From renewable monomer to polymer

Guest lecture University of applied science.

Academy of technology & innovation

02-12-2013, Vlissingen

FOOD & BIOBASED RESEARCH
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Outline

- Introduction to the dream
- Biobased building blocks
  - Existing building blocks
  - New building blocks
- Biobased materials
  - Natural biobased polymers
  - Synthetic biobased polymers
- Mechanical property determination
  - Thermal polymer properties
  - Mechanical polymer properties

Introduction

- Implementation of bio-mass as feedstock in materials production
- Employ concept of biorefinery: co-generation of heat, power, fuel, chemicals and materials
- Two approaches
  - 1: convert biomass into existing chemicals
  - 2: convert biomass into new chemicals

- Approach 1 should lead to implementation on short term
- Approach 2 is a long term route, with opportunities for unique new technologies

Introduction

Approach 1: converting biomass into existing chemicals

- Advantages
  - Can be fully integrated into existing chemical infrastructure
  - Allows for continuation of existing polymers (high level of technological evolution)
  - Focus on O-and N-functionalised monomers (amines, acids) which are difficult to prepare from petrochemicals
- Drawbacks
  - Biomass is oxygen-rich, over-functionalised and hydrophilic with low thermal stability; petrochemicals are mostly apolar, with tailor made functionalities
  - Removal of excess functional groups should not negatively affect atom economy or energy

Introduction

Approach 2: convert biomass into new chemicals

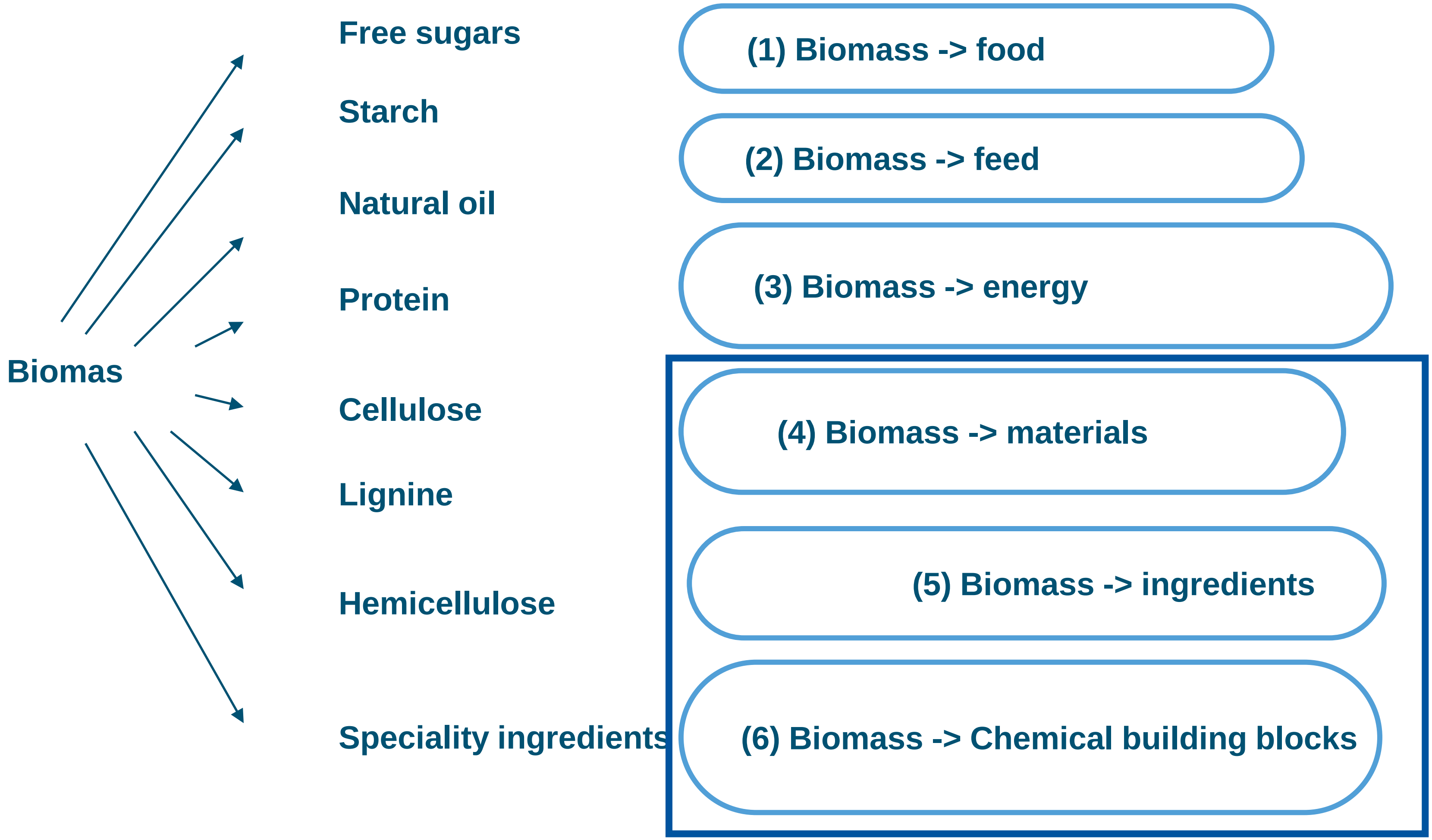
- Advantages
  - Use the intrinsic structure of the biomass and follow the thermodynamically most efficient route
  - Potentially biodegradable
  - New chemicals & materials with new properties
- Drawbacks
  - Requires new processes and technologies
  - New chemicals & materials with unknown properties
  - Unknown risk factors (environmental, toxicological)

Introduction

Which approach should we follow?

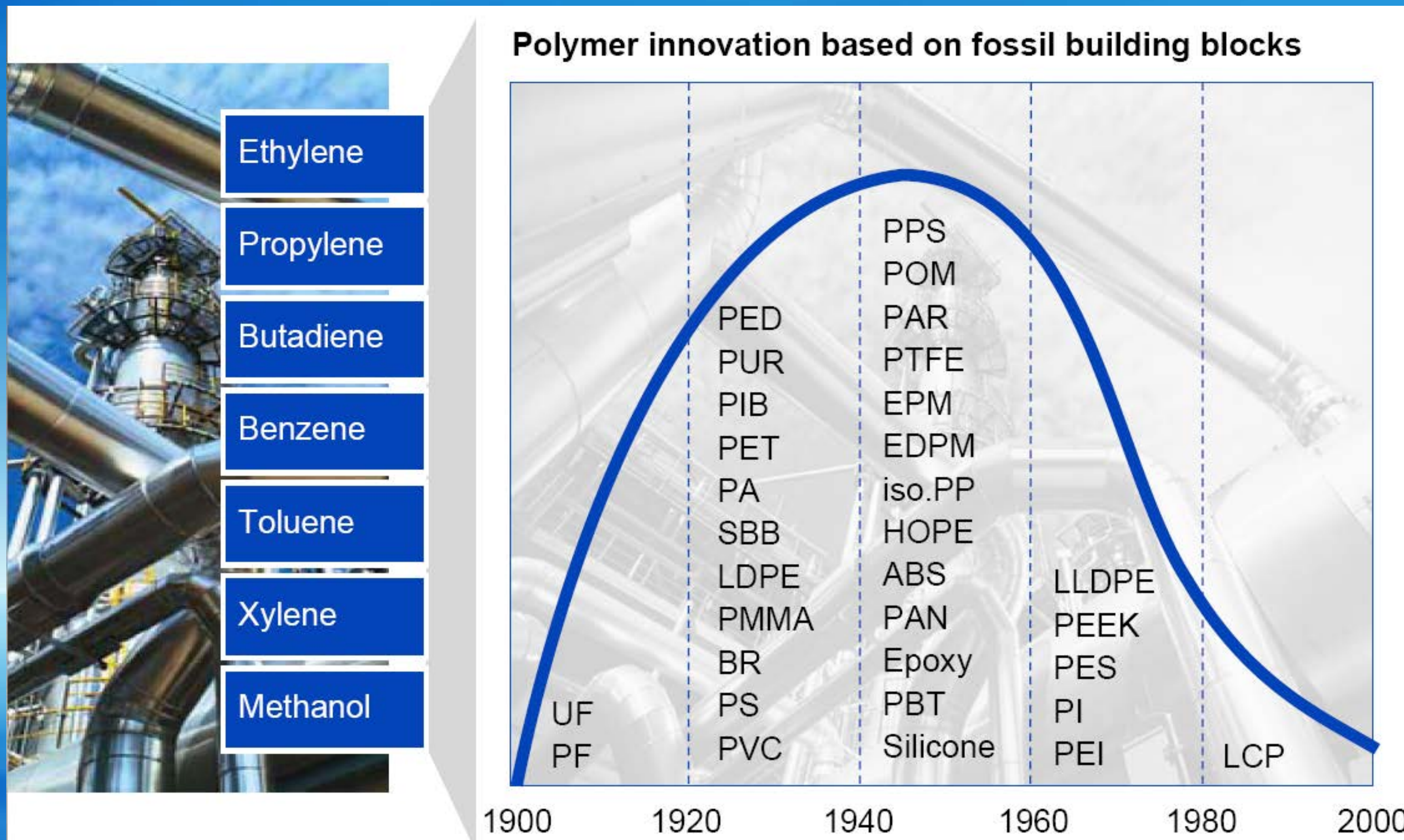
- Both should be explored
- Most current synthetic materials have excellent price performance (prevent reinventing the wheel)
- Large exergy gains possible by clever substitution of functionalised building blocks
- New materials with new (improved) properties are possible

Introduction



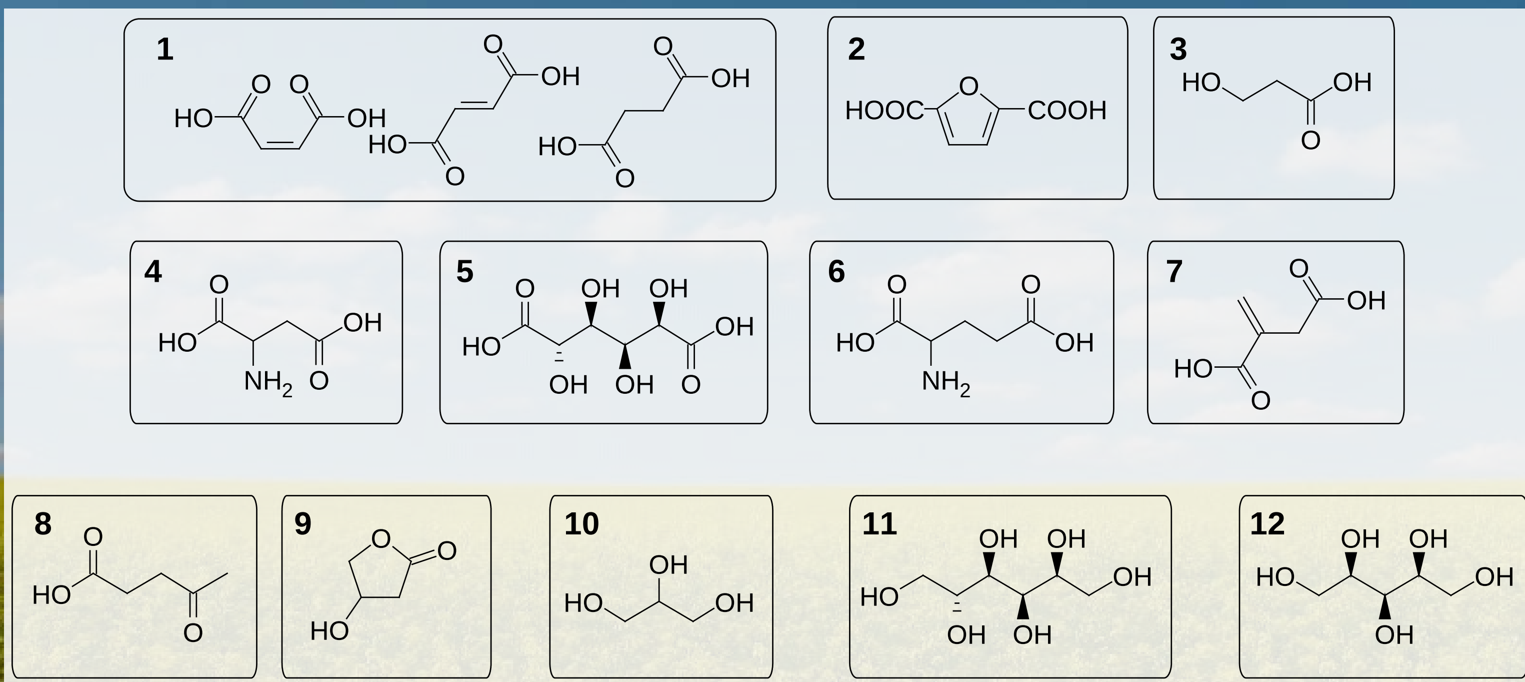
Introduction

- McKinsey: Innovation potential of fossil building blocks appears largely exploited



Introduction

- Top 12 chemicals from biomass (2004 US-DOE study)
  - Based on 2nd approach
  - Scientific fundamentals for certain choices are questionable



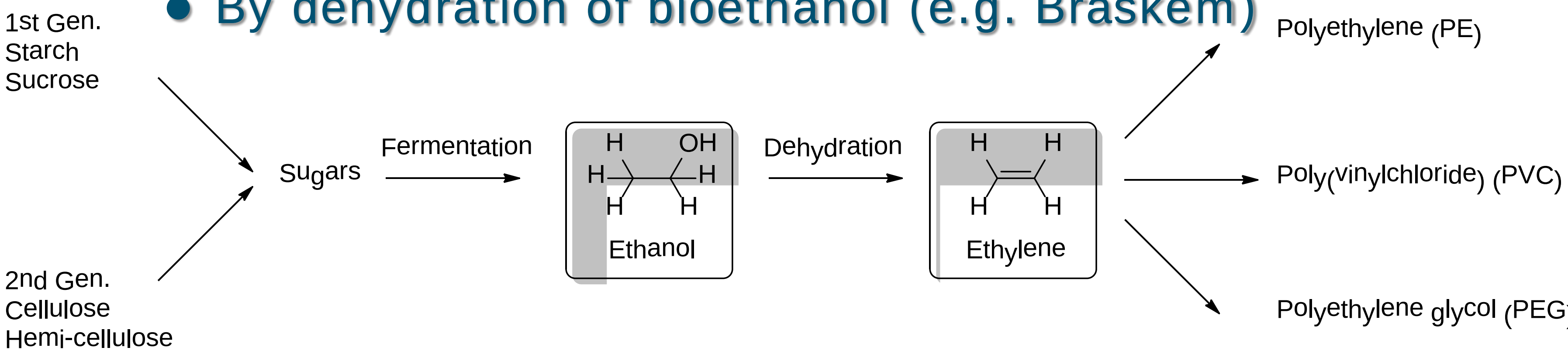
Approach 1:

