DEVELOPMENT OF A BIO-BASED ABLATIVE RESIN FOR THERMAL PROTECTION SYSTEMS

Robin Pouyet

B. Defoort[1], B. Rivières[1], X. Coqueret[2]

1. ArianeGroup – Saint-Médard-en-Jalles, France
2. Institut de Chimie Moléculaire de Reims – UMR CNRS 7312, Reims, France

PhD project: 04/2017 – 03/2020

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05/06/2018

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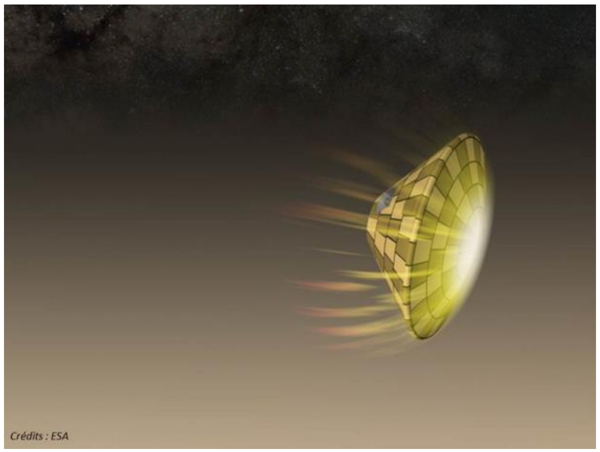
CONLUSION AND PERSPECTIVE

01

CONTEXT AND OBJECTIVES

CONTEXT: ABLATIVE MATERIALS

Thermal protecting materials allowing to withstand **high heat fluxes** and **mechanical erosion** through **progressive pyrolysis**.



Re-entry vehicles

Applications

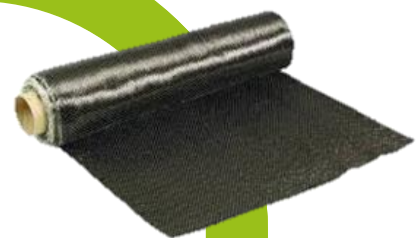
Booster nozzles

CONTEXT: ABLATIVE MATERIALS

Ablative resin

Cork granules

Carbon mat



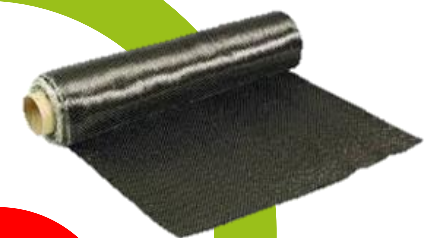
- Phenolic resins

CONTEXT: ABLATIVE MATERIALS

Cork granules

Ablative resin

Carbon mat



- Phenolic resins

REACh

MAIN REQUIREMENTS

UNCURED RESIN

- REACh compliant, industrial production, bio-based
- Viscosity and stability compatible with the manufacturing process

Phenolic resins precursors : CMR 2 and 1B

POLYMERIZATION

- Enthalpy of polymerization < 500 J/g
- No mass loss during polymerization (polyaddition)

Thermal runaway during manufacturing process

Phenolic resins = Polycondensation (up to 30% mass loss)

CURED RESIN

- >50% char yield
- Non-friable char
- Tg > 250°C

02

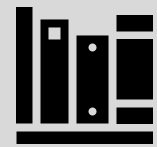
PROPARGYLIC TERMINATED RESINS

PROPARGYLIC TERMINATED RESINS

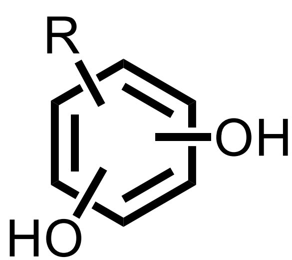
State of the art

Bio-based compound library

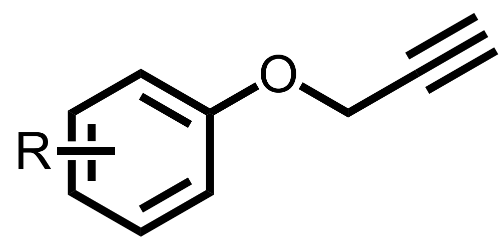
+



Available polyaddition chemistry



Polyphenols



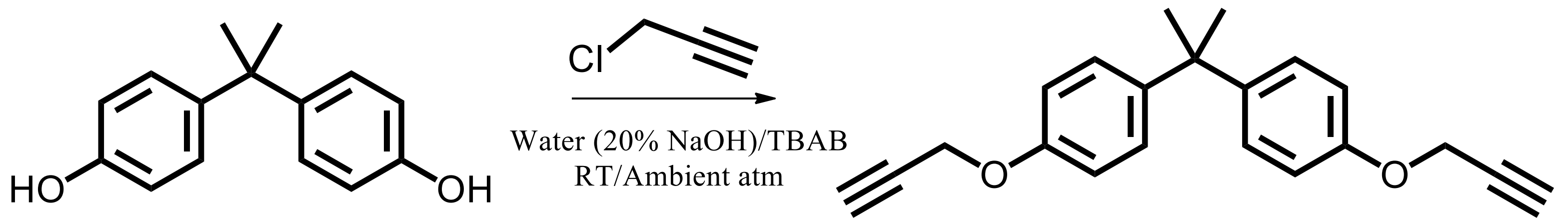
Propargyl aryl ether chemistry

PROPARGYLIC TERMINATED RESINS

(Dirlikov, 1990)

