

# Cellulose: chemical modification

CHEM-E2140



Aalto University  
School of Chemical  
Engineering

Eero Kontturi

17<sup>th</sup> September 2020

# Learning objectives

After this lecture, you will be able to:

- Distinguish the common pathways of cellulose modification: esterification and etherification
- List the most common cellulose derivatives, how they are made, how they dissolve, and what they are used for
- Be aware of the concept of regioselectivity
- Calculate the degree of substitution

# Outline

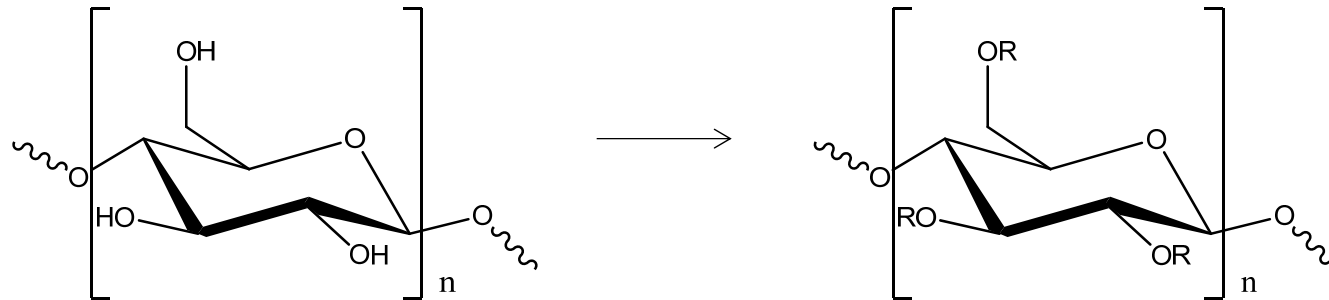
- (1) Chemical modification of cellulose – motivation**
- (2) Background: terminology, challenges**
- (3) Degree of substitution: how to calculate**
- (4) Esterification of cellulose**
- (5) Etherification of cellulose**
- (6) Regioselectivity in chemical modification of cellulose**

# Motivation for cellulose modification

- Preparation of substances that have different properties from cellulose, yet they are of renewable origin and (to an extent) biodegradable
  - One of the most important properties is that most cellulose esters and ethers are *thermoplastic* (cellulose is not)
- Modified cellulose, i.e., cellulose *derivatives* often possess properties that are not easily achieved with totally synthetic polymers
- (With nanocellulose) modify the surface of nanocellulose to achieve better compatibility with its environment (composites etc.) or induce various functionalities (responsivity etc.)

# Basic concepts

- The idea of chemical modification of cellulose is to introduce functional groups in the cellulose backbone



- Usually achieved by substituting the protons in the hydroxyl groups of cellulose to a varying extent

# Basic concepts

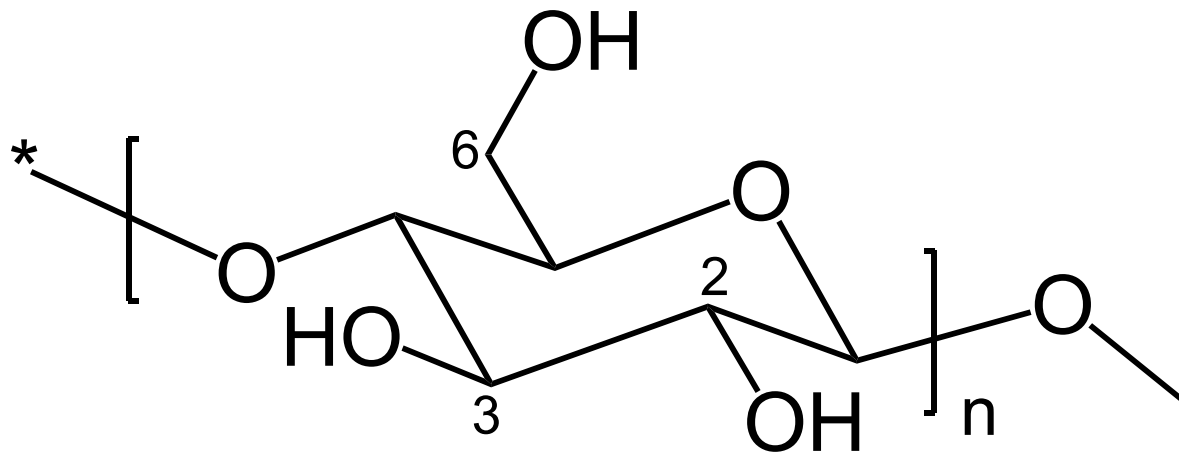
## (1) Homogeneous modification

- Cellulose is dissolved and individualized cellulose chains are modified in a homogeneous solution
- → Uniform, homogeneous modification

## (2) Heterogeneous modification

- Fibres, microfibrils, nanocrystals etc. are modified in a heterogeneous suspension
- → Usually results in surface modification (not necessarily)