From Biomass to *Existing*

Chemicals & Building Blocks

Existing Chemicals & Building Blocks

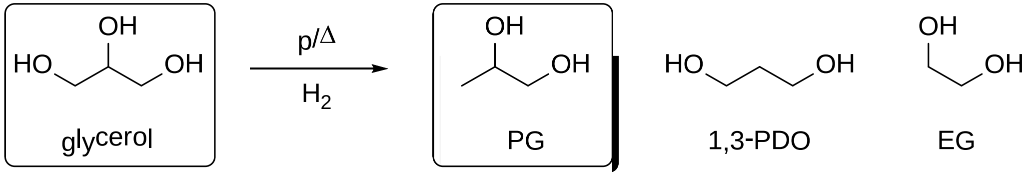
- Bioethylene (for polyethylene or vinyl chloride)
  - By dehydration of bioethanol (e.g. Braskem)



- Only viable in case of cheap bioethanol supply
- Should not compete with food production: 2nd Gen.
- Not enough bioethanol available (yet) for ethylene production (75 MT worldwide in 2005, vs 40 MT ethanol in 2006)

Existing Chemicals & Building Blocks

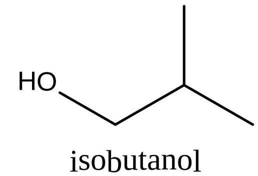
- Propylene glycol (PG)
  - Starting from glycerol or sugars by hydrodeoxygenation (HDO) instead of from propylene oxide (e.g. Cargill/Ashland, ADM)

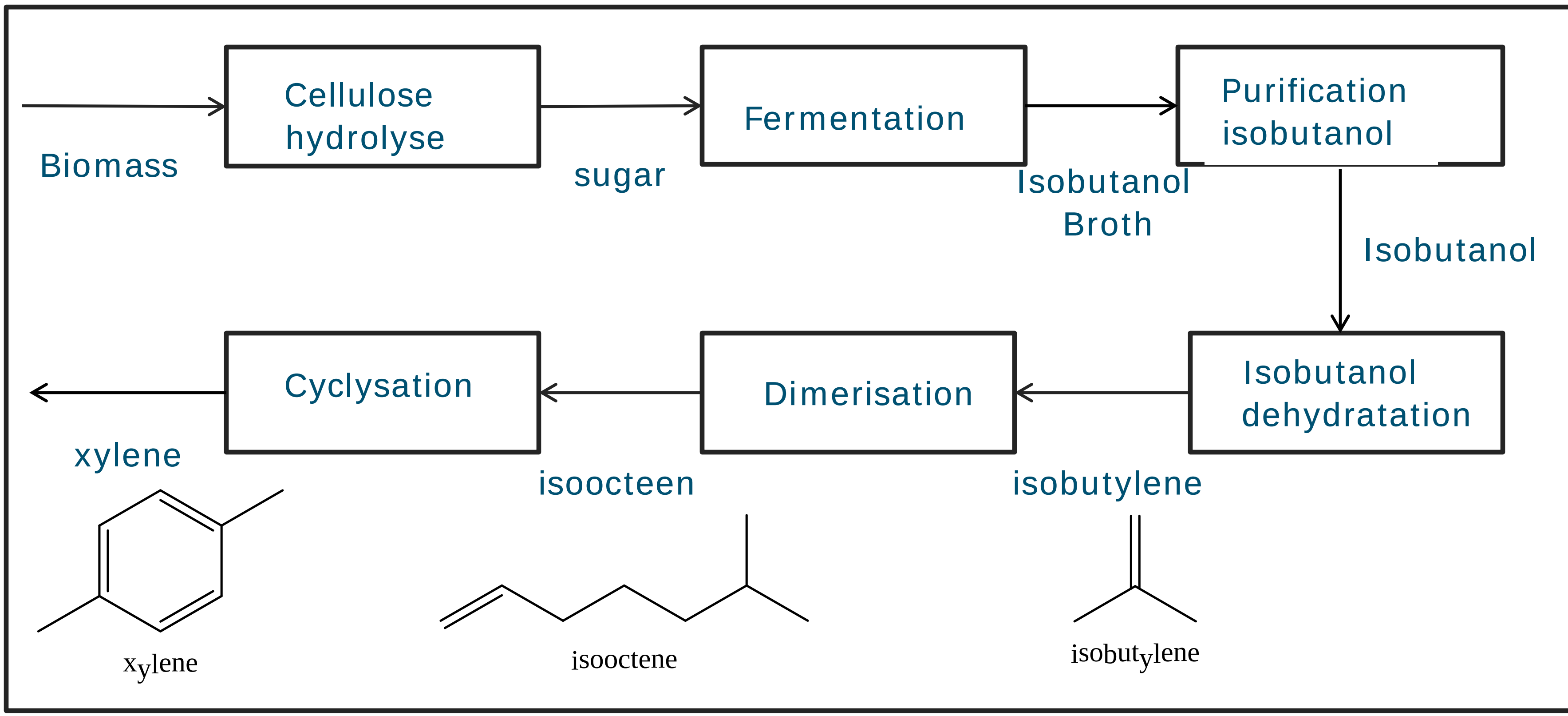


- Glycols are important intermediates
- Find application in various products; e.g. personal care
- Also used as de-icing agent
- However PG does not produce PPO (polyol for polyurethanes)

Existing Chemicals & Building Blocks

- Terephthalic acid





Existing Chemicals & Building Blocks

- Industrial demand for more high-added value, high-volume building blocks
    - Diamines (for polyamides and isocyanates); e.g. from amino acids or sugars
    - Phenols (for polycarbonate, polyepoxides); e.g. from lignin
    - Terephthalic acid (for polyesters, polyamides); from carbohydrates or terpenes
    - Polyols (for polyurethanes); e.g. from glycerol, vegetable oils, carbohydrates, proteins
- WUR-FBR is involved in all of these research areas

Approach 2:

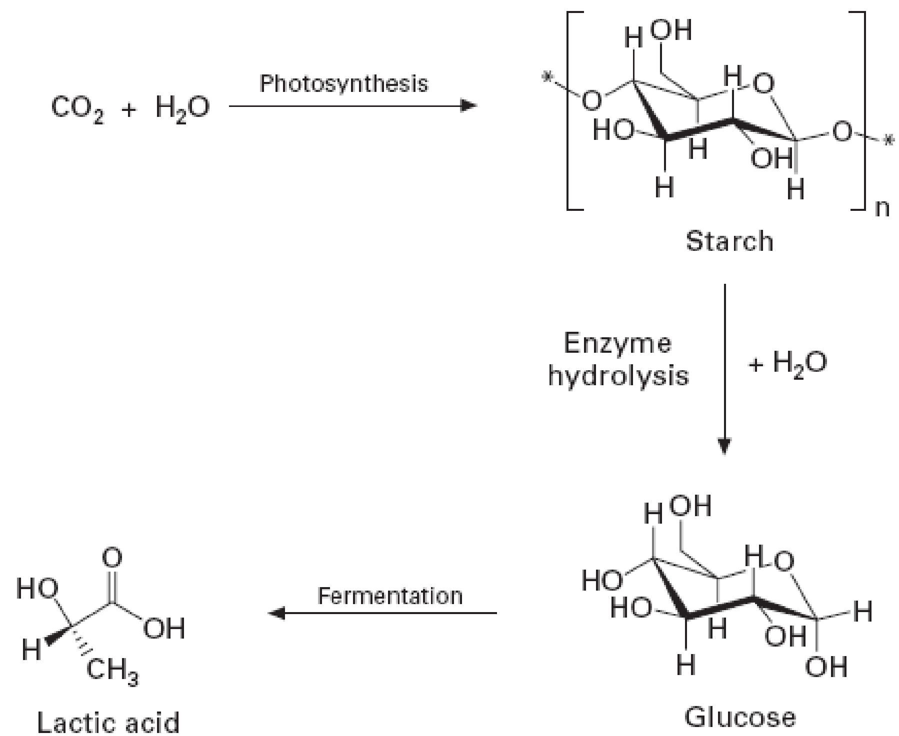
From Biomass to *New*

Chemicals & Building Blocks

New Chemicals & Building Blocks

Lactic acid

- Not really new; important food ingredient
- Produced via fermentation of glucose
- Purity is essential for polymer synthesis
- Enantiomeric purity is important for polymer properties

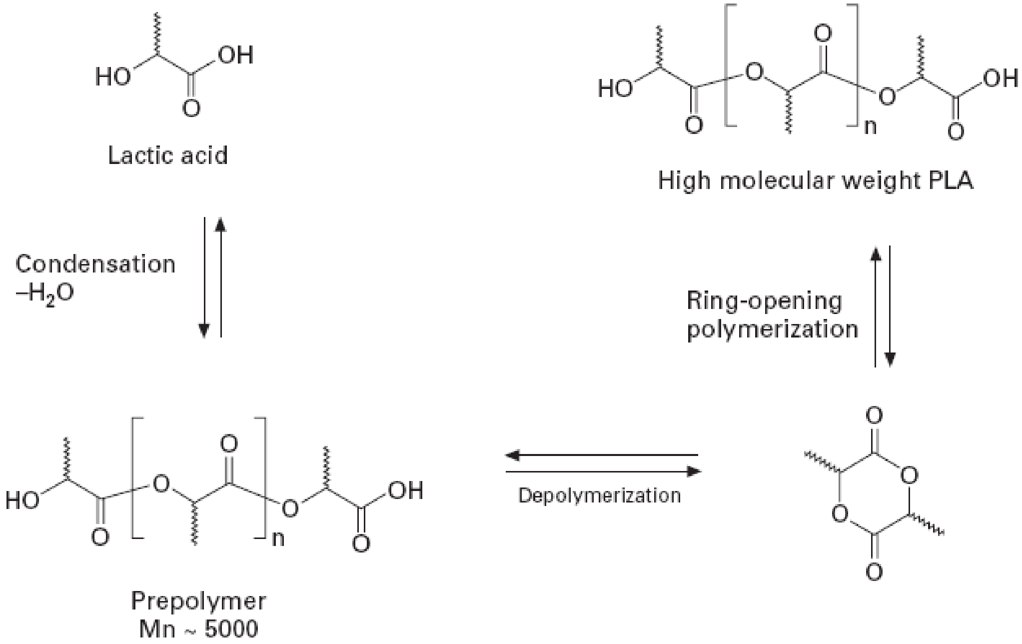


Source: Farrington *et al.* “Poly(lactic acid) fibers.” Biodegradable and sustainable fibres, 2005.

New Chemicals & Building Blocks

Polylactic acid (PLA)

- Used in biomedical applications for years (biodegradable sutures, stents, tissue engineering)
- Produced via ROP



Source: Farrington *et al.* “Poly(lactic acid) fibers.” Biodegradable and sustainable fibres, 2005.

Introduction

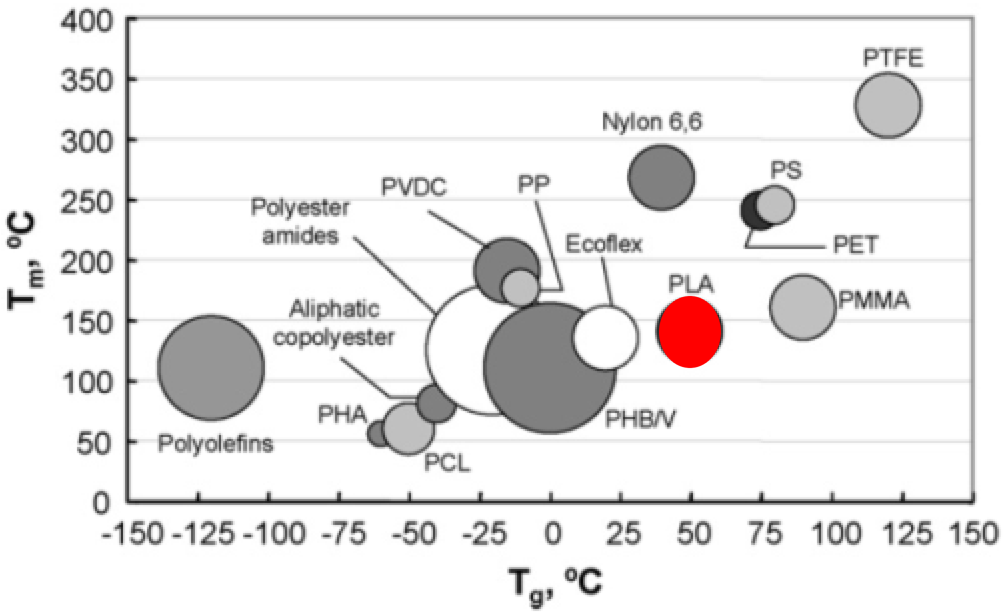
- Mechanical properties PLA

Sample	PLLA 1		PLLA2		PLLA3	
Annealing at 105°C	no	yes	no	yes	no	yes
Molecular weight (Mv, Da)	23,000	20,000	58,000	47,000	67,000	71,000
Tm (°C)	178	178	179	180	181	178
Crystallinity (%)	9	70	9	52	3	45
Tensile properties						
Yield strength (Mpa)	-	-	68	68	70	70
Tensile strength (Mpa)	59	47	58	59	59	66
Yield elongation (%)	-	-	2.3	2.2	2.2	2
elongation at break (%)	1.5	1.3	5	3.5	7	4
Elastic modulus (Mpa)	3550	4100	3750	4050	3750	4150
Impact resitance						
Izod, Notched (KJ/M^2)	1.9	3.2	2.5	7	2.6	6.6
IZOD, UnNotched (KJ/M^2)	13.5	18	18.5	34	19.5	35

Auras, R.; Lim, L. T.; Selke, S. E. M.; Tsuji, H., Eds.
Synthesis, Structures, Properties, Processing and Applications; Wiley & Sons inc., 2010.

