Session: Using biobased sources for new chemicals and materials
Presentation by: Rutger Knoop, *Wageningen Food & Biobased Research*

Title: **High performance polymers based on isoidide**

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Curriculum:
After his master polymer chemistry at the state University Groningen, Rutger Knoop obtained his PhD at the University of Technology Eindhoven in 2009. In December 2008 he joined Wageningen Food & Biobased Research to start up polymer chemistry research. Since then, he was involved in many projects in the field of renewable polymer synthesis, polymer characterisation and polymer modification. He is (co)inventor on 7 patent applications, e.g. polyisoidide furanoate thermoplastic polyester and copolyesters and the use thereof for hot fill applications, and a polymer composition comprising an impact modifier and method of making the same.

Abstract:
Isohexides are a versatile class of monomers suitable for the development of engineering plastics. Isohexides are advocated as a potential monomer to replace bisphenol-A for food packaging applications mainly due to the rigid structure of isohexides. Three different isomers of isohexides exist of which isosorbide is well explored due to its commercial availability. At Wageningen Food & Biobased Research, a technique was developed to transform isosorbide into isoidide, a more reactive and symmetrical isohexide. In this presentation, some insights in the benefits of isoidide over isosorbide will be shown. This will be illustrated with some examples obtained in the BPM-HIPPIE project. This project was a collaborative research project together with ADM, DuPont and Holland Colours.

HIPPIE: High Performance Polymers from Isoidide

June 19th 2019, Willem Vogelzang, Rutger Knoop, Jacco van Haveren

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Outline

- Introduction
  - Project partners
  - Aim of Hippie
  - Isohexides
    - Applications
  - Furandicarboxylic acid (FDCA)
- Results
  - Co-diol isoidide polyesters
- Conclusions
- Future outlook

Partners

- BPM-2 Project
- 3 Partners
  - Archer Daniels Midland (ADM): large agri-food processor
  - DuPont: was the world's fourth-largest chemical company based on terms of sales[1]
  - Holland Colours (HCA): SME, Coloring & Barrier solutions for consumer packaging

[1] https://en.wikipedia.org/wiki/DowDuPont

Introduction (Aim of the project)

1: Develop materials for food packaging applications from isoidide with:

- Glass transition temperature (T_g) > 120°C
- Semi-crystalline; Melting temperature (T_m) ≤ 260°C
- High barrier properties

- Target markets/applications:
  - BPA-PC alternatives and BPA-free food packaging

2: Develop carrier for additives based on isoidide with

- T_m>100°C
- High crystallization rate

Introduction (Background information)

- Bisphenol-A based materials are under debate.
  - Potentially endocrine disruptive
  - Potentially impair the immune systems of (unborn) children
- Bisphenol-A based materials are found in:
  - Construction materials
  - Electronics
  - Bottles
  - Food packaging
  - Medical devices
  - Coatings

Introduction (Commercially available alternatives)

- Mitsubishi DURABIO^{TM} (left) and Eastman Tritan (right)

