MATERIA NOVA Materials R&D Center

UMONS Innovation Center

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Synthesis and water dispersibility of non-isocyanate polyurethane

22 November 2021 – online workshop

Dr Tangi Sénéchal
Tangi.senechal@materianova.be

AVEC LE SOUTIEN DU FONDS EUROPÉEN DE DÉVELOPPEMENT RÉGIONAL
MET STEUN VAN HET EUROPEES FONDS VOOR REGIONALE ONTWIKKELING

http://www.wbdurapaint.eu/

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> 80 scientific experts

> 120 with subsidiaries NANO4 & IONICS

UMONS Innovation Center

UMONS Innovation center

> 140 scientific partners

25 projects/year

250 customers
19 patents
…

ISO 9001
ISO 14001

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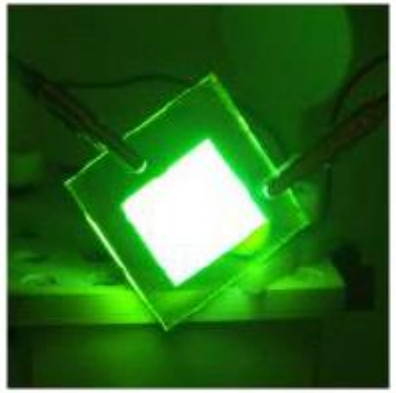


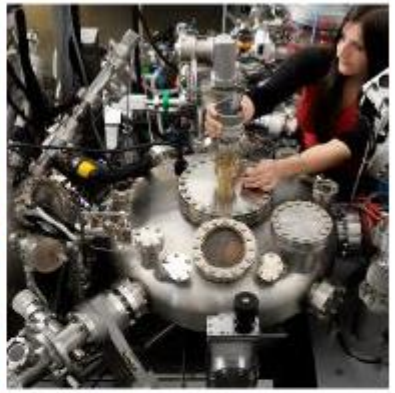
ADVANCED MATERIALS FOR ENERGY APPLICATIONS

INNOVATIVE AND SUSTAINABLE POLYMERIC MATERIALS

CELLS FOR MATERIALS AND MATERIALS FOR CELLS

MULTIFUNCTIONAL SURFACES

LIFE CYCLE THINKING



CHARACTERIZATION PLATFORM

R&D RESEARCH AXES

- White biotechnology, (bio)polymers & (bio)composites
- Sol-Gel & Wet coatings, Metallization
- Plasma technologies
- Electrochemistry, Corrosion
- Organic electronics, Chemical sensors
- Life cycle thinking

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Renewable resources
Polyols from vegetal oils

Waterborne & bio - based
Polyurethanes and Epoxy for Coatings

Project expectations: - More sustainable paints with low toxicity biobased resins for low VOC waterborne

- Replacement of additives for new functionalities

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WBDuraPaint

http://www.wbdurapaint.eu/

Objectives of the project

- Developping new waterborne coating systems with high performances and low environmental impacts
  - → No toxic compounds
  - → Very low volatil organic compounds (VOC) emissions
  - → Enough performances to match the specifications of building and transportation fields

- Two ways of development : **epoxy**-based and **non-isocyanate polyurethane**-based coatings
  - → Various applications targeted (wood, metal, floor, indoor or outdoor)

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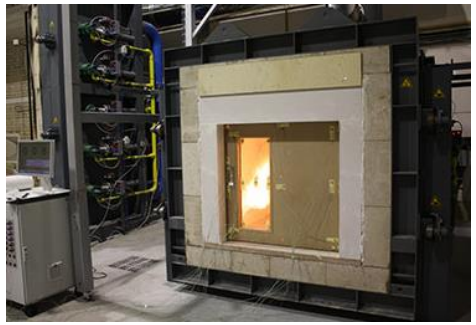
Consortium

Flamac has developped unique and versatile **high-throughput experimentation platforms** to screen new materials and chemical products highly efficiently.

These include **automated synthesis, formulation, application and characterisation platforms**, boosting new product development and shortening time-to-market considerably

CREPIM is one of the major European Laboratories for development and the approval of **materials covered by fire regulations.**

CREPIM **develops, tests and certifies the fire performances** of materials and assemblies for all concerned areas featuring the mass transportation sectors, in the building, electrical, and textile sectors.



