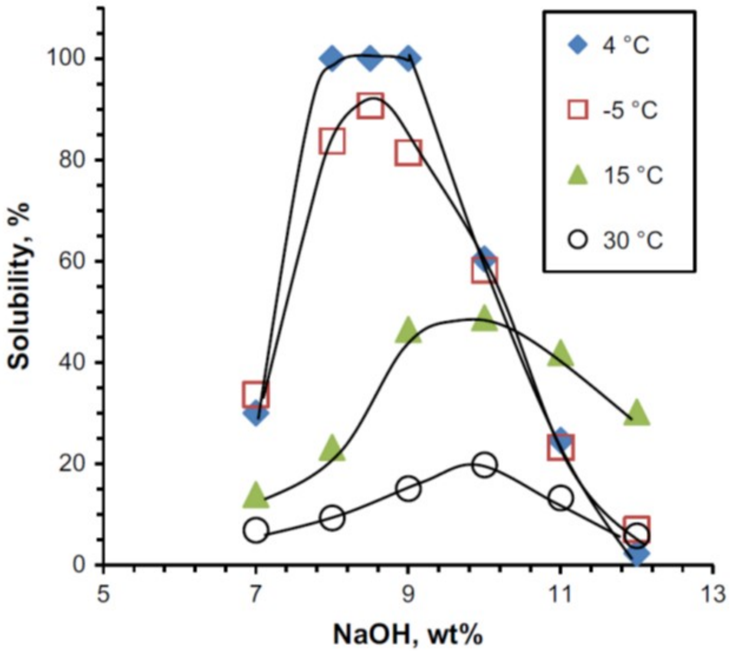
NaOH solutions



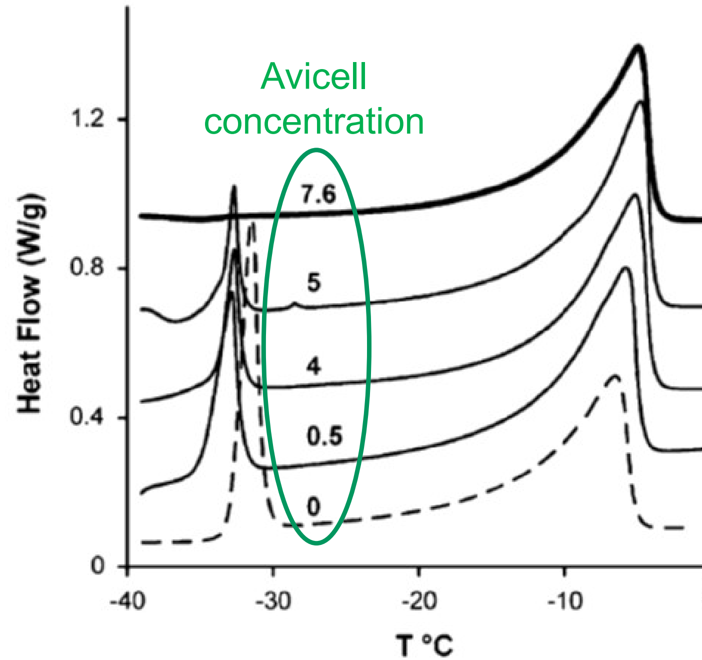
Deconstruction of intramolecular O_3-H…O_5’ and O_2-H…O_6’ H-bonds

Yamashiki *et al. Polym. J.* 1988, 20, 447-457
Kamide *et al. Cell. Chem. Technol.* 1990, 24, 23-31

NaOH solutions

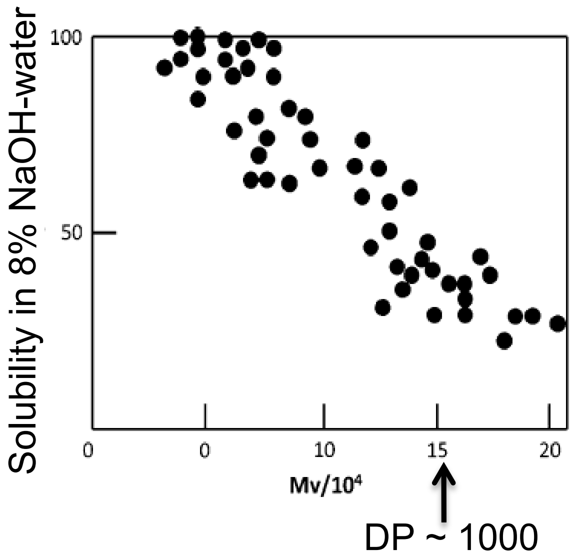


Best dissolution performance of pure NaOH solution at 7-8 wt% NaOH, corresponding to 4 NaOH units per AGU