State of the art: Propargyl ether of Bisphenol A

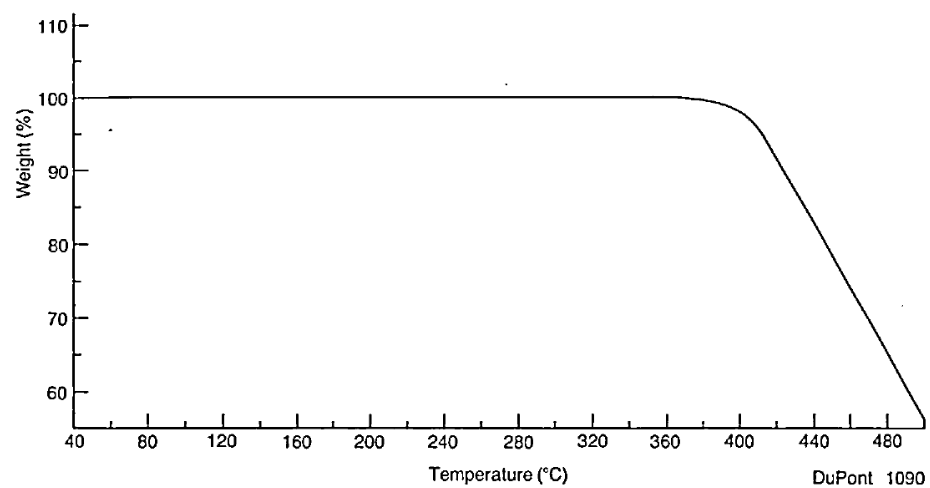
Uncured resin



Yield (purity)	Shelf life at RT (100°C)	Polymerization Enthalpy
Quantitative (<99%)	Unlimited (1 week)	1140 J/g

Cured resin

- No mass loss until 380°C
- Tg > 350°C

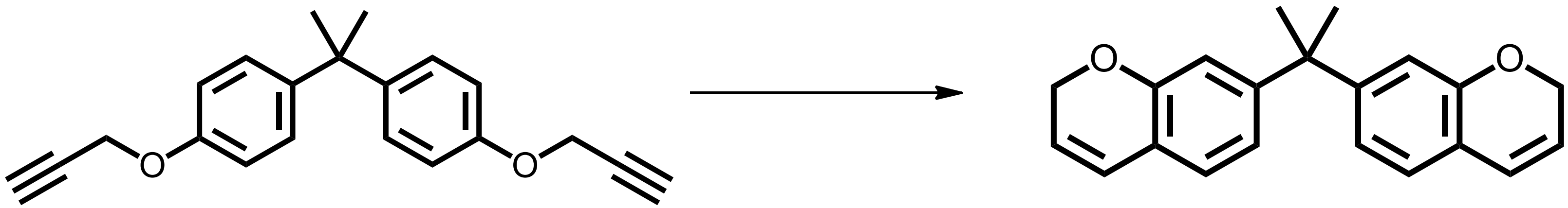


PROPARGYLIC TERMINATED RESINS

(Dirlikov, 1990)

State of the art: Propargyl ether of Bisphenol A

B-staging mechanism



- Chromene structure
- Improved reactivity control

Thermal stability linked to the bisphenol used for its preparation

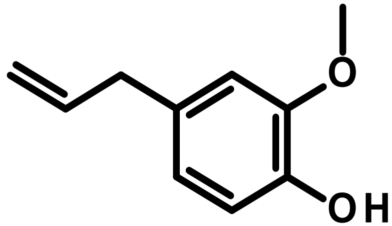
⬇

Why not using biobased polyphenols instead of BPA ?

PROPARGYLIC TERMINATED RESINS (Rivieres, 2016)

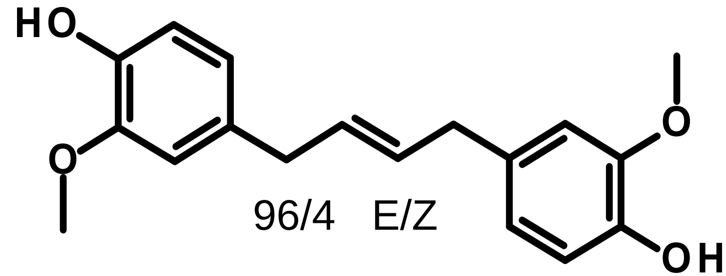
State of the art: Propargyl ether of polyphenols

Molecules **2012**, *17*, 6953–6981.



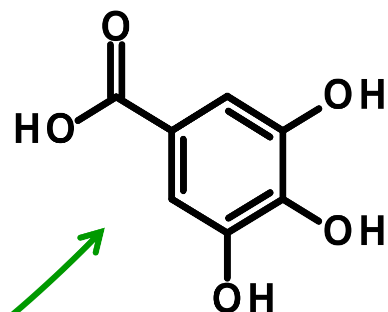
Eugenol

J. Am. Chem. Soc. **2000**, *122*, 58–71.



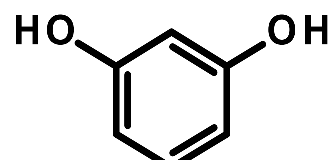
Bisphenol from eugenol

Biotechnol. Lett. **1984**, *6*, 237–242.