Materials and Transformations Unit (UMET) brings the science of materials activities together from Université de Lille

Associate operators

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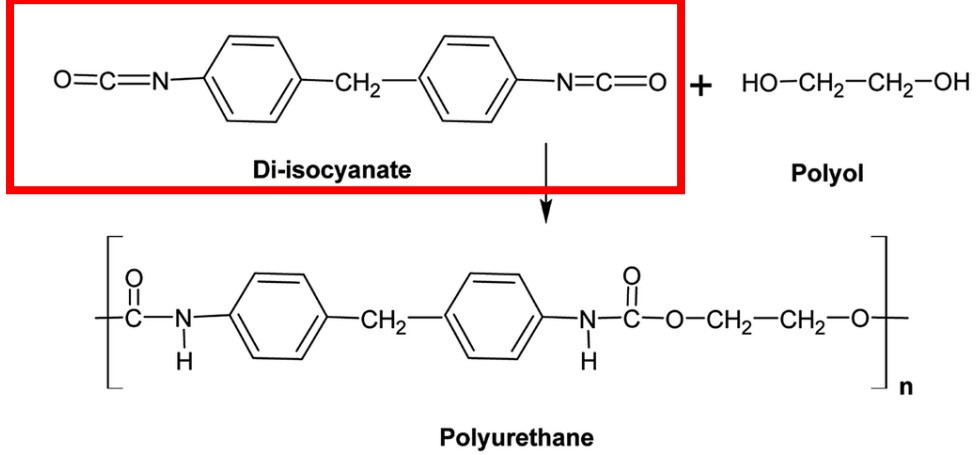
Toxic component

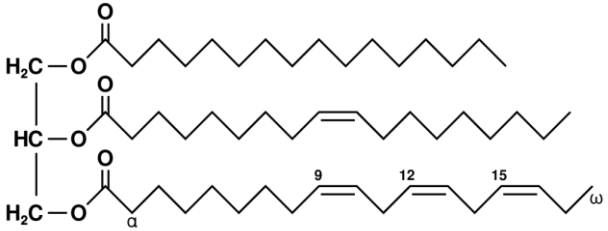


Limitation in biobased content

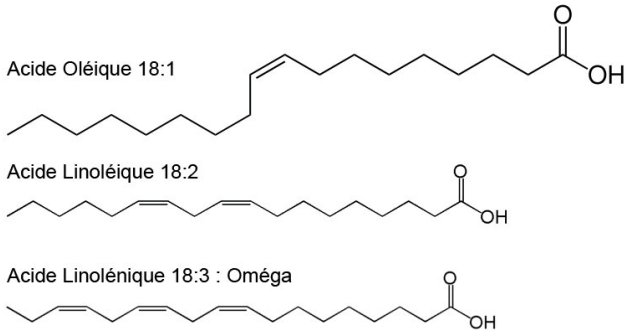
Resin synthesis from vegetable oil

→ Low cost
→ availability
→ Low toxicity

Vegetable oil= triglycerides



Saponification



Fatty acid from linseed oil
→ 1, 2 or 3 unsaturation

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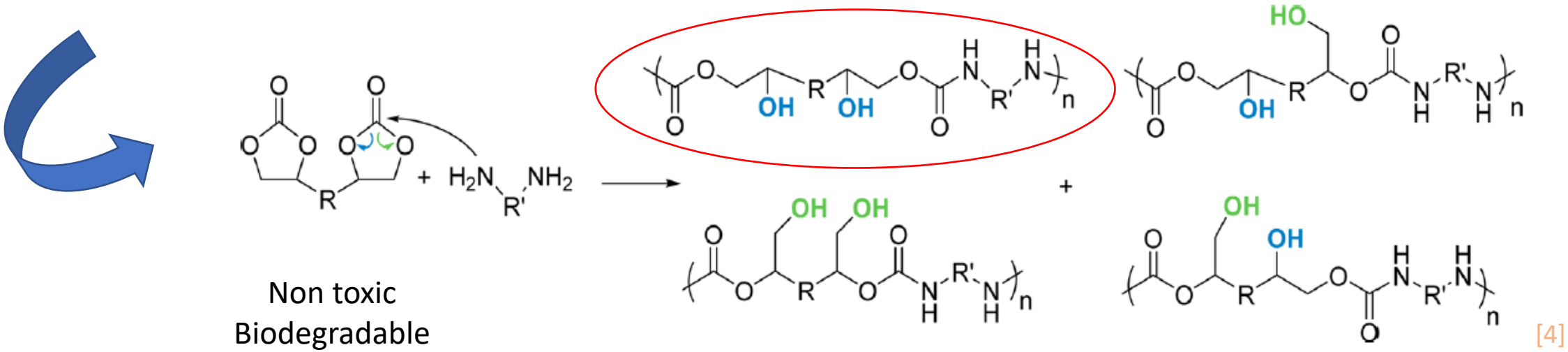
Different NIPUs synthesis pathways :

- Polycondensation
- Rearregment
- Cycle opening polymerisation

Polyaddition of cyclic bicarbonate and amine



[4]

[4] Lombardo VM, Dhulst EA, Leitsch EK, Wilmot N, Heath WH, Gies AP, et al. Cooperative Catalysis of Cyclic Carbonate Ring Opening: Application Towards Non-Isocyanate Polyurethane Materials: Cooperative Catalysis of Cyclic Carbonate Ring Opening.

