Cellulose chemistry: an introduction

Aalto University
School of Chemical Engineering

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Learning outcomes

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

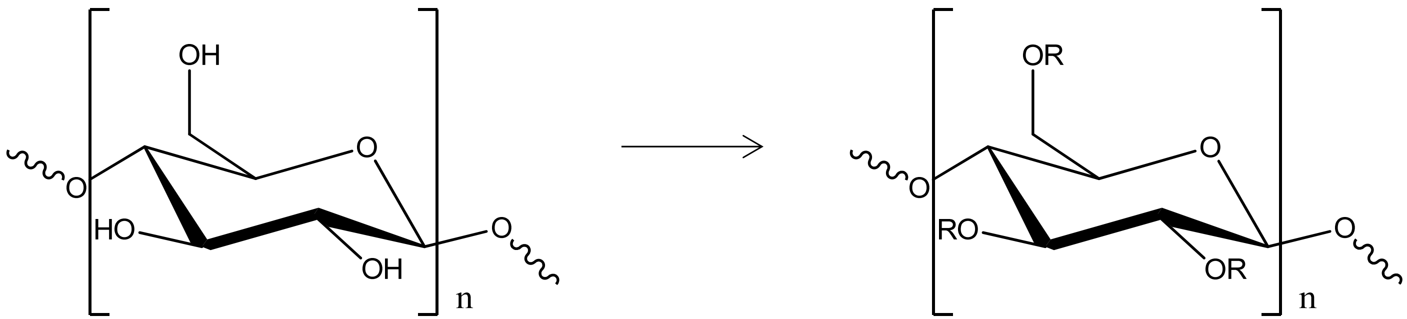
- **Preparation of substances that have different properties from cellulose, yet they are of renewable origin and (to an extent) biodegradable**
  - One of the most important properties is that most cellulose esters and ethers are *thermoplastic* (cellulose is not)

- **Modified cellulose, i.e., cellulose *derivatives* often possess properties that are not easily achieved with totally synthetic polymers**

- **(With nanocellulose) modify the surface of nanocelluose 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

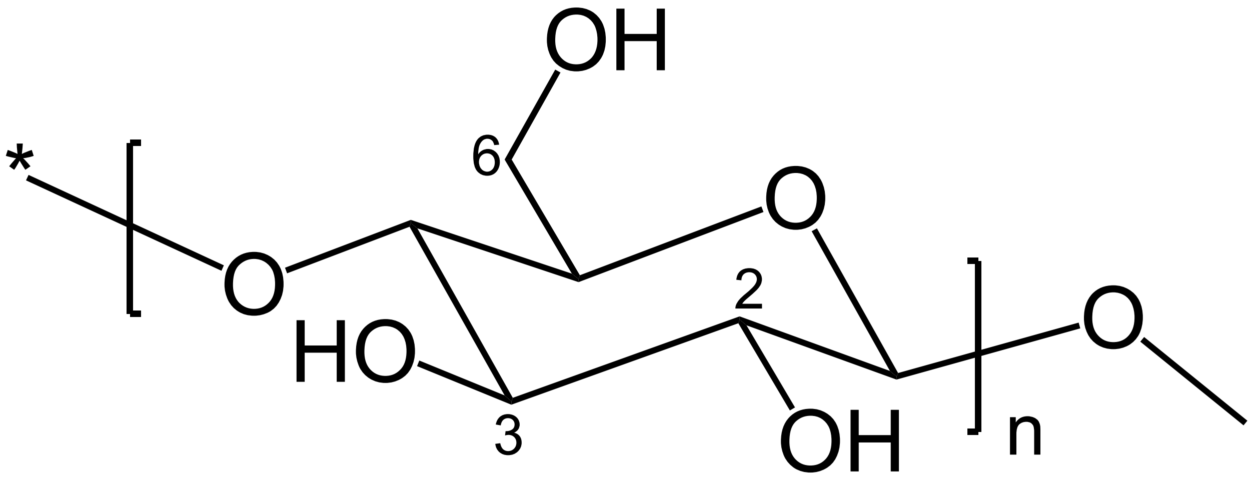
(1)Homogeneous modification

- 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)

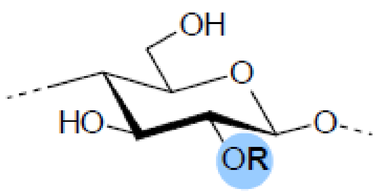
Labelling of hydroxyl groups



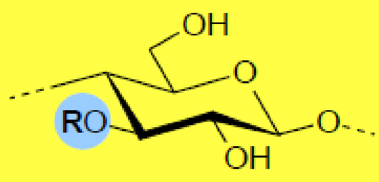
Reactivity in general: 6>2>3

Basic concepts

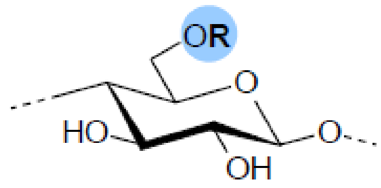
Regioselectivity: which OH group/groups are *selectively* modified



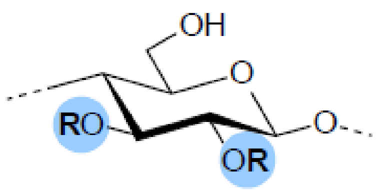
2-mono-O-substituted



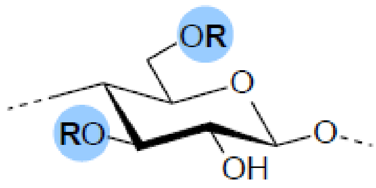
3-mono-O-substituted



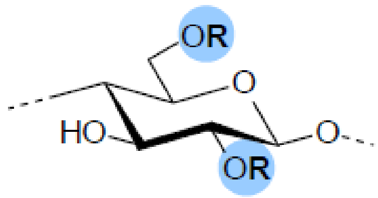
6-mono-O-substituted



2,3-di-O-substituted



3,6-di-O-substituted



2,6-di-O-substituted

Challenges

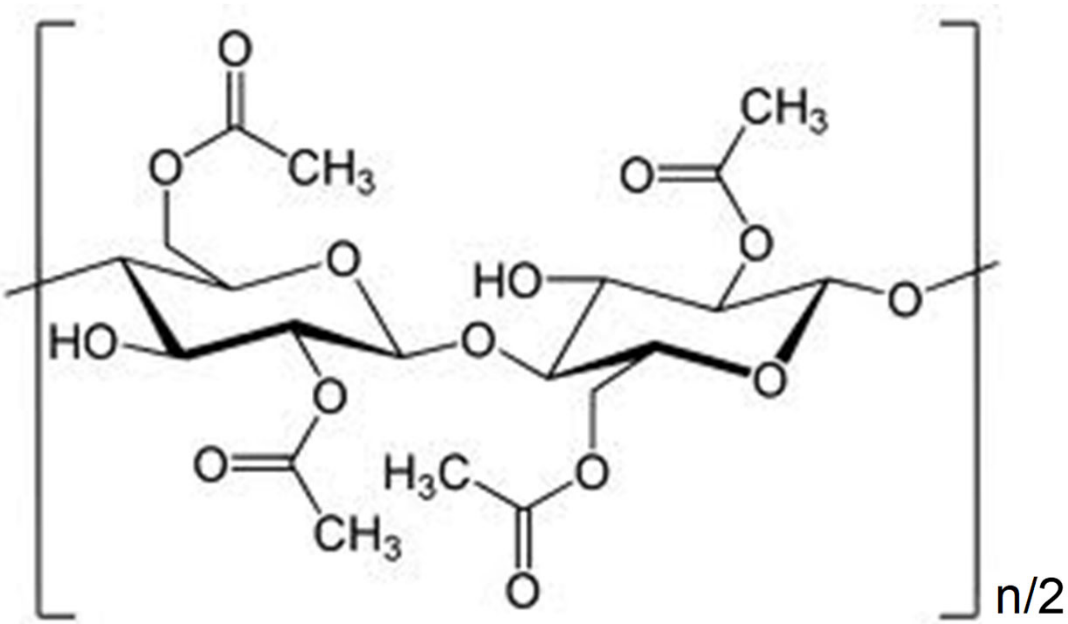
- **The fundamental challenge in chemical modification of cellulose is that cellulose is relatively inert and does not automatically follow the common rules of organic chemistry**
  - Example, cellulose hydroxyl groups are alcohols but they do not form esters with carboxylic acids under normal conditions
- **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



