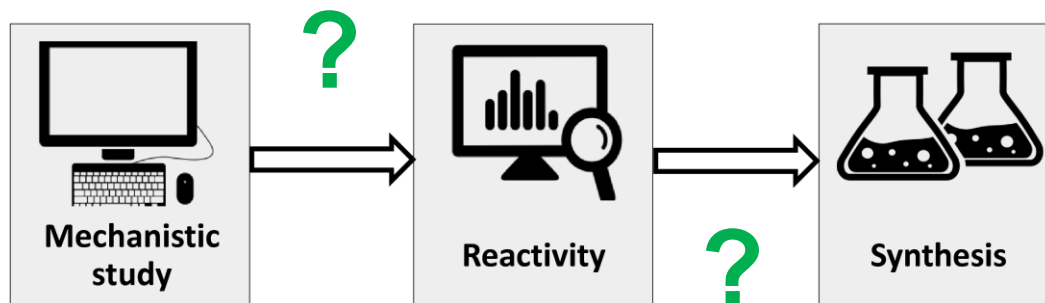


# Molecular Design of **Bio-Based** Polyurethanes



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*HPC for Innovation: When Science Meets Industry*  
**PRACEdays18**

Ljubjana, 29<sup>th</sup> of May 2018

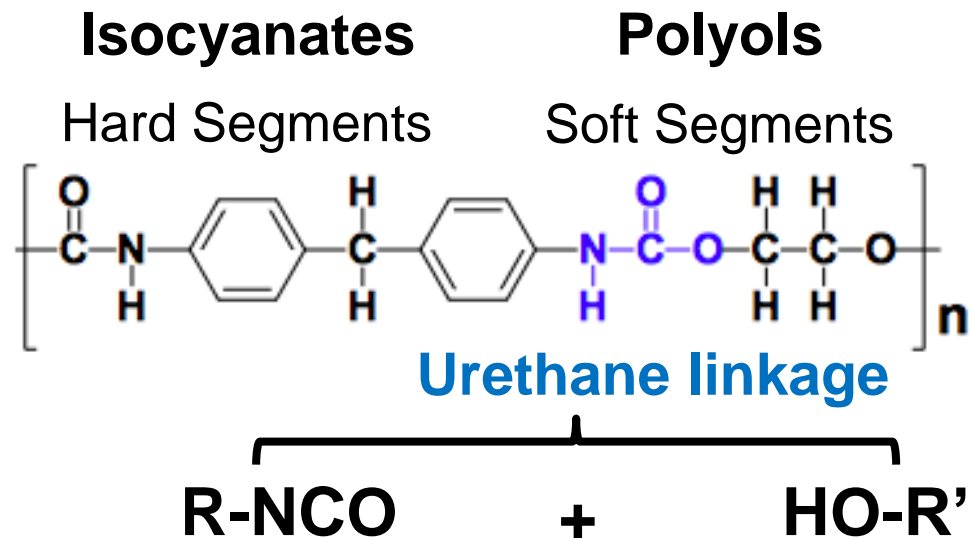


# INTRODUCTION - WHAT AND WHERE?

## What?

Polyurethanes (PUs) – 6<sup>th</sup> most widespread group of polymers, ~18Mt/year

PUs made by reacting di- or oligo-isocyanates with polyols



# INTRODUCTION - WHAT AND WHERE?

## What?

Polyurethanes (PUs) – 6<sup>th</sup> most widespread group of polymers, ~18Mt/year

PUs made by reacting di- or oligo-isocyanates with polyols

## Where?

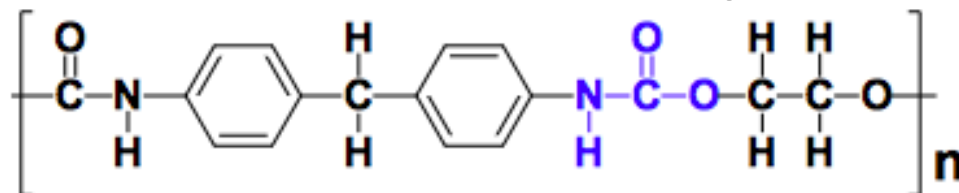
PUs are versatile materials with many applications: elastomeric materials in medical industries [1], heat insulators in construction [2,3], seat cushion in automotive [4].