Gallic acid

J. Am. Chem. Soc. **2000**, *122*, 9042–9043.



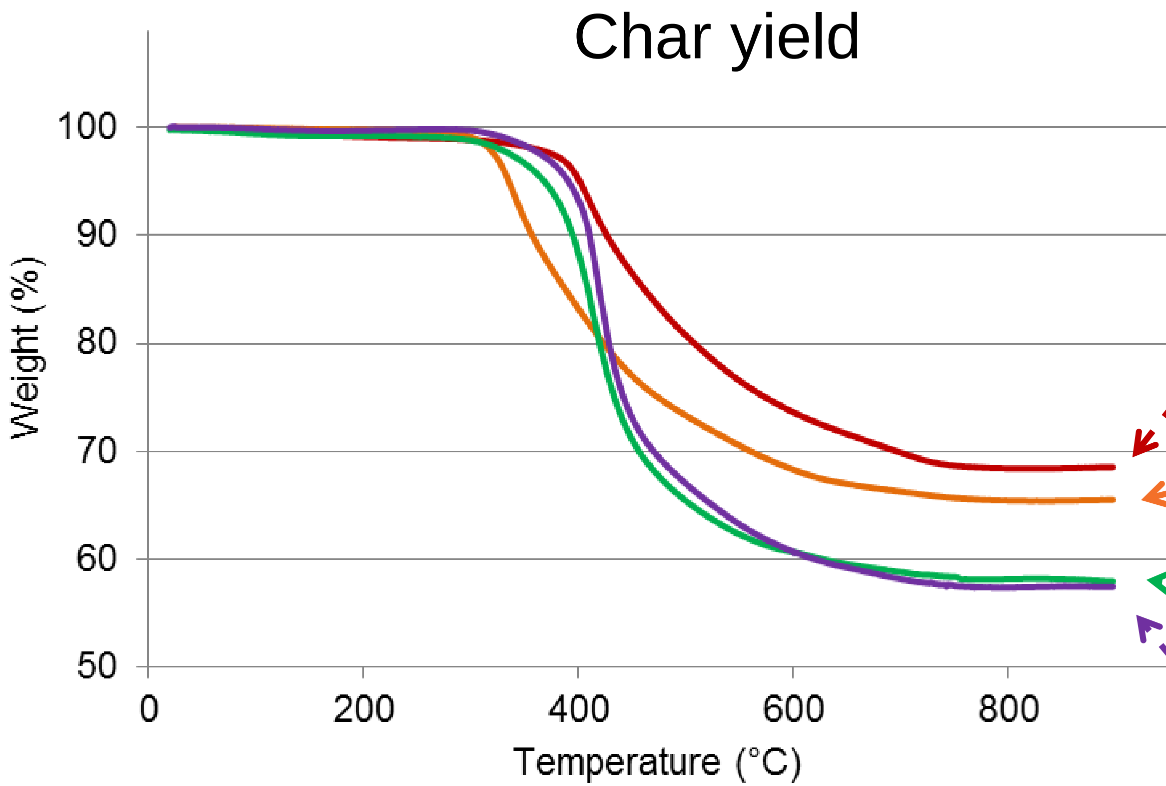
Resorcinol

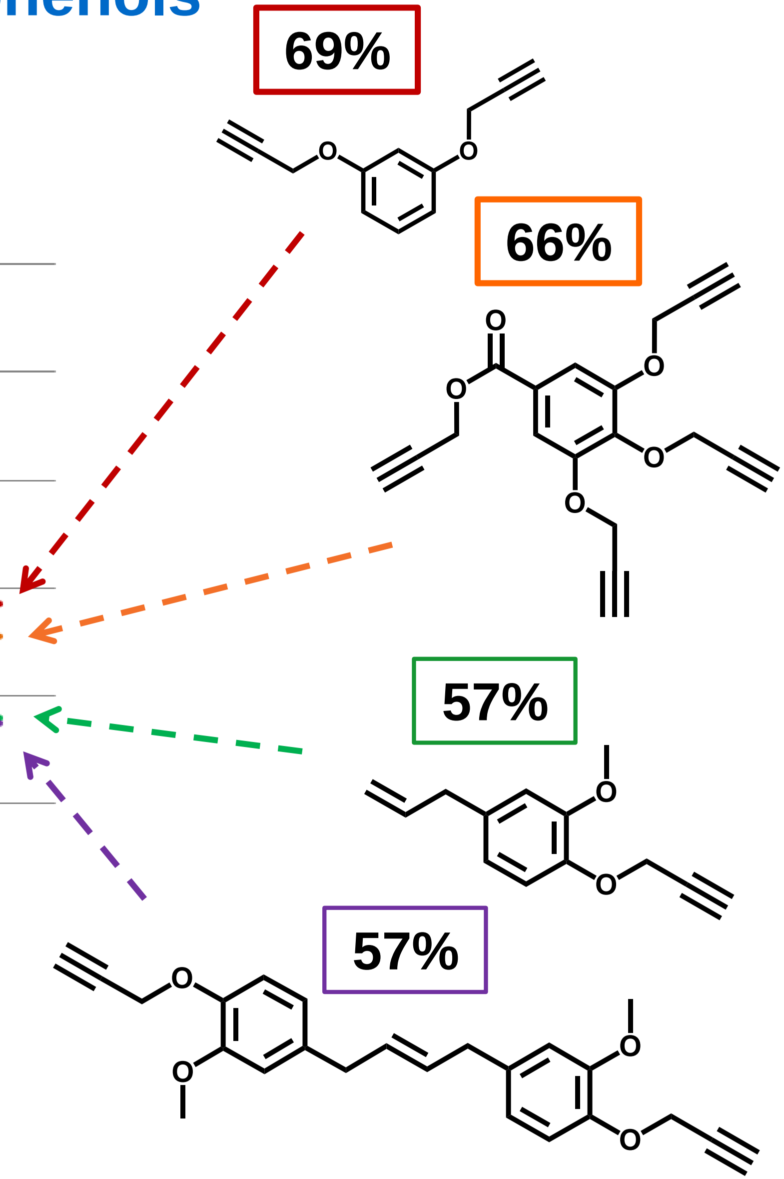
J. Am. Chem. Soc. **2005**, *127*, 5332–5333.