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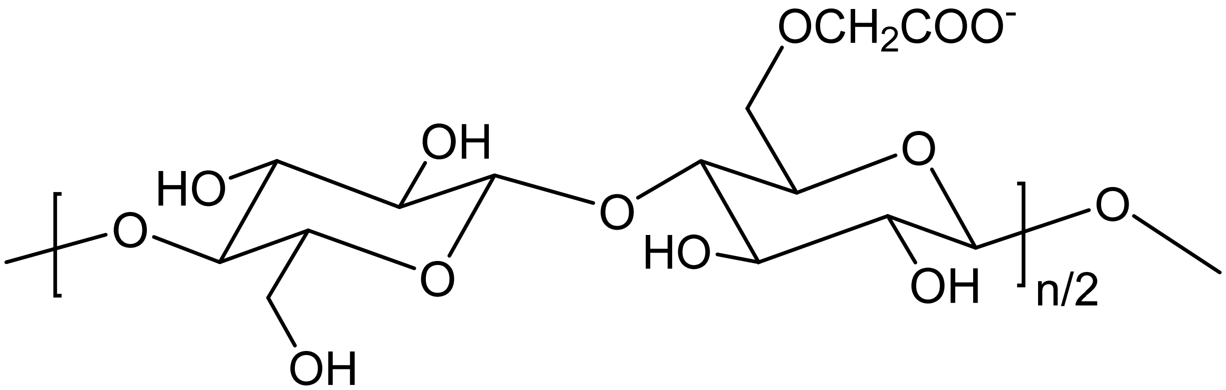
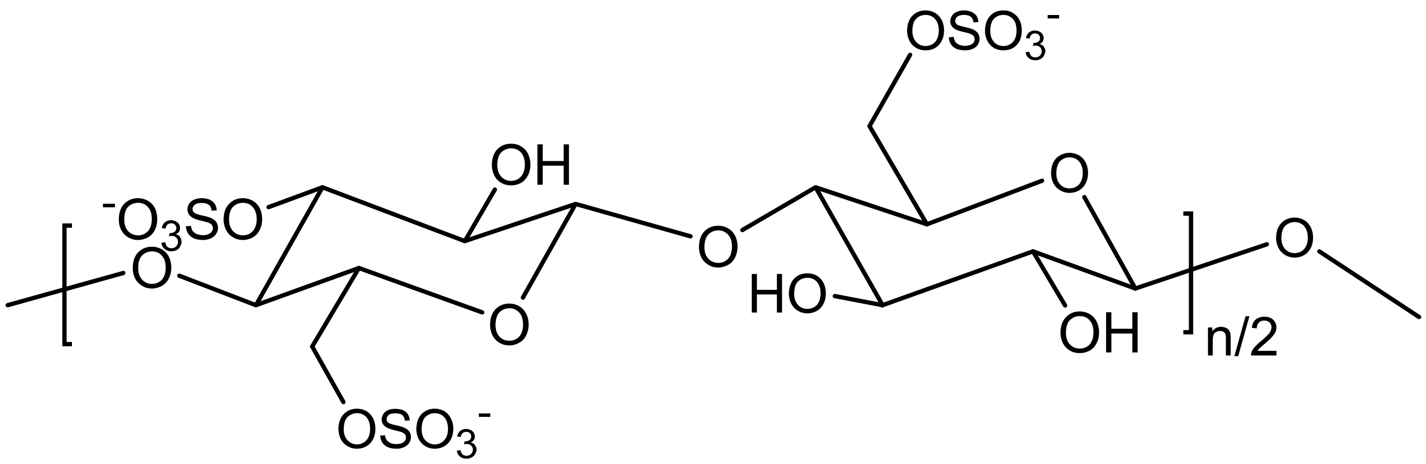
Assignment: calculate DS

Carboxymethyl cellulose



Assignment: calculate DS

Cellulose sulphate



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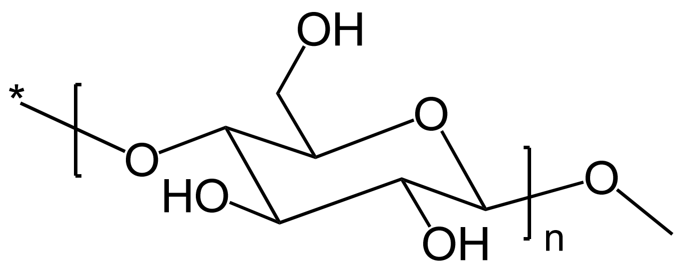
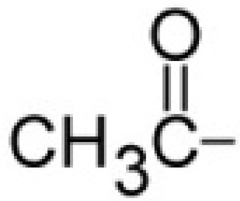
Assignment: calculate DS

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

Aids:



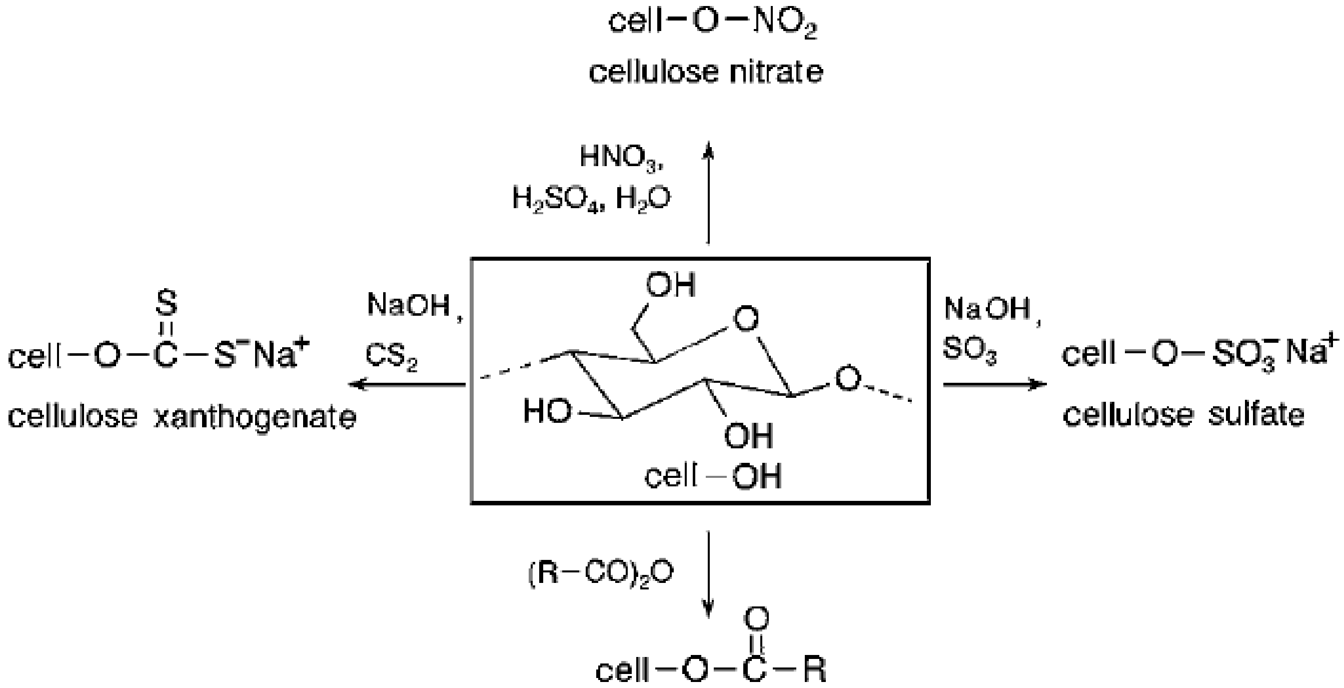


Anhydroglucose (inside brackets)
M=162 g/mol

Acetyl group
M=43 g/mol

Esterification of cellulose

Commercial cellulose esters



R = CH_3: cellulose acetate (CA)

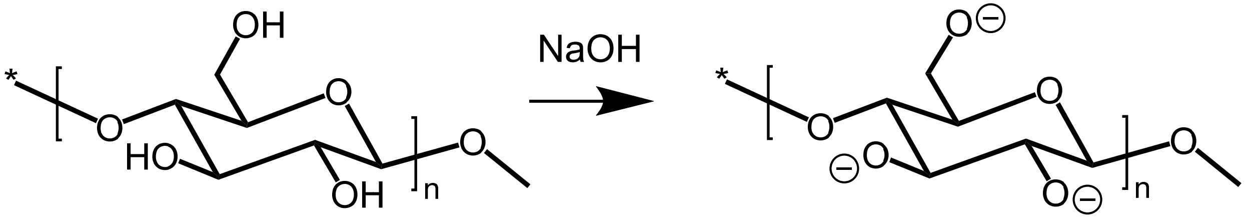
R = CH_3 und CH_2-CH_3 : cellulose acetate propionate (CAP)