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Past projects :
NIPU foams with commercial cyclo carbonates
Biobased PU resins for paint formulation

Synthesis of biobased amines and waterdispersible NIPUs Synthesis

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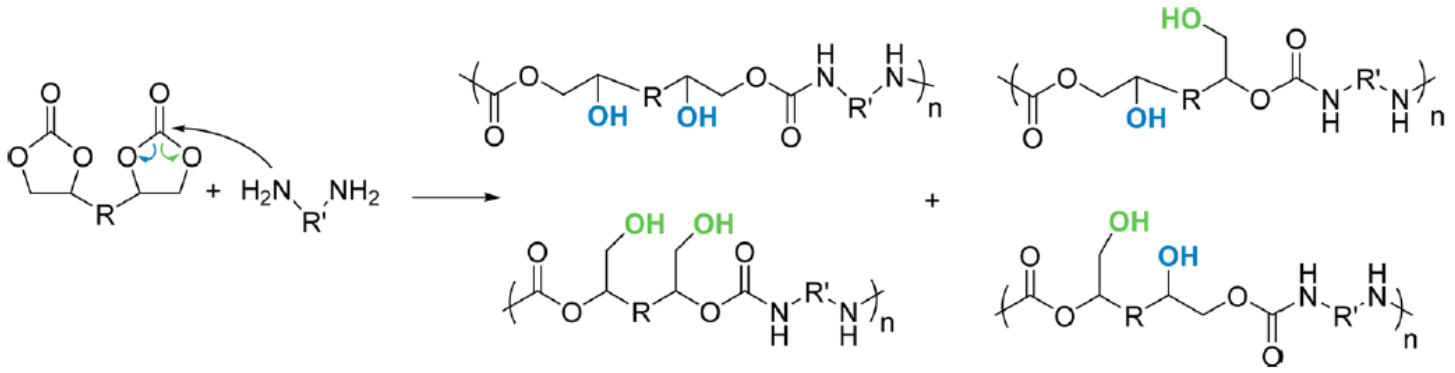
Past projects :
synthesis of biobased resins including epoxy

Synthesis of biobased cyclocarbonates and biobased waterdispersible epoxy



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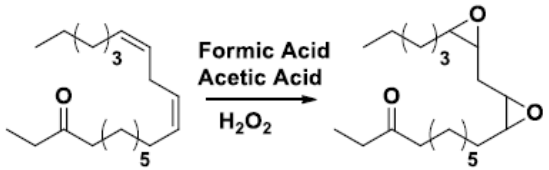
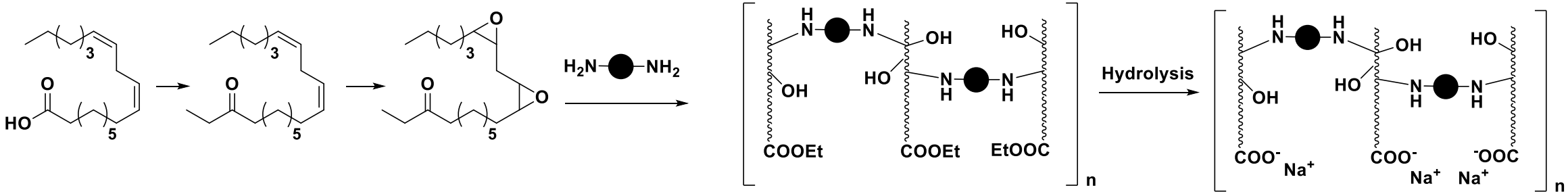
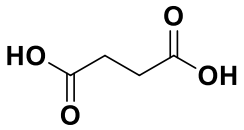
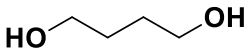




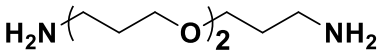
other Linkers :



succinic acid



1,4-butanediol



1,4-bis(3-aminopropoxy)butane

The main effort are dedicated to the increase od the reactivity of molecules to obtain a sufficient molar weight for paint application