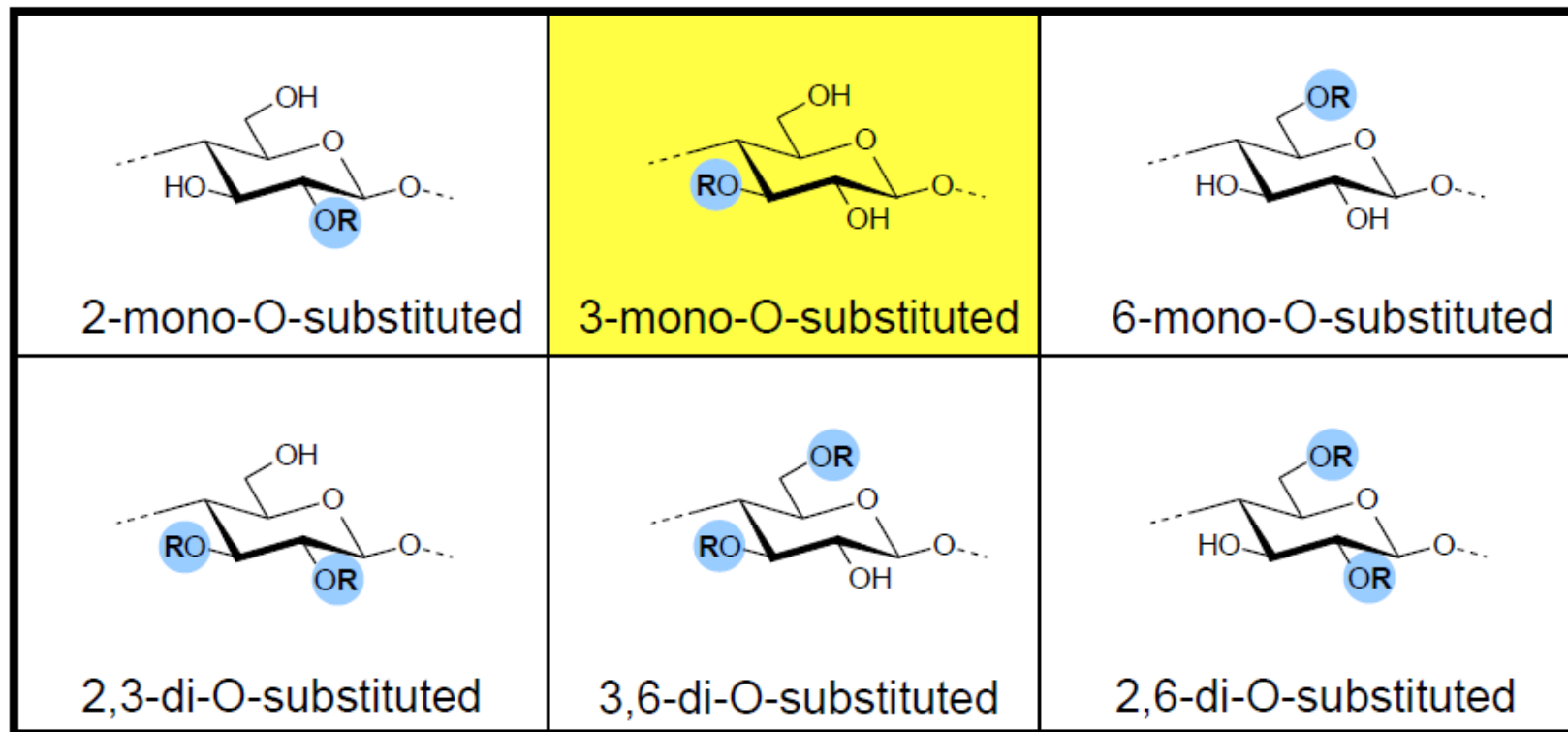
# Labelling of hydroxyl groups



Reactivity in general:  $6 > 2 > 3$

# Basic concepts

Regioselectivity: which OH group/groups are *selectively* modified





# Challenges

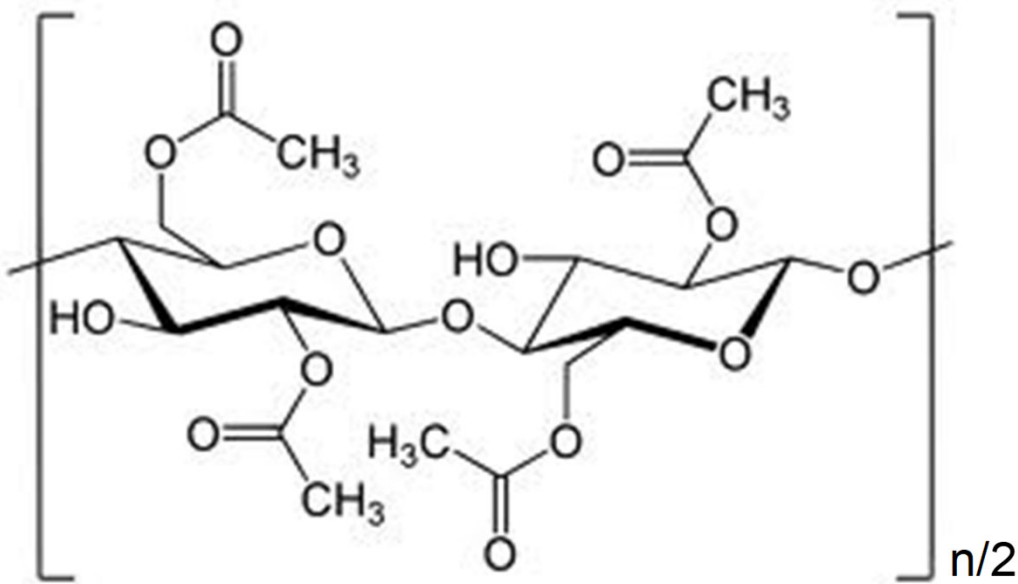
- **The fundamental challenge in chemical modification of cellulose is that cellulose is relatively inert and does not automatically follow the common rules of organic chemistry**
  - Example, cellulose hydroxyl groups are alcohols but they do not form esters with carboxylic acids under normal conditions
- **Reproducible and uniform degree of substitution can be difficult to achieve**
- **Regioselectivity is often difficult to achieve**

# Degree of substitution (DS)

- **Quality which measures the average amount of substituted hydroxyl groups in an anhydroglucose unit**
- **Maximum DS is 3: all 3 hydroxyl groups in all anhydroglucose units have been substituted**
- **On average, if one hydroxyl group per each anhydroglucose unit has been substituted, the DS is 1**
- **If there is only one hydroxyl group substituted per 10 anhydroglucose units, the DS is 0.1**

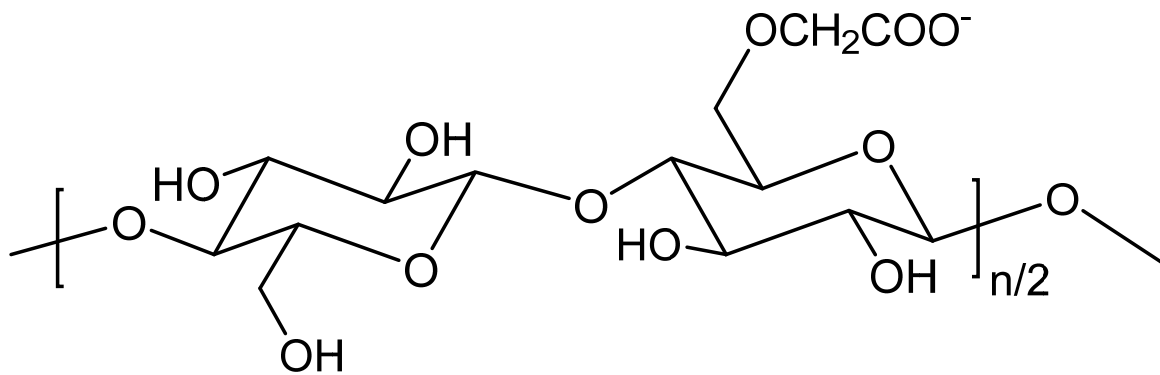
# Assignment: calculate DS

Cellulose acetate



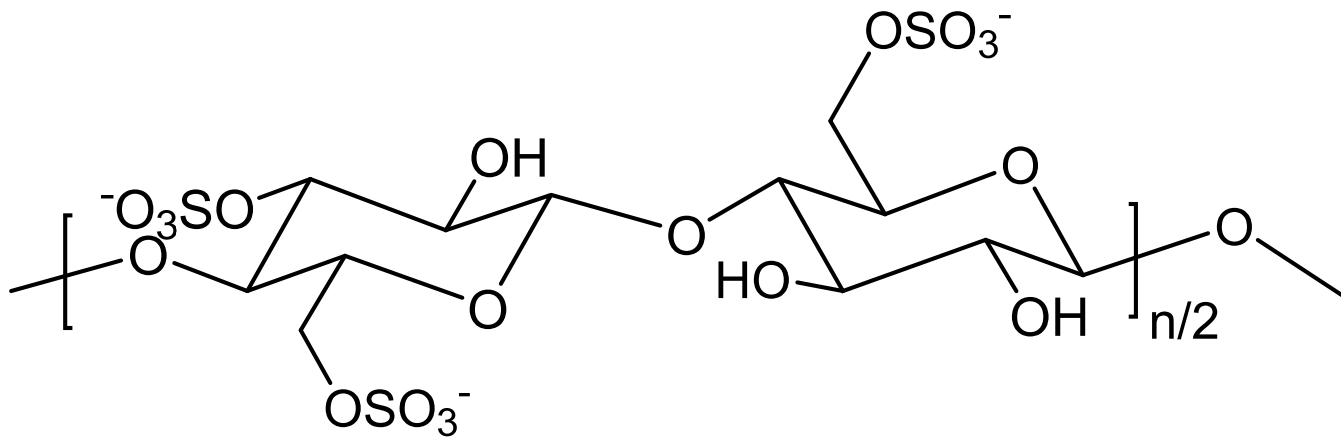
# Assignment: calculate DS

Carboxymethyl cellulose



# Assignment: calculate DS

Cellulose sulphate

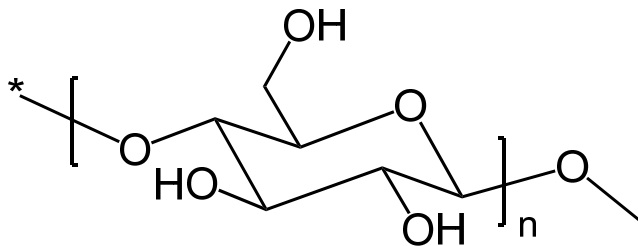


# Assignment: calculate DS

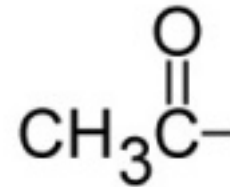
- Cellulose acetate has 39.8% (w/w) acetyl content
- What is the DS?

Aids:

Try it out:  
We'll come back to this  
at the beginning of next  
lecture



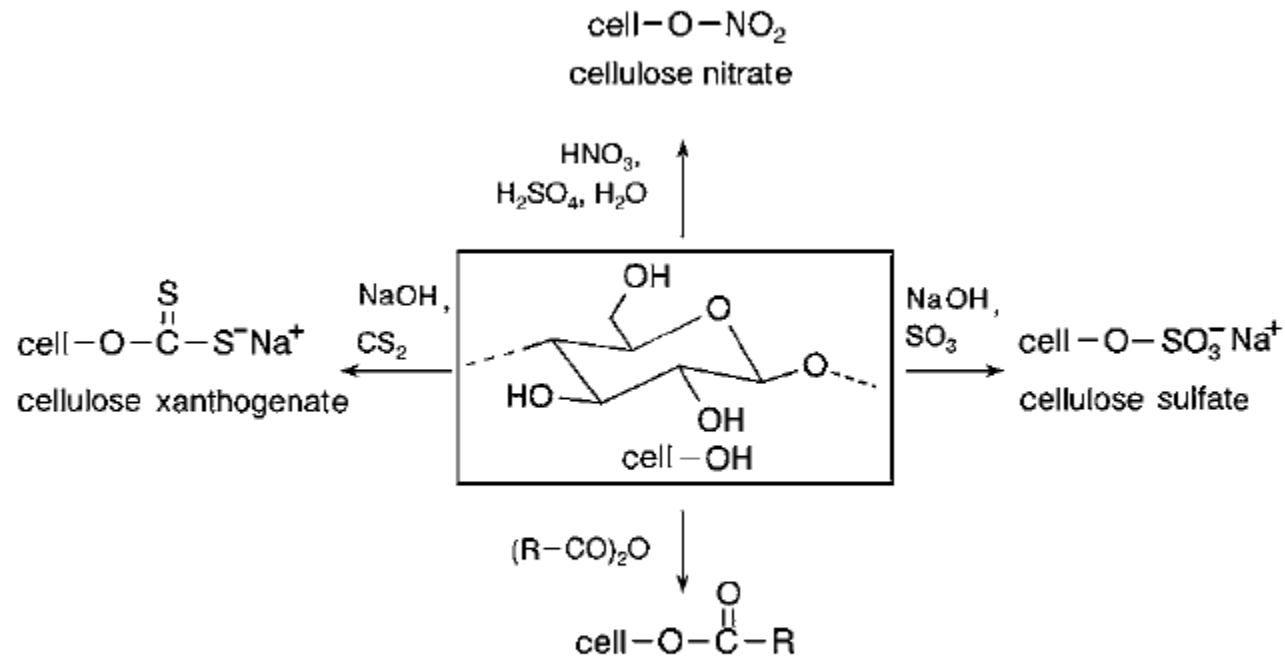
Anhydroglucose (inside brackets)  
M=162 g/mol