R = CH_3 und $CH_2-CH_2-CH_3$: cellulose acetate butyrate (CAB)

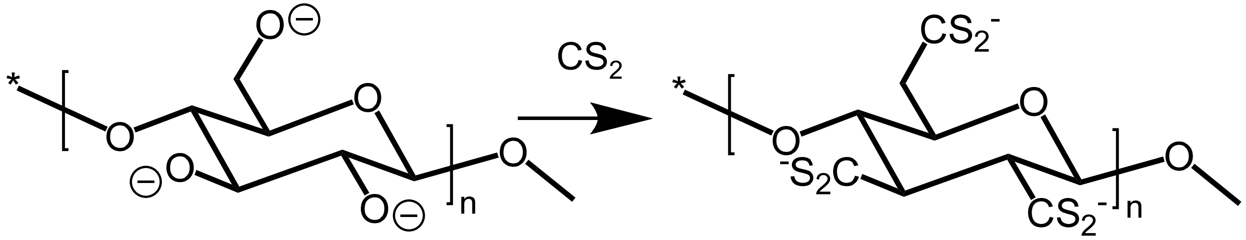
Inorganic cellulose esters

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

Cellulose xanthogenate



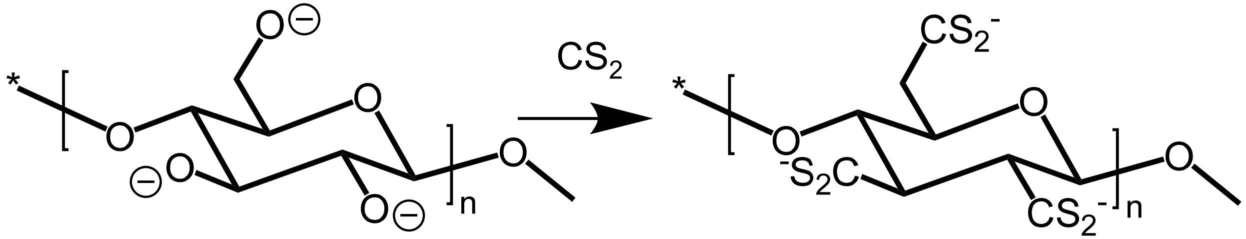
Hydroxyl groups are ionized with strong alkali



Half-ester is created by reacting alkoxy cellulose with CS_2

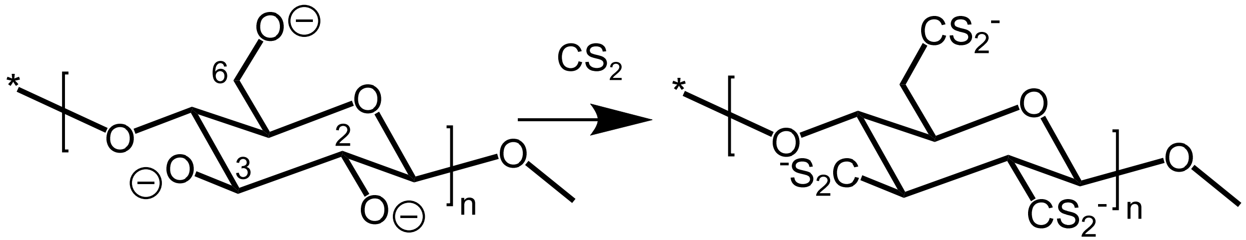
Cellulose xanthogenate is a half-ester, bearing charge
→ Cellulose xanthogenate is a polyelectrolyte

Cellulose xanthogenate



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

Cellulose xanthogenate

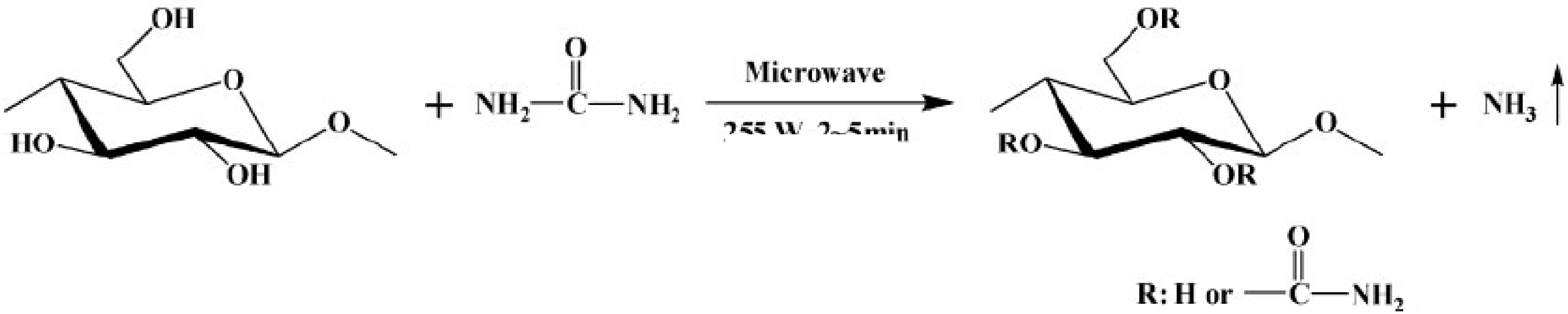


Examples of DS and hydroxyl selectivity at different stages of viscose process

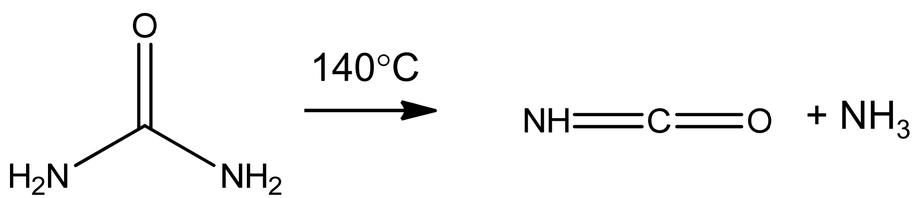
Xanthogenated cellulose material	DS at C-2/C-3	DS at C-6
Fiber xanthogenate (DS 0.61)	0.38	0.17
Viscose, non-ripened (DS 0.58)	0.34	0.24
Viscose, moderately ripened (DS 0.49)	0.16	0.32
Viscose, extensively ripened (DS 0.28)	0	0.32

Klemm et al. *Comprehensive Cellulose Chemistry* Vol. 2, Wiley-VCH, 1998.

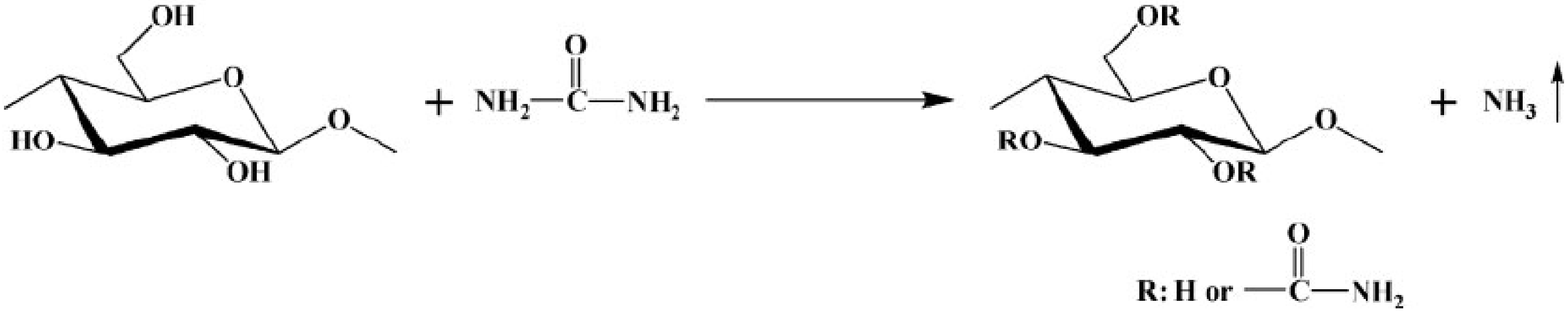
Cellulose carbamate



- High temperature reaction (~140°): 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:



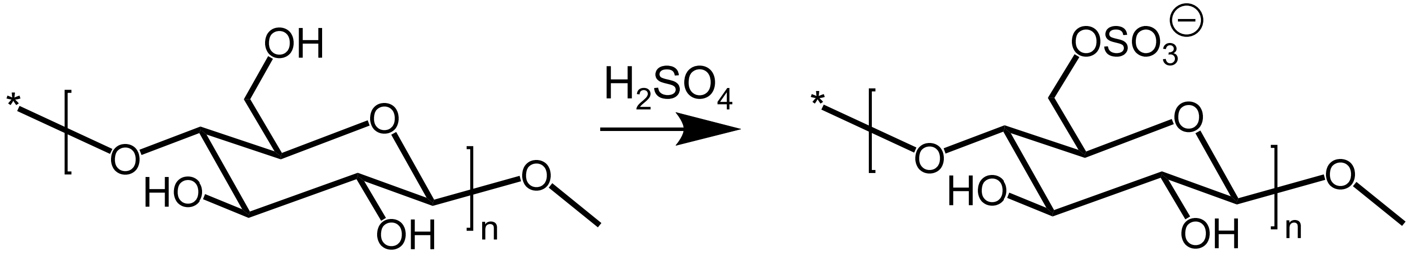
Cellulose carbamate



- Cellulose carbamate with DS 0.2-0.3 can be dissolved in aqueous NaOH

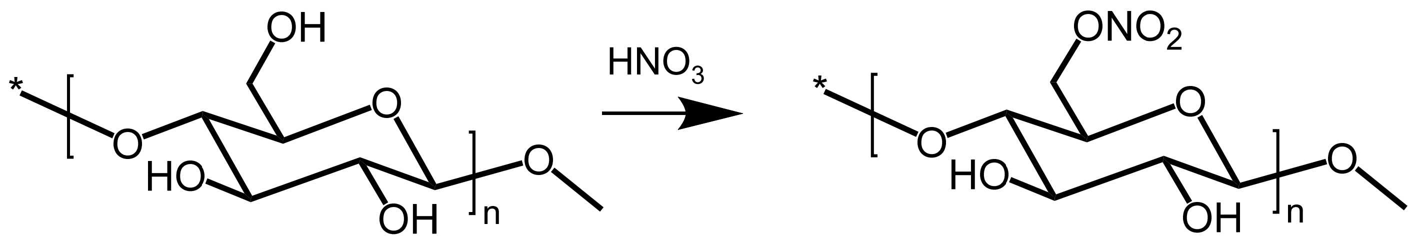
- Basis for the CarbaCell process:
  - Aimed at substituting the environmentally hazardous viscose process
  - Enabled by the effortless conversion of carbamate into cellulose in alkali
  - No commercial applications as of yet

Cellulose sulphate



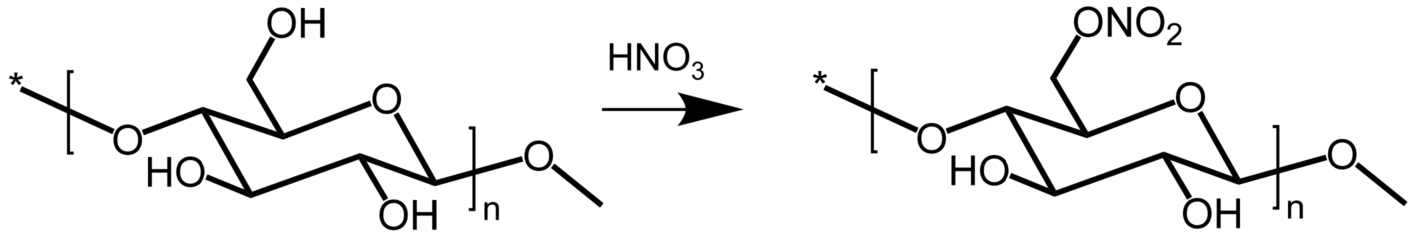
- **Can be prepared in a large variety of systems, usually containing either SO_3 or sulphuric acid**
- **Water soluble at above DS 0.2-0.3**
- **Preparation is generally accompanied by severe chain degradation due to acid hydrolysis**
- **Biomedical applications proposed**

Cellulose nitrate



- **Traditionally produced in a ternary system: $HNO_3/H_2SO_4/H_2O$**
- **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

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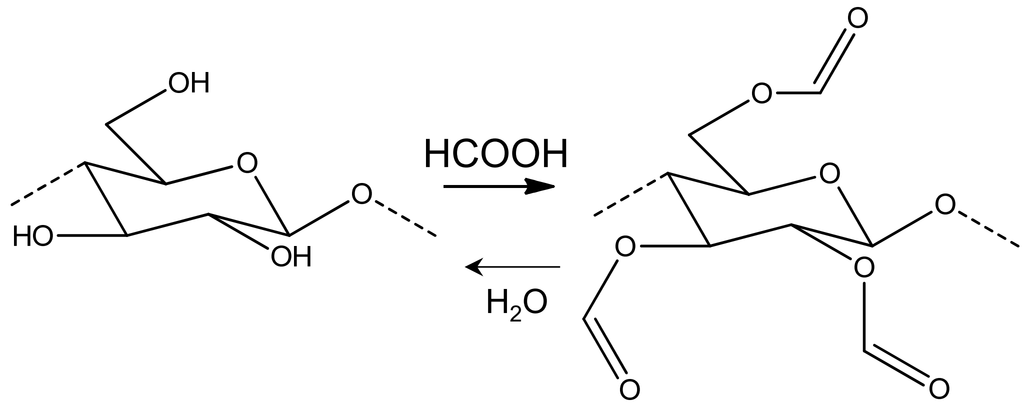
Organic cellulose esters