Kamide *et al. Cell. Chem. Technol.* 1990, 24, 23-31
Eagle *et al. Biomacromolecules* 2007, 8, 2282-2287

NaOH solutions

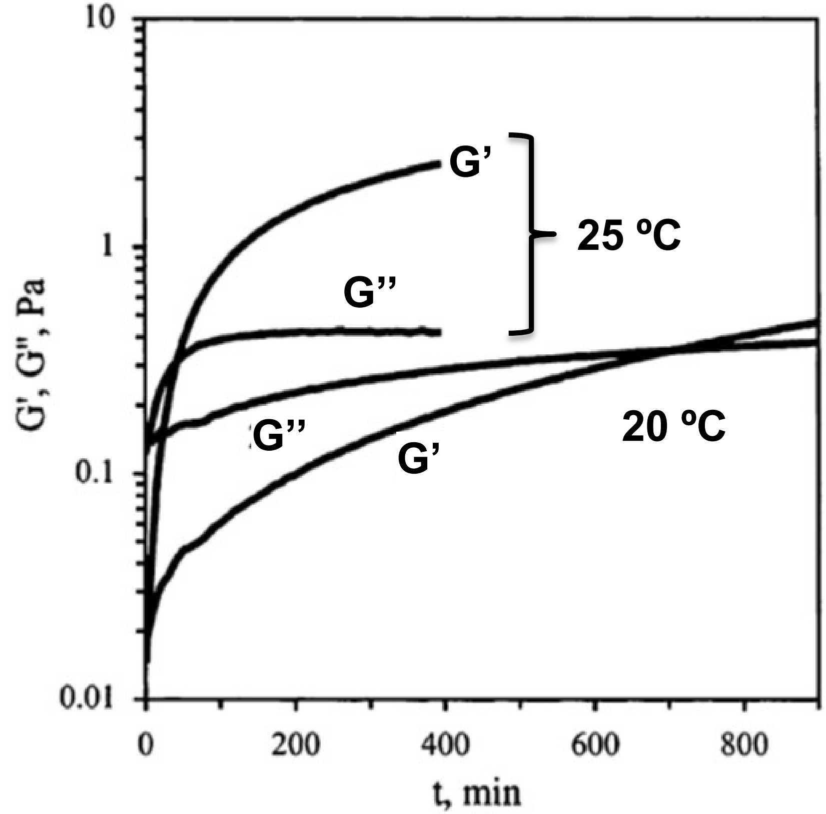


- Major limitation of NaOH as solvent: solubility of cellulose strongly dependent on DP
- Upper limit for relevant cellulose concentration;
- Limited mechanical properties of regenerated products

Budtova, Navard *Cellulose* 2016, 23, 5-55
Kamide *et al. Polym. J.* 1992, 24, 71-96

NaOH solutions

- second limitation of NaOH as solvent: tendency of solutions to gel irreversibly
- Gelling over time
- Pronounced gelling upon temperature increase