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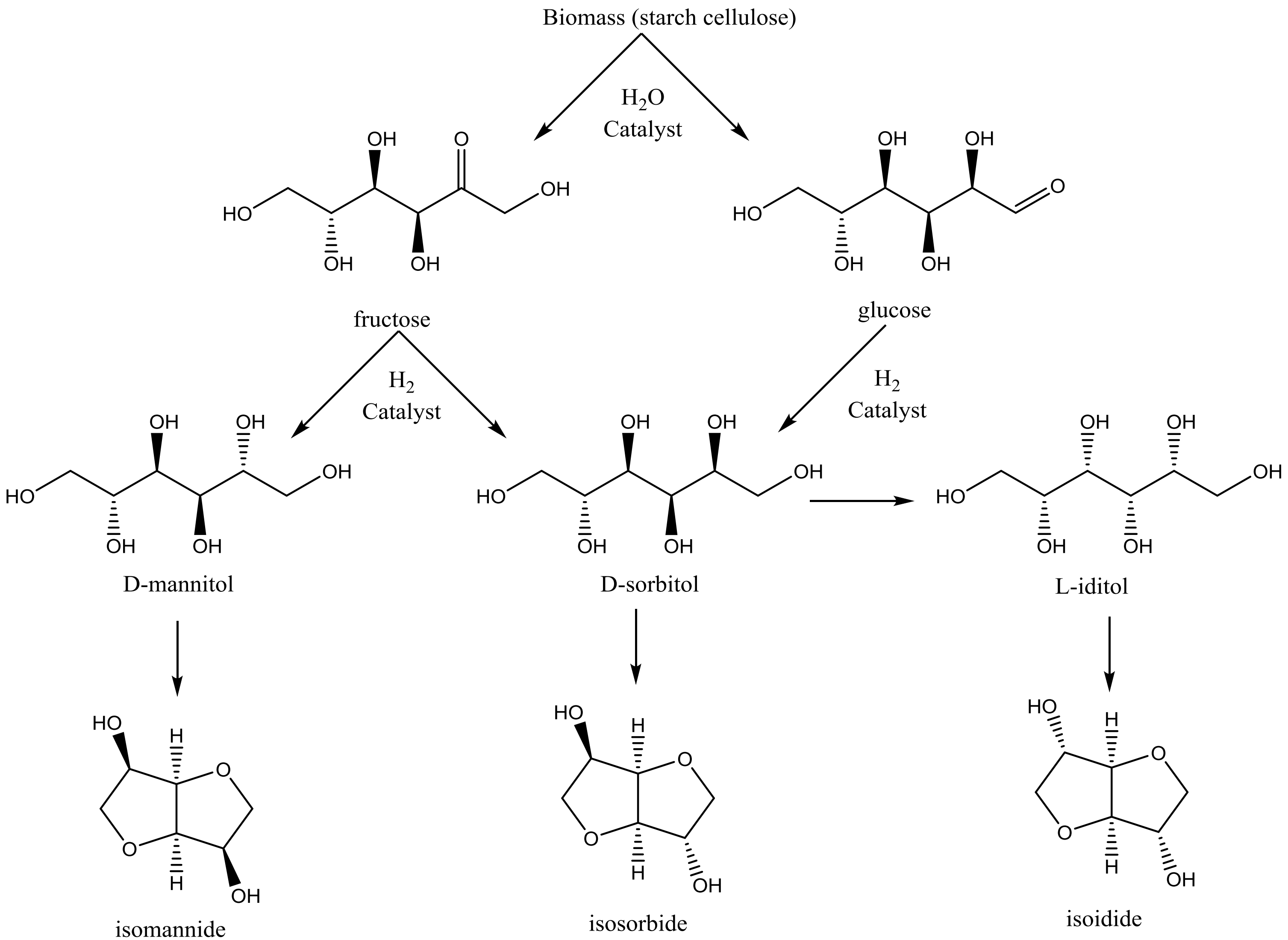
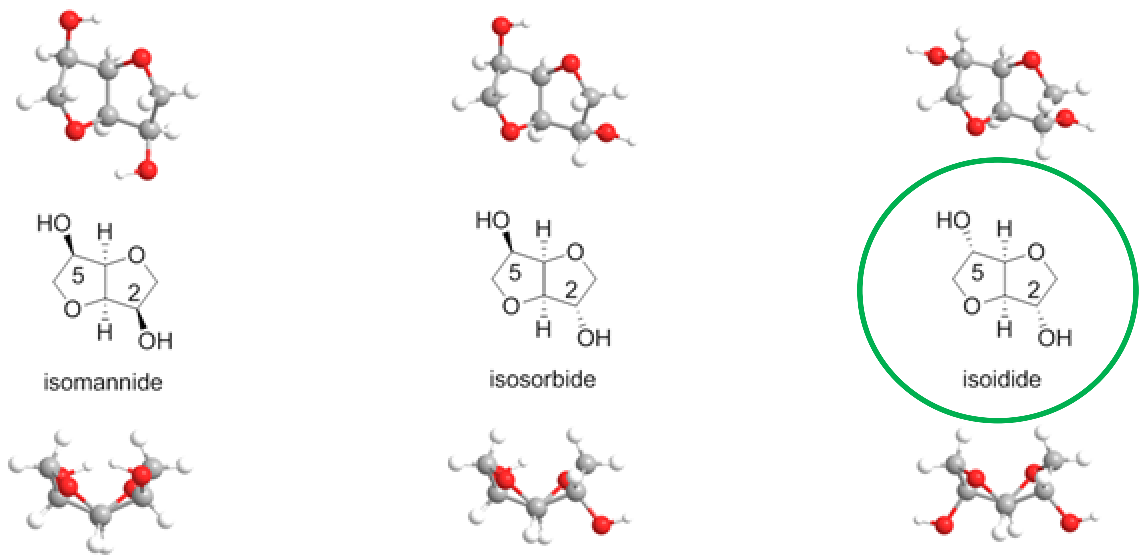
Introduction (Monomers of interest)