## Isocyanates

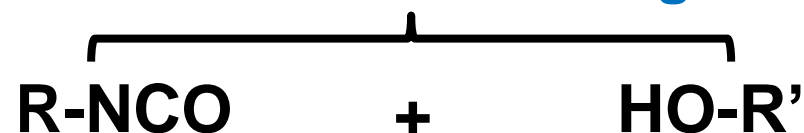
Hard Segments

## Polyols

Soft Segments



Urethane linkage



# INTRODUCTION – ENVIRONMENTAL PROBLEMS & SOLUTIONS

## Problems!

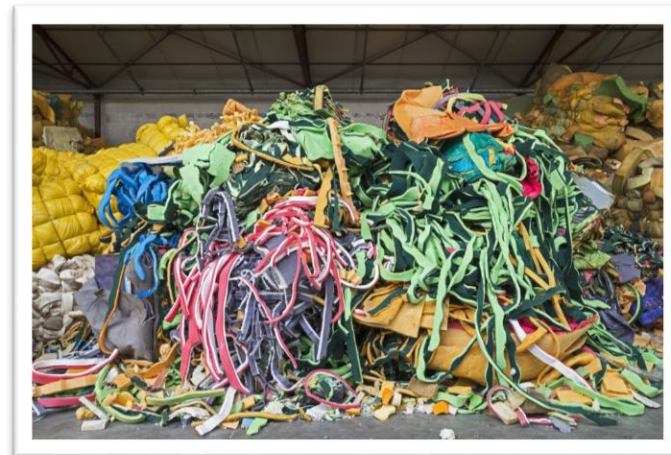
- 1) Recycling of PUs is complicated and expensive
  - thermoset character - difficult to be disintegrate and incorporate back to the environment
- 2) They made from petrochemical based starting materials which raised severe health and environmental concerns



# INTRODUCTION – ENVIRONMENTAL PROBLEMS & SOLUTIONS

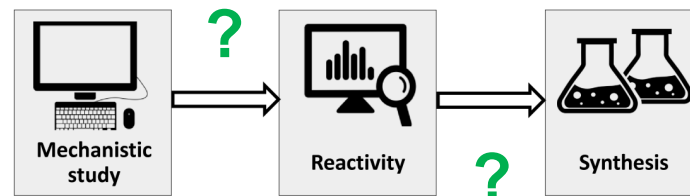
## Problems!

- 1) Recycling of PUs is complicated and expensive
  - thermoset character - difficult to be disintegrate and incorporate back to the environment
- 2) They made from petrochemical based starting materials which raised severe health and environmental concerns



## Solutions?

- 1) Design polyurethanes based on **natural polyols** – easier recycling, cheaper, sustainable production
- 2) Substitution of petro-based polyols with bio-polyols - improve biodegradability and mechanical properties of the polymers.



## Functional Properties

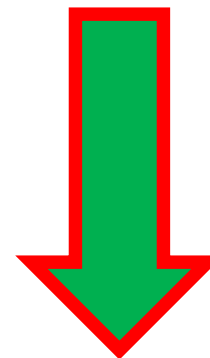
- Non-renewable
- Non-degradable
- Environmental issues

Petro-based

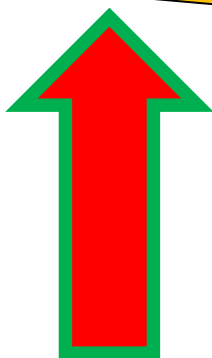


Bio-based

- Abundant
- Promising degradability
- Biocompatible



**Functional Properties**



- Non-renewable
- Non-degradable
- Environmental issues

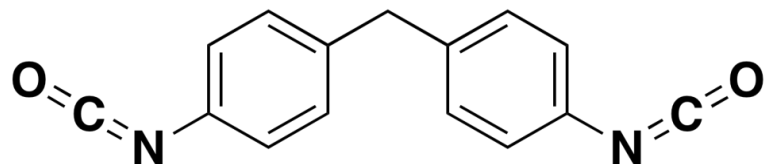
Petro-based

Real System

Carbohydrates

+

Isocyanate



Ongronat<sup>®</sup> 2100

- How the reaction happen?
- Which carbohydrate is the most promising?