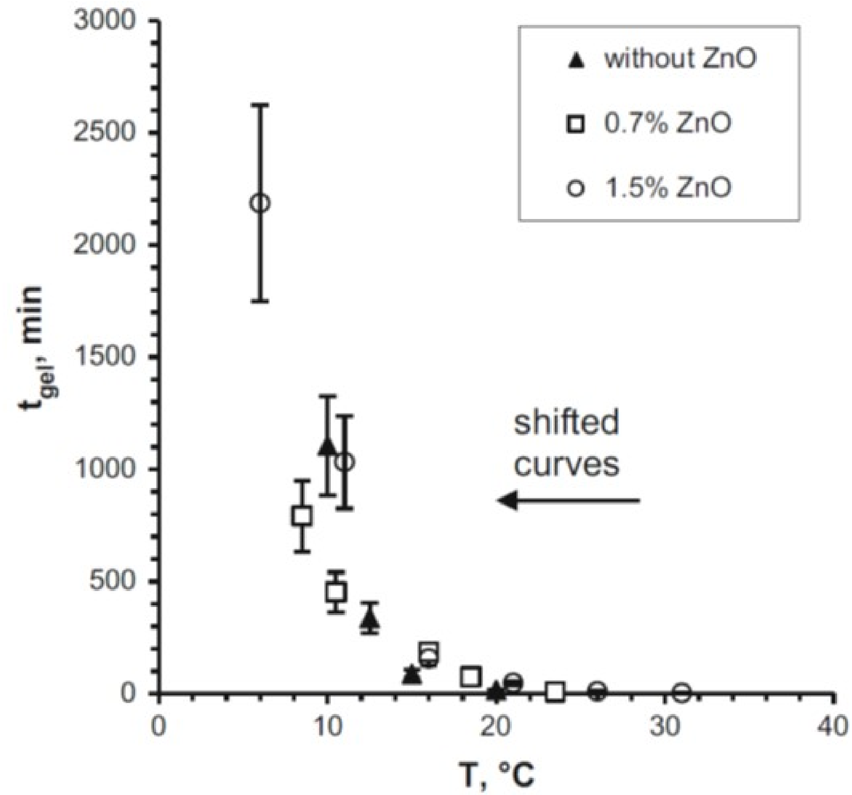
Roy *et al. Biomacromolecules* 2003, 4, 259-264

NaOH solutions – additives

Various additives tested:

- amongst longest know: ZnO
- also urea and thiourea

No confirmed effect on solubility maximum; but stabilization of solution state and hampering of gelation

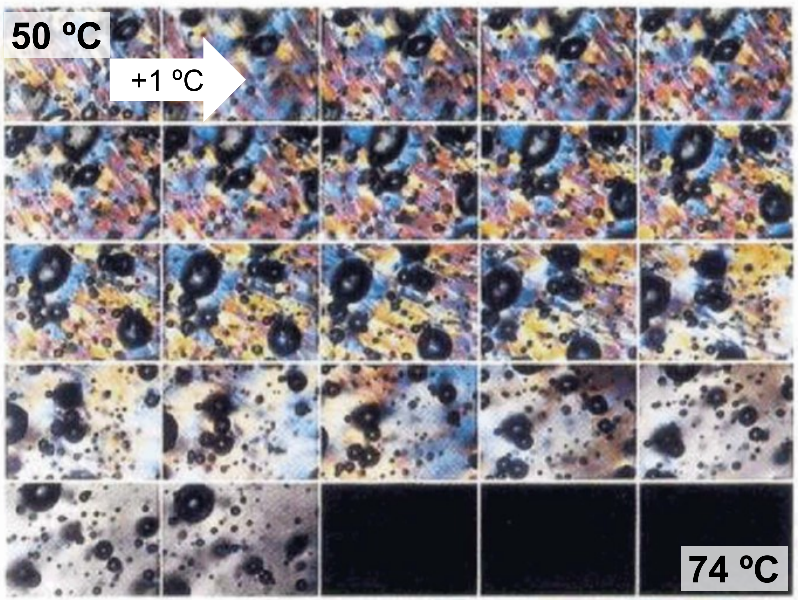


Liu *et al.* *Cellulose* 2011, 18, 663-673

Non-derivatizing – non-aqueous

Superphosphoric acid

phosphoric acid: ca. 54–62% P_2O_5 (75–85% H_3PO_4)
superphosphoric acid*:* 70% P_2O_5 (almost 100% H_3PO_4)