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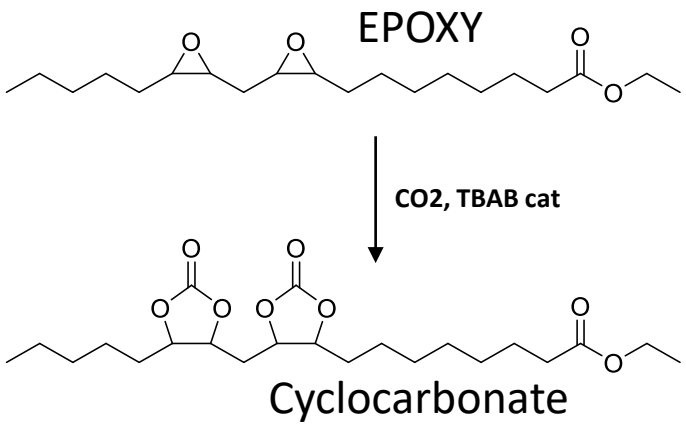
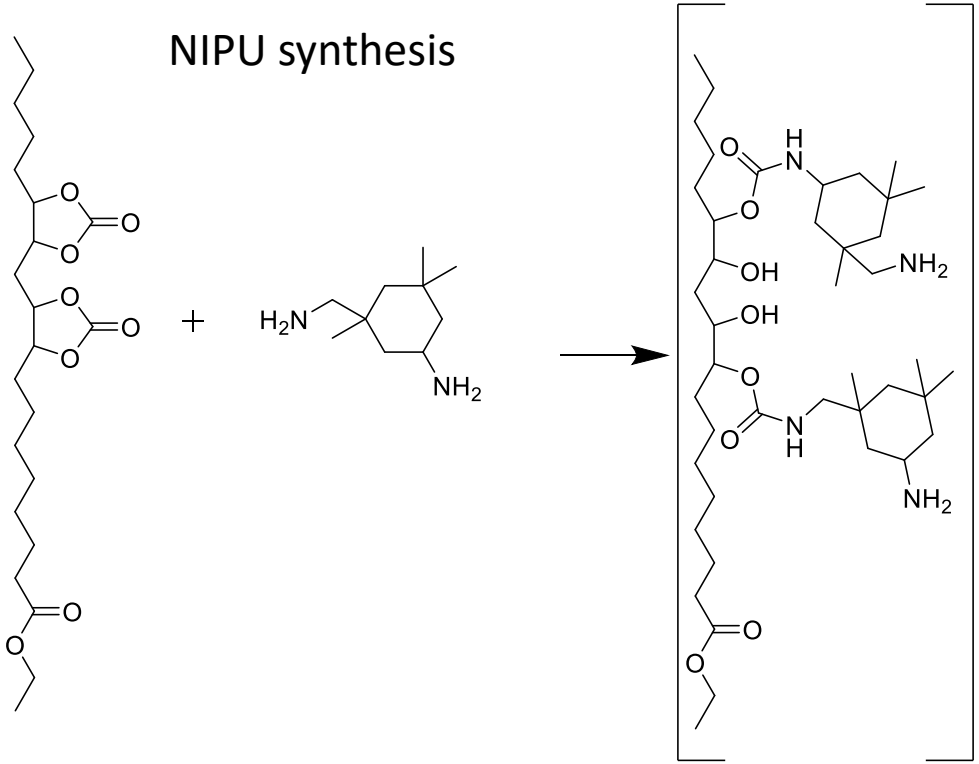
In an attempt to improve the reactivity



Cyclocarbonate compound supposedly more reactive ... but only a slight increase in molecular weight observed in SEC