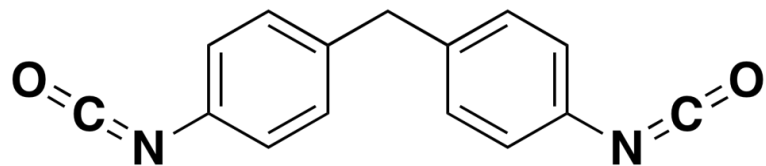


## Real System

Carbohydrates

+

Isocyanate



Ongronat® 2100

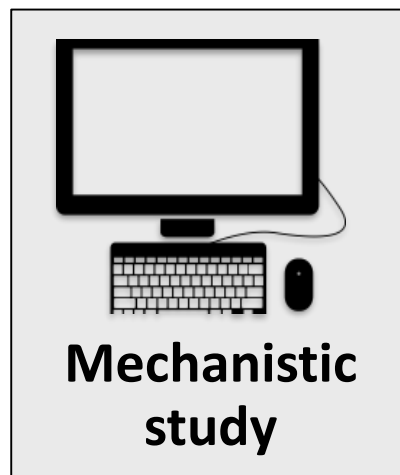
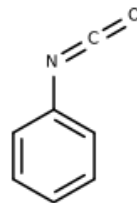
- How the reaction happen?
- Which carbohydrate is the most promising?

## Model

Carbohydrates

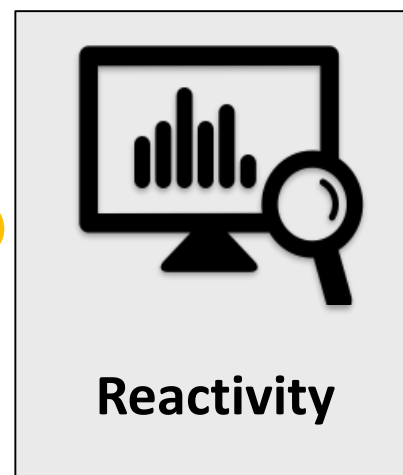
+

Phenyl isocyanate



Mechanistic  
study

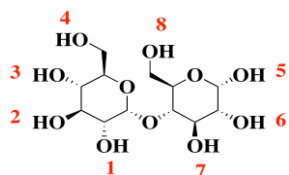
?