Introduction

- Thermal properties PLA



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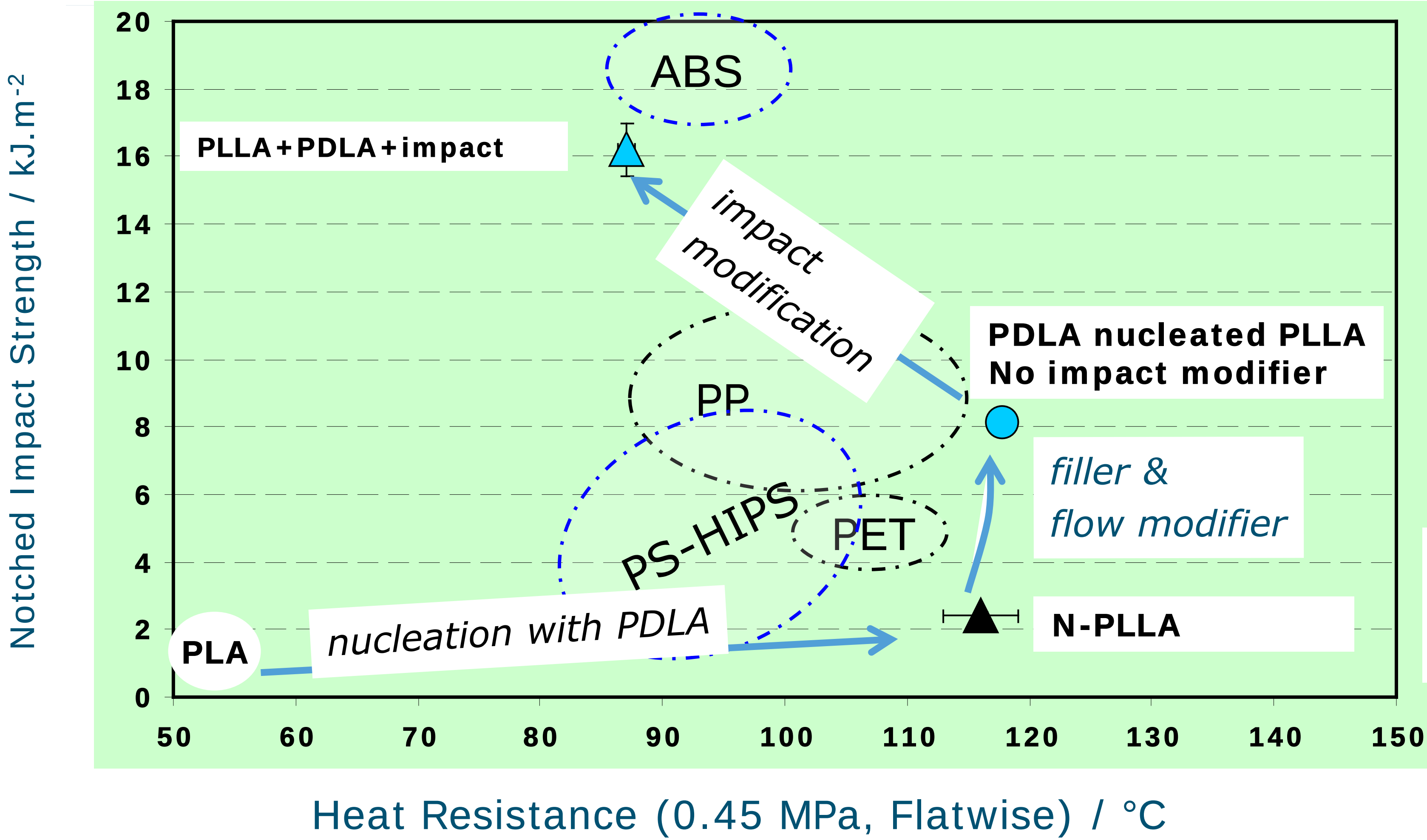
Introduction



purac pure by nature

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New Chemicals & Building Blocks

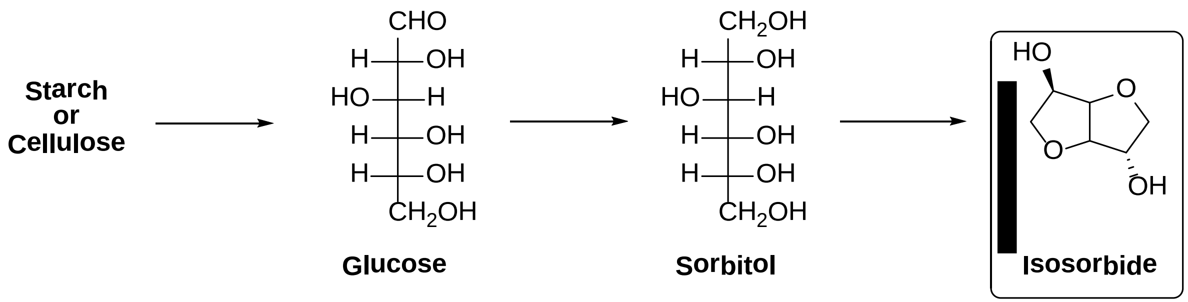
- Now large scale production by NatureWorks; 140kt/a [Mind: European PET production 2010 was approx. 3 MioT]
- Application fields expanded to all kinds of biodegradable materials
  - Packaging films
  - Disposable containers (bottles, cups)
  - Fibres (textile)
  - Foams

- Number of applications limited due to low T_g of approx. 60 °C
- Innovations required for real brake-through

New Chemicals & Building Blocks

Isohexides

- Rigid bicyclic diol



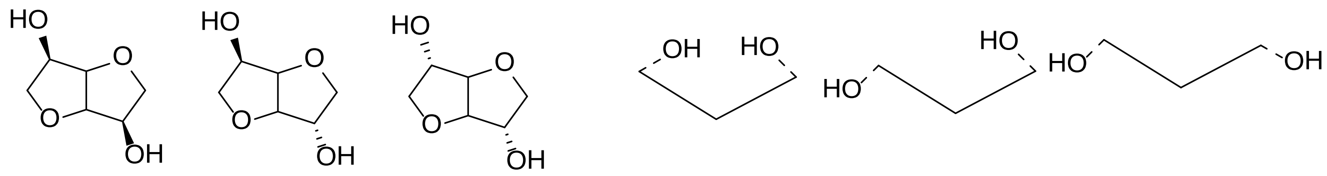
- Prepared by acid catalysed cyclodehydration of sorbitol
- Sorbitol is used on large scale in food, pharmaceuticals and personal care products, produced from glucose

New Chemicals & Building Blocks

- Interesting rigid monomer for e.g. Polyesters and Polycarbonates
- Incorporation in polyesters increases Tg of polymer, which allows for high T applications
- Crystallinity is reduced??
- Major developments by Dupont & Roquette (mid 1990’s-2004)
- 20% incorporation in PET (poly(ethylene terephthalate)) increase Tg > 100°
- Turns PE(I)T into alternative for polycarbonate

New Chemicals & Building Blocks

- However; difficult to incorporate high levels of isohexides into high Mw polymer
  - Secondary diol less reactive then primary diol
  - Difference in reactivity of OH groups (*endo* vs *exo*)



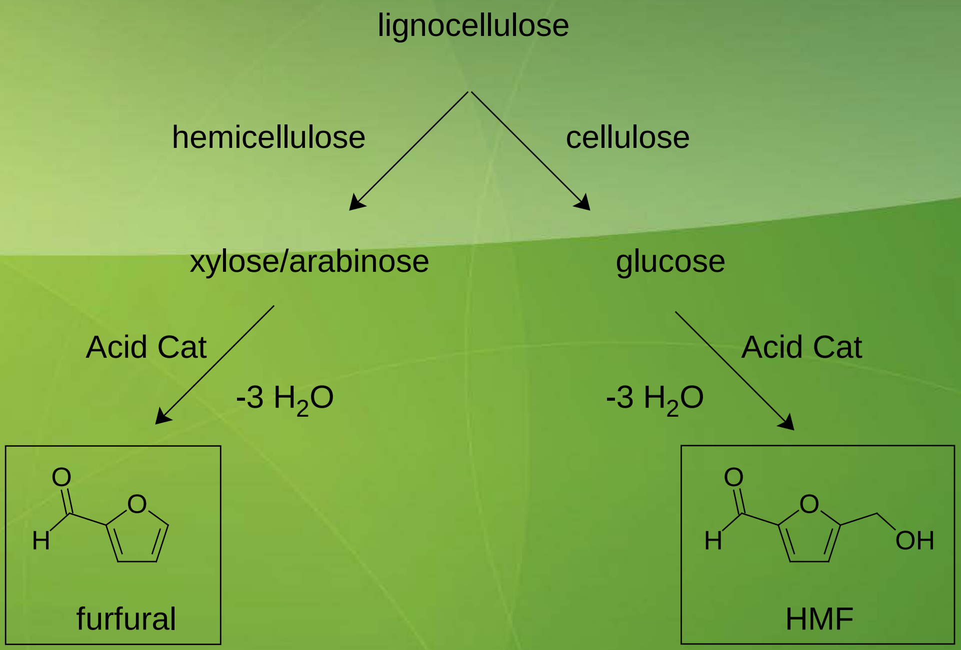
Isomannide Isosorbide Isoidide Isomannide Isosorbide Isoidide

  - Polymers have low degree of crystallinity
  - Severe polymerisation conditions lead to degradation and discolouration, and too low MW
- Further innovations required for break-through

New Chemicals & Building Blocks

Furans

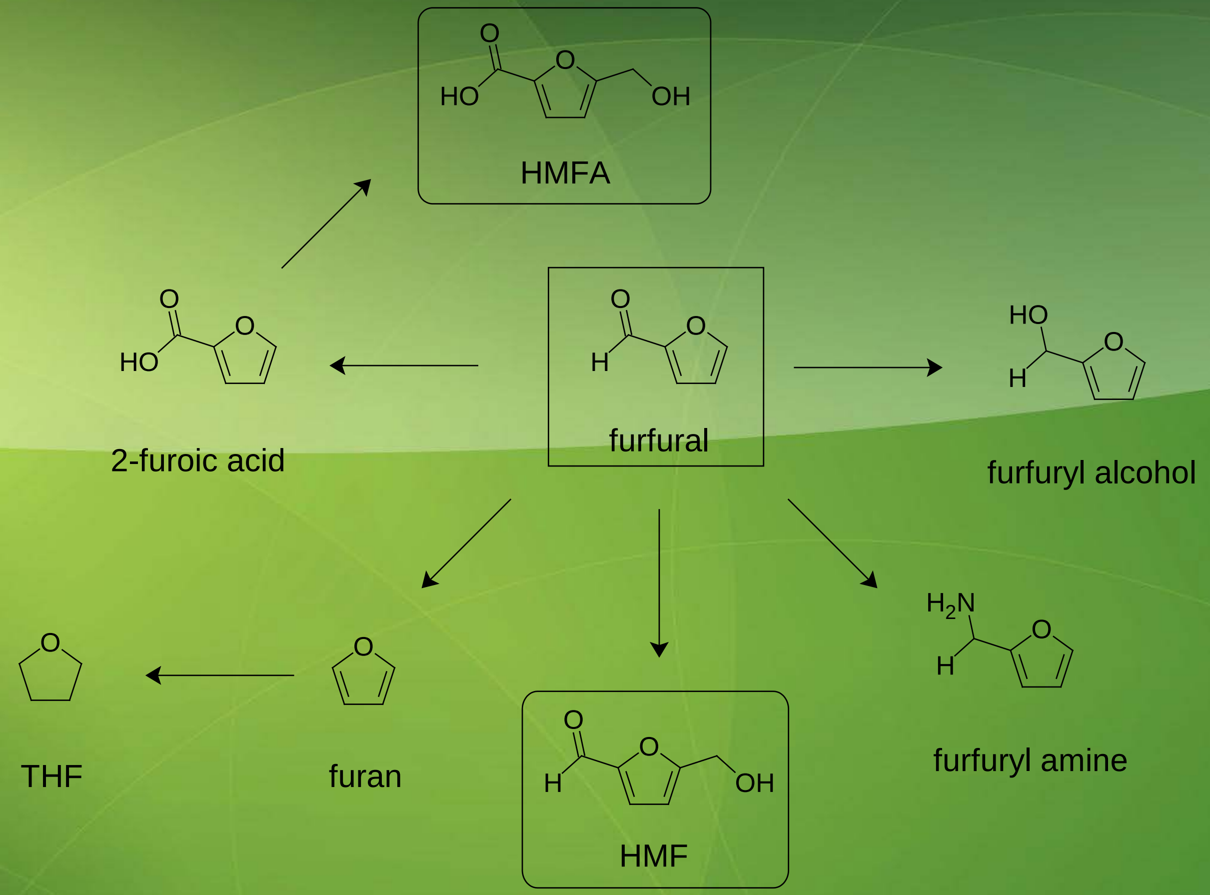
- Acid catalysed cyclodehydration of carbohydrates leads to formation of furans



- Furans are hydrophilic aromatic molecules
- Most furans are also quite reactive (form resins)
- Division into C5 (pentose) or C6 (hexose) sugar based furans