European Polymer Journal **2015**, *73*, 38–49.

PROPARGYLIC TERMINATED RESINS (Rivieres, 2016)

State of the art: Propargyl ether of polyphenols

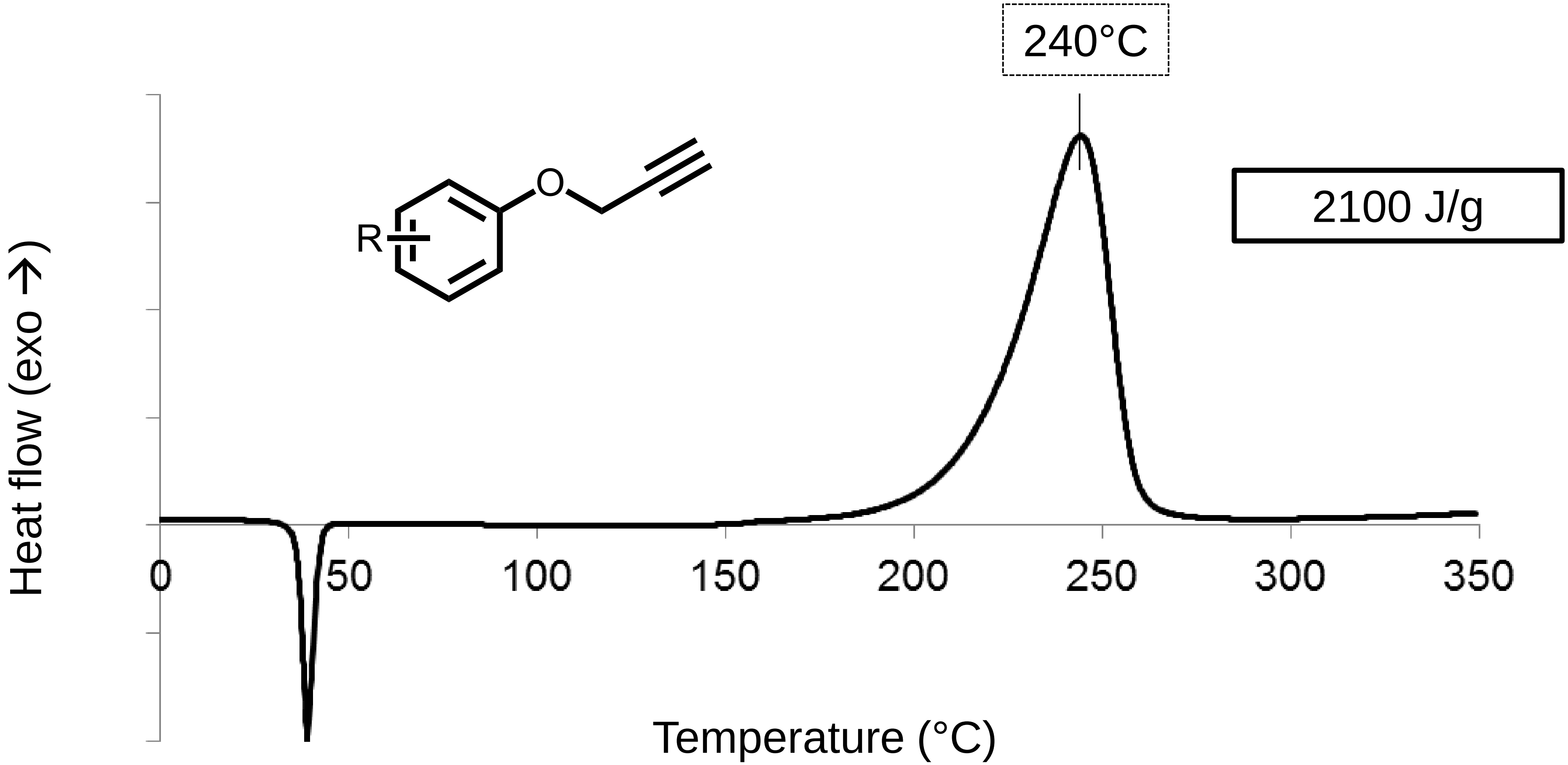




Thermogravimetric analysis, N_2

PROPARGYLIC TERMINATED RESINS (Rivieres, 2016)

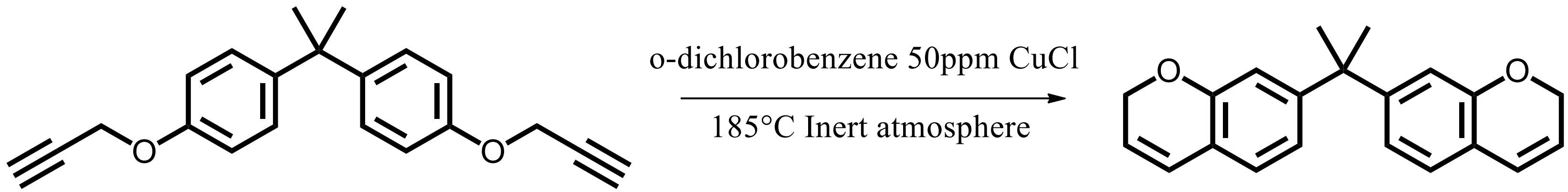
State of the art: Propargyl ether of polyphenols