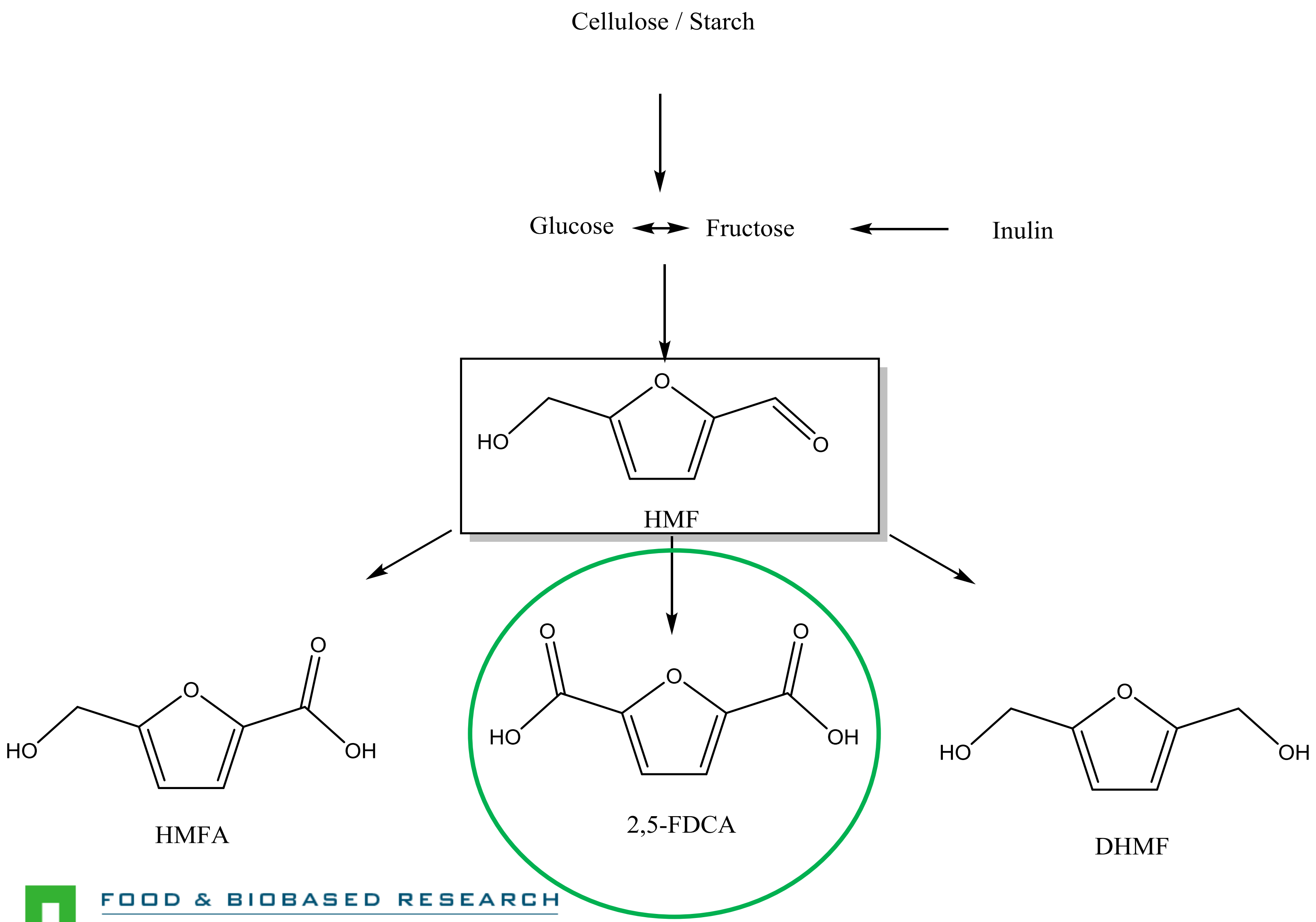
Introduction (Monomers of interest)



- Development of catalytic method to obtain isoidide from isosorbide
  - Resulted in patent application[1a] and scientific paper[1b]

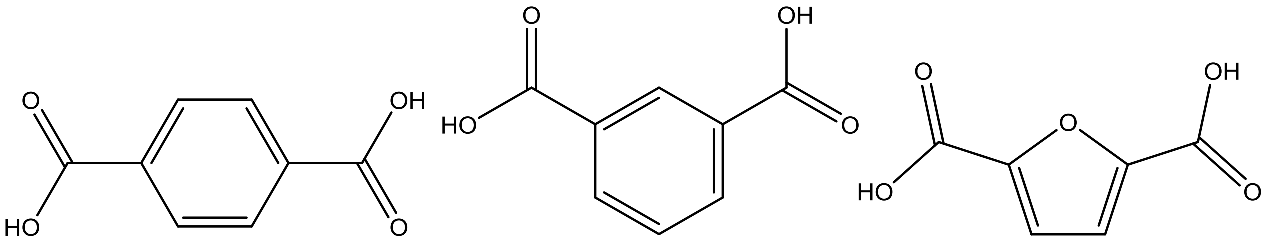
1 a) WO2013125950A1. Method of Making Isoidide. Hagberg, E.; Martin, K.; Le Notre, J.; van Haveren, J.; van Es, D. S. **2013**.
b) Le Notre, J.; van Haveren, J.; van Es, D. S.; Synthesis of Isoidide through Epimerization of Isosorbide using Ruthenium on Carbon. *ChemSusChem* **2013**, *6*, 693 – 700;

Introduction (monomers of interest)



Introduction (Monomers of interest)

- 2,5-FDCA is advocated as alternative for terephthalic acid.