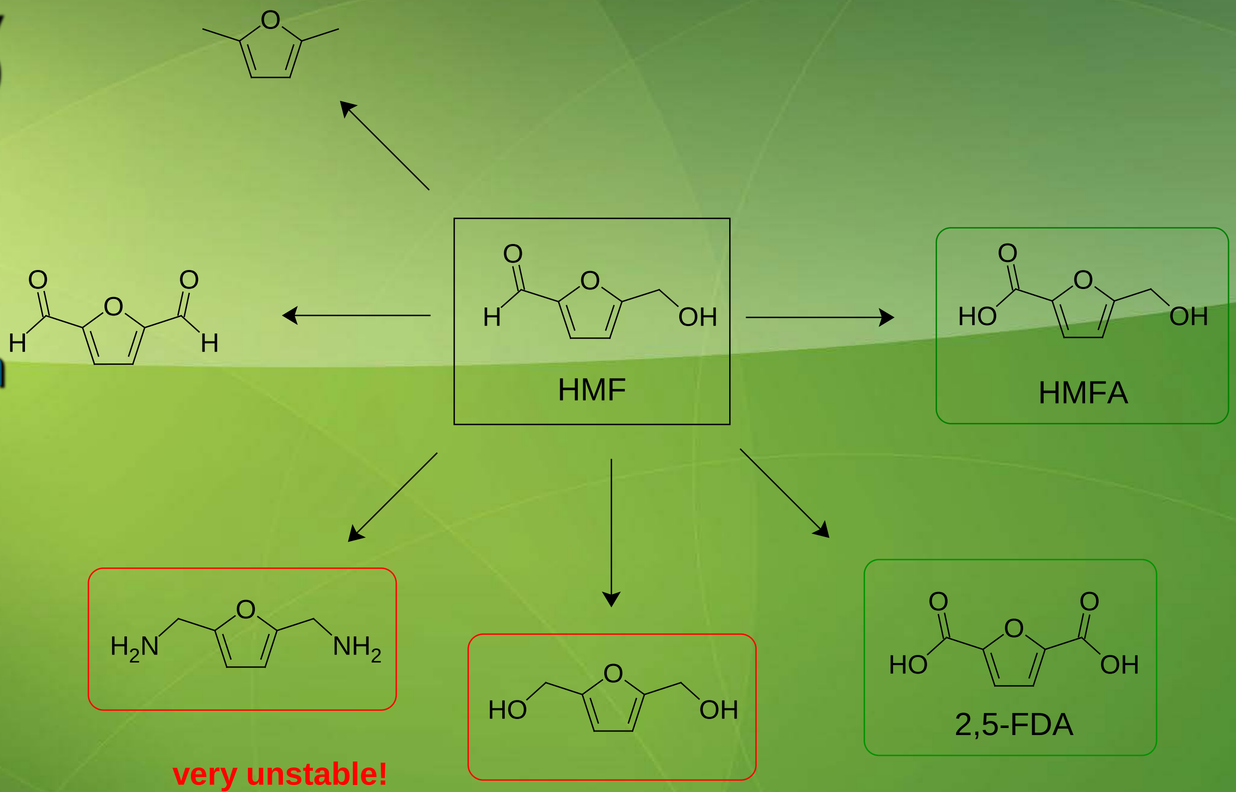
New Chemicals & Building Blocks

- Furfural chemistry is ancient
- Commercial product; 400-500 kt/a worldwide
- Starting point for fine chemicals
- Currently HMF is produced from furfural



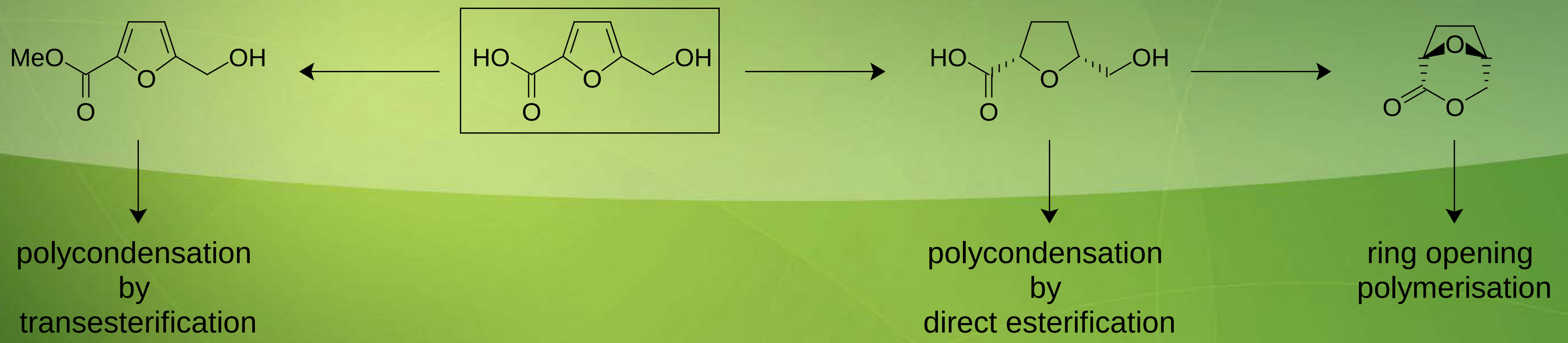
New Chemicals & Building Blocks

- HMF is promising platform chemical, however, not (yet) produced commercially
- Many building blocks proposed in literature not viable
- Only 2,5-FDA and HMFA are stable towards polymerisation



New Chemicals & Building Blocks

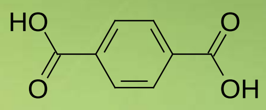
- HMFA (5-hydroxymethyl-2-furoic acid)
  - One of few hydroxy acids
  - Still contains “labile” hydroxymethyl group



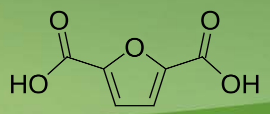
- Chemical/enzymatic polymerisation possible via trans-esterification
- After core hydrogenation lactone can be prepared which can undergo ring opening polymerisation (ROP) under mild conditions

New Chemicals & Building Blocks

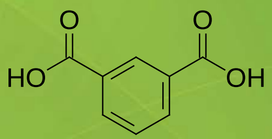
- 2,5-FDA most stable furan building block
- Proposed as renewable alternative to terephthalic acid (TA) for application in e.g. polyester (PET)
- However, angle in TA is 180°, in 2,5-FDA 127°
- More like isophthalic acid



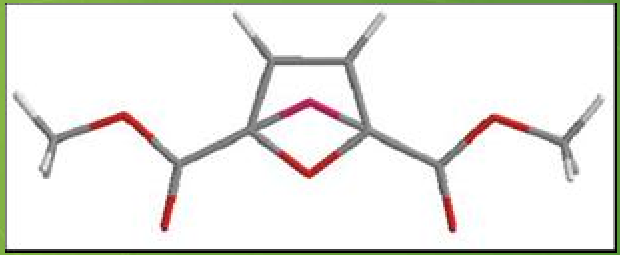
terephthalic acid

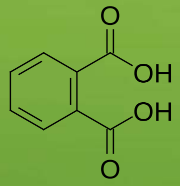


2,5-FDA



isophthalic acid





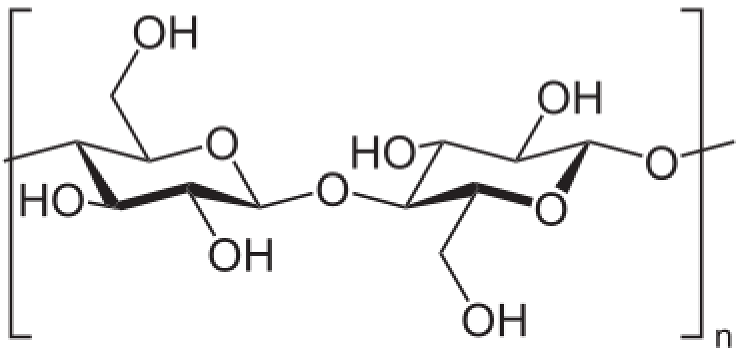
phthalic acid

Natural biobased polymers

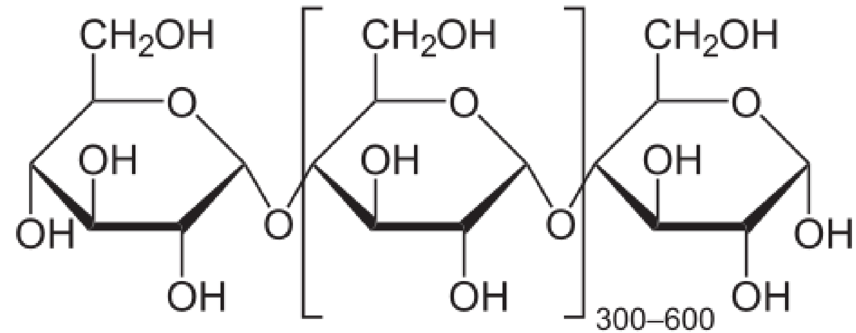
- Natural biobased polymers
  - Cellulose
  - Starch
  - Chitine
  - Rubber (polyisoprene)
  - Polypeptides
  - DNA

Natural biobased polymers

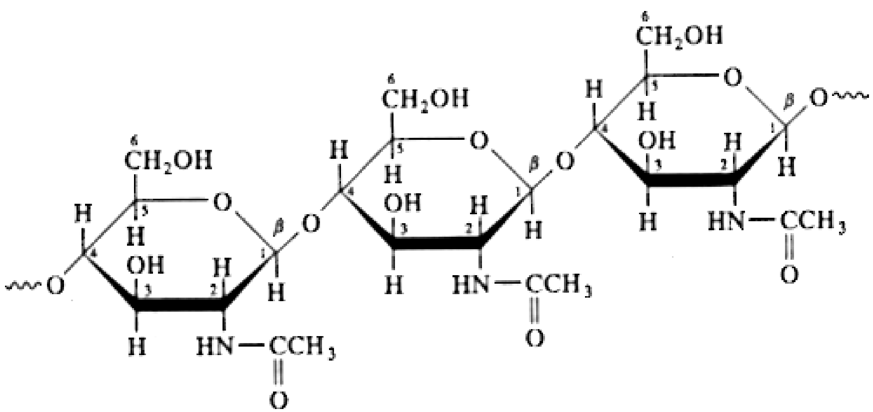
Cellulose



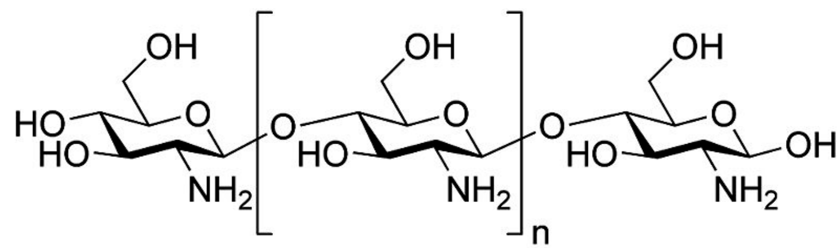
amylose



Chitine



Chitosan



Natural based monomers

- Large diversity of bio-based monomers
  - Directly from nature
  - After fermentation
  - Derived from sugars
  - Derived from peptides
- Large diversity of reactive groups
  - Carbonyl
  - Hydroxyl
  - Amino acids and hydroxy acids
  - Vinyl groups

Natural based polymers from monomers

- Many polymers are possible
    - Amorphous polymers
    - Semi-crystalline polymers
    - Thermoplastics
    - Thermosets
        - Polyesters
        - Polyamides
        - Polycarbonaten
        - Polyurethanen
        - Polyolefinen

Natural based polymers from monomers

- Minimum molecular weight largely depends on application
  - Relatively low molecular weight: coating & composite resins, adhesives
  - High molecular weight: molded parts like cups, bottles etc.
  - Ultra high molecular weight: fibre applications , *high performance* products

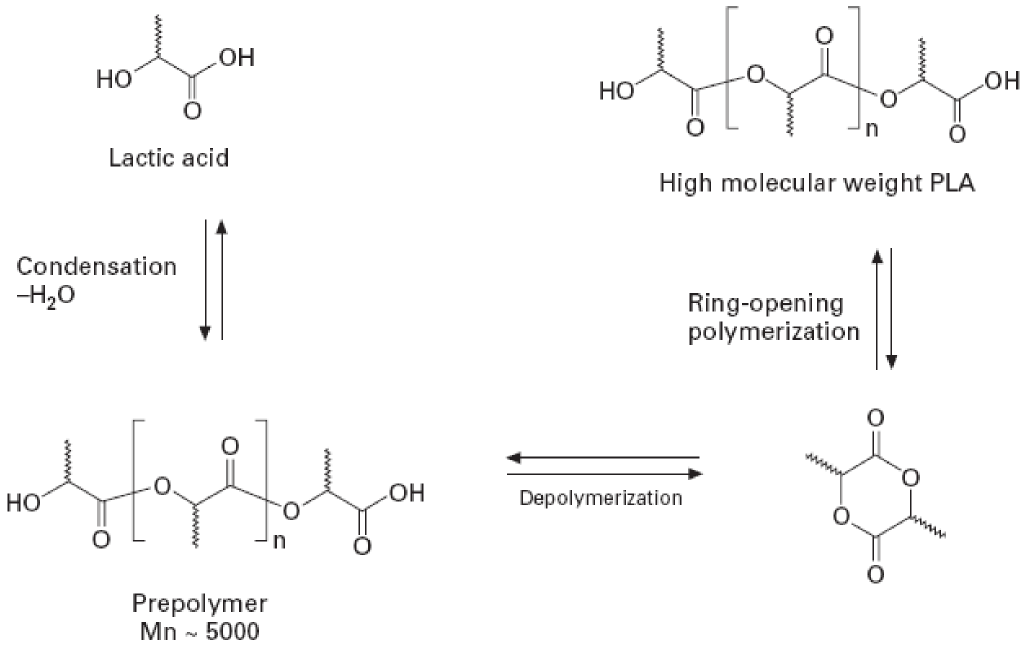
Natural based polymers from monomers

- Polycondensation reactions
  - Purity of the monomers is of main concern
    - Impurities can act as chain stoppers
    - Impurities can cause discoloration
  - Nature based monomers are thermally less stable as the petrol based monomers.
    - Reaction have to be performed at not too high temperatures

Natural based polymers from monomers

- Ring opening polymerisation
- Condensation polymerisation
    - Twee step process
        - Smelt polymerisation
        - Solid state post condensation
- Radical polymerisation
    - Different media
        - Emulsion polymerisation
        - Suspension polymerisatio
        - Bulk polymerisation