NIPU synthesis



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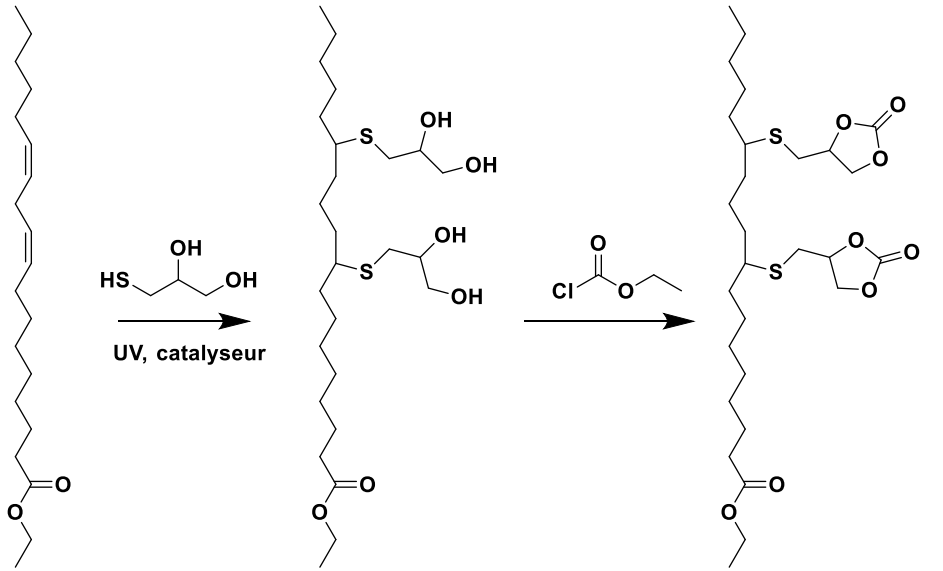
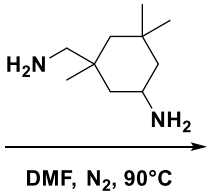
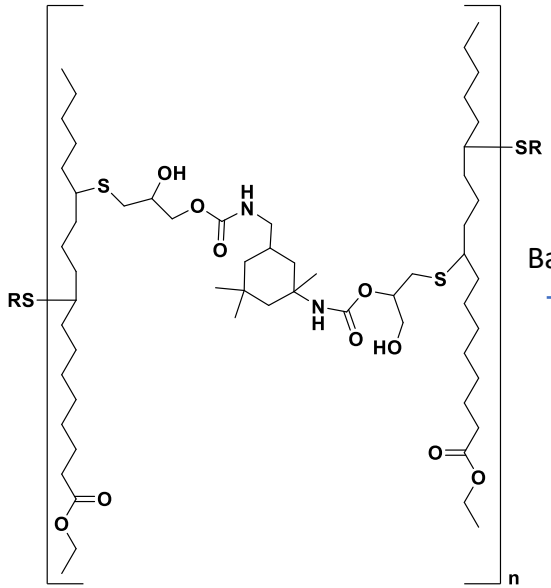
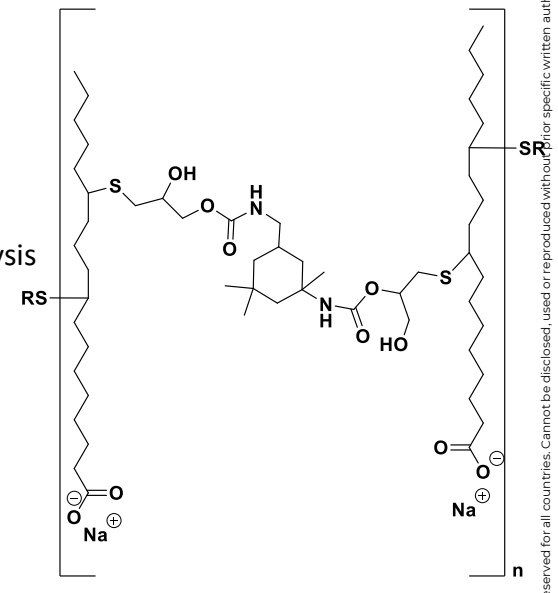
Thioglycerol-cyclocarbonates