Acetyl group  
M=43 g/mol

# Esterification of cellulose

# Commercial cellulose esters



R = CH<sub>3</sub> : cellulose acetate (CA)

R = CH<sub>3</sub> und CH<sub>2</sub>-CH<sub>3</sub> : cellulose acetate propionate (CAP)

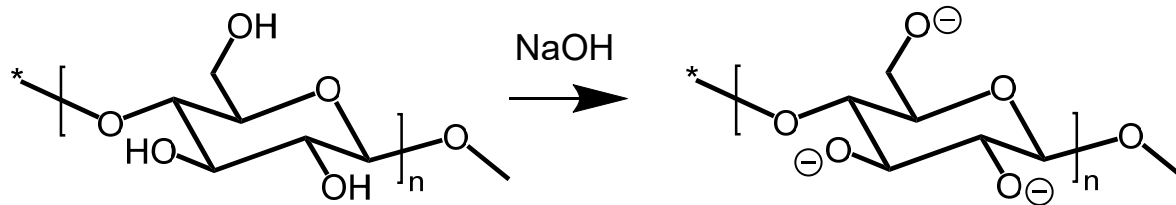
R = CH<sub>3</sub> und CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> : cellulose acetate butyrate (CAB)



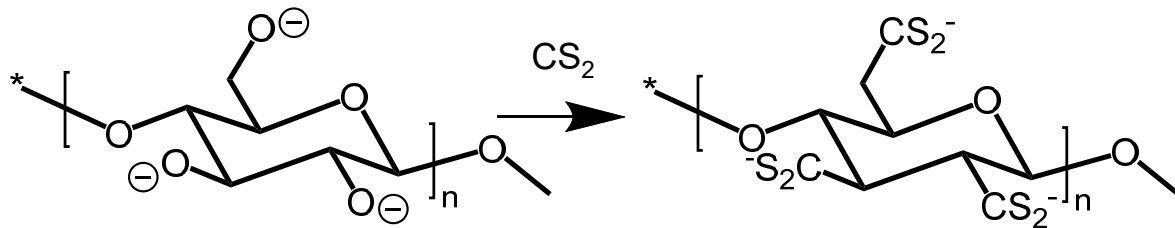
# Inorganic cellulose esters

- Cellulose xanthogenate
- Cellulose carbamate
- Cellulose sulphate
- Cellulose nitrate

# Cellulose xanthogenate



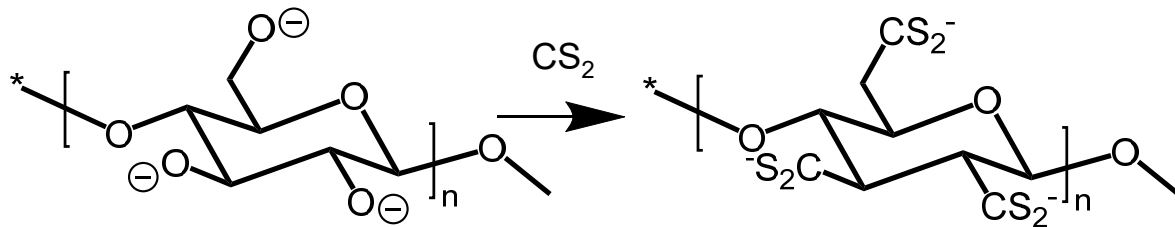
Hydroxyl groups are ionized with strong alkali



Half-ester is created by reacting alkoxy cellulose with CS<sub>2</sub>

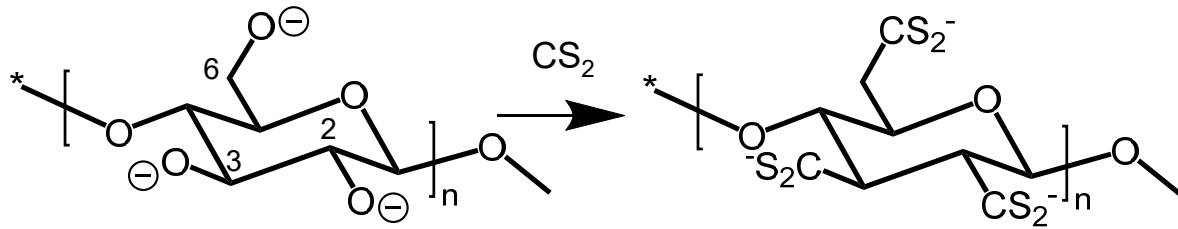
Cellulose xanthogenate is a half-ester, bearing charge  
→ Cellulose xanthogenate is a polyelectrolyte

# Cellulose xanthogenate



- **The reaction is important in practice because of its use in *viscose process***
  - Cellulose xanthogenate is produced from native cellulose
  - Cellulose xanthogenate is dissolved
  - The dissolved xanthogenate is regenerated in acid solution, enabling controlled regeneration of cellulose into fibres and films

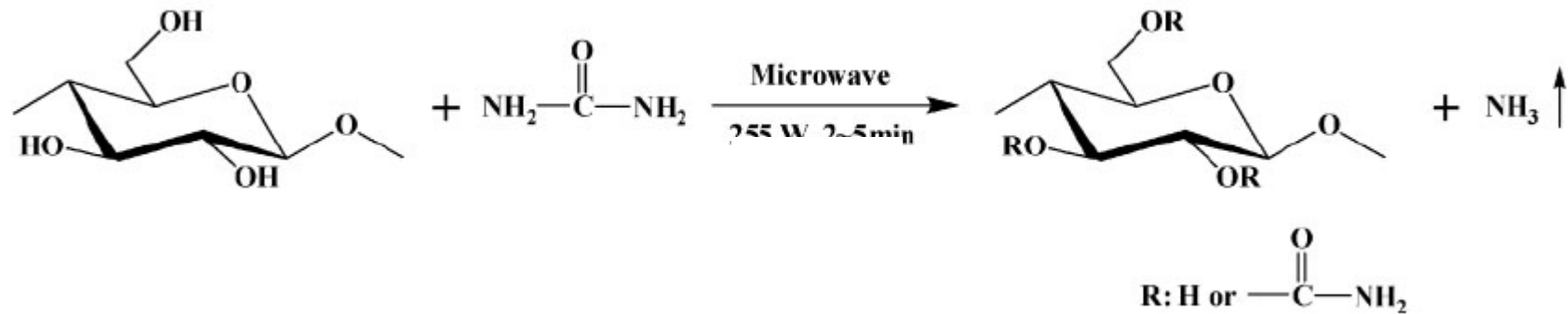
# Cellulose xanthogenate



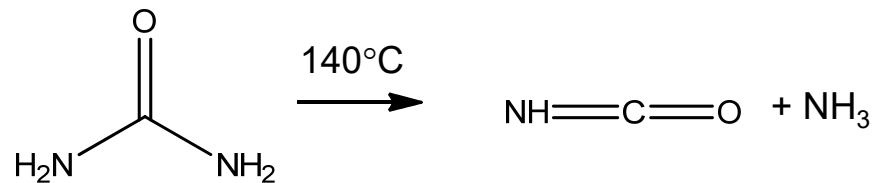
Examples of DS and hydroxyl selectivity at different stages of viscose process

Xanthogenated cellulose material	DS at C-2/C-3	DS at C-6
Fiber xanthogenate (DS 0.61)	0.38	0.17
Viscose, non-ripened (DS 0.58)	0.34	0.24
Viscose, moderately ripened (DS 0.49)	0.16	0.32
Viscose, extensively ripened (DS 0.28)	0	0.32