Polyesters



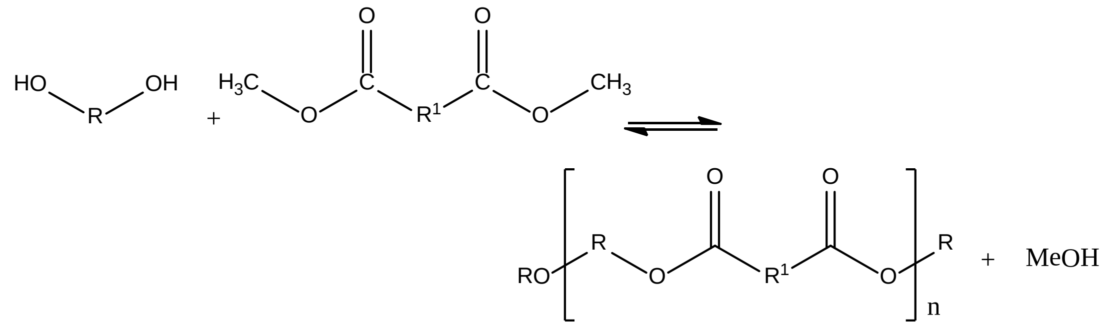
HO
OH
O
Lactic acid
Condensation
$-H_2O$
HO
O
O
O
n
O
OH
O
High molecular weight PLA
Ring-opening
polymerization
HO
O
O
O
n
O
OH
O
Prepolymer
Mn ~ 5000
Depolymerization
O
O
O
O

Polyesters

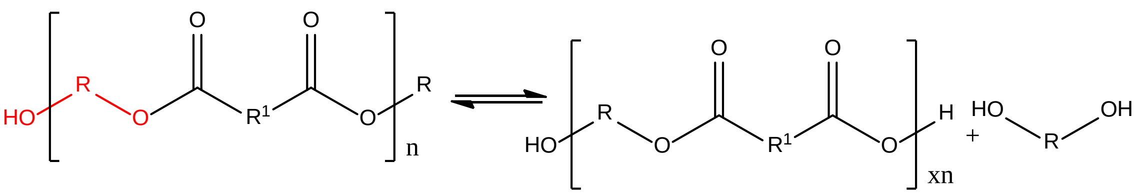
- Polylactic acid
  - Ring opening polymerisation
    - Polymerisation at relatively low T
    - High molecular weight
    - Only 1 end group present
    - Relatively low PDI ($1.3 < PDI < 1.6$)
  - Polycondensation
    - Polymerisation at high T because water has to evaporate
    - Relatively low molecular weight
    - Always 2 end groups present a COOH en OH
    - Polydispersity 2

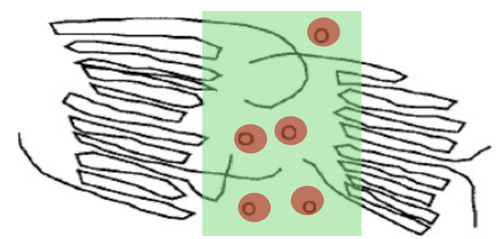
polyester

- Melt polymerization



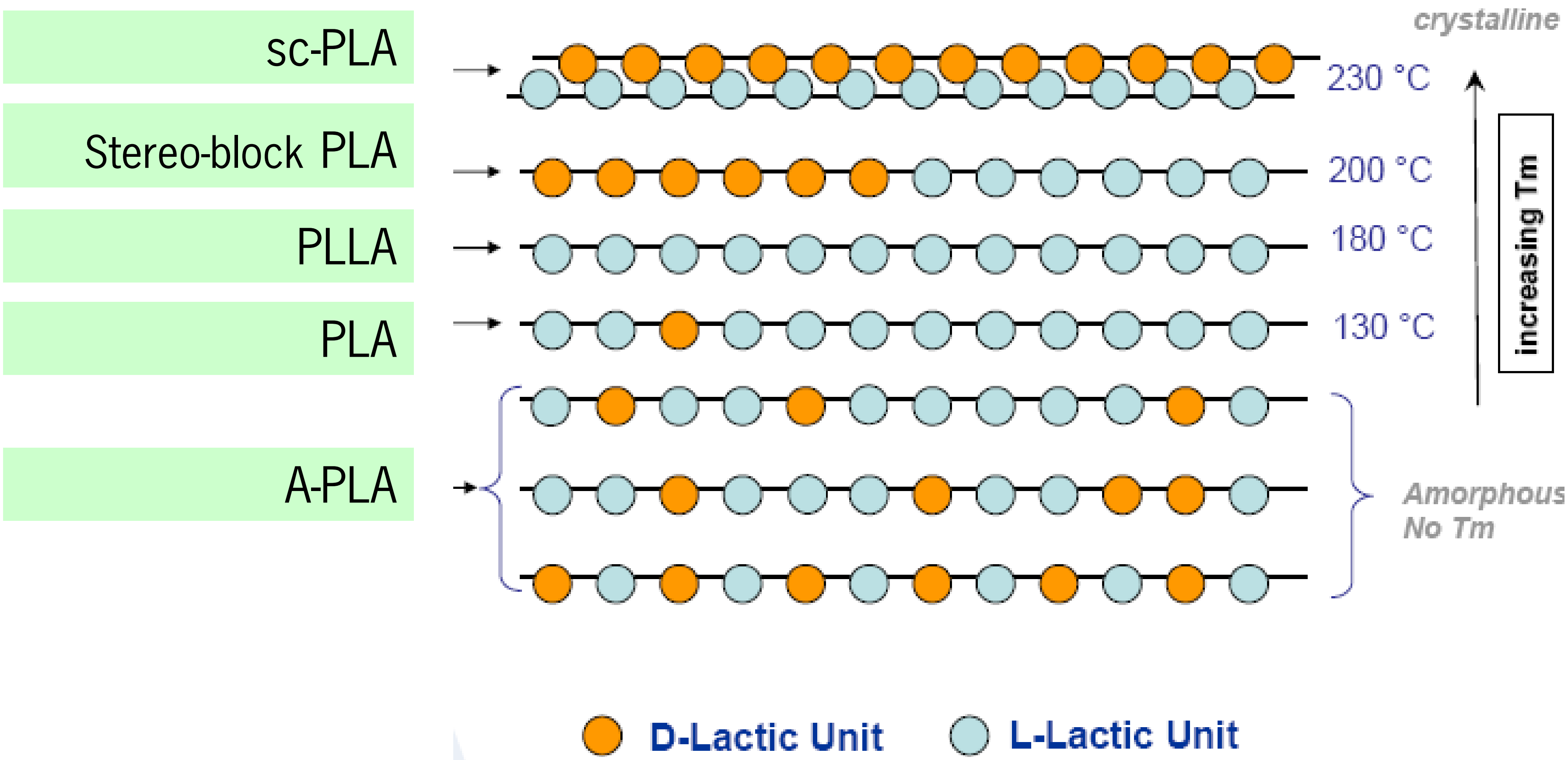
- Solid State Post Condensation (SSPC)
  - Condensation of reactive end-groups in amorphous phase: increase in MW





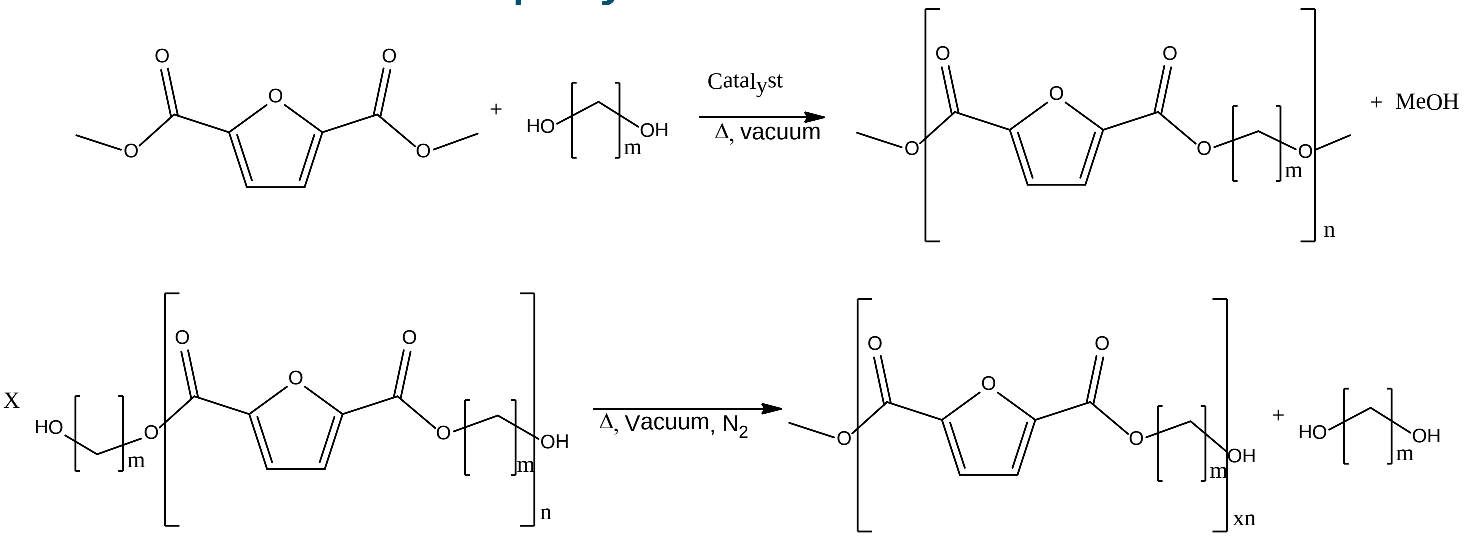
polyesters

- Polylactic acid. Enantiomeric purity



Polyesters

- Furan based polymers



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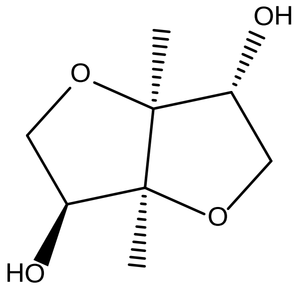
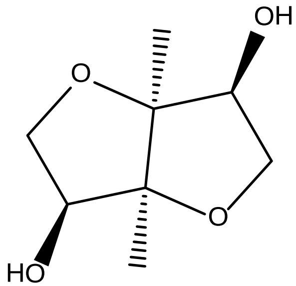
Polyesters

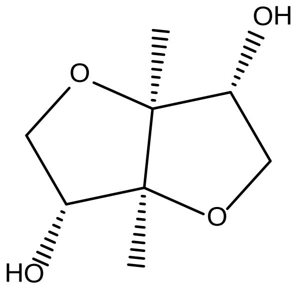
- Isohexides
  - Used to increase the T_g
  - Used to increase the hydrolytic stability