Terephthalic acid | Isophthalic acid | 2,5-FDCA

- Poly(ethylene terephthalate) vs Poly(ethylene furanoate)[1]
  - PEF oxygen barrier is 10 times better than PET
  - PEF carbon dioxide barrier is 4 times better than PET
  - PEF water barrier is 2 times better than PET
  - The Tg of PEF is 86°C compared to the Tg of PET of 74°C
  - The Tm of PEF is 235°C compared to the Tm of PET of 265°C

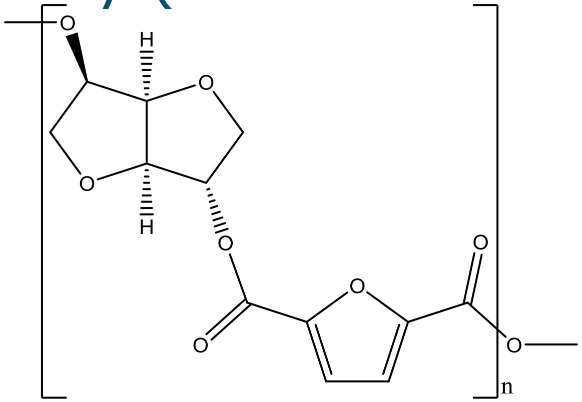
1)https://www.avantium.com/yxy/products-applications/

Introduction (Monomers of interest)

- Research questions
  - Can isoidide increase the glass transition temperature of 2,5-FDCA based polyesters?
  - Can isoidide improve the barrier properties of 2,5-FDCA based polyesters?
  - Does isoidide outperform isorbide in polyesters?

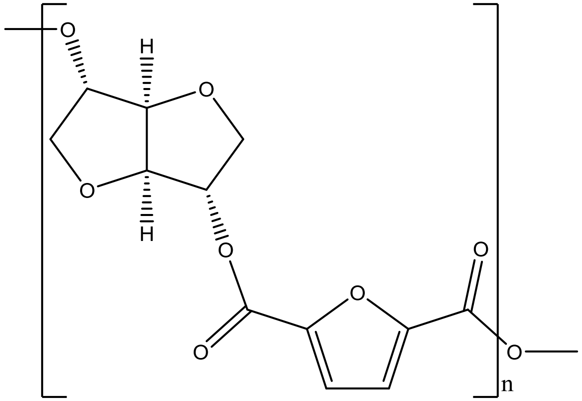
Results isosorbide vs isoidide

- Poly (isosorbide furanoate)



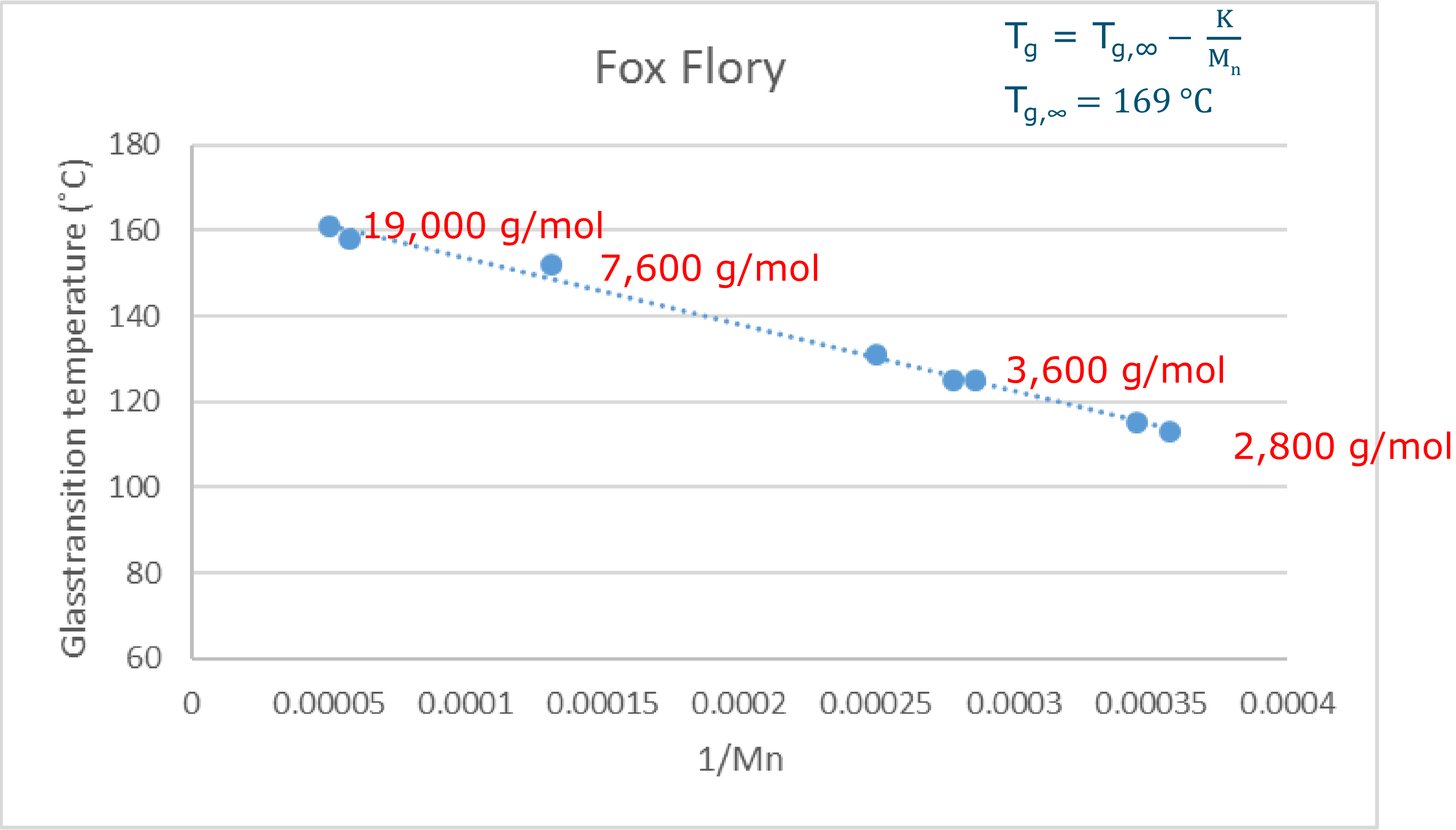
GPC		DSC	
Mn (g/mol)	Mw (g/mol)	Tg (^oC)	Tm (^oC)
1,700	3,800	106	n.o.