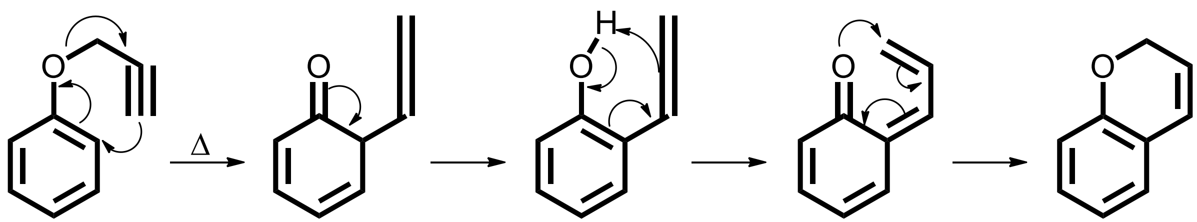


Differential scanning calorimetry

PROPARGYLIC TERMINATED RESINS (EP0350747, 1990)

State of the art: Propargyl ether of Bisphenol A (Sanglar, 1995)





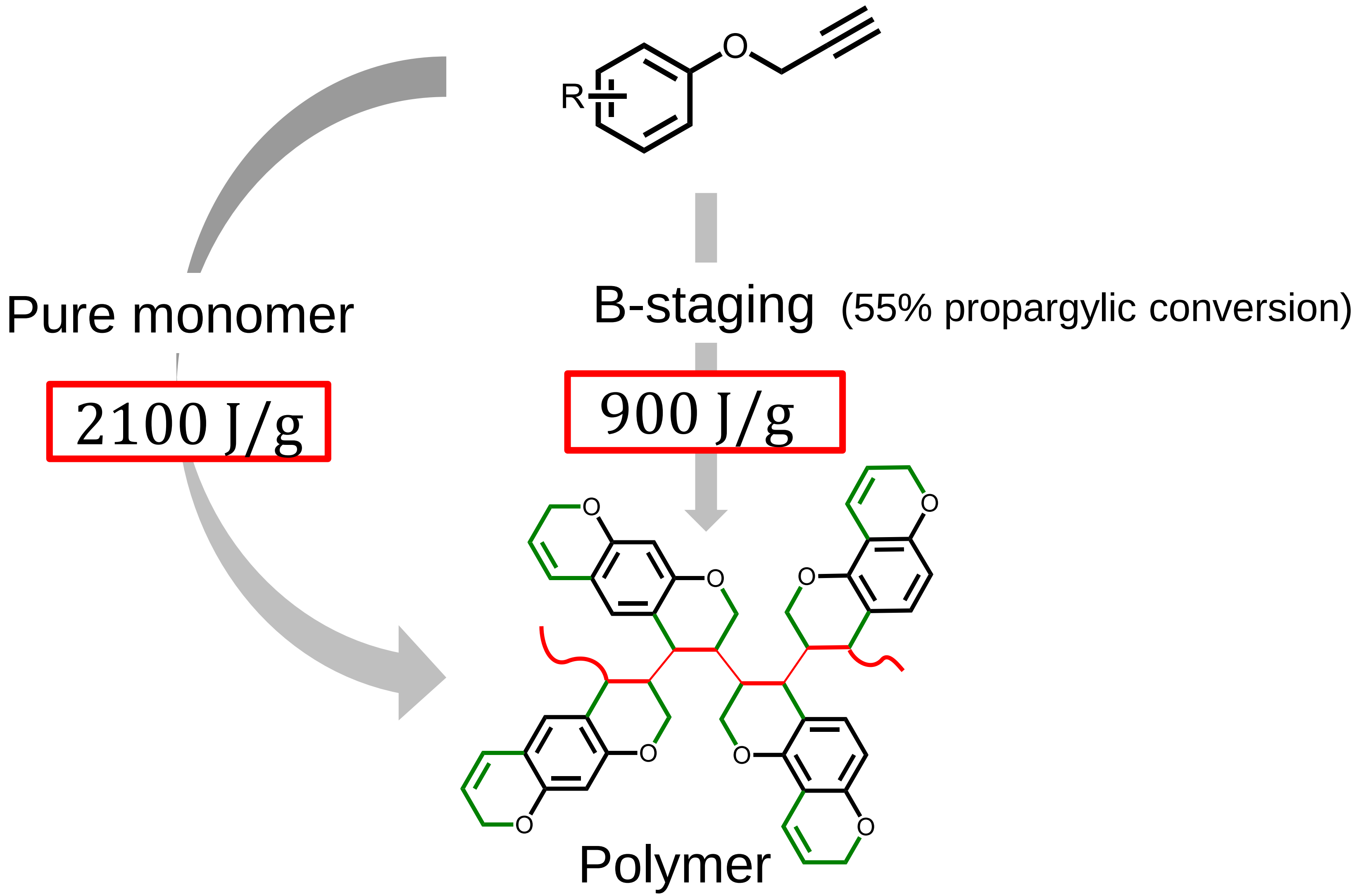
$$\Delta H_{polym}\ (\text{propagylether}) \quad = \quad \mathbf{6} \times \quad \Delta H_{polym}\ (\text{chromene})$$

But

Touchy to find conditions leading to total propargylic conversion without polymerisation

PROPARGYLIC TERMINATED RESINS (Rivieres, 2016)

State of the art: Propargyl ether of polyphenols



PROPARGYLIC TERMINATED RESINS (Rivieres, 2016)

UNCURED RESIN

- **REACh compliant, industrial production, bio-based** ~
- Viscosity and stability compatible to the manufacturing process ✓

POLYMERIZATION

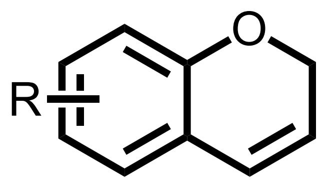
- **Enthalpy of polymerization < 500 J/g** ☹ *(900 J/g)*
- **No mass loss during polymerization (polyaddition)** ~ *(10% mass loss)*