Isosorbide



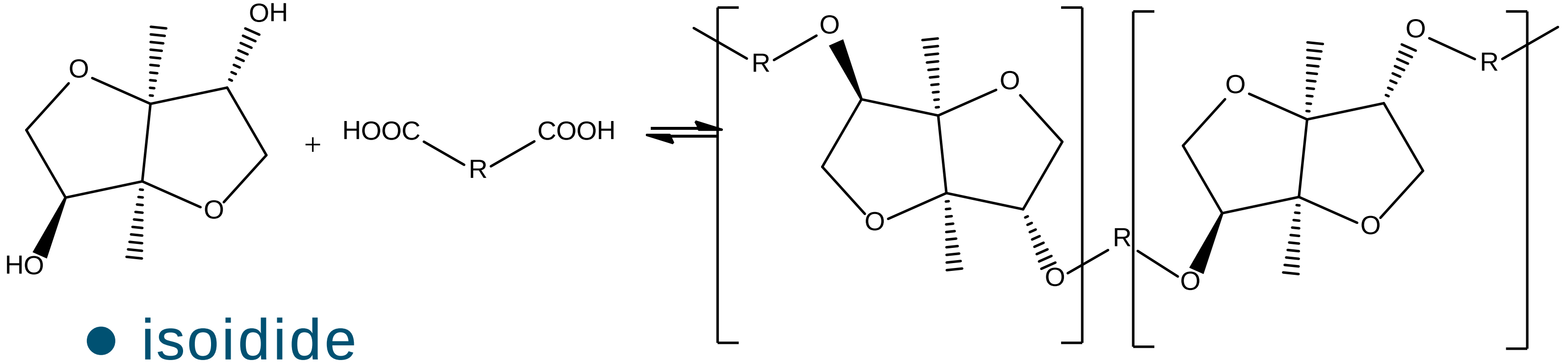
isomannide



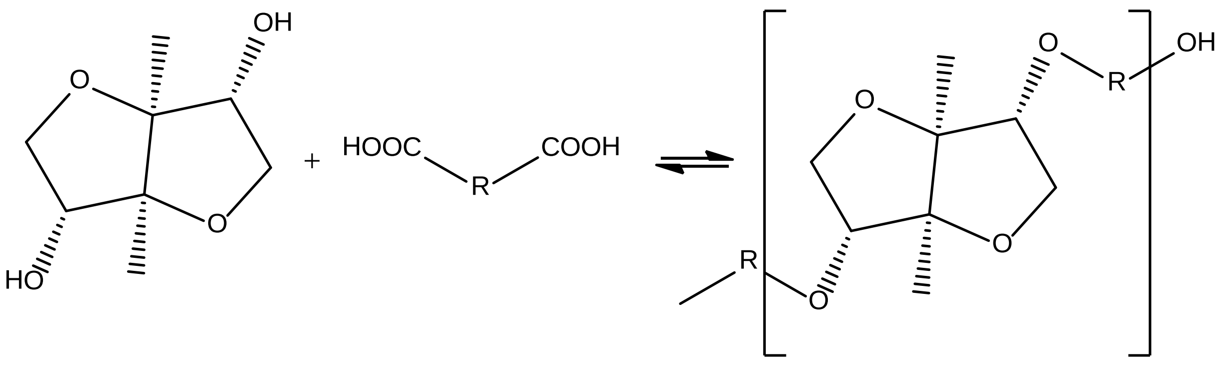
isoidide

Polyesters

- Isohexides
  - Isosorbide

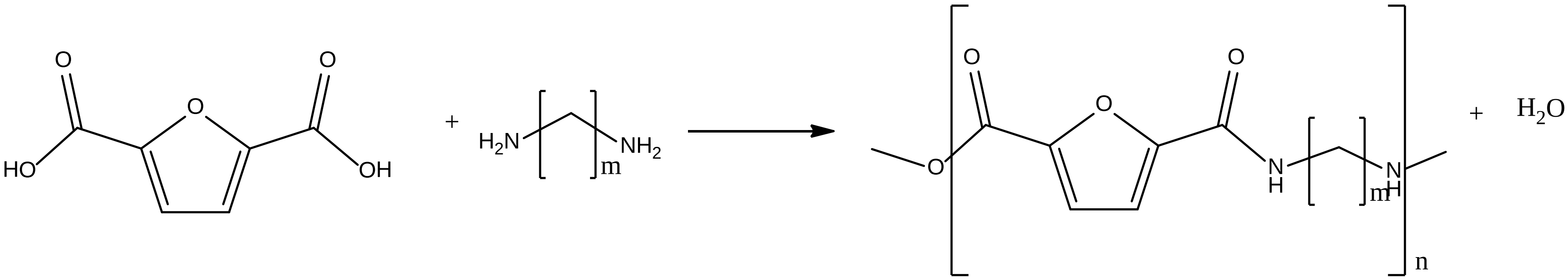


  - isoidide



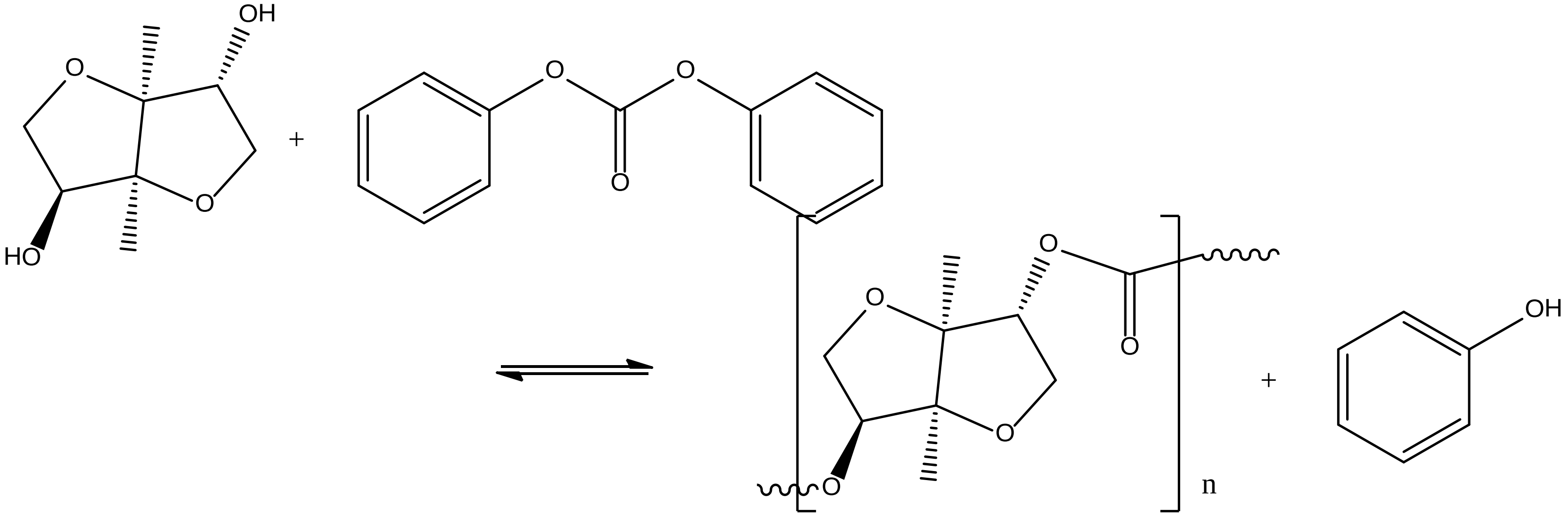
Polyamides

- Furan based polyamide
    - Polycondensation
        - Via the amide salt
        - Via acid chloride (interface polymerisation)



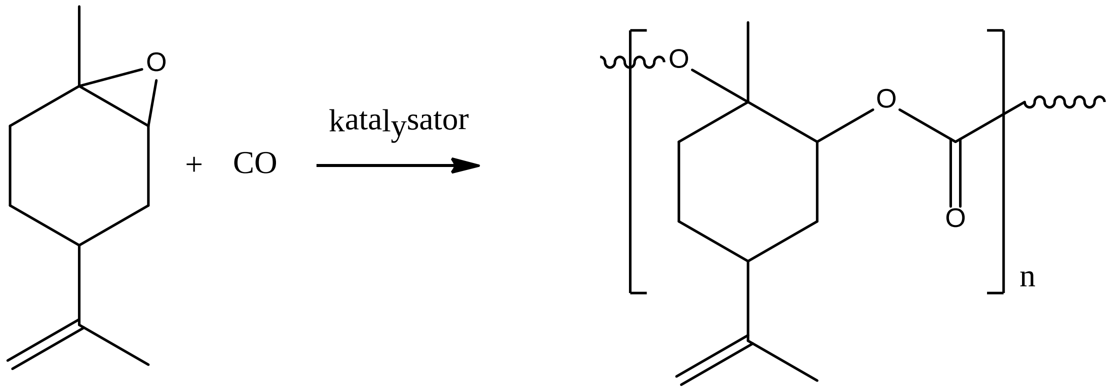
Polycarbonates

- Isosorbide as potential replacement for bisphenol-A
  - Nearly commercialized



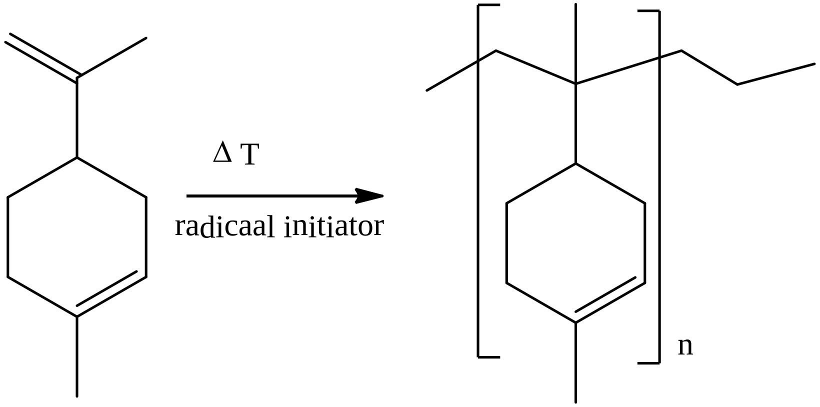
Polycarbonaten

- Limoneen CO



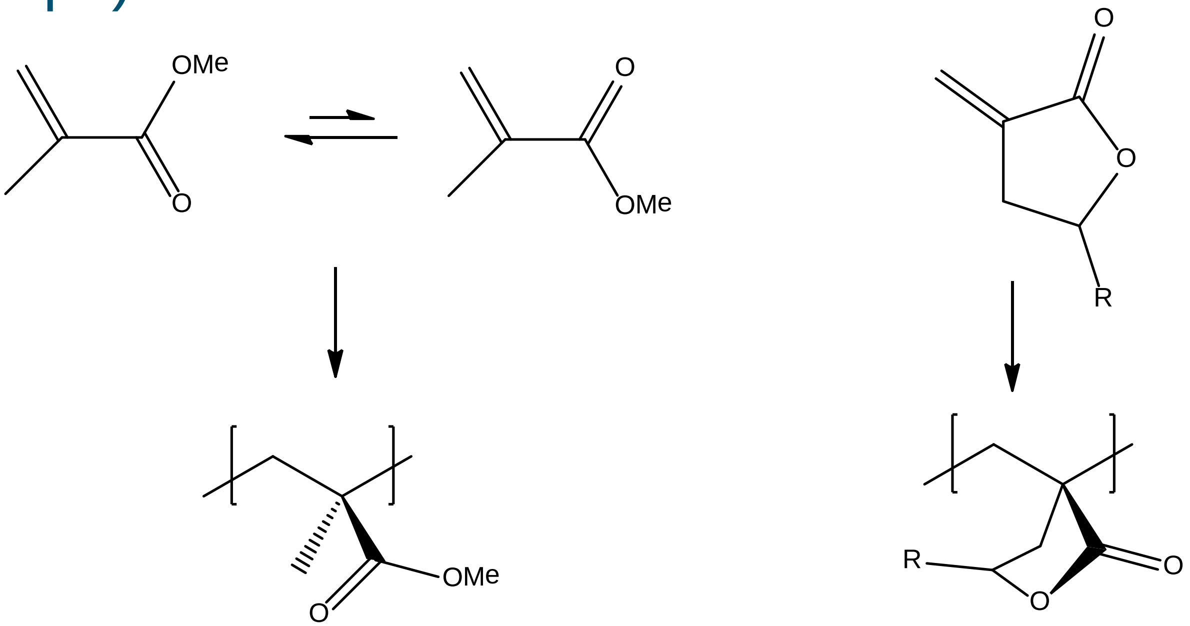
Vinyl polymers

- Radical polymerisation of limonene (isolated from orange peel
- Comparable to polystyrene



Vinyl-polymeren

- Radical polymerisation of tulipaline (monomer origination from tulips)

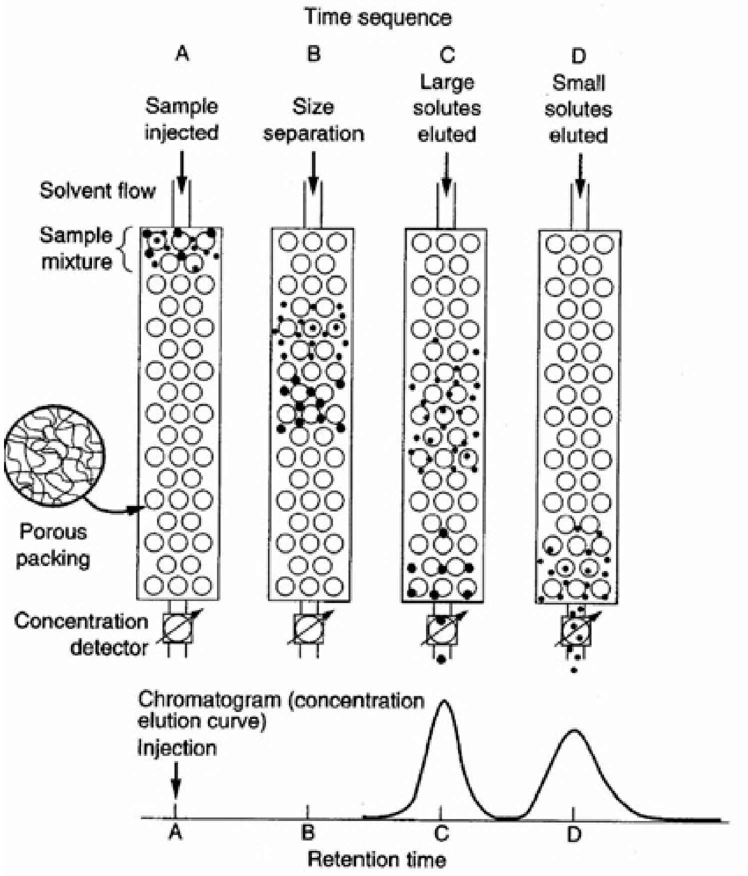


Links: PMMA uit methylmethacrylate (trans en cis conformatie)
rechts: polytulipaline uit tulipaline

Polymers in general

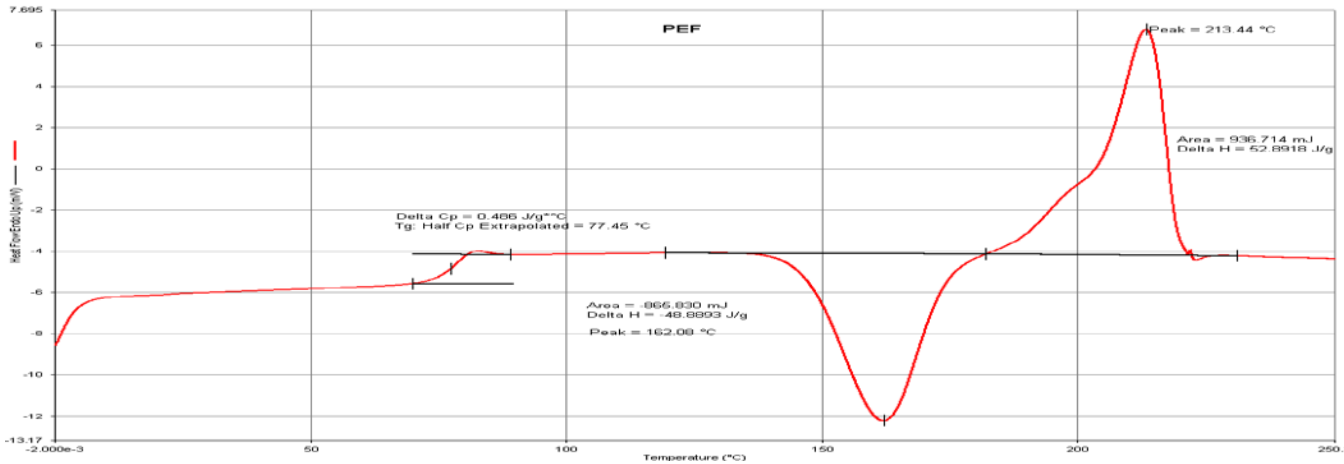
- Polymer back bone influences the thermal and mechanical properties
  - Molecular weight between entanglements determine the minimum MW for good properties
  - Linearity and purity influence the crystallinity
  - Crystallinity influences the HDT.