- poly (isoidide furanoate)



GPC		DSC	
Mn (g/mol)	Mw (g/mol)	Tg (^oC)	Tm (^oC)
2,100	3,600	112	234

Results homo-polymerization



*Fox, T.G.; Flory, P.J., "Second-order transition temperatures and related properties of polystyrene" Journal of Applied Physics, 1950, **21**: 581–591*

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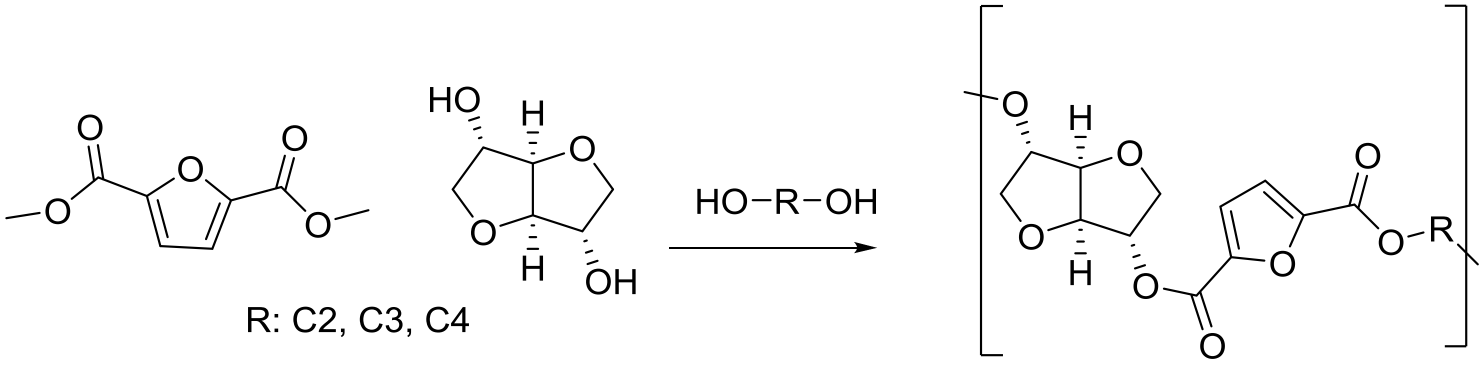
Results homo-polymerization

- Molecular weight increment by solid state post condensation

Entry	T_{SSPC} (°C)	Time (h)	GPC			DSC	
			Mn (g/mol)	Mw (g/mol)	PDI	Tg (°C)	Tm (°C)
PIIF							
1	-	-	1,500	4,000	1.7	111	240
2	230	4	14,200	30,700	2.2	159	274
3	230	16	19,800	44,100	2.2	170	281