- Cellulose formate
- Cellulose acetate

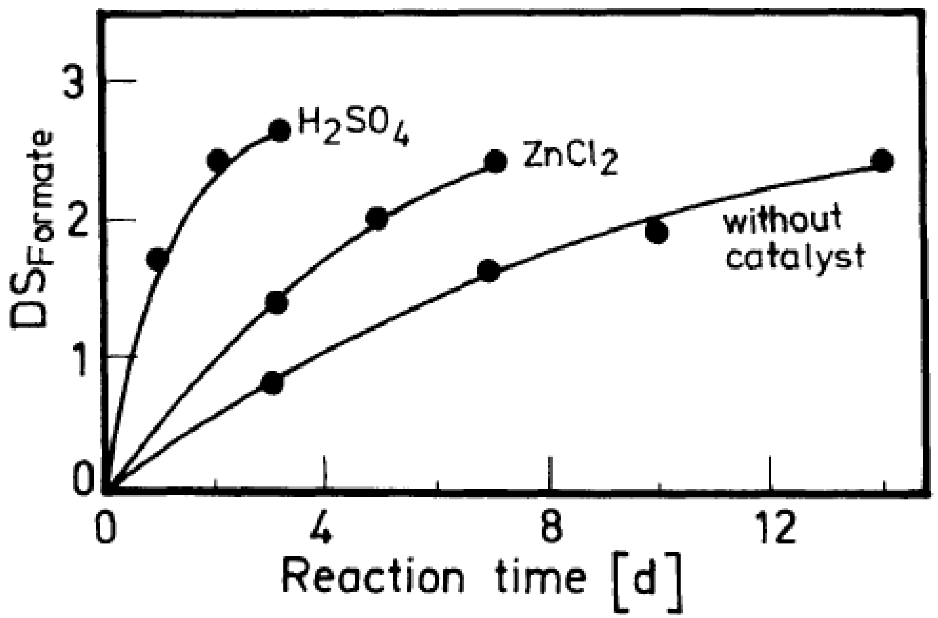
Cellulose formate



- **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

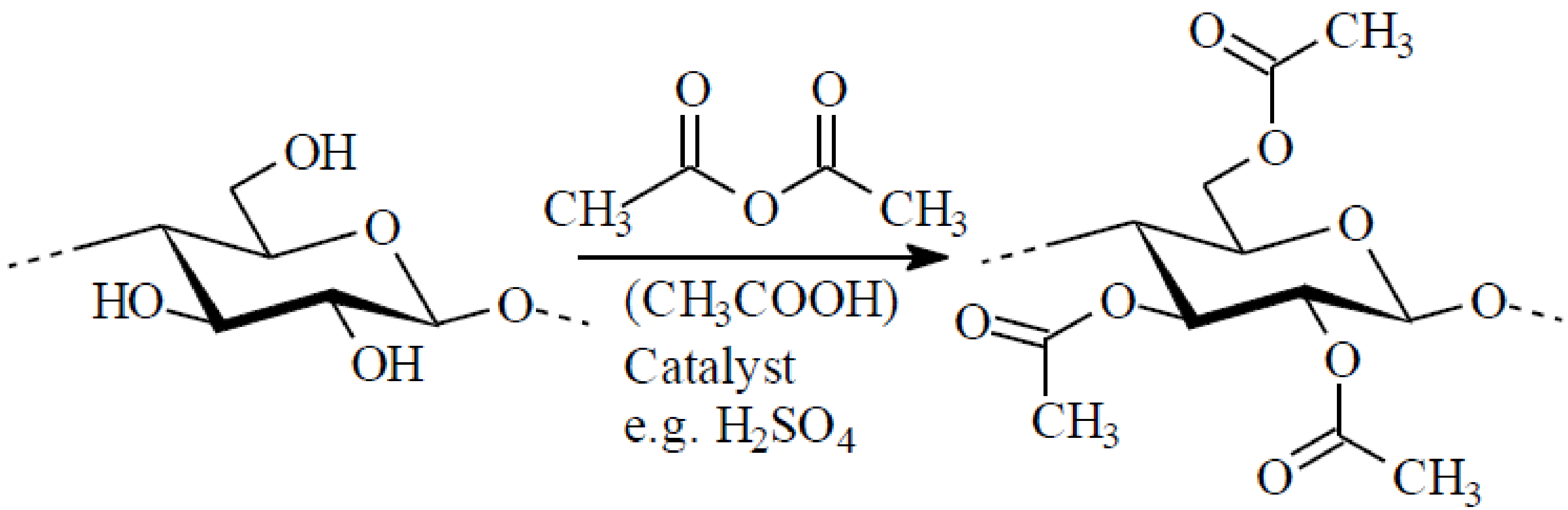
Effect of catalyst on formation



- **Very high DS values of cellulose formate can be achieved**

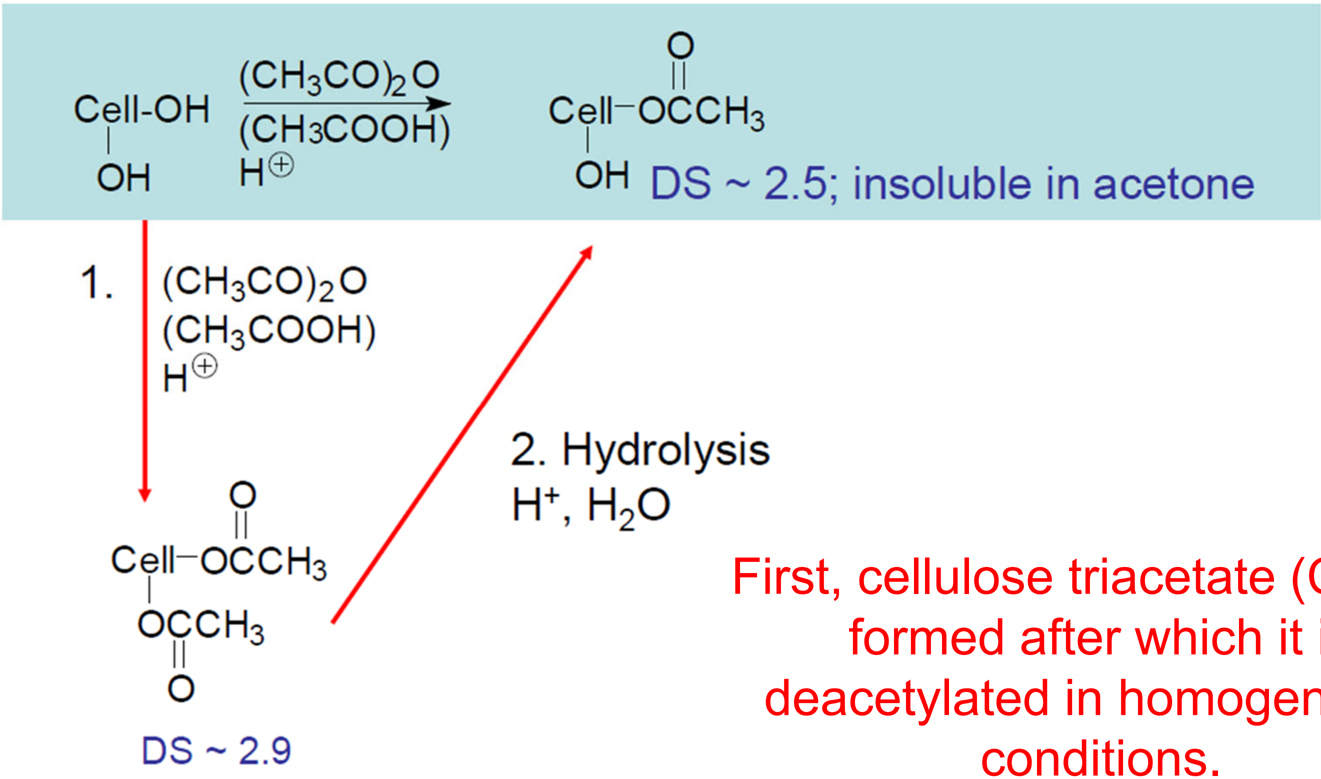
Philipp et al. *Cellulose Chem. Technol.* **1990**, *24*, 667.

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[a]	in C-2/-3 position[b]
Water	0.8–1.0	insoluble
DMF	1.8–2.7	1.3–2.8
Acetone (< 0.01 % H_2O)	insoluble	insoluble
Acetone (1 % H_2O)	2.3–2.6	2.5–2.6
Pyridine	0.8–2.7	1.2–2.8
Pyridine/H_2O (1 : 1 v/v)	0.6–2.0	1.2–1.6
Ethyl lactate	1.6–2.7	2.6–2.8

Klemm et al. *Comprehensive Cellulose Chemistry* Vol. 2, Wiley-VCH, 1998.

Cellulose acetate

Applications

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

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Cellulose ethers

- Methyl cellulose
- Carboxymethyl cellulose

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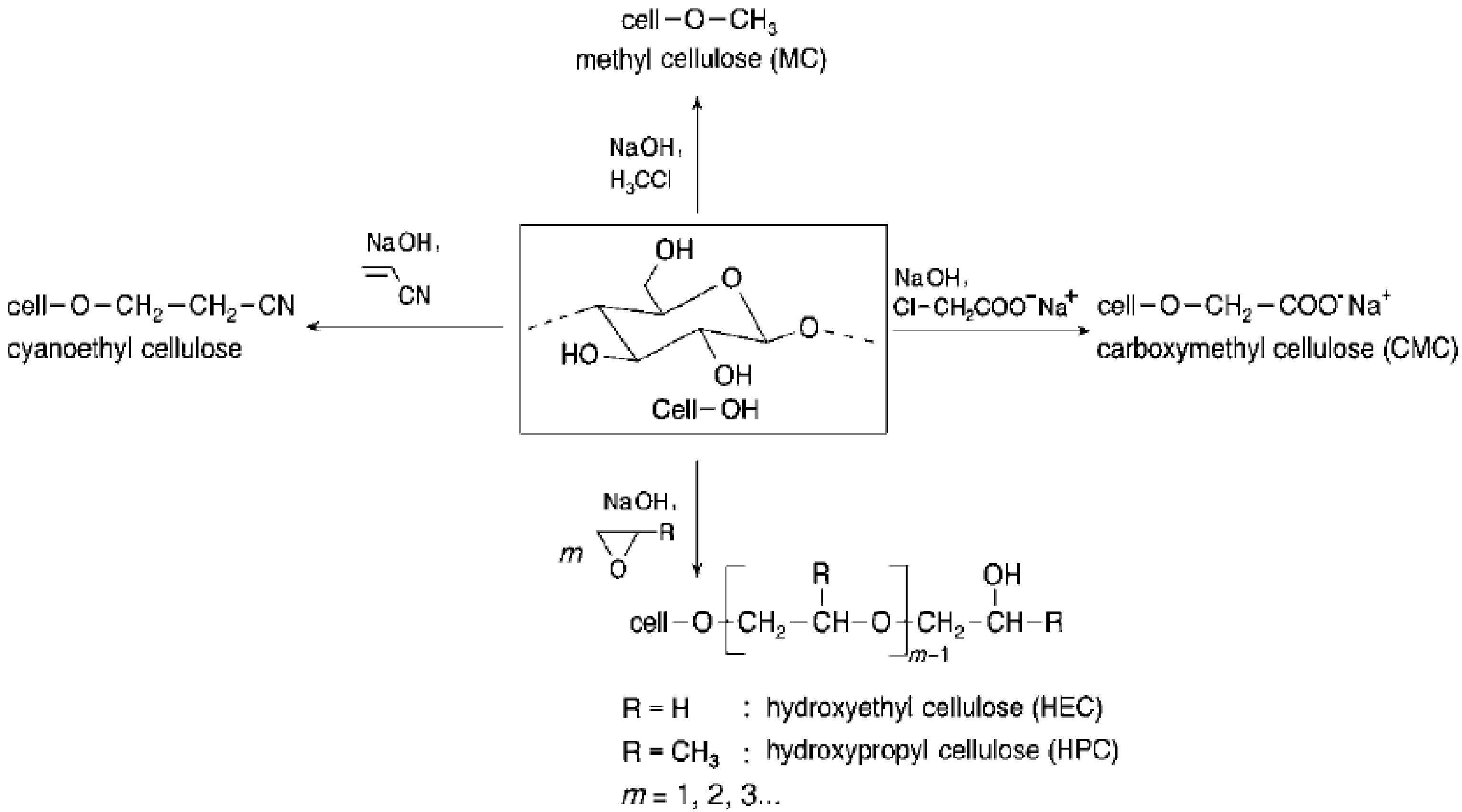
Commercial cellulose ethers