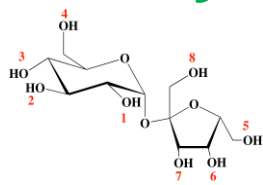
Reactivity

Build a model and compute the reactions & compare the reactivity

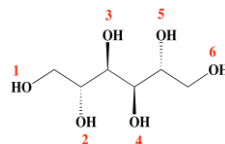
## Carbohydrates = Natural Polyols



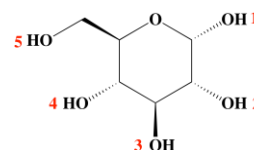
**Sucrose**  
8 OH



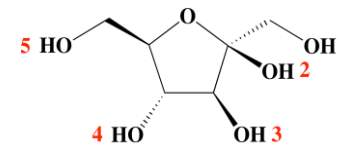
**Maltose**  
8 OH



**Mannitol**  
6 OH

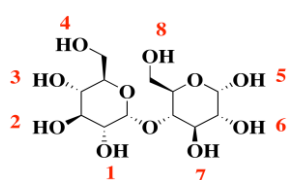


**Glucose**  
5 OH

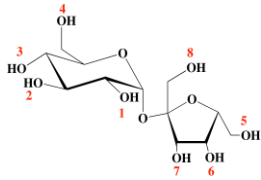


**Fructose**  
5 OH

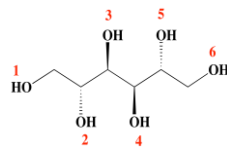
## Carbohydrates = Natural Polyols



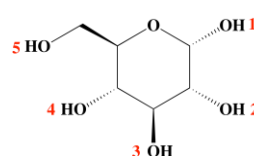
**Sucrose**  
8 OH



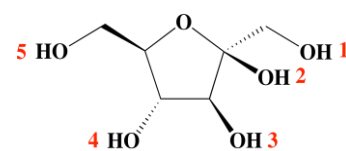
**Maltose**  
8 OH



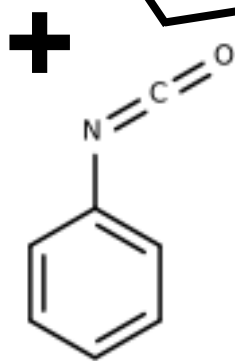
**Mannitol**  
6 OH



**Glucose**  
5 OH



**Fructose**  
5 OH



**Phenyl Isocyanate**

- Reaction between the model isocyanate and every OH group is calculated
- The reactivity of the groups is compared within the carbohydrates and between them

GaussView 5.0

Visualization?