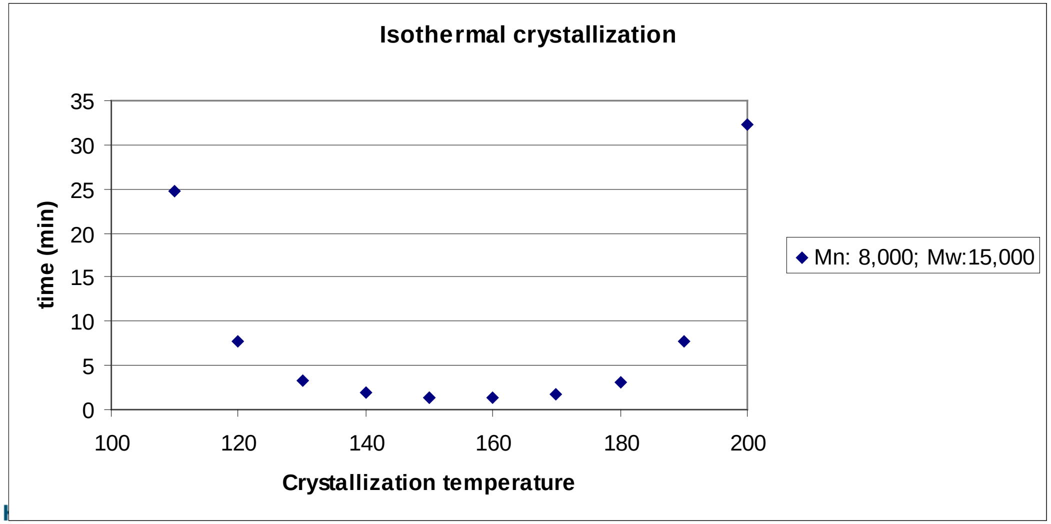
Size exclusion chromatography



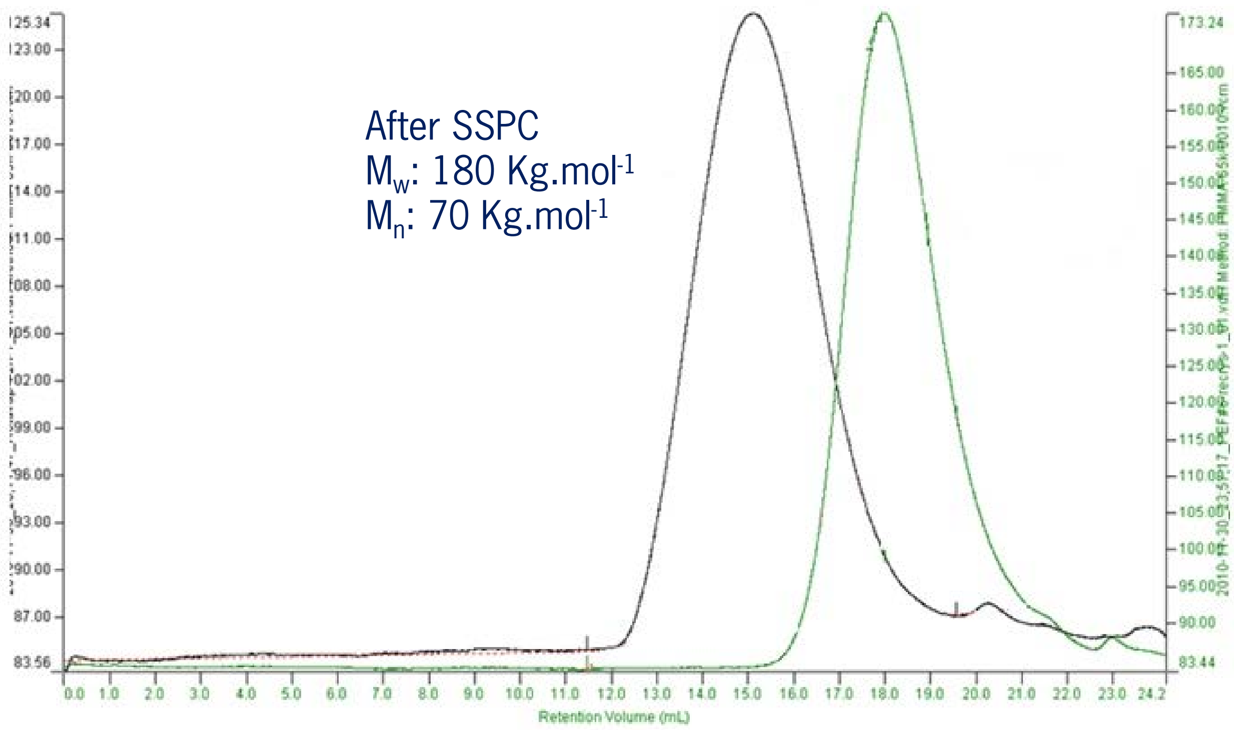
Results (DSC)

- After melt polymerization

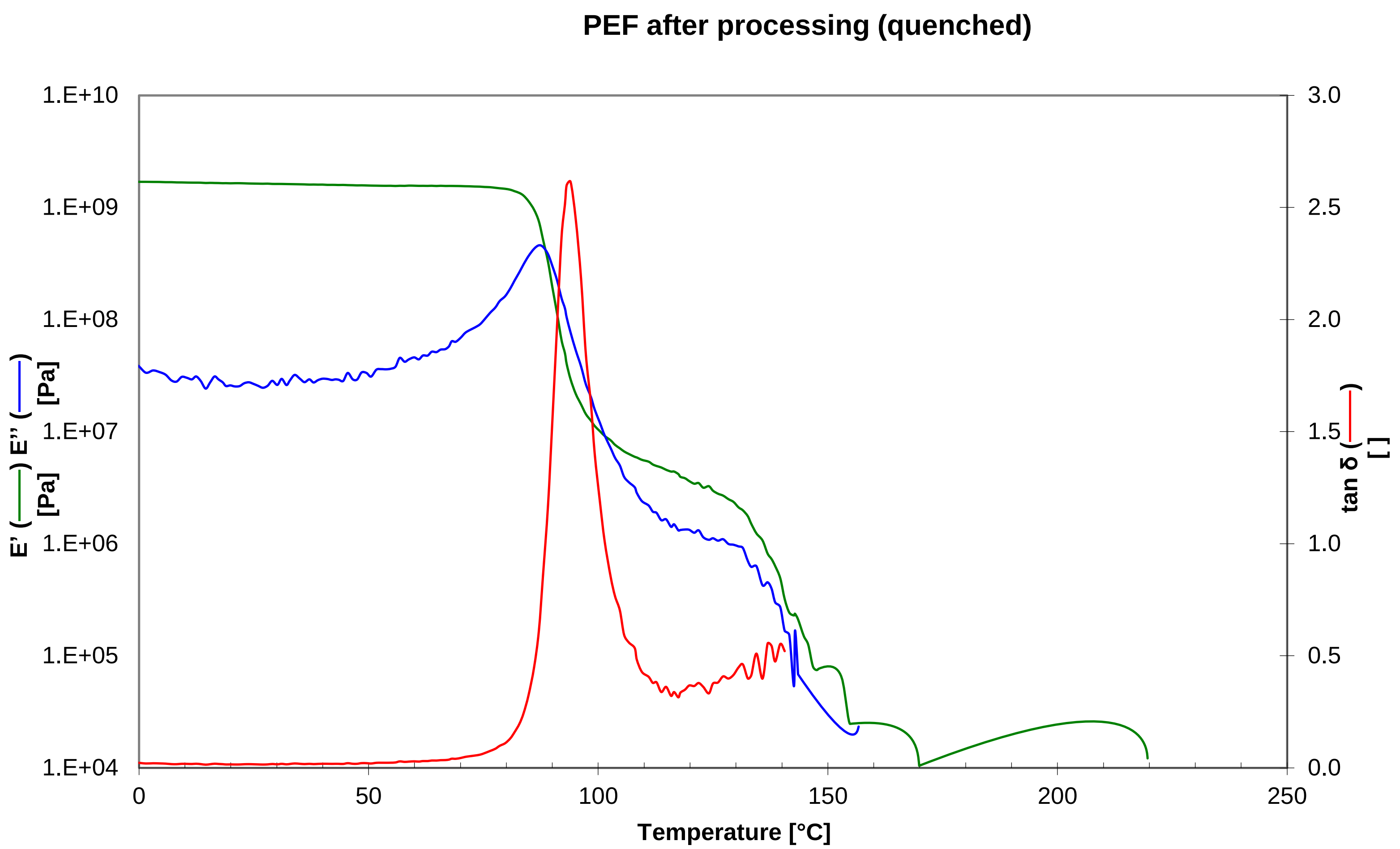




Results (SEC)

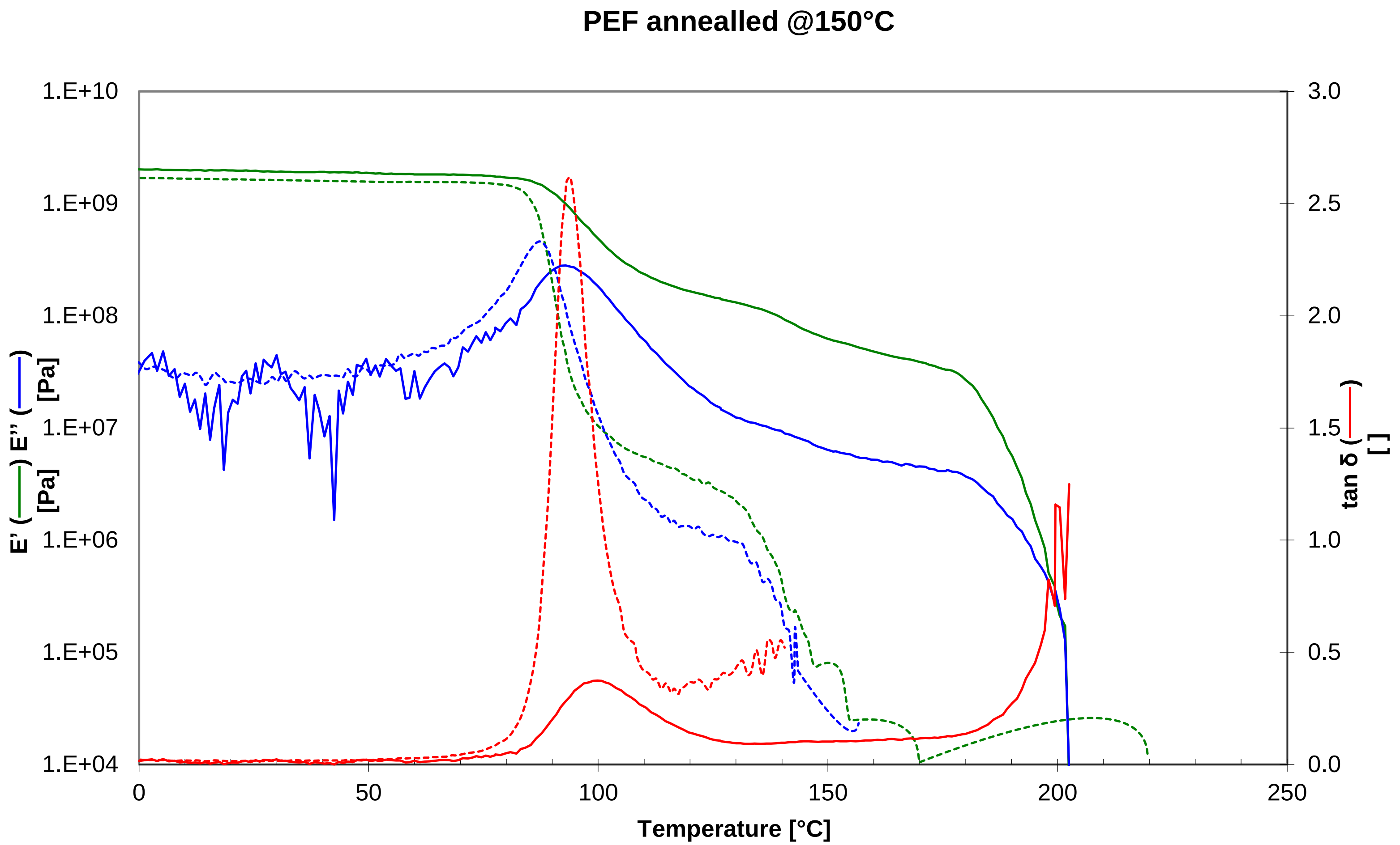


Results (DMTA)



FOOD & BIOBASED RESEARCH
WAGENINGEN UR

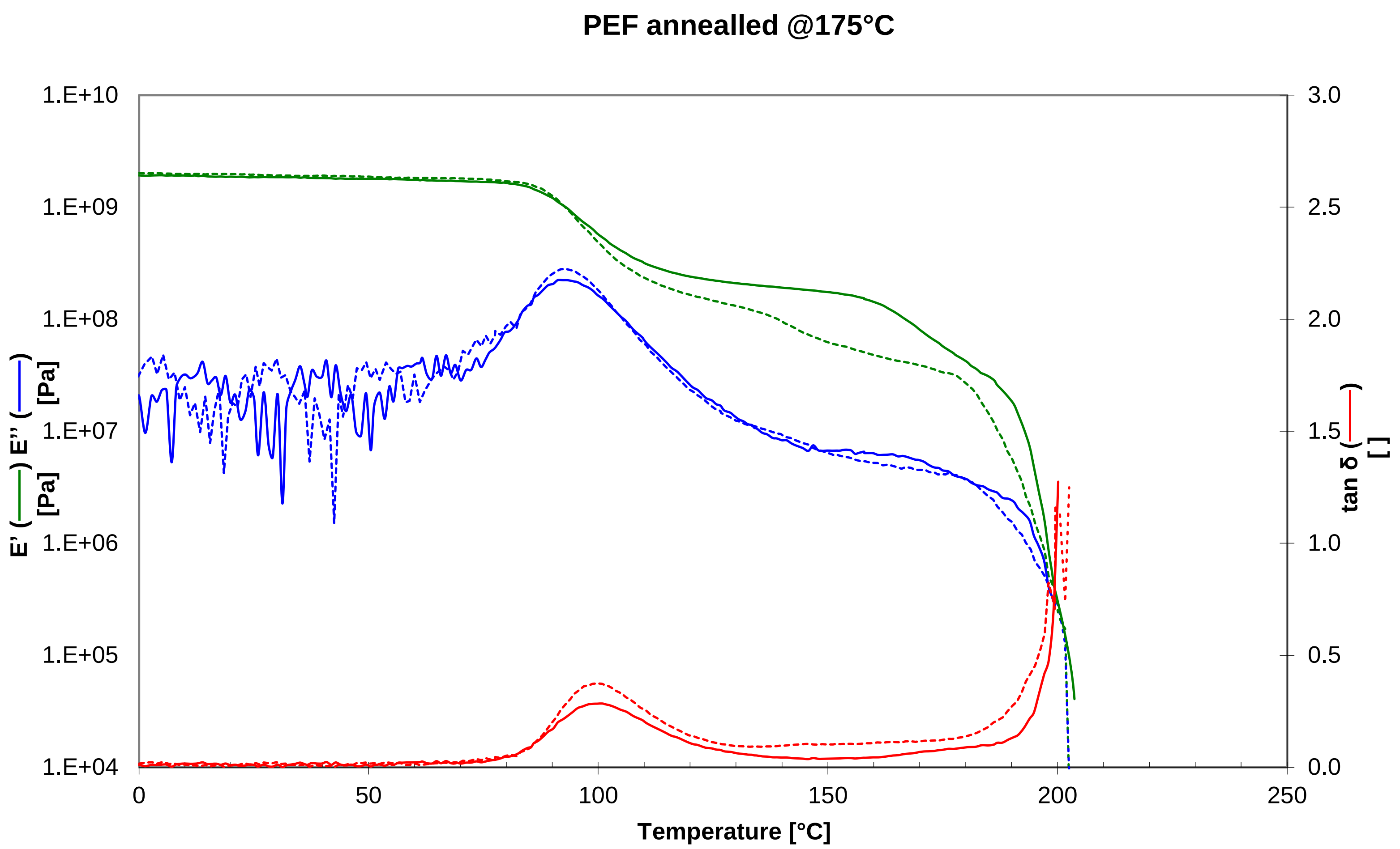
Results (DMTA)