CURED RESIN

- >50% char yield ✓
- Non-friable char ✓
- Tg > 250°C ✓

PROPARGYLIC TERMINATED RESINS

Catalytic rearrangement from propargyl to chromene

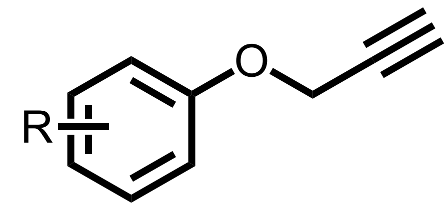


≈ 300 J/g

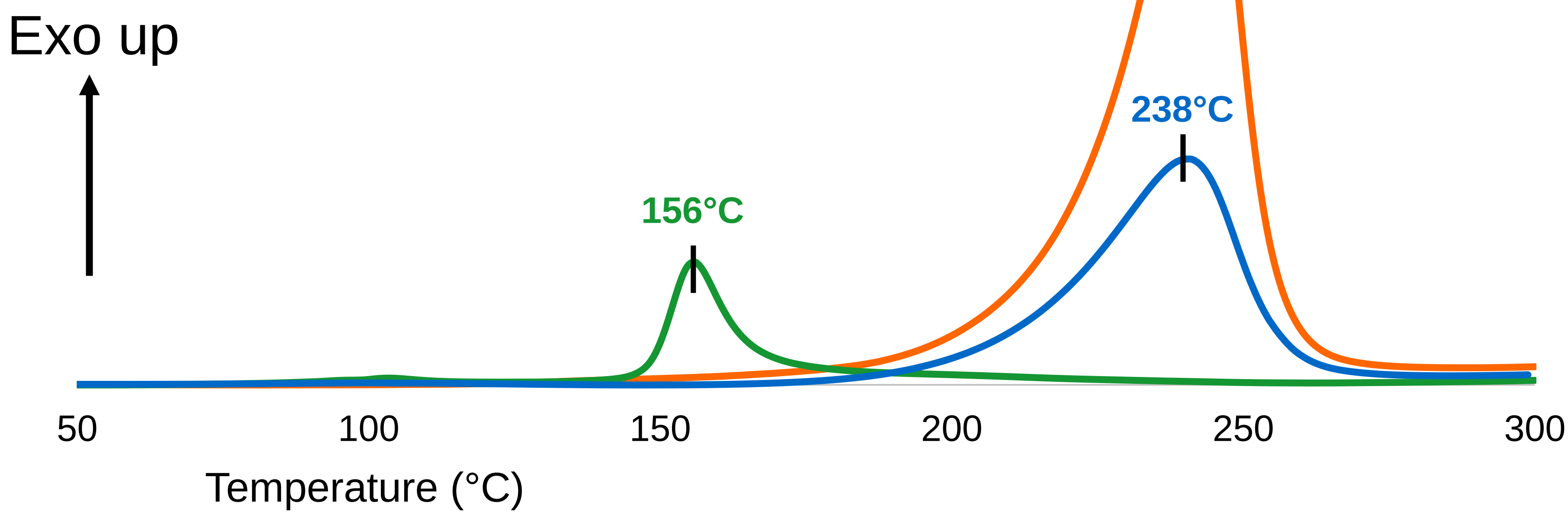
B-staging

Bulk prepolymerization

≈ 900 J/g



≈ 2100 J/g



$$\Delta H_{polym}\,(\text{propagylether}) = 7 \times \Delta H_{polym}\,(\text{chromene})$$