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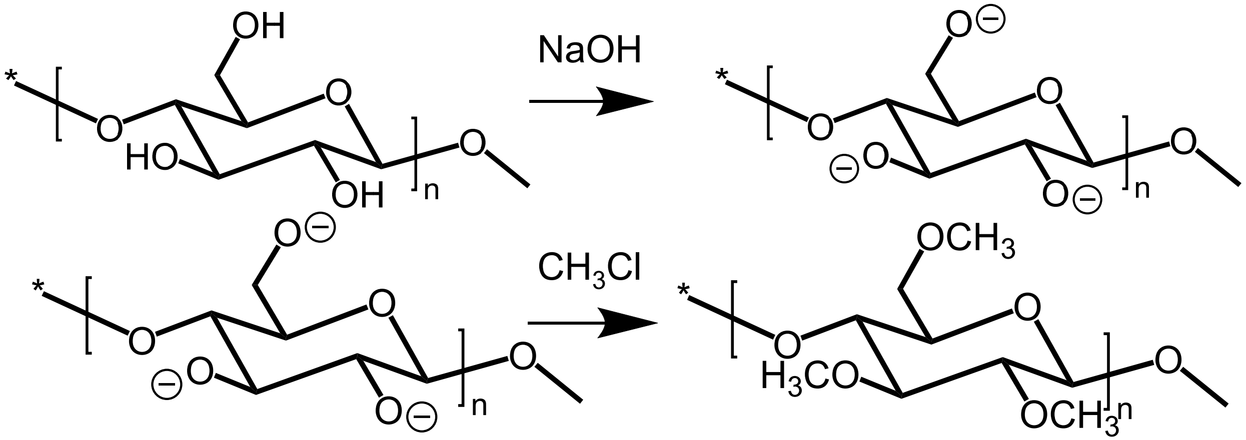
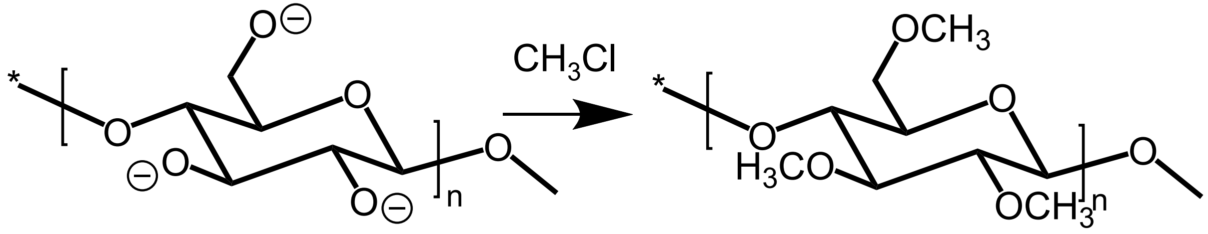
Methyl cellulose



Hydroxyl groups are ionized with strong alkali

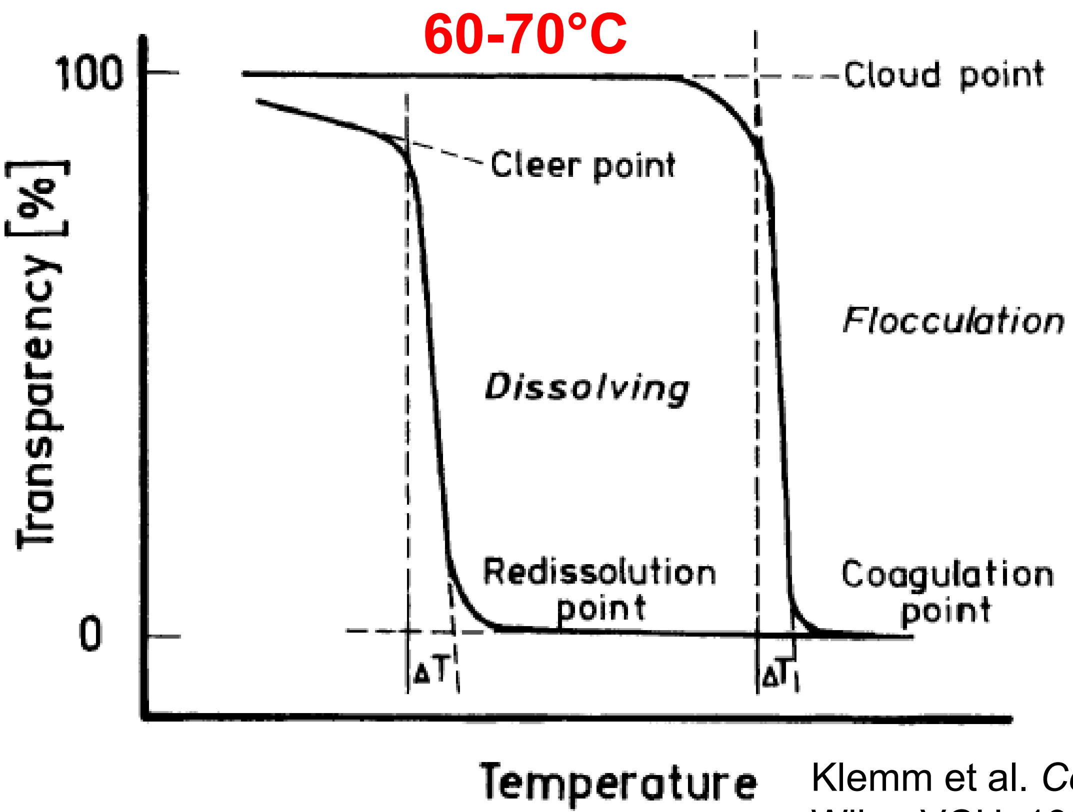
- **Conventional preparation by Williamson reaction with gaseous or liquid chloroform (S_N2 type nucleophilic substitution)**
- **40% NaOH used in the industrial procedure (heterogeneous reaction)**
- **Methylation performed at ca. 70-90°C**

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.