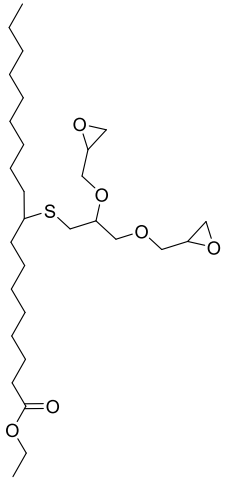


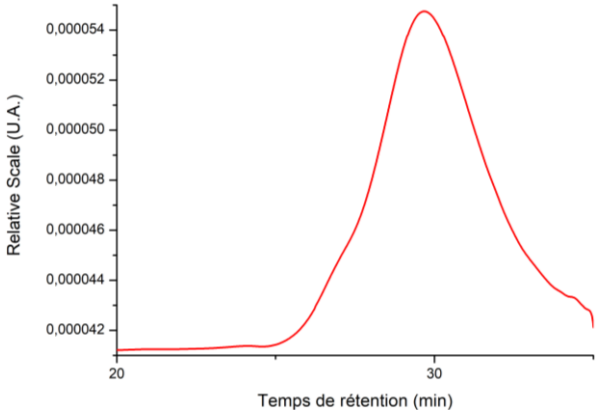
Basic hydrolysis



Water dispersible NIPU

Thioglycerol-epoxy





M_n : 3 x 10^3 g.mol^{-1}
M_w : 5,7 x 10^3 g.mol^{-1}
Ip : 1,85

24h Hydrolysis in alcalin medium

water solubility is obtained

Carboxilic acid function are available for further modifications

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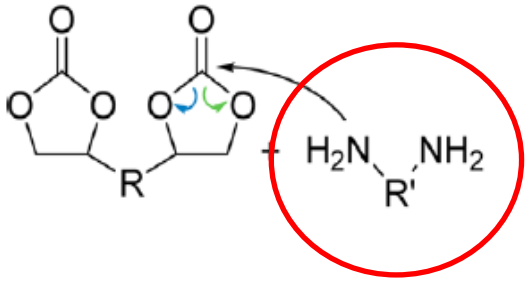
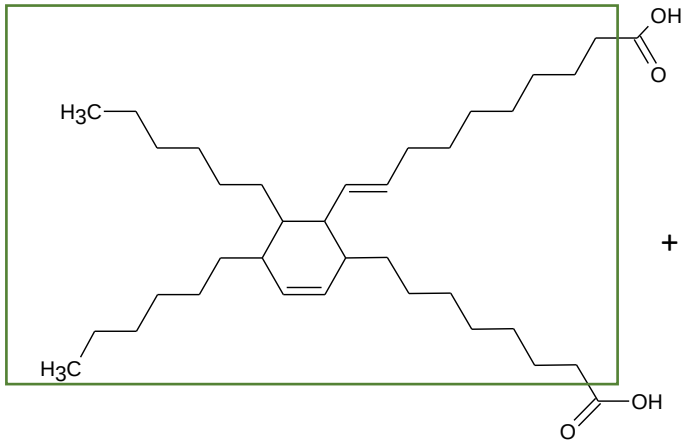


Synthesis of aligamides from a biobased dimer acid and a diamine



Pripol 1013

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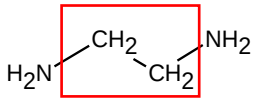
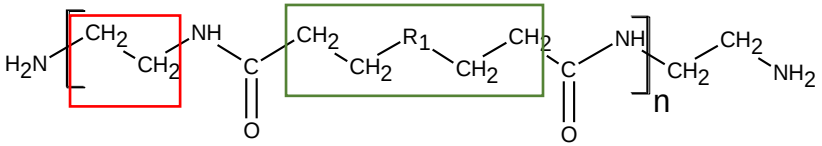


Ethylenediamine (EDA)

190°C – 18h



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H_2O

Oligoamide EDA

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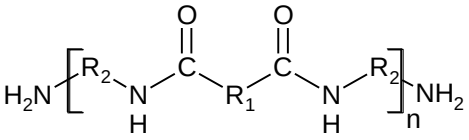
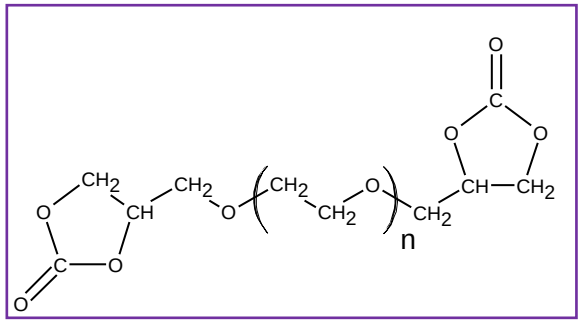


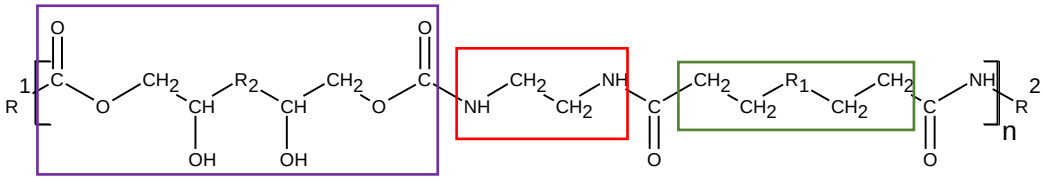
Oligoamide

+



Polyethyloxyde bicyclocarbonate
(PEOBCC)

120°C – 24h →



NonIsocyanatePolyUréthane
(NIPU)

Non Isocyanate Polyurethane resin, synthesized from oligomaide and commercial cyclocarbonate

Synthesis by bulk or solvented

Modification of the oligoamide for waterdispersibility → integration of ionic segments

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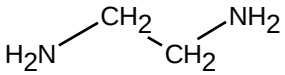
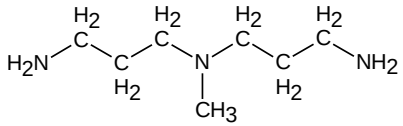
Oligoamides with EDA and DAMDPA Or NIPU synthesized from EDA oligomer and DAMDPA oligomer