03

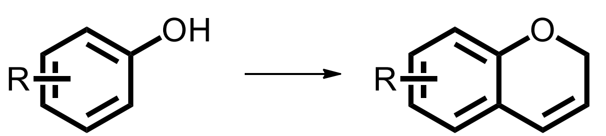
ON THE WAY TO CHROMENE

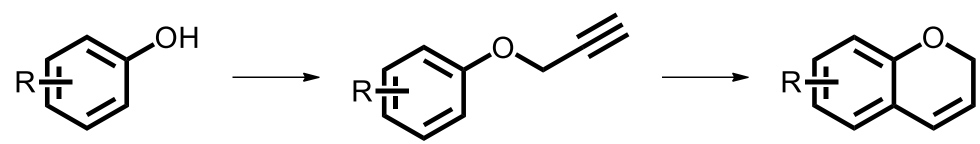
ON THE WAY TO CHROMENE

Two approaches

One-step synthesis of chromene from polyphenols with no propargylic intermediate

Catalytic rearrangement from propargyl to chromene

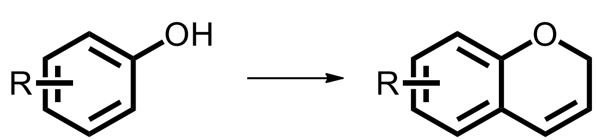




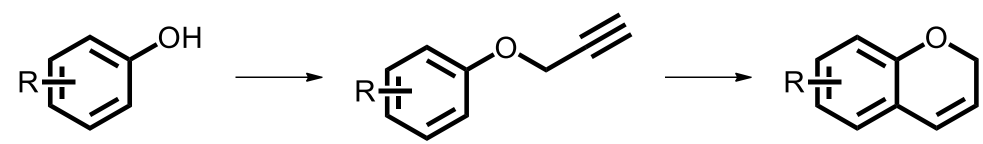
ON THE WAY TO CHROMENE

Two approaches

One-step synthesis of chromene from polyphenols with no propargylic intermediate



Catalytic rearrangement from propargyl to chromene

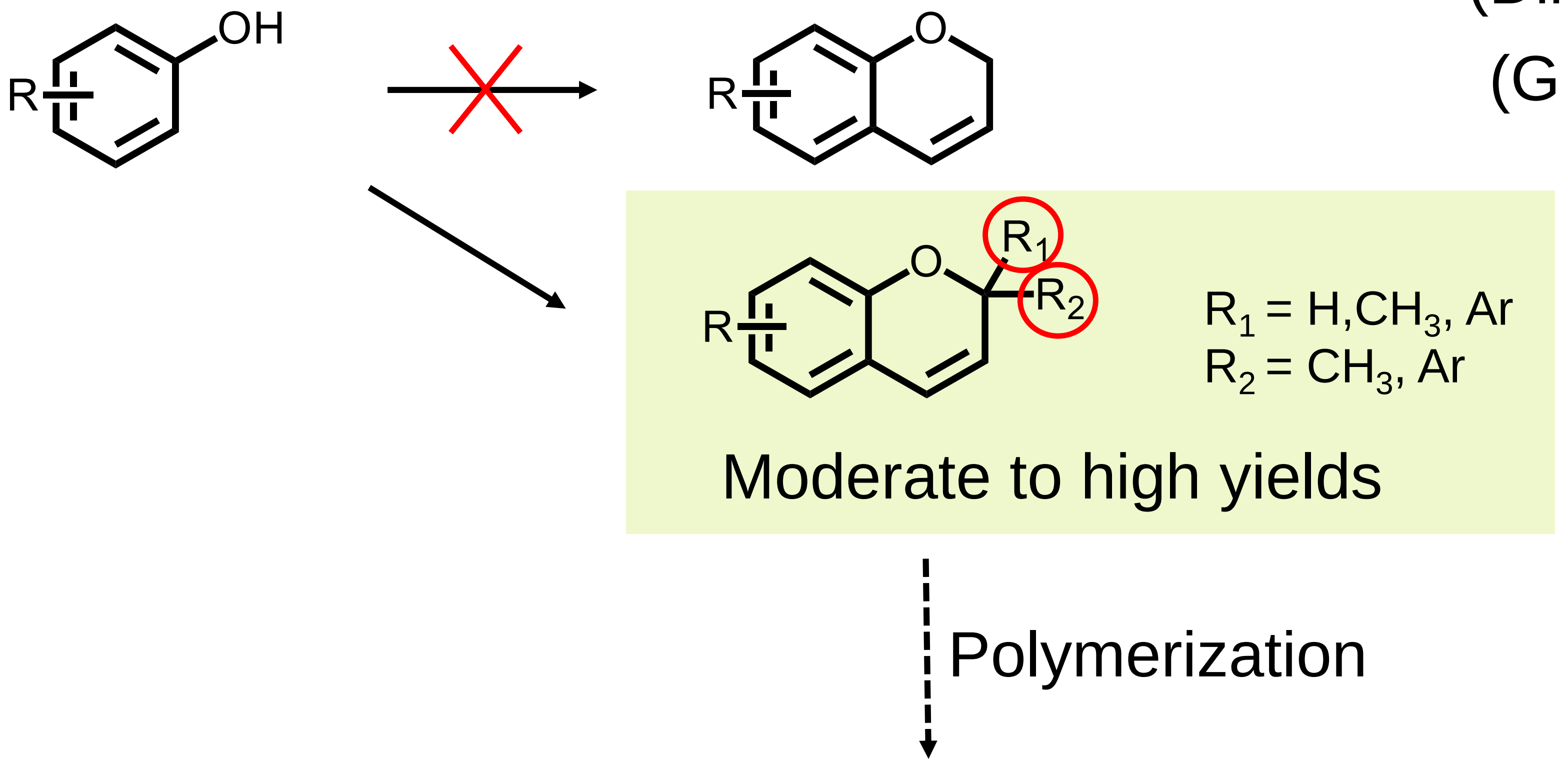


ON THE WAY TO CHROMENE

One step synthesis of chromene from polyphenols

(Dimakos, 2016)

(Ghatak, 2016)