Input/Output

Text Files

Gaussian 10

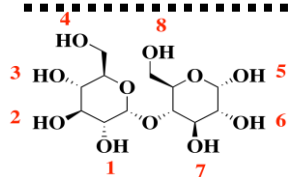
Electronic Structure Calculations

# RESULTS – MOLECULAR DESIGN – REACTIONS

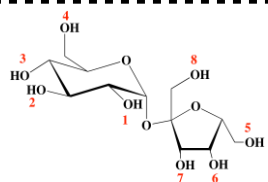
Carbohydrates



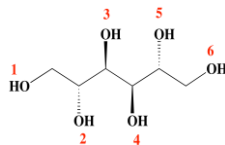
Phenyl Isocyanate



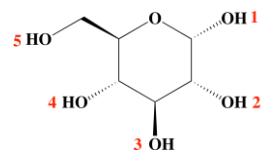
**Sucrose**  
8 OH



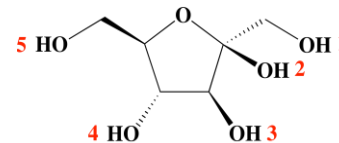
**Maltose**  
8 OH



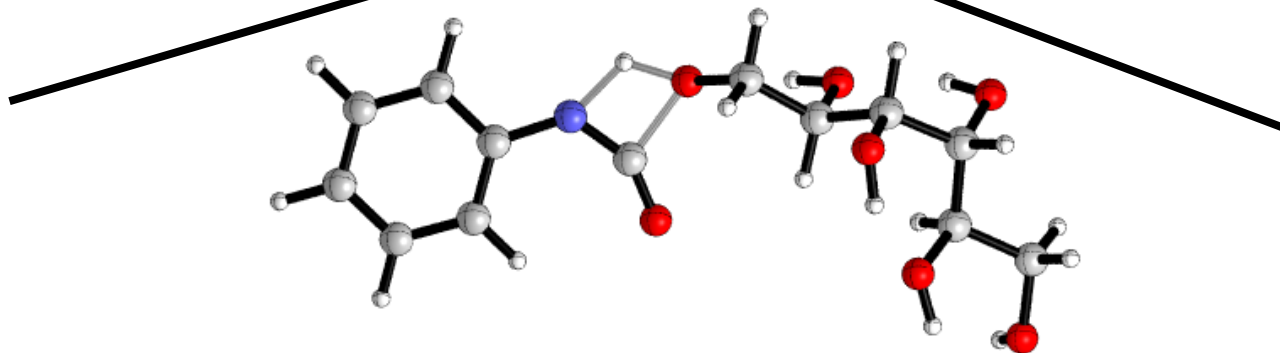
**Mannitol**  
6 OH



**Glucose**  
5 OH



**Fructose**  
5 OH

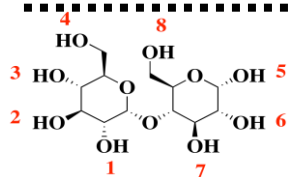


# RESULTS – MOLECULAR DESIGN – REACTIONS

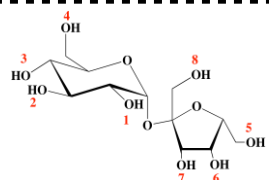
**Carbohydrates**



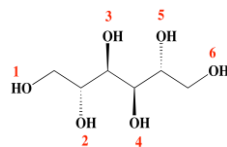
**Phenyl Isocyanate**



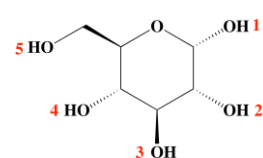