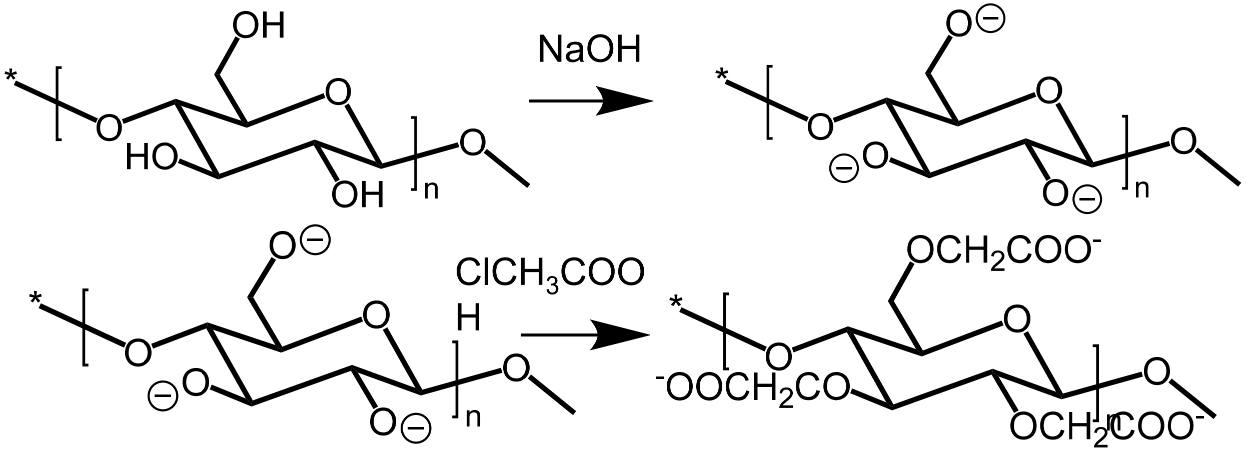
Klemm et al. *Comprehensive Cellulose Chemistry* Vol. 2, Wiley-VCH, 1998.

Engineering

Methyl cellulose applications

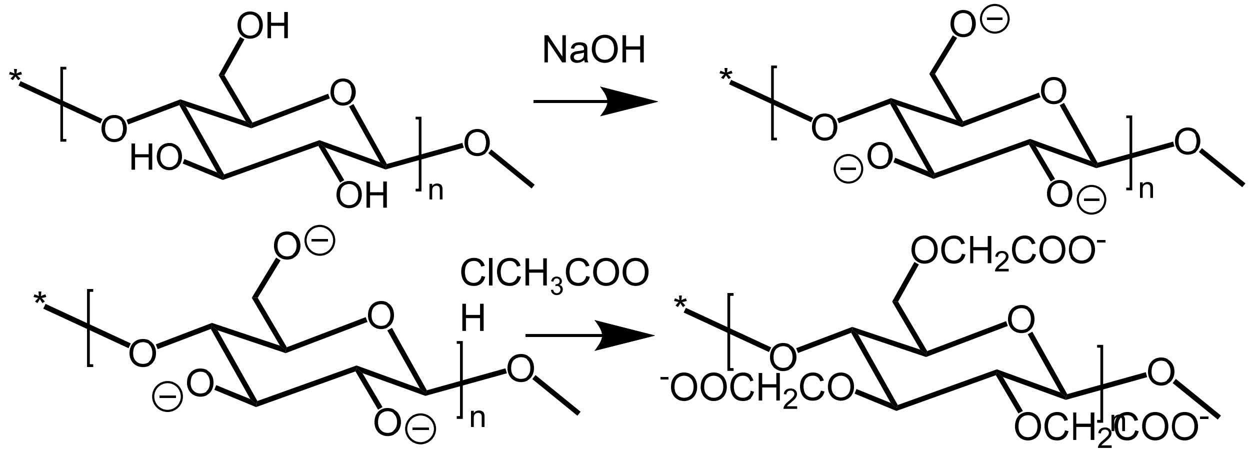
Application area	Proportion (%)
Building industry	47
Dispersion paints	21
Wall paper paints	14
Cosmetics	5
Polymerization	5
Detergents	4
Other	4

Carboxymethyl cellulose



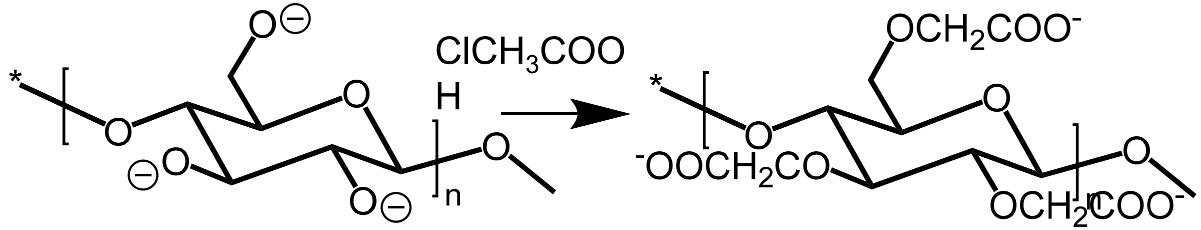
- **Generally produced by a substitution reaction of monochloroacetic acid to alkoxy cellulose**

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 %
- **Main application areas**
  - paper and board
  - oil drilling
  - paints
  - mining

- CMC-content min. 99,5 %
- **Main application areas**
  - food
  - dental
  - pharmaceutical

- **Technical CMC**
  - CMC-content 55 – 75 %
- **Main application areas**
  - detergent
  - oil drilling
  - paper and board
  - mining
  - construction

Information from CPKelco

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Regioselective modification of cellulose

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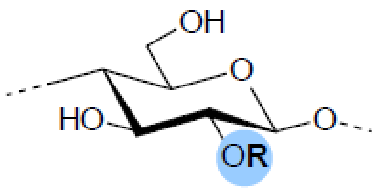
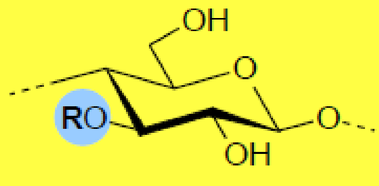
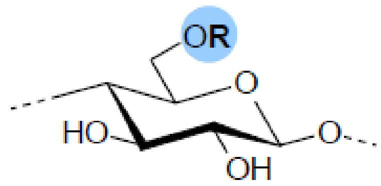
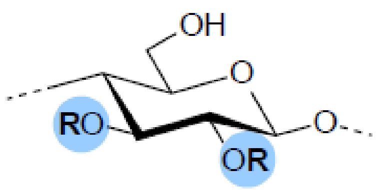
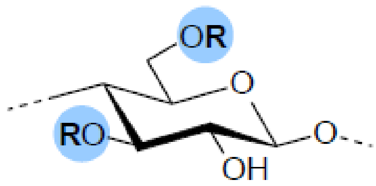
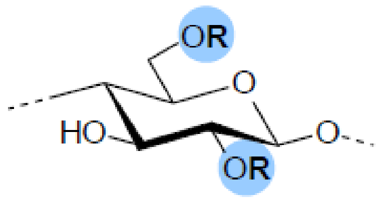
Regioselectivity issues

- 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

 2-mono-O-substituted	 3-mono-O-substituted	 6-mono-O-substituted
 2,3-di-O-substituted	 3,6-di-O-substituted	 2,6-di-O-substituted

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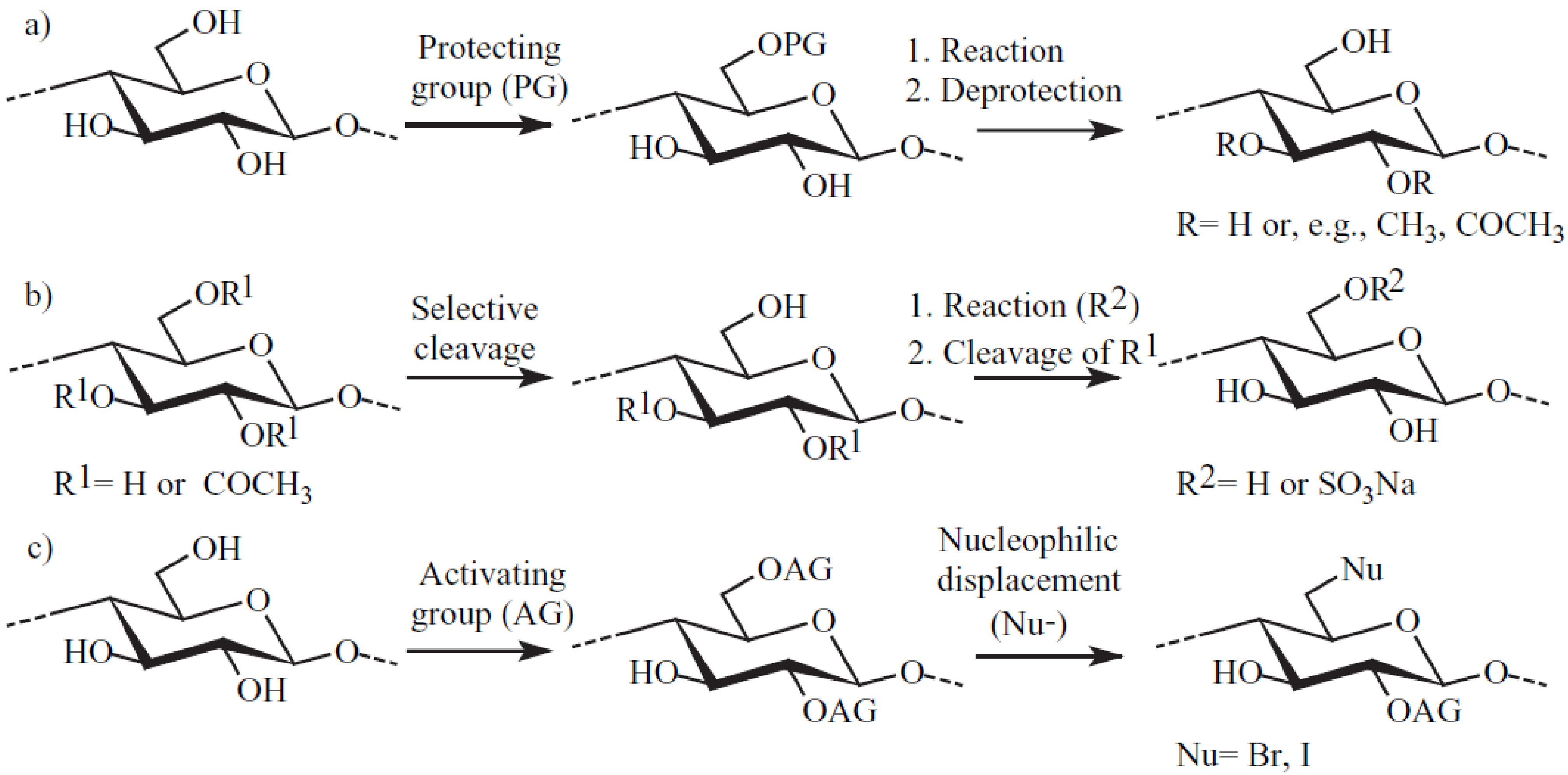
Pathways to regioselectivity