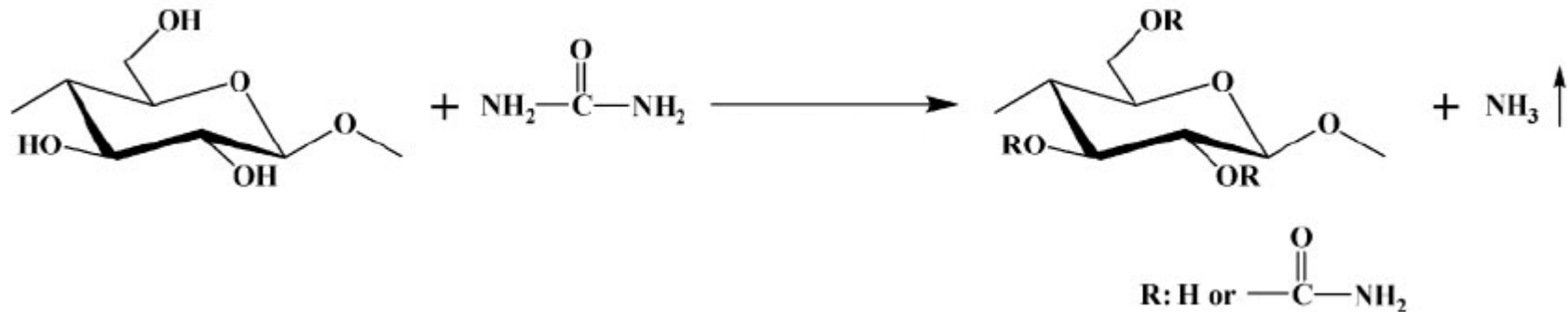
# Cellulose carbamate



- High temperature reaction ( $\sim 140^\circ$ ): processed above the melting point of urea
- Catalyzed by metal salts, particularly zinc sulphate is used
- Urea forms isocyanic acid which is the actual reagent with cellulose:

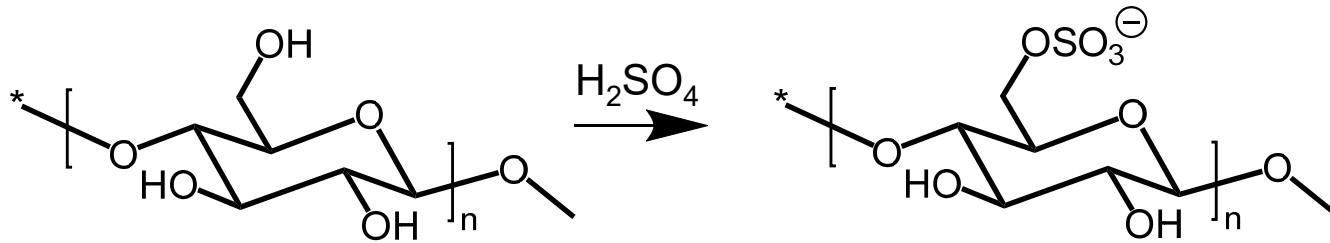


# Cellulose carbamate



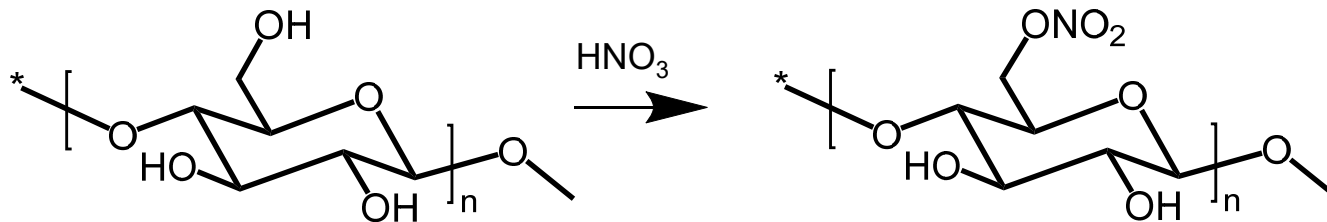
- Cellulose carbamate with DS 0.2-0.3 can be dissolved in aqueous NaOH
- Basis for the CarbaCell process:
  - Aimed at substituting the environmentally hazardous viscose process
  - Enabled by the effortless conversion of carbamate into cellulose in alkali
  - No commercial applications as of yet

# Cellulose sulphate



- Can be prepared in a large variety of systems, usually containing either  $SO_3$  or sulphuric acid
- Water soluble at above DS 0.2-0.3
- Preparation is generally accompanied by severe chain degradation due to acid hydrolysis
- Biomedical applications proposed

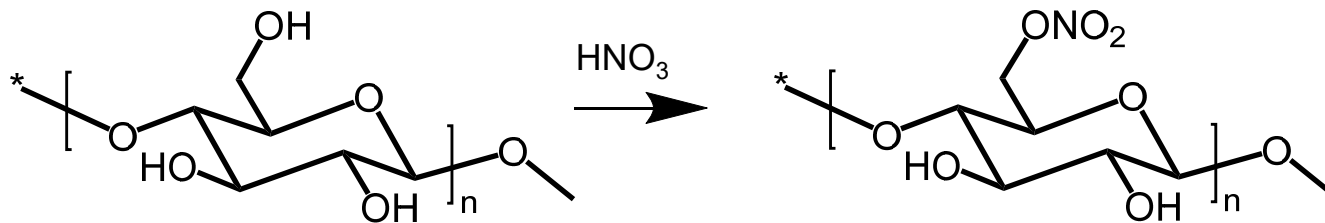
# Cellulose nitrate



- Traditionally produced in a ternary system:  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$
- Nitrogen contents of commercial cellulose nitrates range from 10.5-13.6%



# Cellulose nitrate



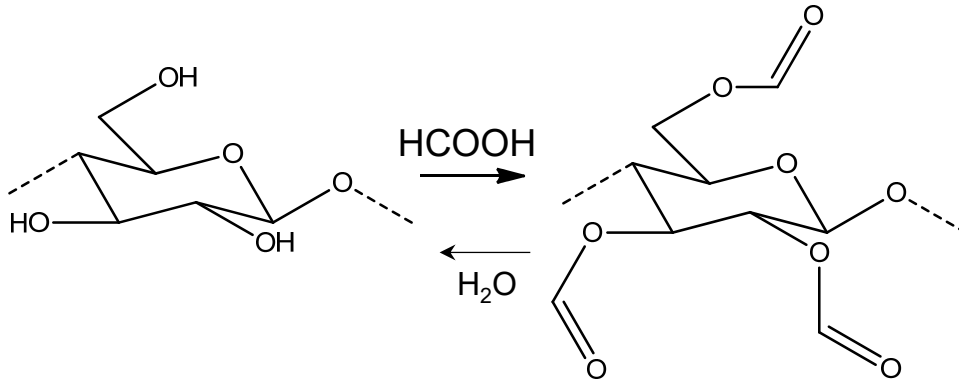
## Applications

- Celluloid (combs, hair ornaments, ping pong balls)
- Explosives (nitrogen content above 12.6%)
- Filters, membranes
- Component in lacquers

# Organic cellulose esters

- Cellulose formate
- Cellulose acetate

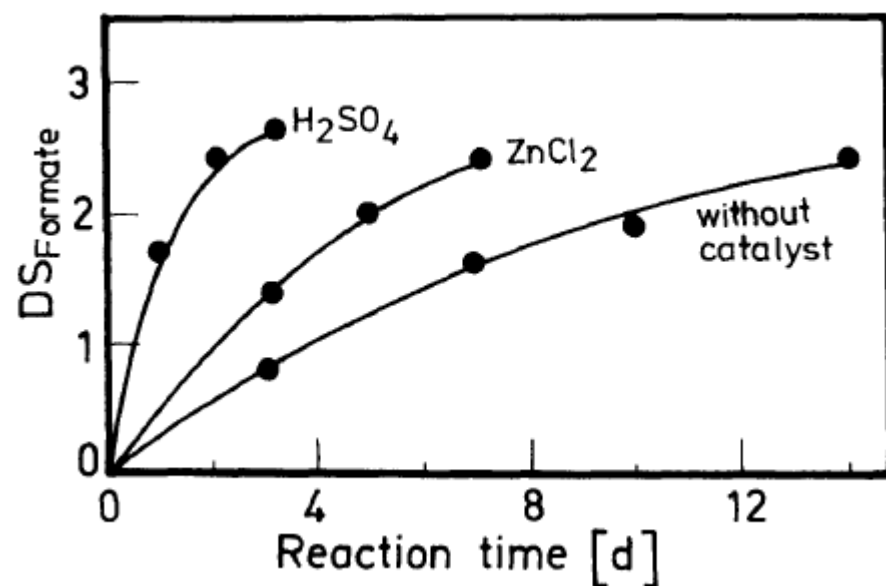
# Cellulose formate



- Among the only organic esterifications that proceed spontaneously with the free acid itself
- Cellulose formate is unstable: cellulose formate with DS 2.0-2.5 is decomposed to cellulose and formic acid in 10 h in boiling water