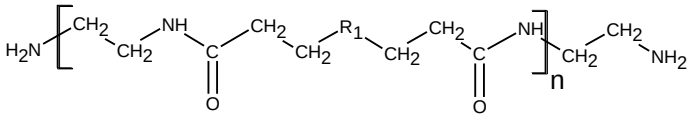
EDA



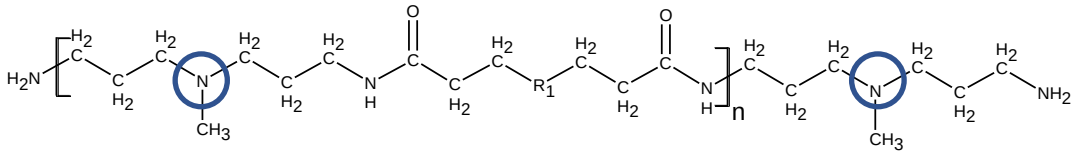
DAMDPA

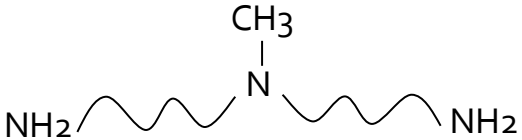


Oligoamide EDA



Oligoamide DAMDPA



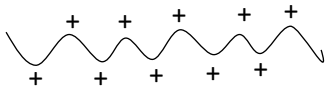


NIPUs – acidic hydrolysis

100/0 50/50 0/100

slighlty charged

locally charged



Homogeneously charged

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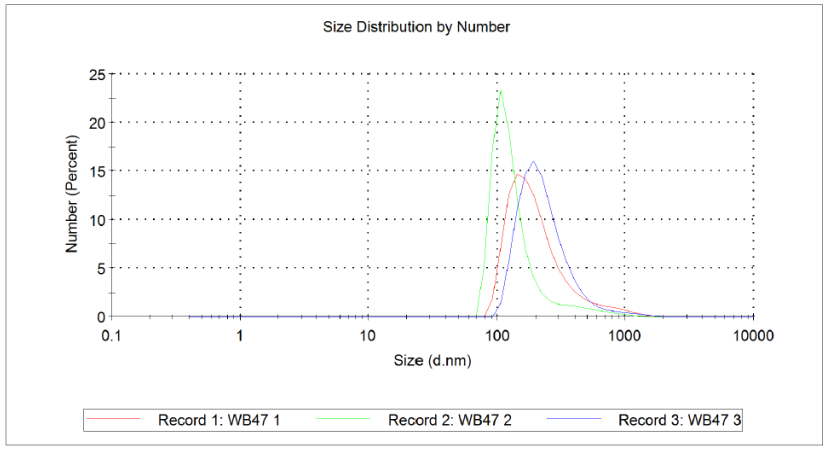
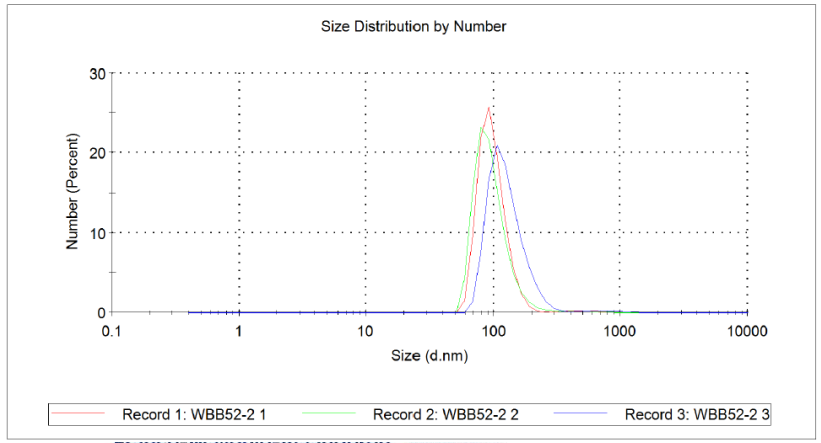
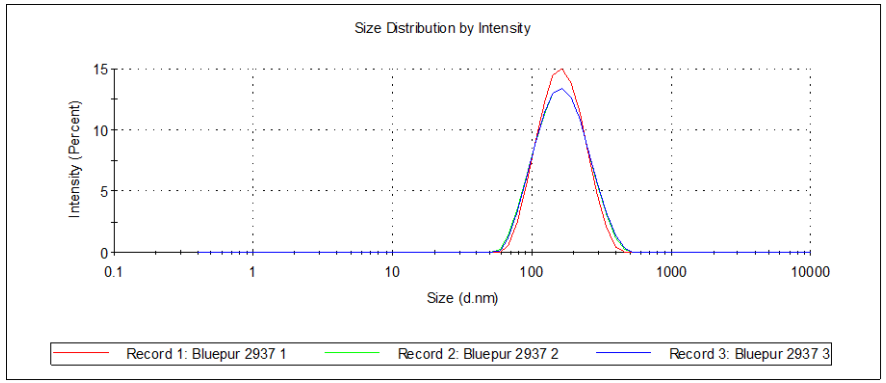
Latex NIPU 100% EDA
$\overline{M_n}$ (GPC) = 7000 g.mol^{-1}
20 wt% resin in water