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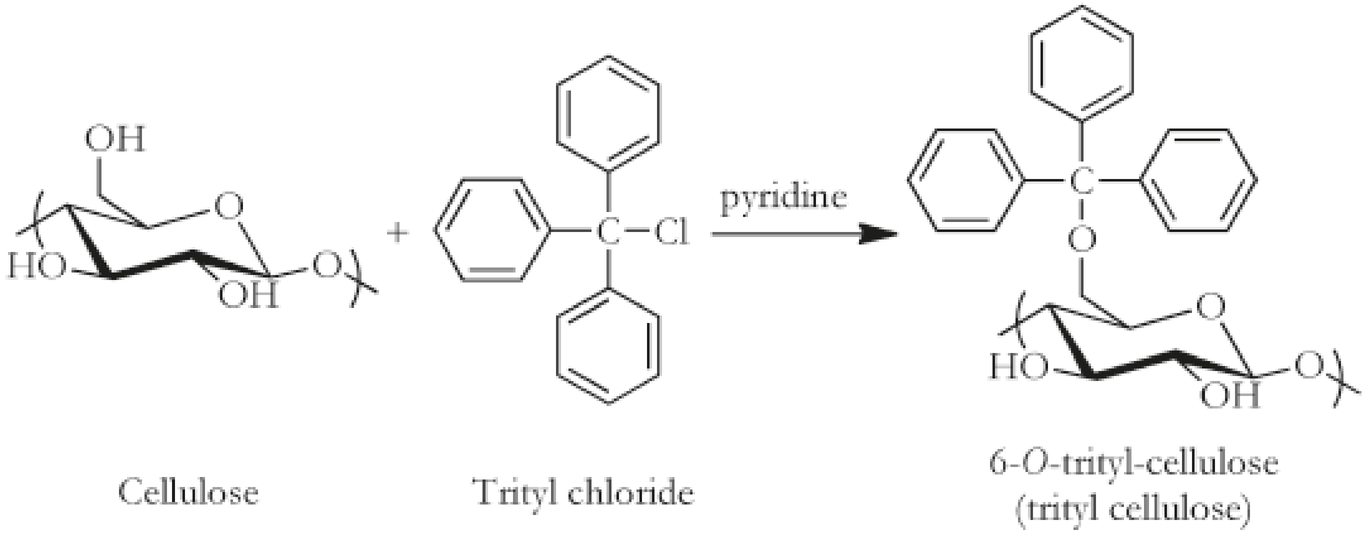
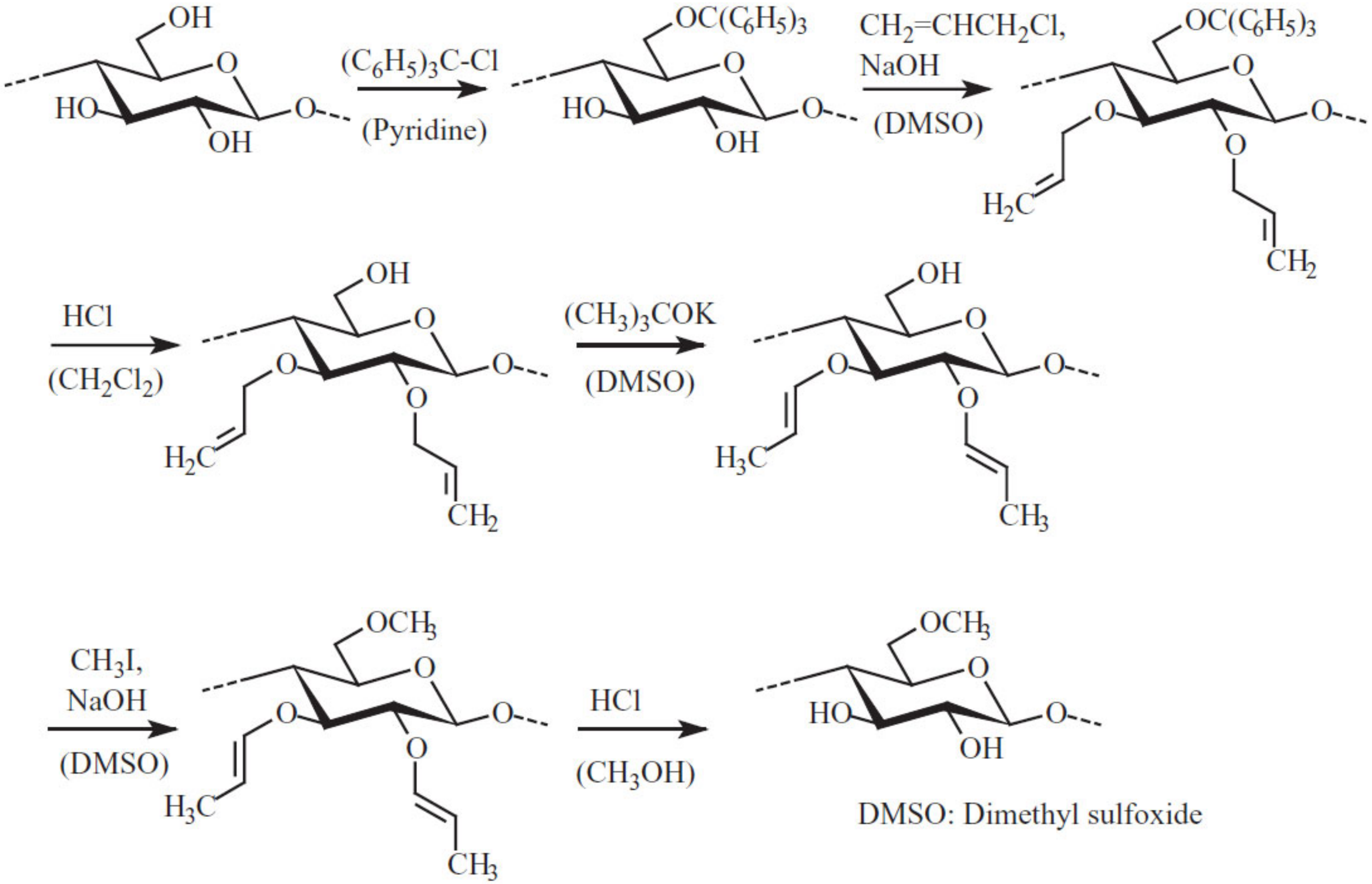
Koschella et al. *Macromol. Symp.* **2006**, *244*, 59.

Protective group: trityl

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



6-mono-O-methyl cellulose



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Kondo et al. *Carbohydr. Res.* **1993**, *238*, 231.

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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