FOOD & BIOBASED RESEARCH

WAGENINGEN UR

Results (DMTA)



FOOD & BIOBASED RESEARCH
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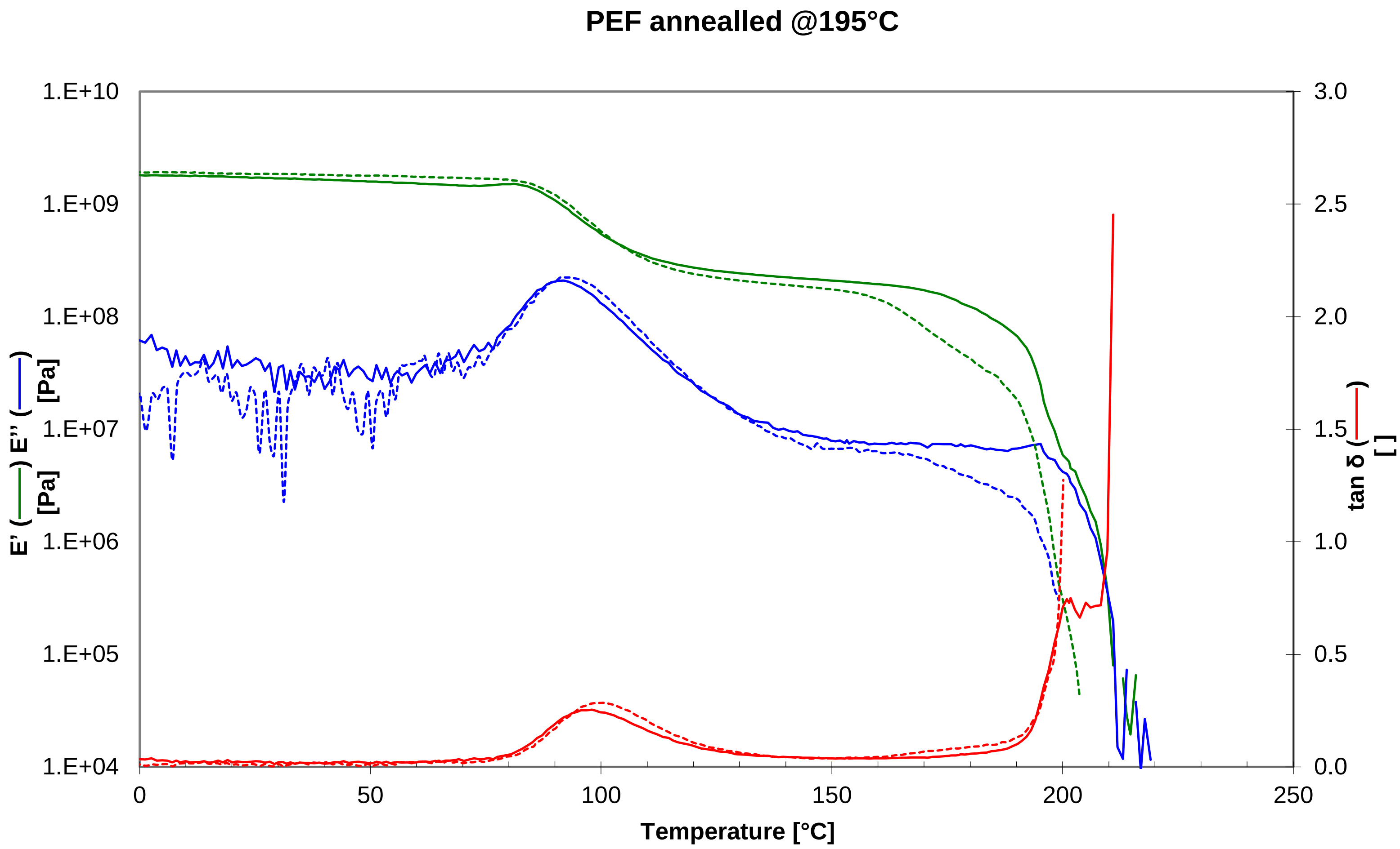
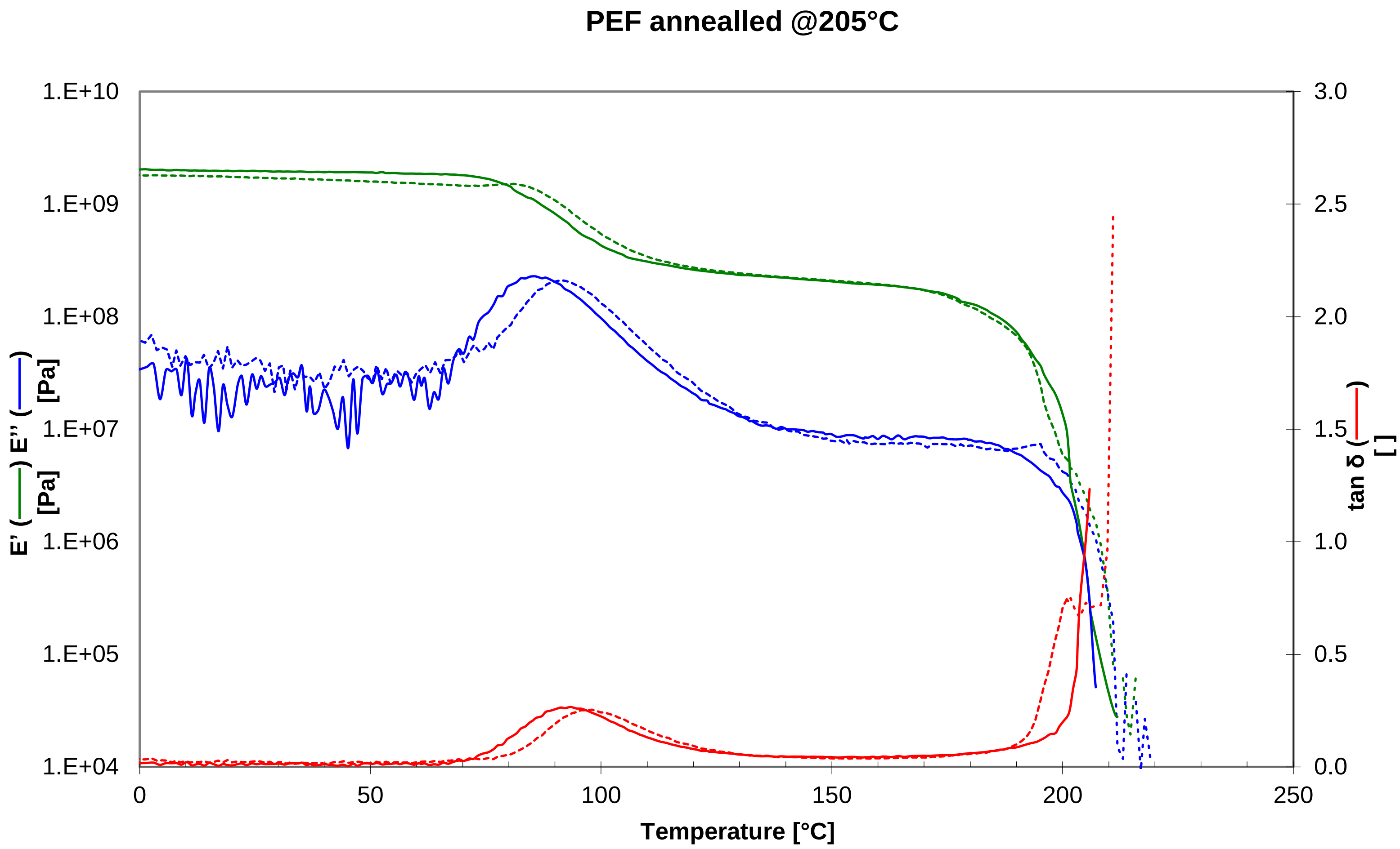
Results (DMTA)



FOOD & BIOBASED RESEARCH
WAGENINGEN UR

Results (DMTA)



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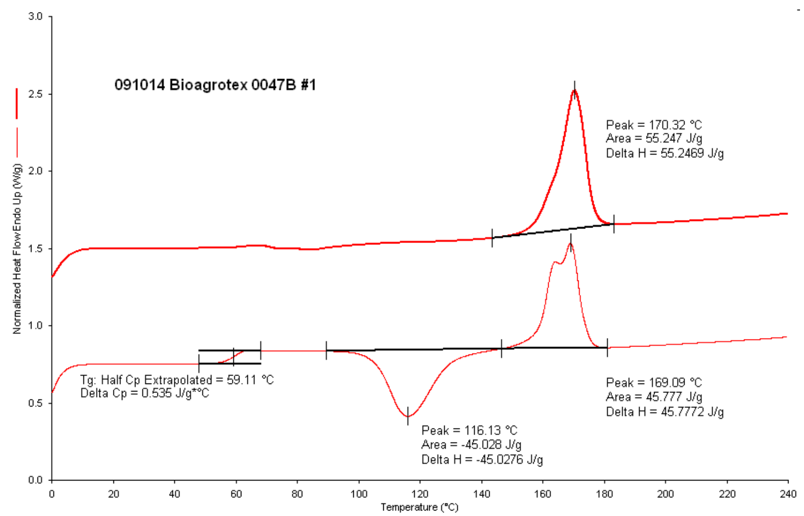
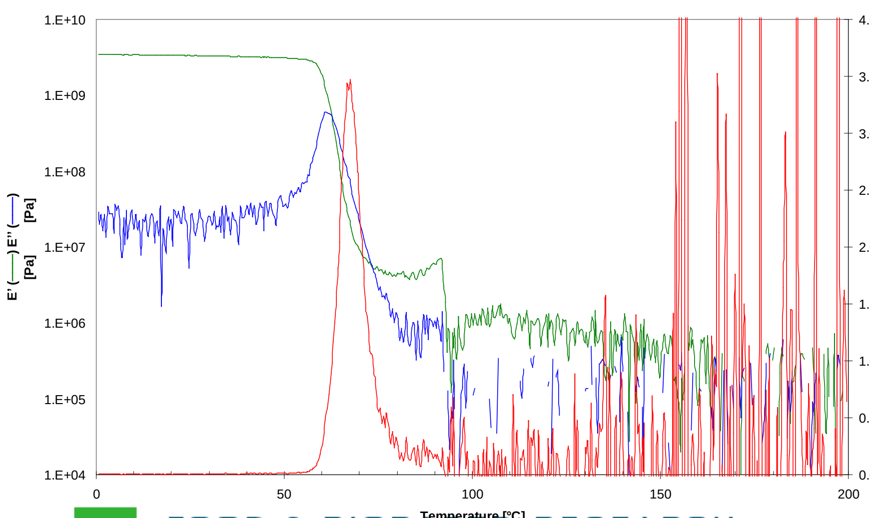
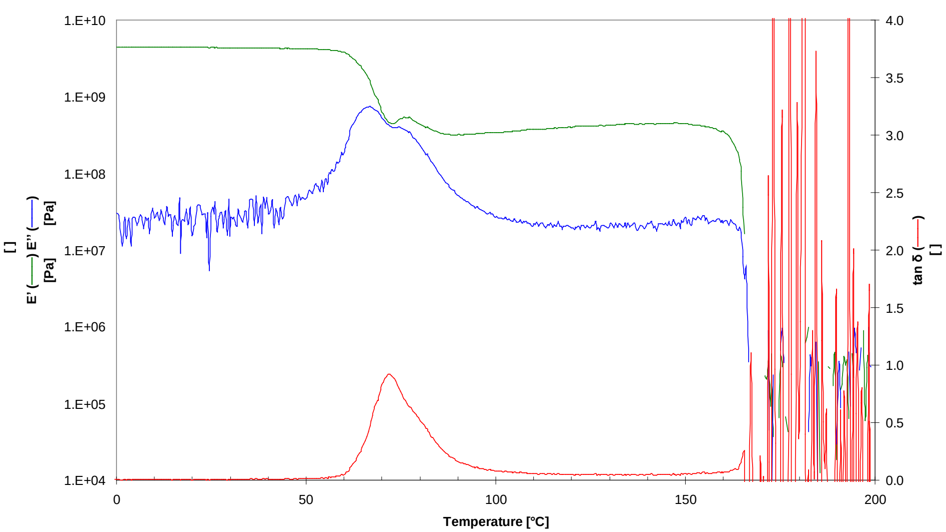
Thermal-mechanical analysis



Bioagrotex PLA 6201D 4x verstrekt (115°C) 0047C



Bioagrotex PLA 6201D 4x verstrekt (90°C) 0047A



Questions

Thanks to

Daan van Es

Karin Molenveld

Gerald Schennink