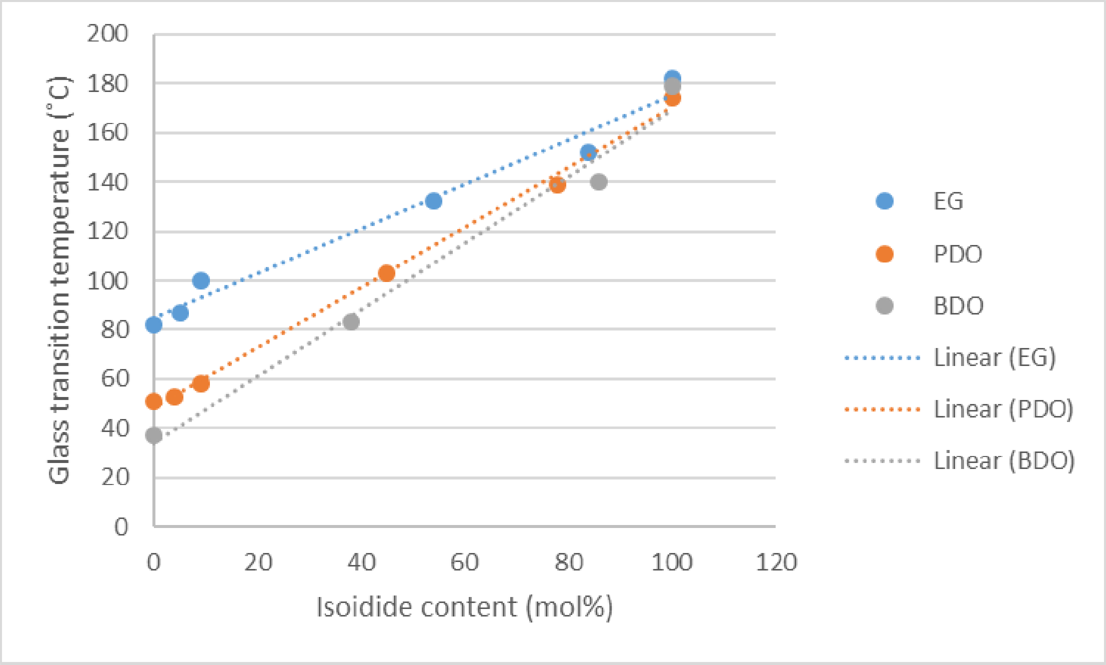
Results co-polymerization

- Semi-crystalline and amorphous co-polyesters based on isoidide and 2,5-FDCA

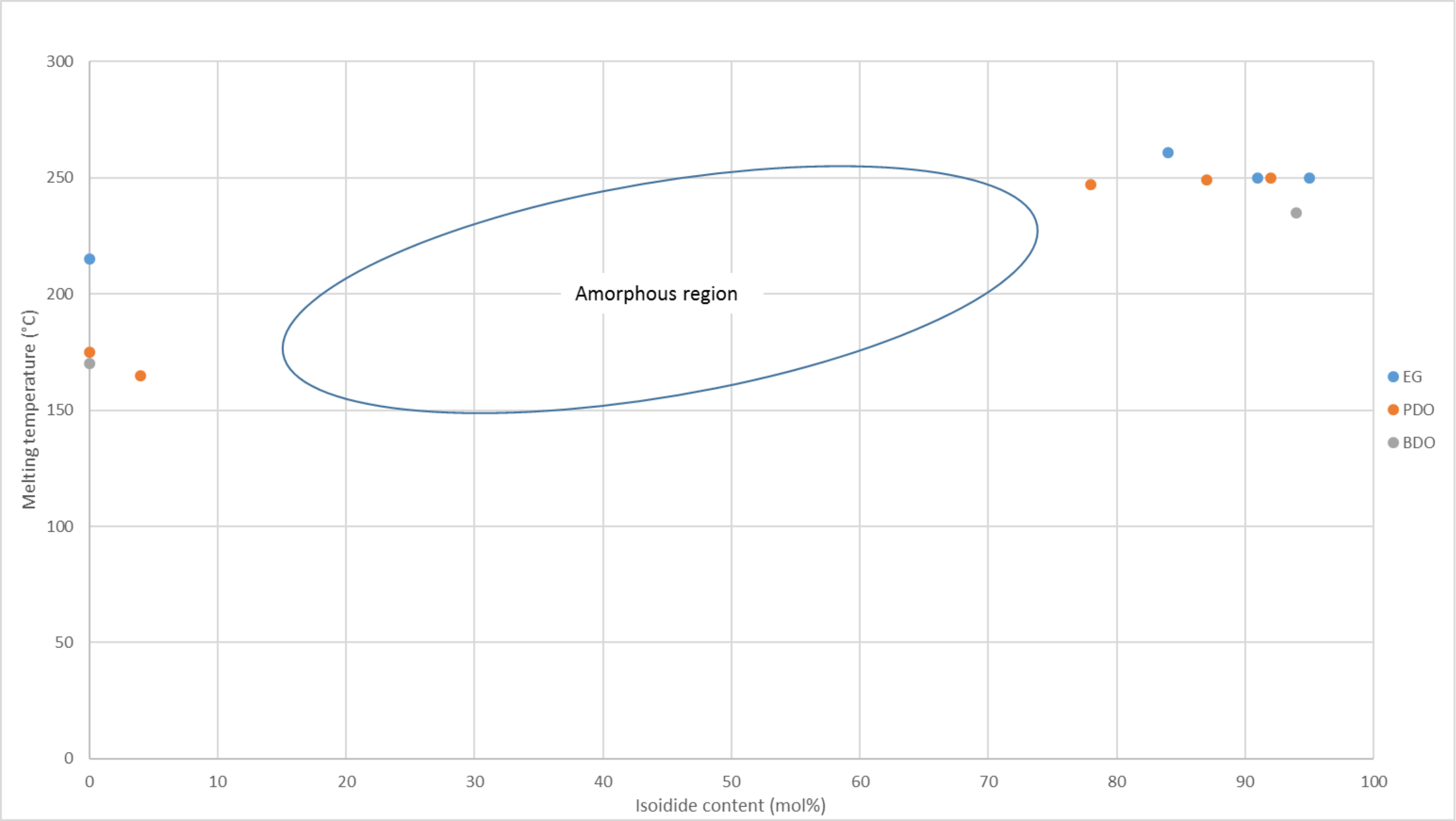


Results co-polymerization

- Glass transition temperature as function of isoidide content in
  - poly(ethylene-co-isoidide furanoate)
  - poly(propylene-co-isoidide furanoate)
  - poly(butylene-co-isoidide furanoate)



Results co-polymerization



Intermediate conclusions

- Homo-polymerization of isoidide and 2,5-FDCA.
  - Highly crystalline polyester with:
    - T_g: 169-175°C
    - T_m: >250°C (slightly high for processing)
- Homo-polymerization of isosorbide and 2,5-FDCA
  - Amorphous polyester with:
    - T_g: 169-175°C
- Co-polymerization of isoidide with aliphatic diols.
  - Glass transition temperature increases with isoidide content
  - Remain semi-crystalline for
    - 15%<isoidide content (mol %)<85%