**Sucrose**  
8 OH



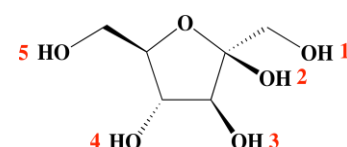
**Maltose**  
8 OH



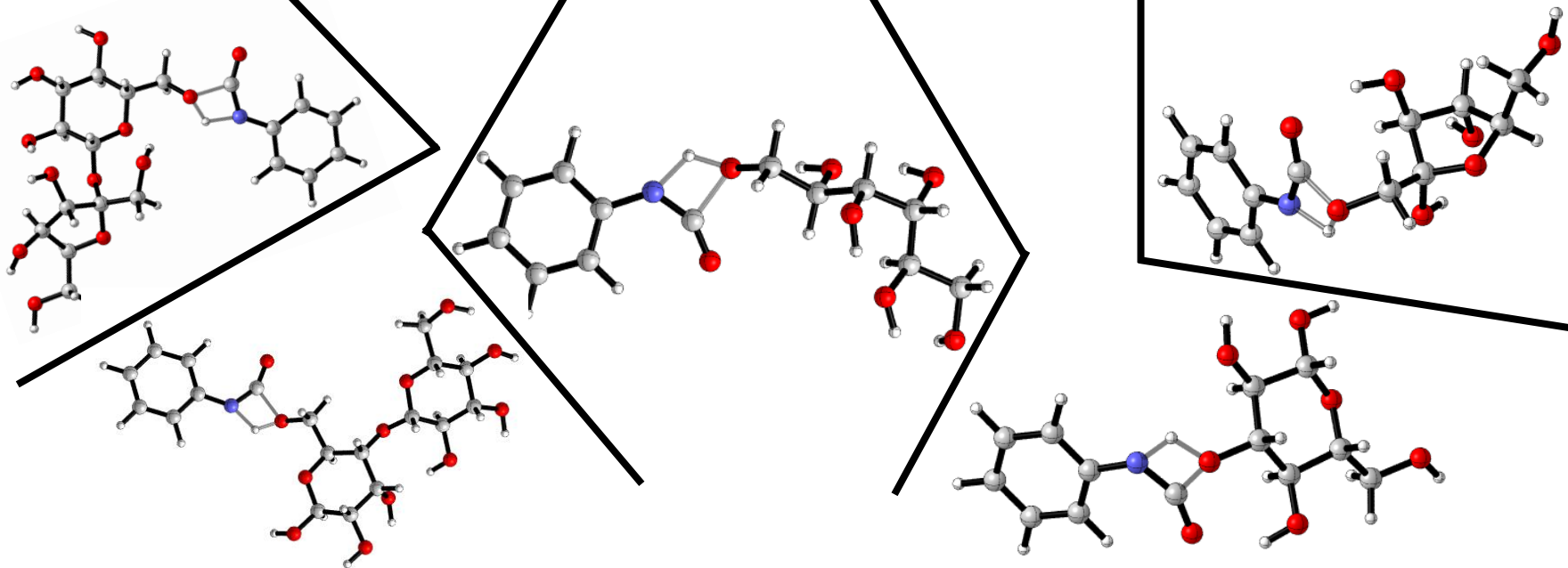
**Mannitol**  
6 OH



**Glucose**  
5 OH



**Fructose**  
5 OH

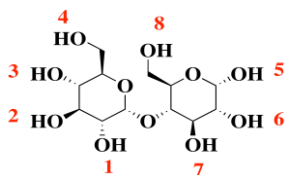


# RESULTS – MOLECULAR DESIGN – REACTIVITY

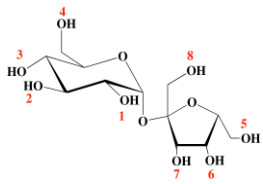
Carbohydrates



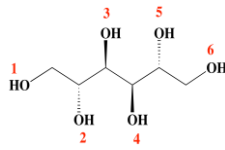
Phenyl Isocyanate



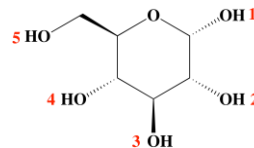
Sucrose



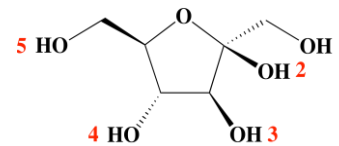
Maltose



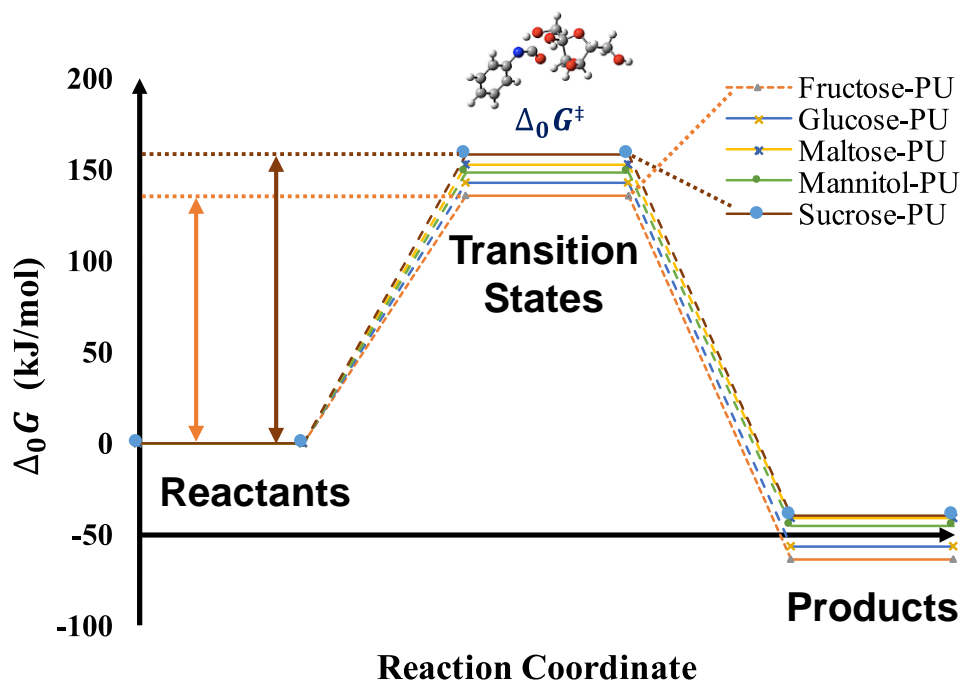
Mannitol



Glucose



Fructose

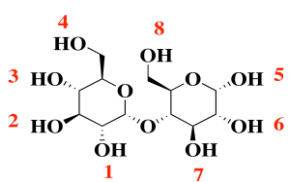


- Higher the barrier height  
→ lower the reactivity
- Lower the barrier height  
→ higher the reactivity