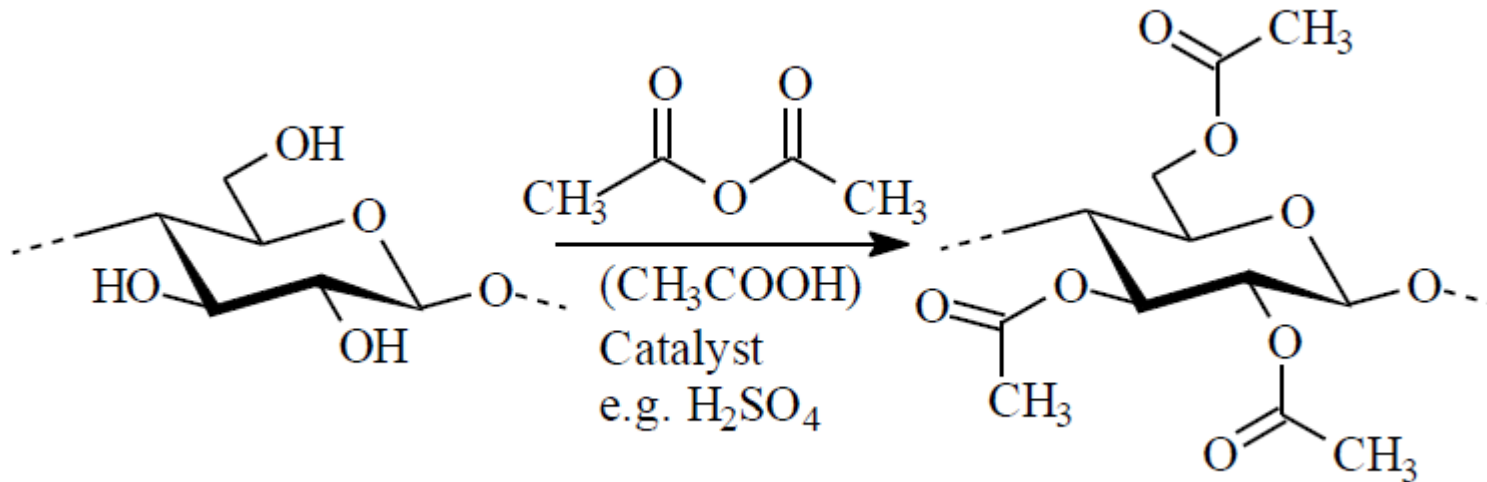
# Cellulose formate

## Effect of catalyst on formation



- Very high DS values of cellulose formate can be achieved

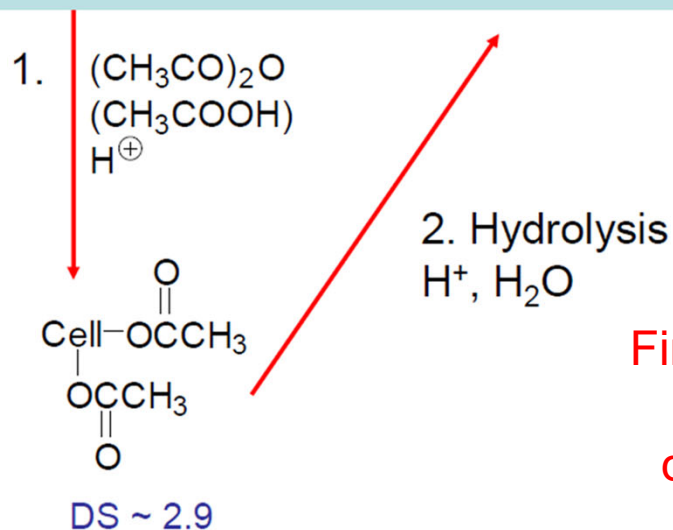
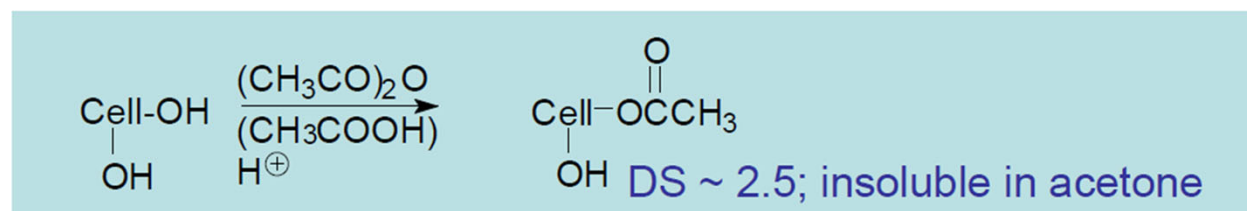
# Cellulose acetate



- Cellulose acetylation proceeds with acetic anhydride and a suitable catalyst in water-free conditions
- Acetic acid alone is not sufficient to acetylate cellulose

# Cellulose acetate (DS 2.5)

## Commercial synthesis



First, cellulose triacetate (CTA) is formed after which it is deacetylated in homogeneous conditions.

# Cellulose acetate solubility

- Strong dependence on DS and position

Liquid	$DS_{Ac}$ range of solubility for partially deacetylated cellulose acetate	
	in C-2/-3/-6 position <sup>a</sup>	in C-2/-3 position <sup>b</sup>
Water	0.8–1.0	insoluble
DMF	1.8–2.7	1.3–2.8
Acetone (< 0.01 % H <sub>2</sub> O)	insoluble	insoluble
Acetone (1 % H <sub>2</sub> O)	2.3–2.6	2.5–2.6
Pyridine	0.8–2.7	1.2–2.8
Pyridine/H <sub>2</sub> O (1 : 1 v/v)	0.6–2.0	1.2–1.6
Ethyl lactate	1.6–2.7	2.6–2.8

# Cellulose acetate

## Applications

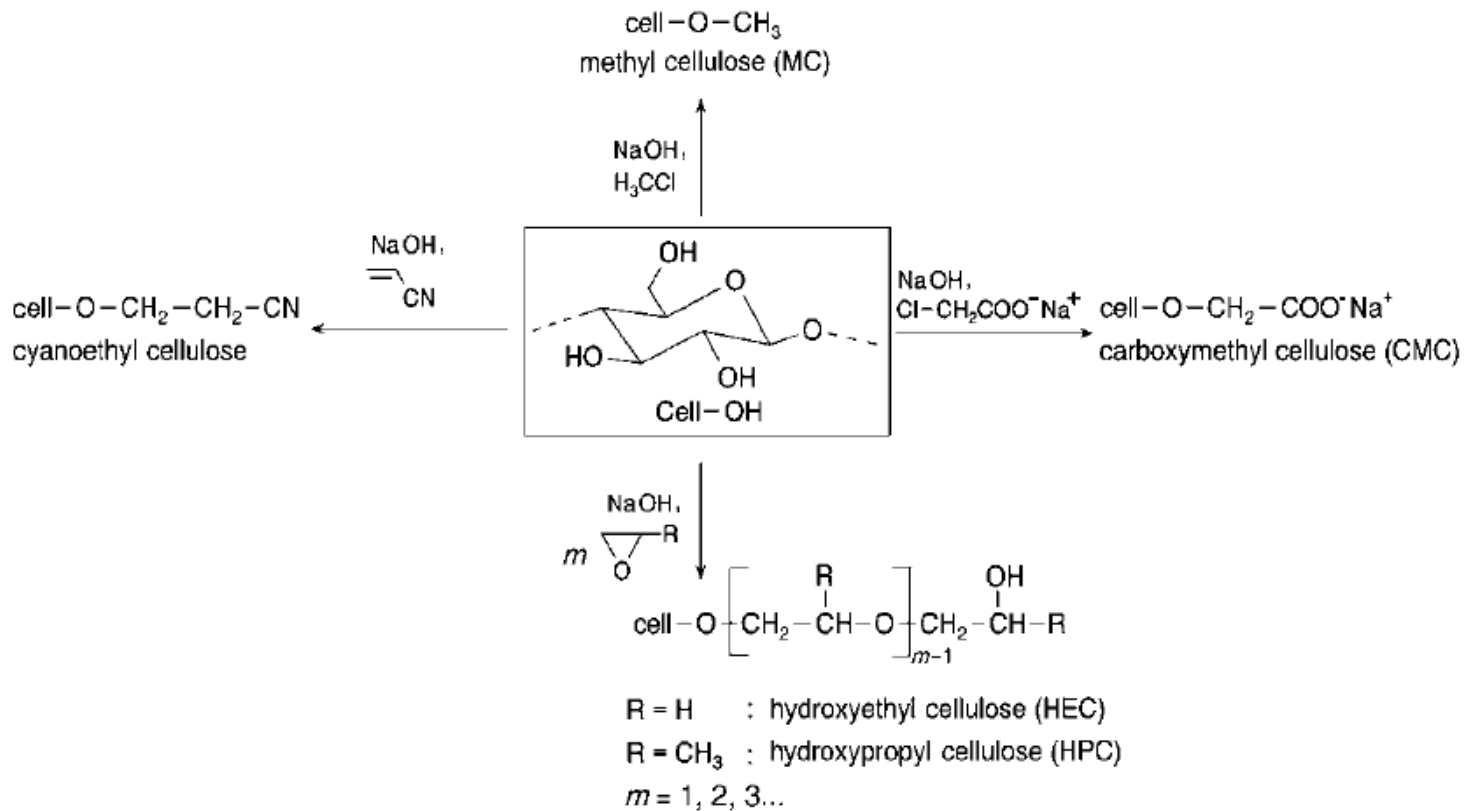
- **Coatings (LCD displays)**
- **Photographic films**
- **Thermoplastic compounds**
- **Isolation foils**
- **Cigarette filters**