Intermediate conclusions

- Development of isoidide based polyesters
  - Resulted in patent application on polyisoidide furanoate (PIIF) homo-polyester and co-polyesters[1]
  - Solid State Postcondensation (SSPC) was used to increase MW
  - Concept proven that isoidide allows for producing semi-crystalline polymers

1)polyisoidide furanoate thermoplastic polyester
and copolyesters and the use thereof for hot fill applications. (WO20156607 A1)

Reduction of the melting temperature

- The melting temperature of isoidide based polyesters is slightly too high for processing.
    - Reduction of melting temperature by introduction of additional co-monomers

Results co-polymerization

Mn: 27,900 Da
Mw: 56,300 Da
PDI: 2.1

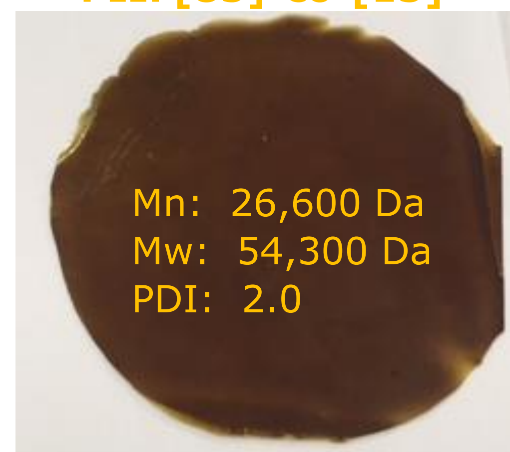
phase 1 — Quenching — 285-290 °C

phase 2 — Compression moulding — 250 °C

Mn: 32,000 Da
Mw: 72,000 Da
PDI: 2.1

PIIF[85]-co-[15]

PIIF[85]-co-[15]