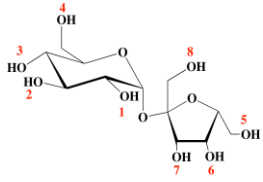


# RESULTS – MOLECULAR DESIGN – REACTIVITY

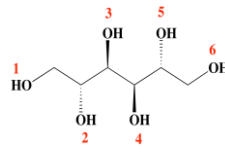
## Carbohydrates + Phenyl Isocyanate



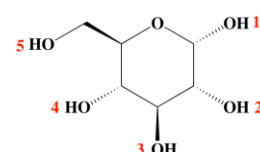
Sucrose



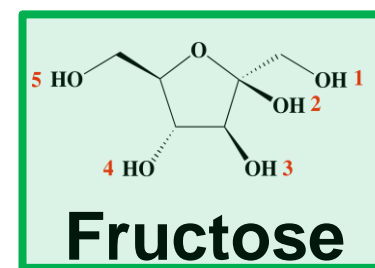
Maltose



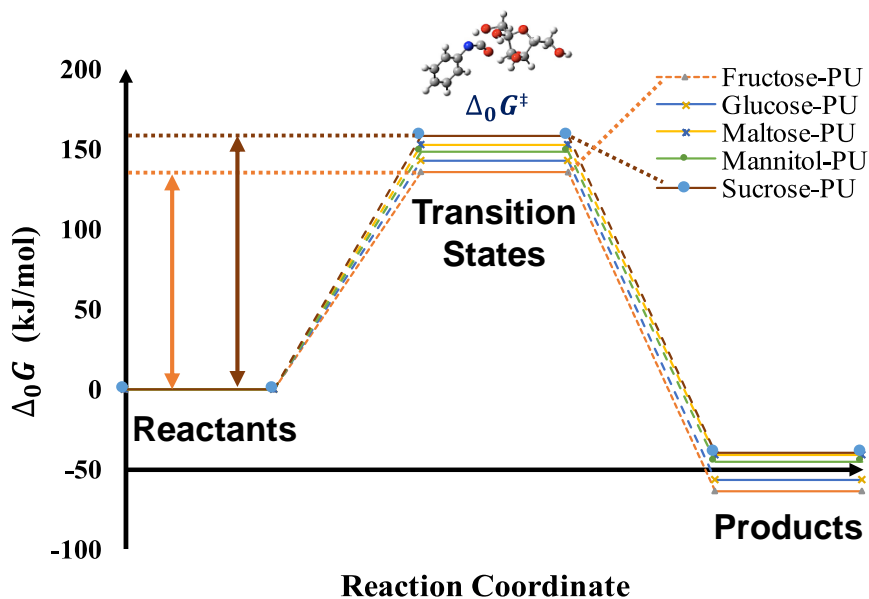
Mannitol



Glucose



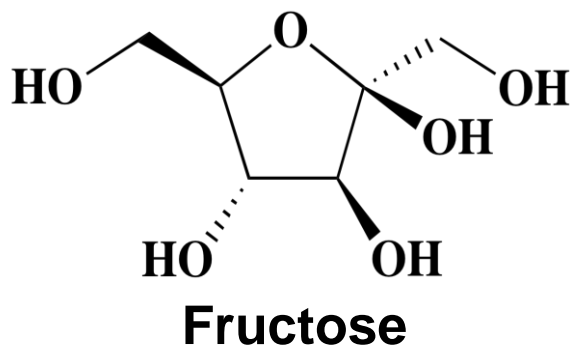
Fructose



- Higher barrier height  
→ lower reactivity
- Lower barrier height  
→ higher reactivity