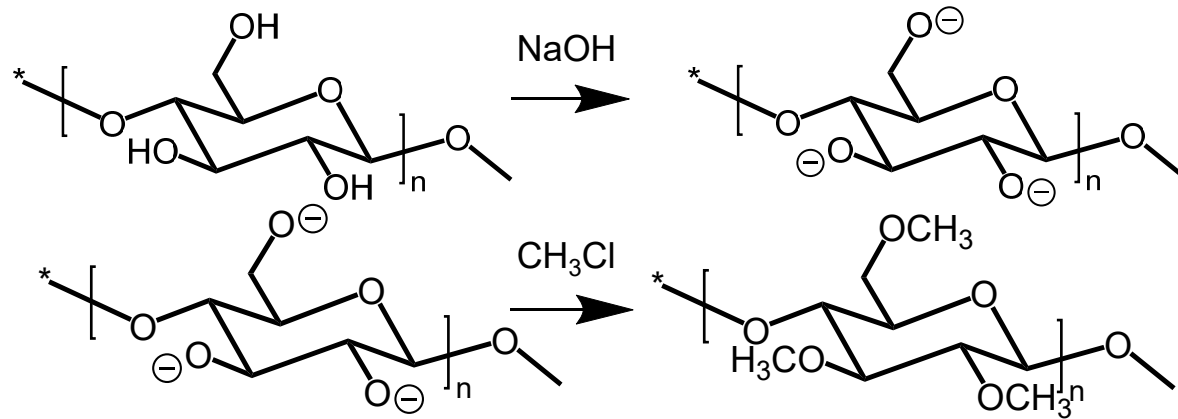
# Cellulose ethers

- Methyl cellulose
- Carboxymethyl cellulose

# Commercial cellulose ethers



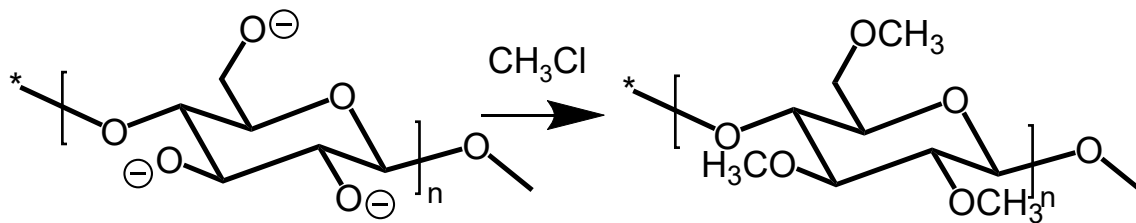
# Methyl cellulose



Hydroxyl groups are ionized with strong alkali

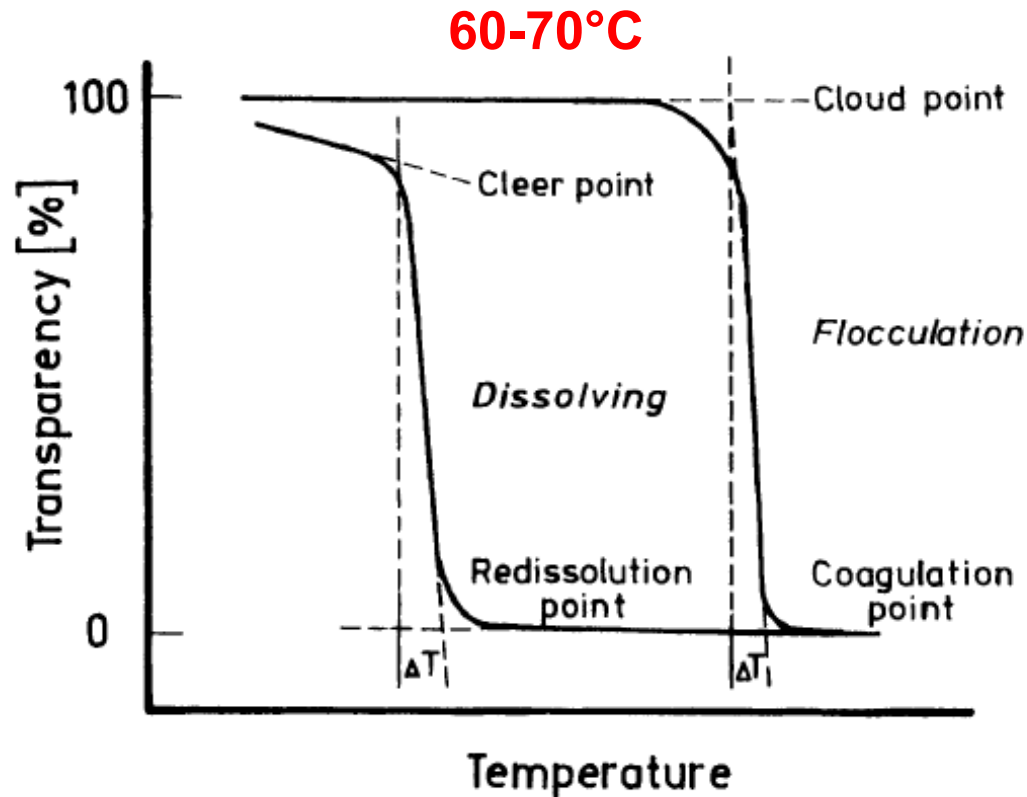
- Conventional preparation by Williamson reaction with gaseous or liquid chloroform ( $S_N2$  type nucleophilic substitution)
- 40% NaOH used in the industrial procedure (heterogeneous reaction)
- Methylation performed at ca. 70-90°C

# Methyl cellulose



- **DS 1.5-2.0 are produced commercially**
- **Water soluble at DS 1.4-2.0**
- **Coordination of water around hydrophobic methyl groups induces water solubility**

# Methyl cellulose – thermal response



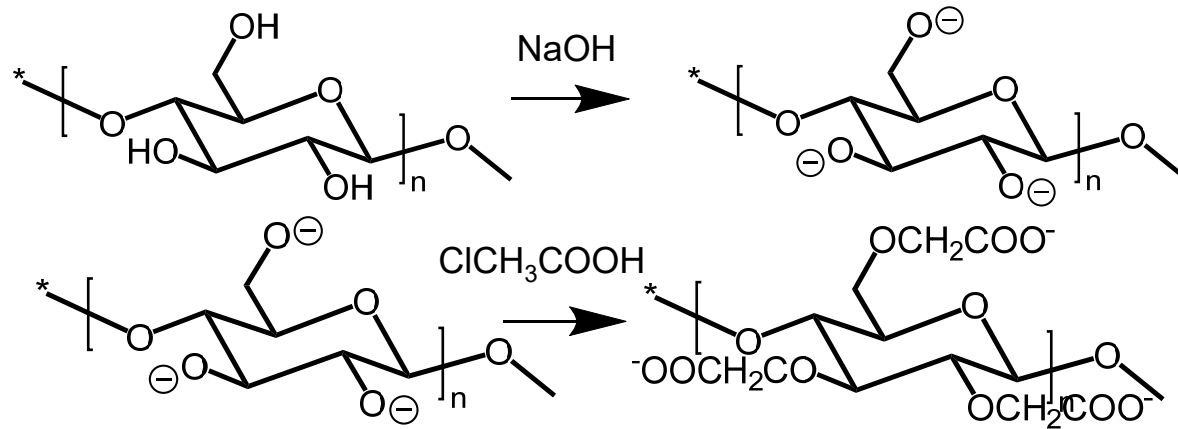
**Between DS 1.7-2.3**

- Solubility is temperature sensitive.
- Gels form above a critical temperature and the gelation is reversible.