17.1 wt% cellulose in 74.4% P_2O_5

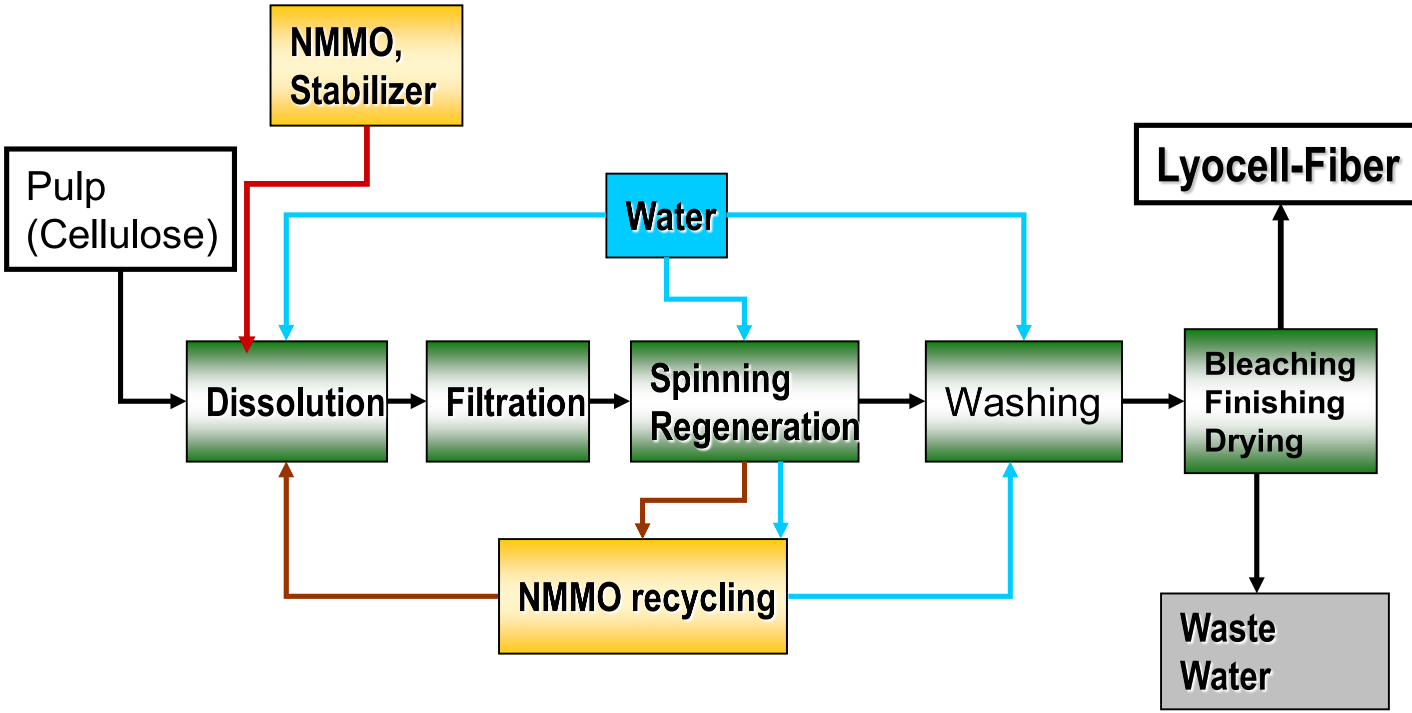
Cellulose dissolved in SPA forms anisotropic solutions (liquid crystalline-like) i.e. cellulose have structured; structure lost upon heating.

Clearing temperature depending on DP and concentration

Pre-orientation can be used to prepare highly orientated cellulose products such as fibers = Fiber B (Bocell): 90 cN/tex

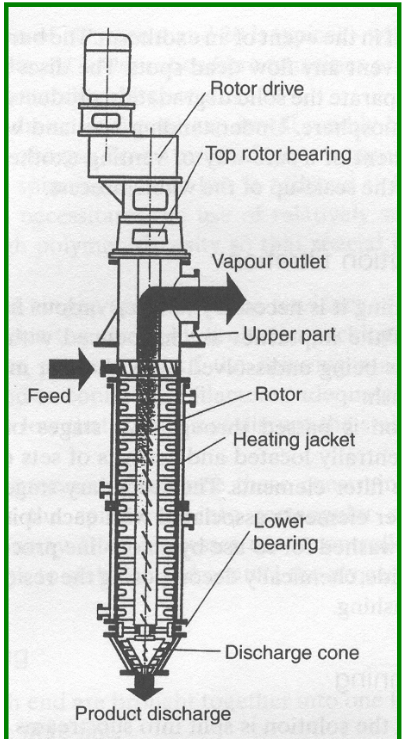
Boerstoel *et al. Polymer* 2001, 42, 7371-7379