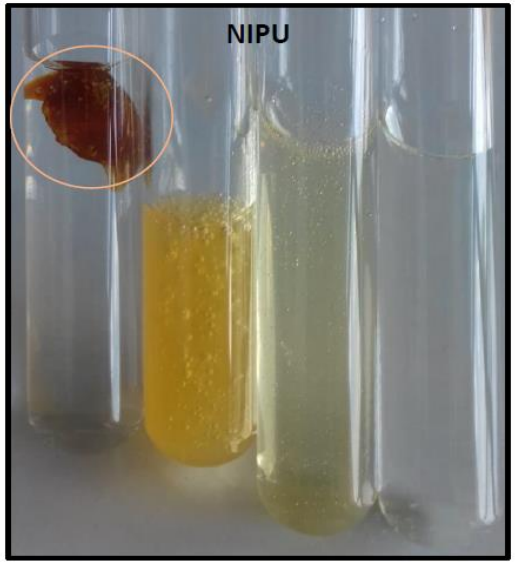
Commercial Latex PU



Improvement of water solubility with ionic charge

NIPU size around 100 nm diameter in water

Water solubility of Latex with charge modification



France-Wallonie-Vlaanderen EUROPESE UNIE

WBDuraPaint

Avec le soutien du Fonds européen de développement régional
Met steun van het Europees Fonds voor Regionale Ontwikkeling

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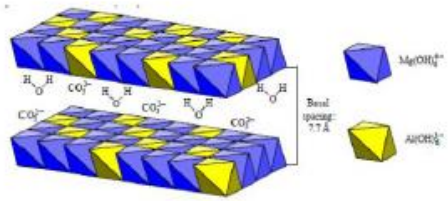
Other activities in the Consortium

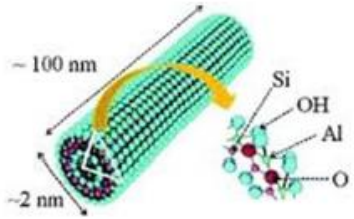
Partial substitution of TiO_2
By clay containingof corrosion inhibitor

Anionic clays : Pural MG 61 (lamellar)

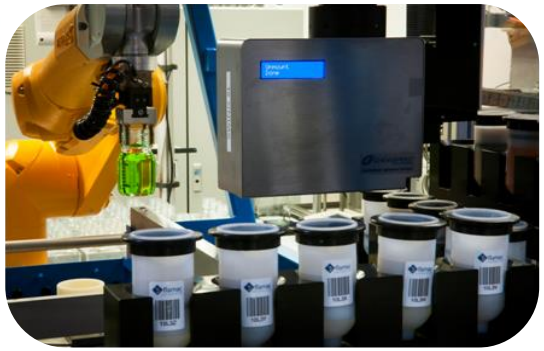


5-10 wt% of Mo in Pural Mg 61

Halloysites/aluminosilicate nanotube ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) (tubular)



8-10 wt% of benzotriazole (BTA) in halloysite



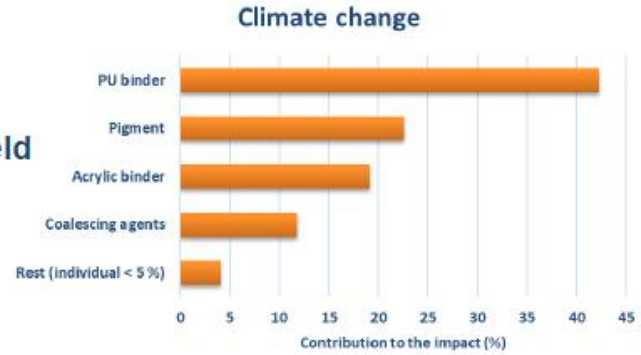
Q Panels – bare coat 200 µm

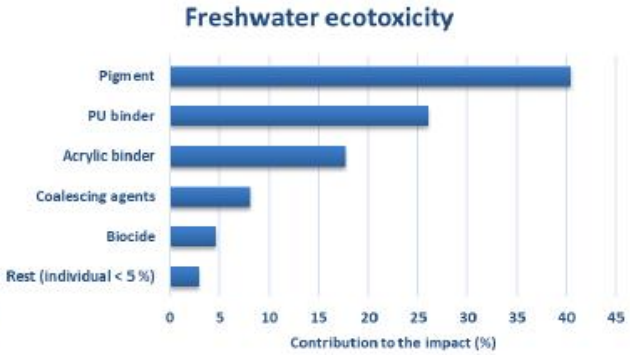
Ecodesign thanks to Life Cycle Assesment

Identifying hotspots for raw materials

Exemple for 2 impact indicators for a PU commercial paint

Application example in coatings field





flamac materials exploration

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Synthesis and water dispersibility of non-isocyanate polyurethane

22 November 2021 – online workshop

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