# Methyl cellulose applications

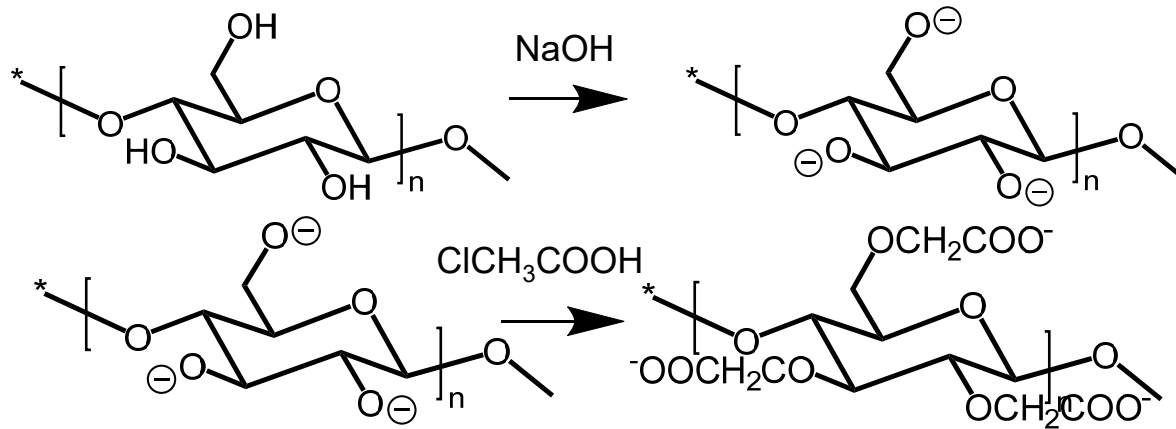
Application area	Proportion ( %)
Building industry	47
Dispersion paints	21
Wall paper paints	14
Cosmetics	5
Polymerization	5
Detergents	4
Other	4

# Carboxymethyl cellulose



- **Generally produced by a substitution reaction of monochloroacetic acid to alkoxy cellulose**

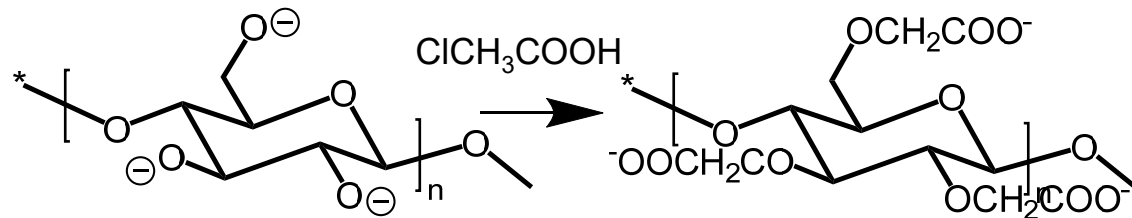
# Carboxymethyl cellulose



- **20-30% NaOH concentration**
- **Temperature 50-70°C**
- **Exothermic process**
- **Heterogeneous process in water/isopropanol (or water/t-butanol)**



# Carboxymethyl cellulose



- Commercial grades possess DS values 0.4-0.8
- CMC is water-soluble when DS>0.4
- Aqueous CMC solution does not usually represent a complete dissolution down to the molecular level

# Carboxymethyl cellulose

- **Purified CMC**

- CMC-content min. 98 %

- CMC-content min. 99,5 %

- **Technical CMC**

- CMC-content 55 – 75 %

- **Main application areas**

- paper and board
- oil drilling
- paints
- mining

- **Main application areas**

- food
- dental
- pharmaceutical

- **Main application areas**

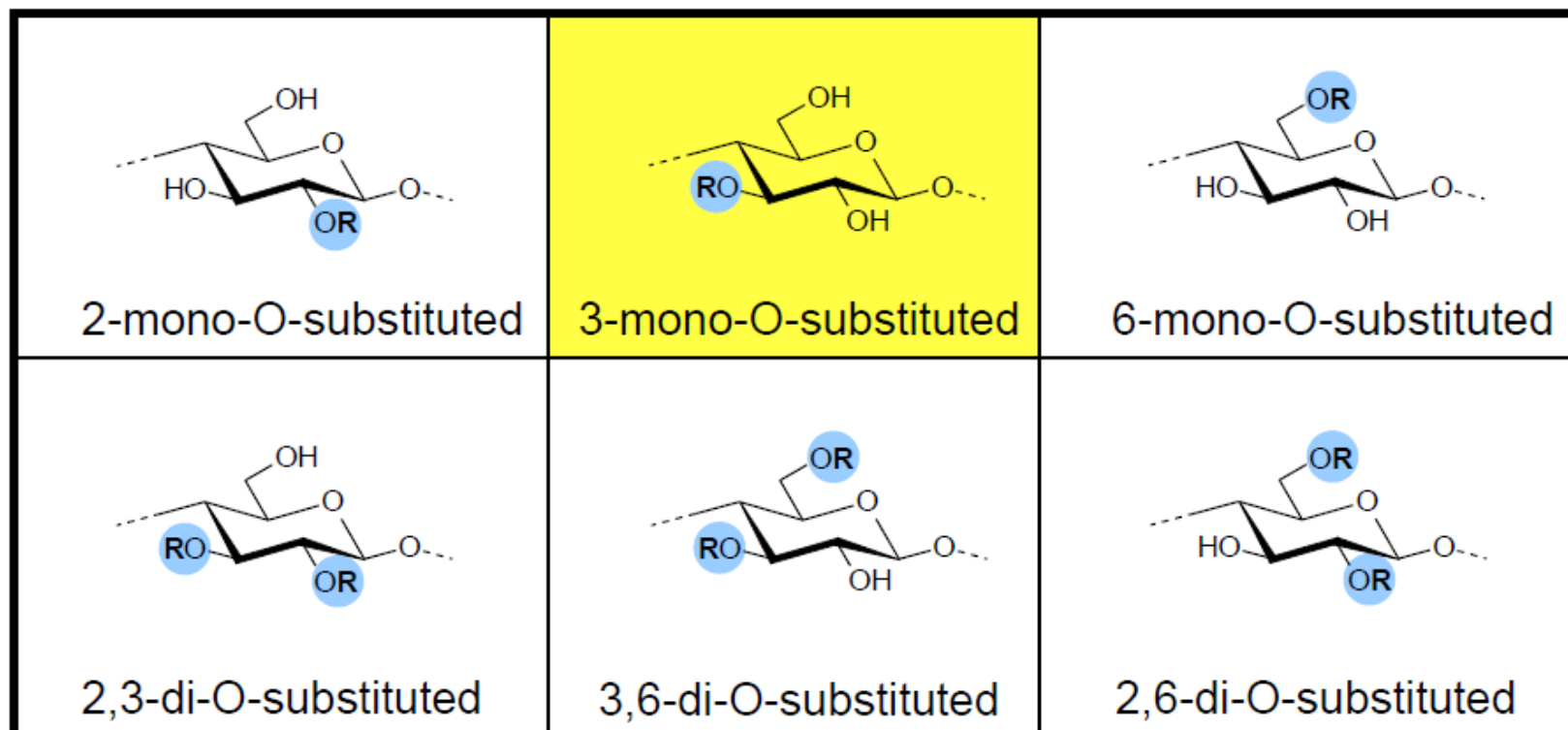
- detergent
- oil drilling
- paper and board
- mining
- construction