Retaining 70-75% initial MW after compression moulding

Tensile properties polyesters

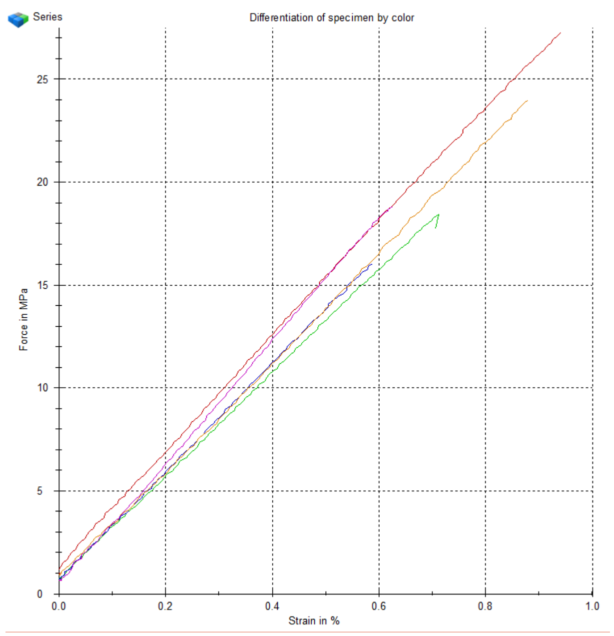
PIIF copolyester A

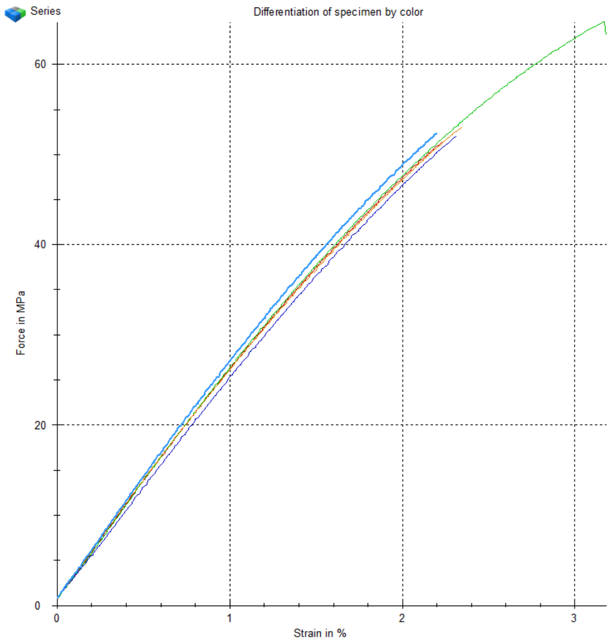
PIIF copolyester B

Polymer	E-modulus (GPa)	Tensile strength (MPa)	Stress at break (%)	T_g (°C)
PIIF copolyester A	2.6	21	0.7	160
PIIF copolyester B	2.6	55	2.5	140
BPA-PC[1]	2.0-2.4	55-75	80-150	150

1) https://en.wikipedia.org/wiki/Polycarbonate

Tensile properties





Sample	Composition		E-Modulus (MPa)	Stress-max (MPa)	Strain at break (%)
WVHIP55		PiIF[85]-co[15]	2640 [191]	20.9 [4.6]	0.7 [0.2]
WVHIP60		PiIF[85]-co[15]	2562 [115]	54.7 [5.6]	2.5 [0.4]

Conclusions

- Polyesters based on isoidide and 2,5-FDCA in combination with other co-monomers can result in materials with a $T_g > 125^{\circ}C$
- Semi crystalline materials for compositions for II and
  - FDCA : other co-monomer = 80:20 up to 100:0
- All co-polyesters with other co-monomers show slow crystallization rates
- All co-polyesters with other co-monomers can be processed into:
  - Foils
  - Tensile bars
- Mechanical properties of all co-polyesters can be tuned by composition of c-monomers

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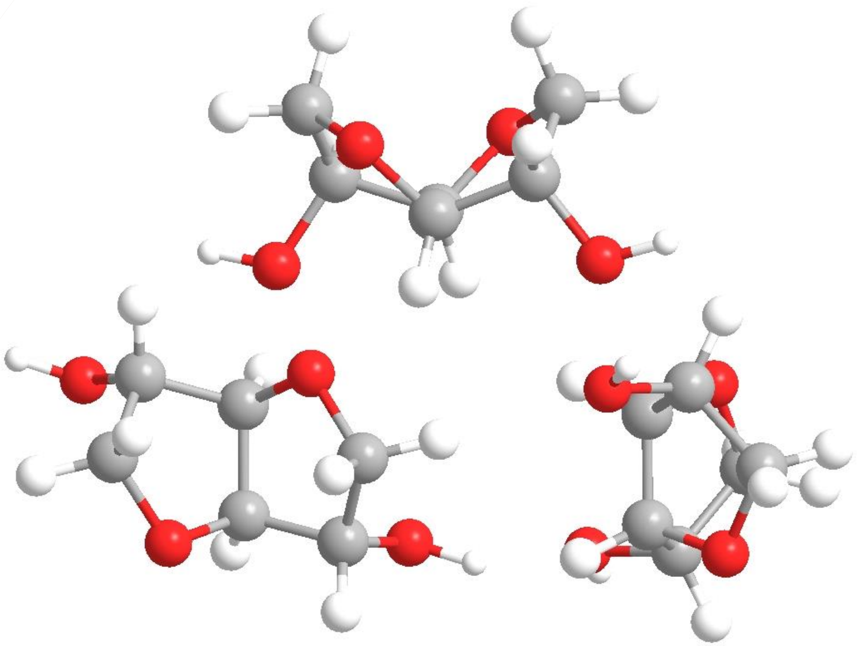

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