## Fructose-based Polyurethane



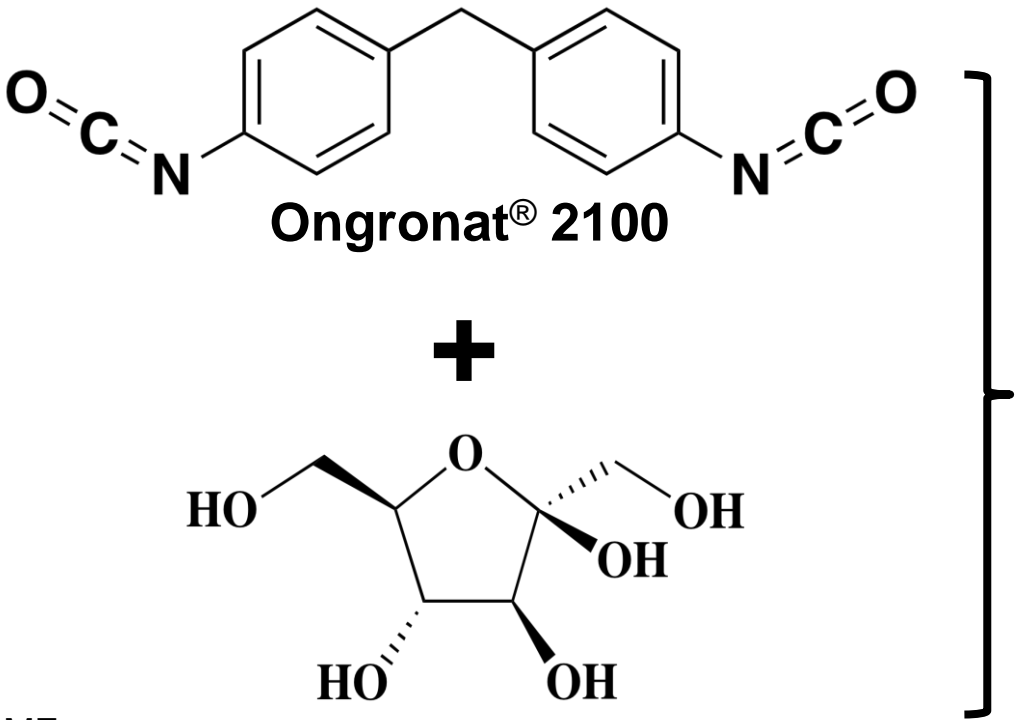
Solvent: DMF

Blowing agent: Water

Catalyst: DMCHA



## Fructose-based Polyurethane



Solvent: DMF  
Blowing agent: Water  
Catalyst: DMCHA

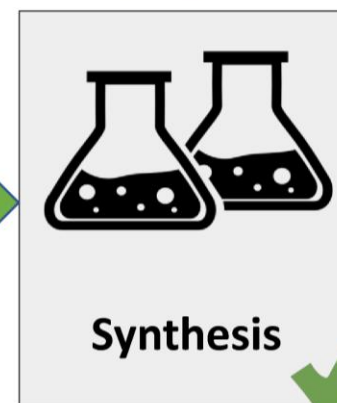
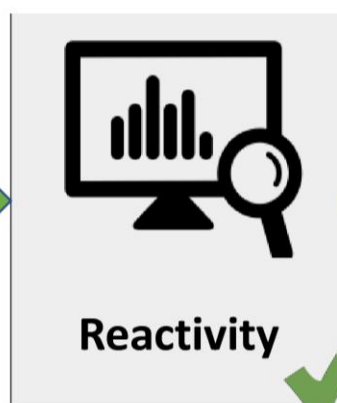
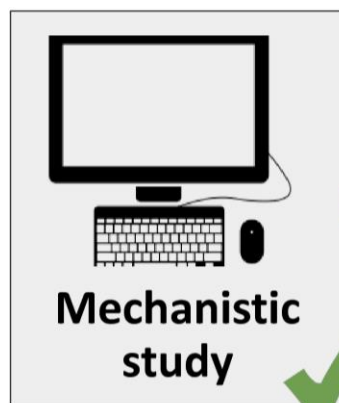
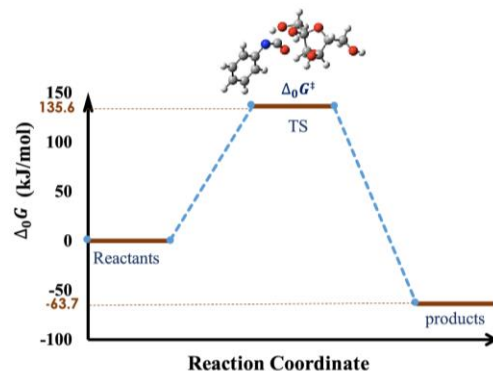
# CONCLUSIONS

Carbohydrates

+

Isocyanate

Fructose-based  
Polyurethane



# THANKS



Nemzeti  
Tehetség Program

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National Talent Programme.  
Project ID: **NTP-NFTÖ-16-1098**.



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**GINOP-2.3.4-15-2016-00004** project,  
aimed to promote the cooperation between  
the higher education and the industry.



GITDA

Governmental Information-  
Technology Development  
Agency, Hungary



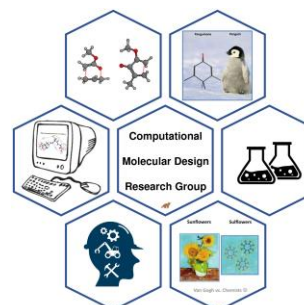
University of Miskolc,  
Hungary



Financial support by the New  
National Excellence Program  
of the Ministry of Human  
Capacities (HU) under the  
**ÚNKP-17-4-I-ME/17** project.



EMBERI ERŐFORRÁSOK  
MINISZTERIUMA



HUNGARIAN CHAPTER



Danke

ありがとう

Hvala

Gracias

Eskerrik

Bedankt

Děkuji

asko

kiitos

Спасибо

Köszönöm

Дякуємо

Merci

谢谢

Takk