# Regioselective modification of cellulose

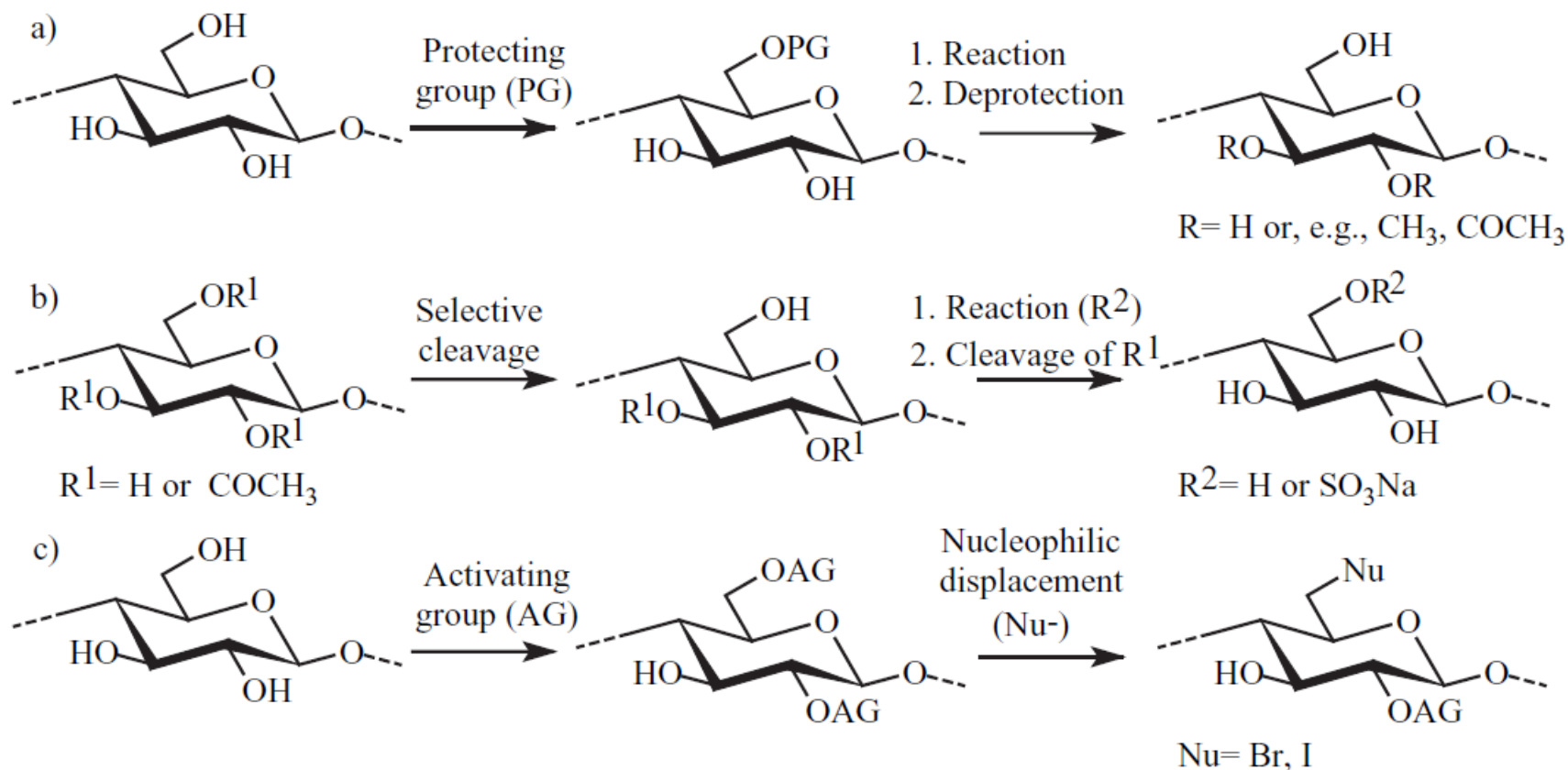
# Regioselectivity issues

- **Generally, cellulose hydroxyl groups react in the order O6>O2>O3**
- **Reactivity of different hydroxyl groups can be tuned by reaction conditions but they are rarely exclusive**
- **Regioselective synthesis applies various pathways to achieve nearly complete regioselectivity of certain OH group / groups**
- **Regioselectively prepared cellulose derivatives yield information on the structure-property relationship of polysaccharides and the function of the different hydroxyls on cellulose**

# Regioselectivity nomenclature

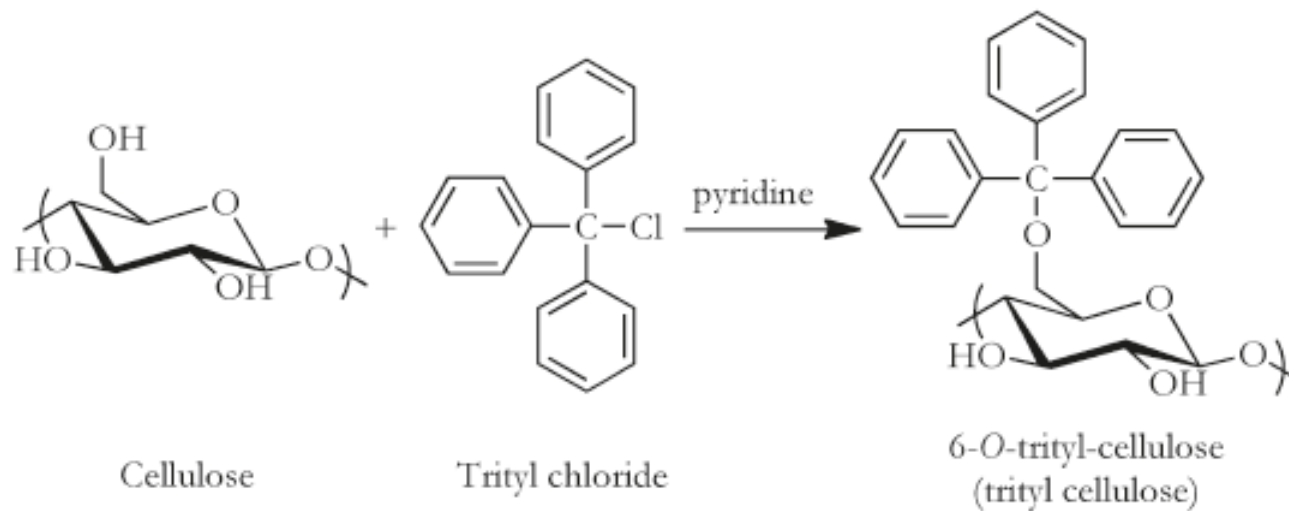


# Pathways to regioselectivity

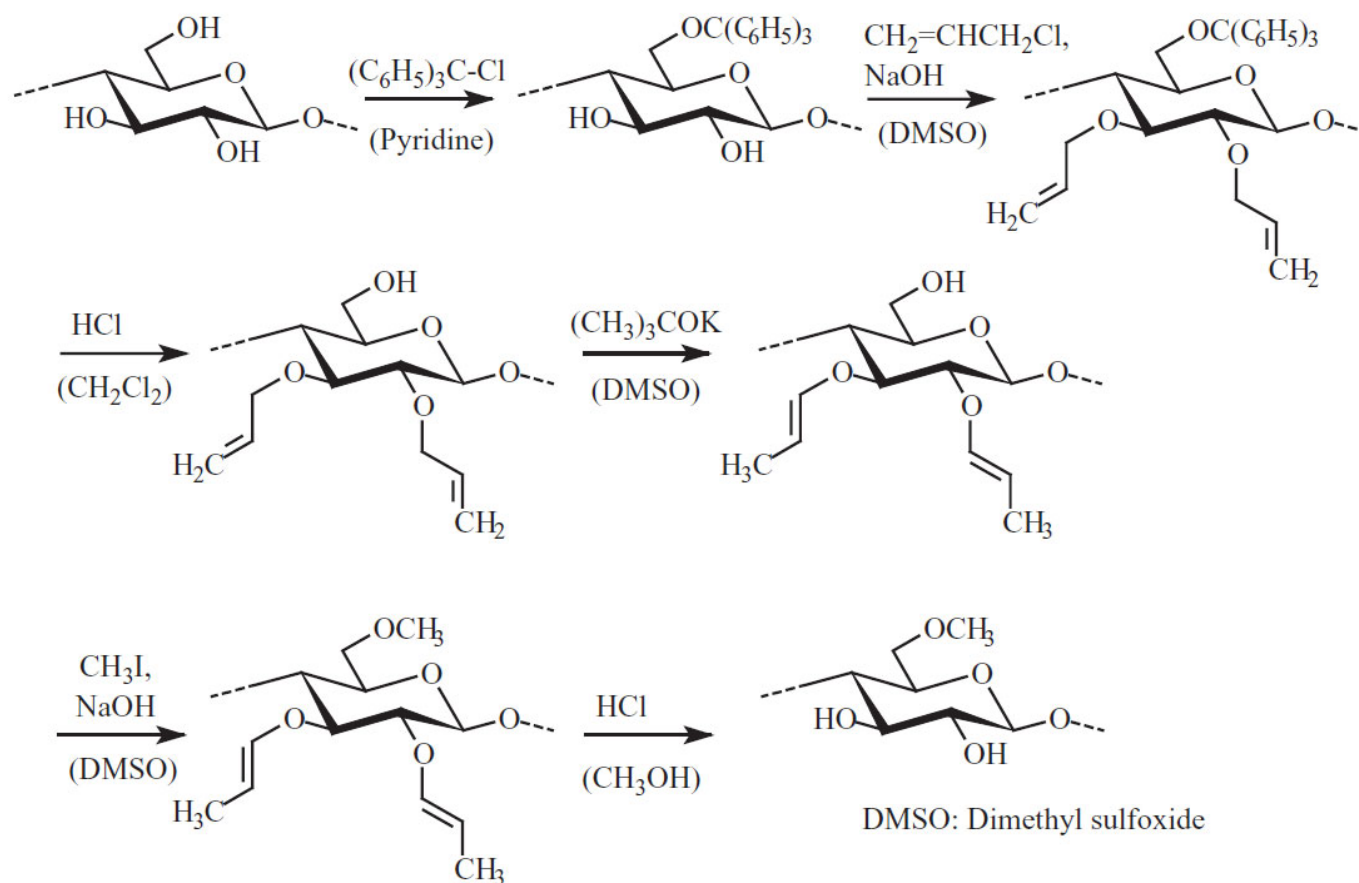


# Protective group: trityl

One of the most popular protective groups for regioselective modification is triphenylmethyl (trityl)



# 6-mono-O-methyl cellulose





# Summary

- **Organic esterification of cellulose requires a more reactive reagent than carboxylic acid, such as acetic anhydride**
- **Etherification of cellulose proceeds generally via alkoxy ion, generated with harsh alkaline conditions**
- **Regioselective cellulose modification is a modern trend; it is an important scientific advance in cellulose modification**