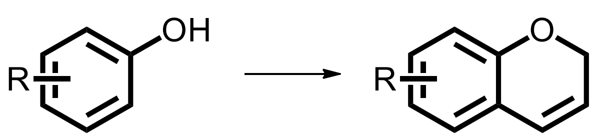


- Important mass loss
- Friable polymer

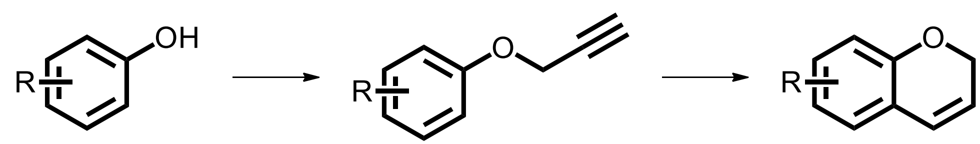
ON THE WAY TO CHROMENE

Two approaches

One-step synthesis of chromene from polyphenols with no propargylic intermediate

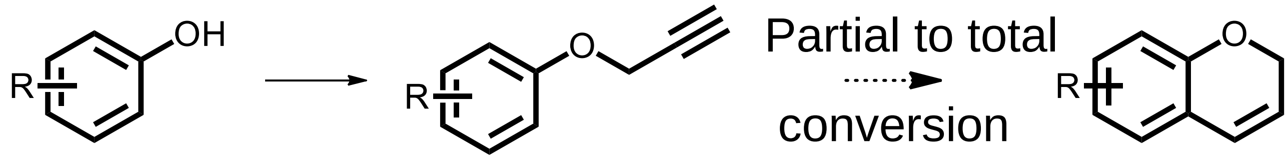


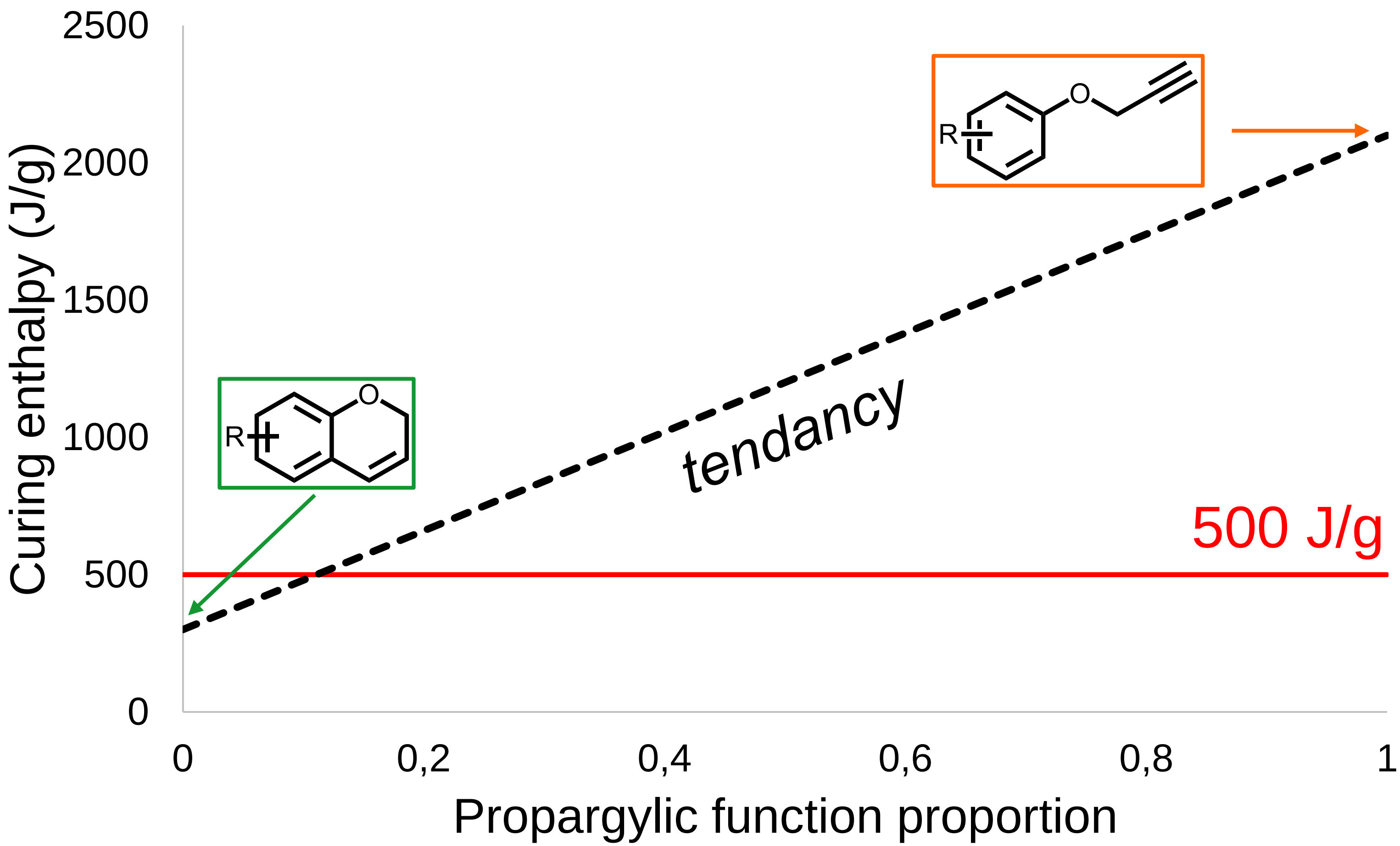
Catalytic rearrangement from propargyl to chromene



ON THE WAY TO CHROMENE

Catalytic rearrangement from propargyl to chromene





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CONCLUSION AND PERSPECTIVE

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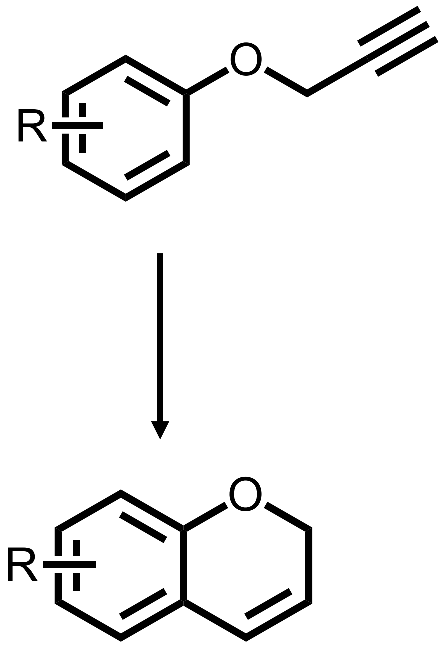
Conclusion



Promising ablative properties

- >50% char yield ✓
- Non-friable char ✓
- Tg > 250°C ✓

Reactivity to control

Polymerization enthalpy : 300 J/g ✓

Promising processes have been found to get chromenes in high yields and purity

Perspective

Formulation with enthalpy < 500 J/g : viscosity, DMA, composites

Scale-up for the most promising synthesis arianeGROUP

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UMR CNRS 7312

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dépasser les frontières

THANK YOU FOR YOUR ATTENTION

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05/06/2018

robin.pouyet@univ-reims.fr

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