Lyocell Process



Video Lab Spinning

Lyocell Dope Preparation

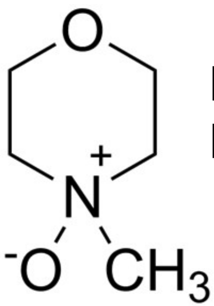


Buss Filmtruder

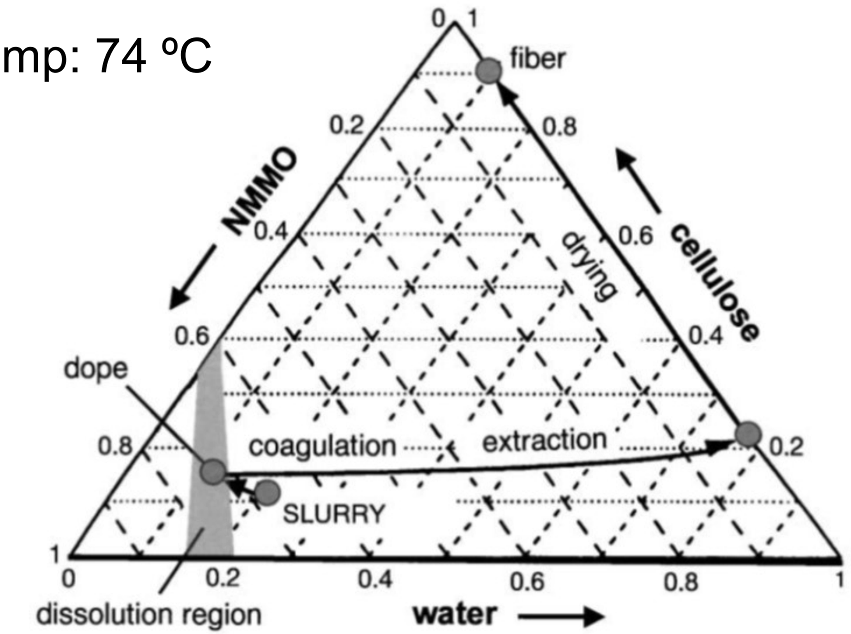
Long vertical vessel with steam heating in jackets around the vessel.

A shaft down the center of the vessel with blades attached to its circumference is rotated to smear the material around the heated surface to promote the evaporation process.

N-methylmorpholine *N*-oxide monohydrate



Neat NMMO: mp 170 ºC
NMMO.H_2O (13.3 wt% H_2O): mp: 74 ºC



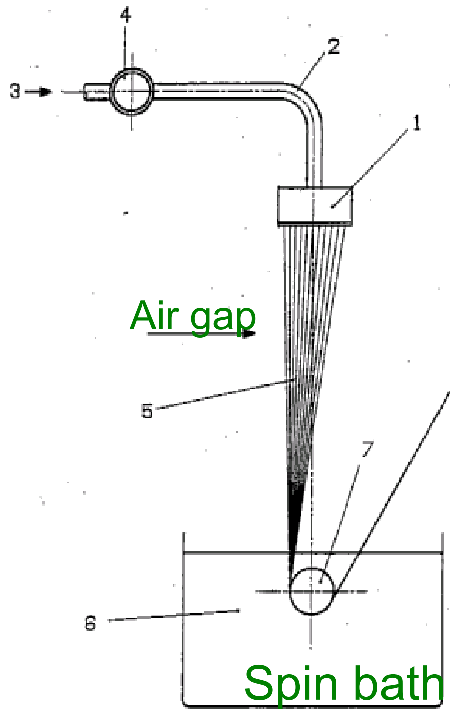
Initial development started at the very end of the 1960s by American Enka/Akzona Inc.

It took until 1992 when Courtauld started its first full-scale production plant in Mobile (USA), followed by Lenzing AG in Heiligenkreuz (Austria) in 1997.

Today, Lenzing owner of all spinning sites (Grimsby, UK)

Instability of NMMO

Dry-jet Wet Spinning (CLY)



- Extrusion of the hot solution via an air gap into an cold aqueous spin bath (20 – 30% solvent).
- The polymer chains are highly oriented through the ratio between take-up velocity and the extrusion velocity (draw ratio between 4 and 20).
- Coagulation takes place when the gel enters the spin bath. No further stretching is necessary.

Spinning, Precipitation

Spinneret, airgap:
chain orientation

Coagulation bath:
Spinodal decompostion, re-formation of hydrogen bonds -> **highly swollen gel in fibrillar form -> fibrillar cellulose II crystal structure**

Structure Formation:
Build-up of a fibrillar network.
Phase separation time < relaxation time

H.A. Coulsey, S.B. Smith. LenzBer, 75, 51-61 (1996)

Summary questions

- What is the difference between regeneration and coagulation?
- Which cellulose derivatives are (or have been) of importance?
- Advantages and drawbacks of the viscose process?
- Examples for non-derivatizing cellulose solvents?
- Advantages and limitations of aqueous NaOH solution as cellulose solvent?
- What is the Lyocell process